

STATISTICAL MECHANICS FOR THE LIQUID STATE

JEAN-LOUIS BRETONNET



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By

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Foreword

Statistical mechanics is the name used for the discipline devoted to studying systems composed of a large number of particles in order to calculate their macroscopic properties including energy, pressure, entropy... It deals as such with both *equilibrium systems* whose particles are either independent or strongly interacting and *non-equilibrium systems*. In most cases, two different approaches are used to develop a theory of the equilibrium properties of liquids based on the principles of statistical mechanics: (i) the systematic cluster expansion formalism applied to fluids at a density as high as one-third of normal liquid densities, and (ii) the integro-differential equations formalism determining the relationship between the distribution functions and the effective pair interactions. The discussion of the non-equilibrium phenomena have also made significant headway with the sophisticated calculations of the Chapman-Enskog solution for the Boltzmann equation and, more recently, with the linear response theory that provides the transport coefficients in terms of correlations among fluctuations.

Statistical mechanics is a relatively new science that developed in the mid nineteenth century with the scientific works of Clausius, Maxwell and Boltzmann. Clausius laid the foundation of the theory of gases in 1857. Two years later, Maxwell established the law of velocity distribution of molecules in gases. In 1872, Boltzmann went through a harsh period against the supporters of the theory of energy and changed the law of the Maxwell velocity distribution by taking the external fields into account.

The basic grounding in statistical mechanics was actually provided by Gibbs [1] in a book entitled *The principles of statistical mechanics* which almost went unnoticed when it was published in 1902. In this work, Gibbs justified for any system containing interacting particles

the results obtained by Maxwell and Boltzmann by following a different path than what the predecessors had used and offering more rigorous mathematical and logical consistency based on the *concept of ensemble*. Gibbs' distribution is based exclusively on assuming the canonical ensemble to derive the laws of distribution, and makes no use of empirical results about the nature of the intermolecular forces. Any new statistical theory is inspired in some way by Gibbs distribution, and it is not an overstatement to say that it holds the same position as Newton's equation in classical mechanics or Maxwell's equations in electromagnetism.

In 1907, a milestone was passed when Einstein combined the ideas of statistical mechanics and quantum mechanics to explain the specific heat of solids at low temperature. Shortly later, von Neumann established rigorously the link between statistical mechanics and quantum mechanics. Nevertheless, when realizing that the Maxwell-Boltzmann distribution is a limiting case of the Bose-Einstein and Fermi-Dirac distributions, the scope of statistical mechanics has been widely extended. It would be difficult to compile a full list of fields where statistical mechanics identified applications. Statistical mechanics is used in a wide range of fields including radiation (Planck, Bose, Einstein...), Brownian motion (Brown, Einstein, Smoluchowski...), electronic theory of metals (Drude, Sommerfeld, Lorentz...), magnetism (Langevin, Brillouin, Weiss...), specific heat (Einstein, Debye...), semiconductors (Bardeen, Shockley...), superconductivity (Cooper, Schrieffer, Josephson...), superfluidity (Landau...), astrophysics (Fowler, Chandrasekhar...), phase transitions (Domb, Fisher, Wilson...), polymers (Kuhn, Flory...), dense fluids (Kirkwood, Yvon, Green...), etc.

The purpose of this book is primarily to examine and study the structural and thermodynamic properties of dense fluids and their transport properties. It is important to note that the statistical mechanics of dense fluids is divided into two parts. The first one investigates the *equilibrium systems* and makes it possible to calculate their thermodynamic properties and static structure. The second one focuses on the *out-of-equilibrium systems* and open the way to studying individual and collective motions of particles together with determining their transport properties. Regarding the equilibrium systems, there are two distinct ways to calculate the thermodynamic properties. The first one - based on knowledge on the *partition function* - is elegant but it applies to diluted fluids and is the only path to investigate the thermodynamic properties. The second way rest on the use

of *spatial correlation functions*. In addition to the fact that they give access to the thermodynamic properties of dense fluids, they are likely to extract the static structure provided that the interactions between particles are reduced to a sum of pair potentials. Over and beyond that fact, they fall under a more general theory involving the *spatial and temporal correlation functions* that make it possible to calculate the atomic transport properties such as the coefficients of diffusion, viscosity or thermal conductivity.

The aim of this publication is mainly to try and pinpoint what there is behind the seemingly anarchistic proliferation of phenomena observable in liquid state together with the sequence of causes and effects and, where appropriate, identify the general principles and underlying rules governing them. To facilitate the understanding of the microscopic theory of liquids, the tests made often refer to specific cases calling for only easy reasoning and concepts whose aim is not to display the mathematical rigour of the theory, but rather to the implementation of the models under consideration. Nevertheless, numerous details of the calculations are produced to exempt the reader from repeating the demonstrations.

And last but not least, let me express my thanks and gratitude to my colleagues and graduate students for numerous discussions and helpful comments. When writing this book, the purpose was to provide a pre-measured dosage of statistical mechanics to make the reading easier and appetizing and raise interest among students for the liquid theory. Many thanks also go to Jean-Pierre Hansen, Ian McLaughlin and Andrei Postnikov, who displayed much patience and solid expertise when reading over the manuscript and suggesting numerous improvements.

1 The basics of classical statistical mechanics

Unlike classical mechanics and quantum mechanics, adapted to systems with a few degrees of freedom, the statistical mechanics makes it possible for us to study systems containing many particles such as gases, dense fluids and solids. In classical mechanics, the past and future history of systems is fully determined when external forces and initial conditions are known. In contrast to this in statistical mechanics, we should be content with admitting that the initial conditions are always subject to uncertainties due to the large amount of data. Therefore, it is impossible to find a rigorous solution to the equations of motion so that the methods of mathematical statistics become indispensable. In other words, the differences between statistical mechanics and classical mechanics lie in having no knowledge of initial conditions.

The statistical analysis is not restricted to systems containing a large number of particles. It can be also used in classical mechanics with numerical simulation methods. For instance, the Monte Carlo method, when tracking the motion of a small number of particles, merges the advantages of classical mechanics and statistical mechanics.

Whereas the molecular behaviour of matter is described by *microscopic laws* involving coordinates and momenta, the *macroscopic laws* of thermodynamics use an appropriate set of physical properties such as volume, pressure, temperature, density... One of the major objectives of statistical mechanics aims specifically at making the link between the laws of mechanics and the laws of thermodynamics. Gibbs was first to develop the general treatment to express the relevant thermodynamic properties of any chemical system in terms of

the microscopic properties of molecules. Formalism is based on the *concept of ensemble* and the *probability density*. Given that the treatment can lead to severe discrepancies when compared with results of experiments (particularly for specific heats), it has been necessary to introduce the ideas of quantum mechanics to remove the shortcomings.

The purpose of this chapter is to offer a brief reminder of classical mechanics and quantum mechanics that play a central role in the development of the statistical mechanics. Then, we present the concept of ensembles and of probability density conveniently introduced by Gibbs through the phase space considerations. Finally, we state the first postulate of statistical mechanics showing correspondence between the time average and the ensemble average in ergodic systems. Nothing is more solid and effective than a theorem whose validity has been carefully tested.

1.1 Classical mechanics and phase space

Newtonian formalism

The classical mechanics is based on Newton's equation :

$$\mathbf{F}_i = m \frac{d^2 \mathbf{r}_i}{dt^2}, \quad (1.1)$$

in which $\mathbf{F}_i$ is the force acting on the i th particle of a system that contains N particles, m the mass of the particle and $\mathbf{r}_i$ its radius vector. This equation can describe the motion of the particle and be reduced to three second-order differential equations whose solutions $x_i(t)$, $y_i(t)$ and $z_i(t)$ are determined when the force $\mathbf{F}_i$ and the initial conditions are known.

For example, to study the motion of the linear harmonic oscillator, the differential equation is:

$$m \frac{d^2 X}{dt^2} = -kX, \quad (1.2)$$

where $X(= x - x_0)$ represents the elongation proportional to the force $F(= -kX)$. The solution of this differential equation is $X = X_0 \cos(\omega t + \varphi)$, where the angular frequency $\omega = \left(\frac{k}{m}\right)^{1/2}$ depends on

the characteristics of the system, while X_0 and φ are two constants of integration determined from the initial conditions. In practice, this corresponds to the oscillatory motion of a frictionless mass m attached to a spring of stiffness k .

In order to compare meaningfully the different formalisms of classical mechanics, we consider the motion of a particle of mass m in a central field. The potential energy is $U(r) = \frac{k}{r}$ and the force deriving from it is $\mathbf{F} = -\mathbf{grad}U = -k\frac{\mathbf{r}}{r^3}$, so that Newton's equation that governs the motion of the particle is:

$$m \frac{d^2 \mathbf{r}}{dt^2} = -k \frac{\mathbf{r}}{r^3}. \quad (1.3)$$

If the trajectory is located in the plane (xy) , the projections of this vectorial equation are:

$$m \frac{d^2 x}{dt^2} = -k \frac{x}{(x^2 + y^2)^{3/2}}, \quad (1.4)$$

$$m \frac{d^2 y}{dt^2} = -k \frac{y}{(x^2 + y^2)^{3/2}}. \quad (1.5)$$

The nature of the problem and the form of the equations require the use of polar coordinates (r, θ) to solve the system of differential equations. After making the change of variables $x = r \cos \theta$ and $y = r \sin \theta$, the system of differential equations written above becomes:

$$\left[m(\ddot{r} - r\dot{\theta}^2) + \frac{k}{r^2} \right] \cos \theta - m(r\ddot{\theta} + 2\dot{r}\dot{\theta}) \sin \theta = 0, \quad (1.6)$$

$$\left[m(\ddot{r} - r\dot{\theta}^2) + \frac{k}{r^2} \right] \sin \theta + m(r\ddot{\theta} + 2\dot{r}\dot{\theta}) \cos \theta = 0. \quad (1.7)$$

To simplify these equations, we perform their sum after multiplying the first equation by $\cos \theta$ and the second one by $\sin \theta$, and then carry out their difference after the first equation has been multiplied by $\sin \theta$ and the second one by $\cos \theta$. This produces the following two equations:

$$m(\ddot{r} - r\dot{\theta}^2) + \frac{k}{r^2} = 0, \quad (1.8)$$

$$m(r\ddot{\theta} + 2\dot{r}\dot{\theta}) = 0. \quad (1.9)$$

The second equation is an exact differential equation that can be integrated immediately into the form:

$$mr^2\dot{\theta} = l. \quad (1.10)$$

It is obvious that the quantity $mr^2\dot{\theta} = l$ corresponds to the angular momentum of the particle that is a constant of motion. In eliminating $\dot{\theta}$ between equations (1.8) and (1.10), we obtain the radial equation:

$$m\ddot{r} = -\frac{k}{r^2} + \frac{l^2}{mr^3}. \quad (1.11)$$

It should be noted that the solution $r(t)$ to this differential equation can be expressed - at least at a matter of principle - in terms of the constants k and l . By comparing equations (1.11) and (1.3), we can also notice the presence of the additional term $\frac{l^2}{mr^3}$ in equation (1.11) that can be interpreted as a fictitious force (centrifugal force), which does not result from an external force, but rather arises from the mode of representation adopted. The centrifugal force and Coriolis force appearing in the coordinate systems in rotation are two examples of fictitious forces.

Lagrangian formalism

The motion of a particle - or more generally of a material system - can also be studied with the Lagrange formalism. This approach is used when the variables are angles or complicated functions of conventional coordinates rather than Cartesian coordinates of individual particles. In this formalism, a system of N particles interacting with each other is defined by its $3N$ generalized coordinates q_i , where $i = 1, 2, \dots, 3N$. However, before describing the motion of particles, it is appropriate to calculate the following function known as the *Lagrangian* of the system:

$$L(q_1, q_2, \dots, q_{3N} ; \dot{q}_1, \dot{q}_2, \dots, \dot{q}_{3N} ; t) = T - U, \quad (1.12)$$

depending on *generalized coordinates* q_i , *generalized velocities* $\dot{q}_i$ and, possibly, on the time t . At the right side of equation (1.12), T is the kinetic energy and U the potential energy of the system. The kinetic energy T is a quadratic function of generalized velocities:

$$T = \frac{1}{2} \sum_{k=1}^N m_k \dot{q}_k^2, \quad (1.13)$$

and the potential energy U depends only on generalized coordinates when the system is conservative. Knowing the kinetic and potential energies of the system, the equations of motion can be derived using the Lagrange equations that arise in the following form:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0 \quad \text{where} \quad i = 1, 2, \dots, 3N. \quad (1.14)$$

By way of illustration, the equations of motion can be derived within the Lagrangian formalism of the two systems previously treated with the Newtonian formalism. In this case it is unnecessary to calculate the applied forces. For the linear harmonic oscillator, we use the generalized coordinate $q_1 = X$. The kinetic energy is $T = \frac{1}{2}m\dot{X}^2$ and the potential energy is $U = -\int(-kX)dX = \frac{1}{2}kX^2$, so that the Lagrangian is :

$$L(X, \dot{X}) = \frac{1}{2}m\dot{X}^2 - \frac{1}{2}kX^2. \quad (1.15)$$

As far as the equation of motion is concerned, the Lagrange equation (Eq. 1.14) is written:

$$\frac{d}{dt}(m\dot{X}) + kX = 0, \quad (1.16)$$

which coincides with equation (1.2).

Now we consider the particle of mass m in a central field. Its potential energy is $U = \frac{k}{r}$ and its kinetic energy $T = \frac{1}{2}mv^2$ is expressed in terms of generalized coordinates $q_1 = r$ and $q_2 = \theta$. As the square of the velocity - in polar coordinates - has the following expression $v^2 = \dot{r}^2 + r^2\dot{\theta}^2$, the corresponding Lagrangian reads :

$$L(r, \theta, \dot{r}, \dot{\theta}) = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) + \frac{k}{r}. \quad (1.17)$$

In terms of the coordinates r and θ , the use of the Lagrange equations leads directly to :

$$\frac{d}{dt}(m\dot{r}) - mr\dot{\theta}^2 + \frac{k}{r^2} = 0, \quad (1.18)$$

$$\frac{d}{dt}(mr^2\dot{\theta}) = 0. \quad (1.19)$$

These equations coincide with equations (1.10) and (1.11). Contrary to the Newtonian formalism, the knowledge of actual and fictitious

forces is not required. In particular, the centrifugal force $mr\dot{\theta}^2 = \frac{l^2}{mr^3}$ results understandably from the Lagrangian and this is considered as an advantage over the Newtonian formalism in which the presence of fictitious forces makes things more complex when deriving the equations of motion.

Another advantage of the Lagrangian formalism is offering an identification of quantities called *first integrals* and retained during the motion. A first integral of the motion is particularly important when the Lagrangian does not depend explicitly on time. Let us show it by calculating the total derivative of L with respect to time:

$$\frac{dL}{dt} = \sum_i \frac{\partial L}{\partial q_i} \frac{\partial q_i}{\partial t} + \sum_i \frac{\partial L}{\partial \dot{q}_i} \frac{\partial \dot{q}_i}{\partial t} + \frac{\partial L}{\partial t}. \quad (1.20)$$

According to the Lagrange equation, $\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) = \frac{\partial L}{\partial q_i}$, and the relation $\frac{\partial q_i}{\partial t} = \dot{q}_i$, equation (1.20) is rewritten:

$$\begin{aligned} \frac{dL}{dt} &= \sum_i \left[\dot{q}_i \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) + \frac{\partial L}{\partial \dot{q}_i} \frac{\partial \dot{q}_i}{\partial t} \right] + \frac{\partial L}{\partial t}, \\ &= \sum_i \frac{d}{dt} \left(\dot{q}_i \frac{\partial L}{\partial \dot{q}_i} \right) + \frac{\partial L}{\partial t}, \end{aligned} \quad (1.21)$$

$$\text{hence} \quad \frac{\partial L}{\partial t} = -\frac{d}{dt} \left(\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L \right). \quad (1.22)$$

However, if the Lagrangian does not depend explicitly on time ($\frac{\partial L}{\partial t} = 0$), the above equation reduces to:

$$\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L = H = \text{const.} \quad (1.23)$$

The quantity H , being retained when L does not depend explicitly on time, is a very important first integral of analytical mechanics. Similarly and for instance, if the Lagrangian L is independent of a generalized coordinate q_j , the variation of L with respect to $\dot{q}_j$ is a constant, i.e. $\frac{\partial L}{\partial \dot{q}_j} = \text{const.}$ Following Lagrange's equation (Eq. 1.14), $\frac{\partial L}{\partial q_j} = 0$ is indeed equivalent to $\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_j} \right) = 0$ or $\frac{\partial L}{\partial \dot{q}_j} = \text{const.}$ Accordingly, each generalized coordinate q_i is associated to its *conjugate momentum* $\frac{\partial L}{\partial \dot{q}_i} = p_i$ whose leads to the Hamiltonian formalism.

Hamiltonian formalism

In the Lagrangian formalism, the independent variables are the generalized coordinates q_i defining the system state at any moment. They are functions of time that are themselves solutions of a system of $3N$ second order differential equations. By contrast, the independent variables in the Hamiltonian formalism are the generalized coordinates q_i and the conjugate momenta $p_i = \frac{\partial L}{\partial \dot{q}_i}$. Replacing $\frac{\partial L}{\partial \dot{q}_i}$ by the conjugate momenta p_i into equation (1.23) does not bring any obvious advantage, except to define a new function H , called the *Hamiltonian* of the system:

$$H(q_i, p_i, t) = \sum_i \dot{q}_i p_i - L, \quad (1.24)$$

which has the same unit as L , i.e. energy.

The interest in the Hamiltonian is to be a first integral when the Lagrangian does not depend explicitly on time (Eq. 1.23) and to represent, in most cases, the total energy E of the system. For a conservative system, the potential energy $U(= T - L)$ is indeed a function of the generalized coordinates q_i which allows us to write the conjugate momenta as:

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial(T - U)}{\partial \dot{q}_i} = \frac{\partial T}{\partial \dot{q}_i}. \quad (1.25)$$

Moreover, considering that the kinetic energy T is a quadratic function of the generalized velocities (Eq. 1.13), we can write:

$$\sum_i \dot{q}_i \frac{\partial T}{\partial \dot{q}_i} = 2T, \quad (1.26)$$

by virtue of Euler's theorem. Remember that Euler's theorem stipulates that if a function $f(\lambda x_1, \lambda x_2, \dots, \lambda x_i)$ is a homogeneous polynomial of degree m in x_i , namely:

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_i, \dots) = \lambda^m f(x_1, x_2, \dots, x_i, \dots), \quad (1.27)$$

f is related to its partial derivatives by the equation:

$$\sum_i x_i \frac{\partial f}{\partial x_i} = m f. \quad (1.28)$$

To demonstrate this, it is just necessary to differentiate equation (1.27) with respect to λ and to write down $\lambda = 1$, as follows:

$$\begin{aligned}
 \frac{\partial f}{\partial \lambda x_1} \frac{\partial \lambda x_1}{\partial \lambda} + \frac{\partial f}{\partial \lambda x_2} \frac{\partial \lambda x_2}{\partial \lambda} + \dots + \frac{\partial f}{\partial \lambda x_i} \frac{\partial \lambda x_i}{\partial \lambda} + \dots \\
 = m \lambda^{m-1} f(x_1, x_2, \dots, x_i, \dots), \\
 x_1 \frac{\partial f}{\partial x_1} + x_2 \frac{\partial f}{\partial x_2} + \dots + x_i \frac{\partial f}{\partial x_i} + \dots \\
 = m f(x_1, x_2, \dots, x_i, \dots). \quad (1.29)
 \end{aligned}$$

Given that the kinetic energy T is a homogeneous polynomial of degree two of $\dot{q}_i$, this yields equation (1.26). Therefore, by combining equations (1.24), (1.25) and (1.26), the Hamiltonian of a conservative system reduces to the total energy E :

$$\begin{aligned}
 H &= \sum_i \dot{q}_i \frac{\partial T}{\partial \dot{q}_i} - L, \\
 &= 2T - L = T + U = E. \quad (1.30)
 \end{aligned}$$

To establish the equations of motion in the Hamiltonian formalism, we must calculate the total differential of the Hamiltonian $H(q_i, p_i, t)$:

$$dH = \sum_i \frac{\partial H}{\partial q_i} dq_i + \sum_i \frac{\partial H}{\partial p_i} dp_i + \frac{\partial H}{\partial t} dt. \quad (1.31)$$

As the element dH is also given by the differential of equation (1.24), it can be written again under the following form with the help of equation (1.20):

$$dH = \sum_i d\dot{q}_i p_i + \sum_i \dot{q}_i dp_i - \left[\sum_i \frac{\partial L}{\partial q_i} dq_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i + \frac{\partial L}{\partial t} dt \right]. \quad (1.32)$$

By using the Lagrange equations (Eq. 1.14), namely $\frac{\partial L}{\partial q_i} = \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right)$, and the conjugate momenta ($p_i = \frac{\partial L}{\partial \dot{q}_i}$), the term in square brackets in the above equation transforms into

$$\left[\sum_i \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}_i} \right) dq_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i + \frac{\partial L}{\partial t} dt \right] = \sum_i \dot{p}_i dq_i + \sum_i p_i d\dot{q}_i + \frac{\partial L}{\partial t} dt, \quad (1.33)$$

and equation (1.32) simplifies to:

$$\begin{aligned} dH &= \sum_i d\dot{q}_i p_i + \sum_i \dot{q}_i dp_i - \left[\sum_i \dot{p}_i dq_i + \sum_i p_i d\dot{q}_i + \frac{\partial L}{\partial t} dt \right], \\ &= \sum_i \dot{q}_i dp_i - \sum_i \dot{p}_i dq_i - \frac{\partial L}{\partial t} dt. \end{aligned} \quad (1.34)$$

Identifying the terms of equations (1.31) and (1.34) yields the Hamilton equations:

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i}, \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i}, \\ \frac{\partial L}{\partial t} &= -\frac{\partial H}{\partial t}. \end{aligned} \quad (1.35)$$

The last of these equations shows that if the Lagrangian does not depend explicitly on the time, the Hamiltonian does not depend on it either. As for the two first equations, they constitute the equations of motion in the Hamiltonian formalism. They form a system of $6N$ first order differential equations that require knowledge of $6N$ initial conditions ($3N$ for p and $3N$ for q). They replace the $3N$ second order differential equations in the Lagrangian formalism, which also require $6N$ initial conditions. The Hamilton equations do not represent an improvement relative to the Lagrange equations; their only advantage is to provide an appropriate basis for the development of quantum mechanics and statistical mechanics. In the Hamiltonian formalism, a $6N$ dimensional space, called the *phase space* Γ , is introduced, where a point defined by $3N$ variables q_i and $3N$ variables p_i describes a trajectory that allows us to follow the evolution of the system over time.

To illustrate the method, consider again the linear harmonic oscillator with the Lagrangian (Eq. 1.15) written as :

$$L(q, \dot{q}) = \frac{1}{2}m\dot{q}^2 - \frac{1}{2}kq^2. \quad (1.36)$$

The conjugate momentum is $p = \frac{\partial L}{\partial \dot{q}} = m\dot{q}$ so that the Hamiltonian $H = p\dot{q} - L$ reduces to :

$$\begin{aligned} H &= m\dot{q}^2 - \left(\frac{1}{2}m\dot{q}^2 - \frac{1}{2}kq^2 \right), \\ &= \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}kq^2, \end{aligned} \quad (1.37)$$

and the equations of motion become:

$$\dot{q} = \frac{\partial H}{\partial p} = \frac{p}{m}, \quad (1.38)$$

$$\dot{p} = -\frac{\partial H}{\partial q} = -kq. \quad (1.39)$$

After having substituted $\dot{p} (= m\ddot{q})$ in the second equation, we can proceed to the integration of the second order differential equation and draw successively q and p as:

$$q = q_0 \cos(\omega t + \varphi), \quad (1.40)$$

$$p = m\dot{q} = -m\omega q_0 \sin(\omega t + \varphi), \quad (1.41)$$

where $\omega^2 = \frac{k}{m}$. Since the system is conservative, we can also calculate the total energy by equation (1.37):

$$\begin{aligned} E &= H = \frac{1}{2}\frac{p^2}{m} + \frac{1}{2}m\omega^2 q^2 \\ &= \frac{1}{2m}[-m\omega q_0 \sin(\omega t + \varphi)]^2 + \frac{1}{2}m\omega^2 [q_0 \cos(\omega t + \varphi)]^2 \\ &= \frac{1}{2}m\omega^2 q_0^2. \end{aligned} \quad (1.42)$$

It should be noted that the evolution of the system can be represented in the phase space in two dimensions by plotting p versus q . Assuming that the phase φ is zero at the initial moment, the expressions of q and p (Eqs. 1.40 and 1.41) reduce in terms of E (Eq. 1.42) as:

$$q = \frac{1}{\omega} \sqrt{\frac{2E}{m}} \cos \omega t, \quad (1.43)$$

$$p = -\sqrt{2mE} \sin \omega t. \quad (1.44)$$

It is easy to verify that the trajectory in the phase space describes an ellipse moving clockwise.

1.2 Quantum mechanics

Introduction

Classical mechanics is used to determine the motion of a classical particle – or a set of particles – by solving the equations of motion, when the initial positions and initial velocities are known. However, during the 1920s it became apparent that it was impossible to determine precisely and simultaneously the position and velocity of quantum particles: this is known as the *Heisenberg uncertainty principle*. For these particles, the description of classical mechanics does not apply. In particular, the representative point of the dynamic state in the phase space, at a given moment, cannot be pinpointed. Other considerations apply that are the aim of quantum mechanics.

The fundamental concept of quantum mechanics resides in the *wave function* $\psi(\mathbf{q}, t)$, which is defined in terms of generalized coordinates $\mathbf{q} = (q_1, q_2, \dots, q_{3N})$ and time t . Strangely, the wave function is a feature that does not refer to the movement of particles but to the probability of finding particles in a given region of space. Thus the elementary probability that the system is, at a given moment, in the region of space limited to $d\mathbf{q}$, bounded by q_1 and $q_1 + dq_1$, q_2 and $q_2 + dq_2$, ..., q_{3N} and $q_{3N} + dq_{3N}$ is:

$$\psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)d\mathbf{q}, \quad (1.45)$$

where $\psi^*(\mathbf{q}, t)$ is the complex conjugate of $\psi(\mathbf{q}, t)$.

The *first postulate* of quantum mechanics states that the square modulus of the wave function $|\psi(\mathbf{q}, t)|^2 = \psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)$ represents a probability density function. According to mathematical statistics, this means that the wave function satisfies the normalization condition:

$$\int \psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)d\mathbf{q} = 1. \quad (1.46)$$

This relationship reflects the fact that the particle is found with certainty in the area considered, since the probability is equal to unity. The wave function is not an observable quantity and never enters the final result. It must be regarded only as a mathematical tool used in the calculation of dynamic quantities such as position, momentum, energy...

The *second postulate* of quantum mechanics stipulates that any dynamic quantity L is associated with a linear operator $\hat{L}$. When the dynamic quantity L is involved, the corresponding operator $\hat{L}$ has to be applied to the wave function $\psi(\mathbf{q}, t)$. However, if one is interested only in stationary states of the system (time-independent states), the only observable results of the physical property are the eigenvalues λ of $\hat{L}$ that satisfy the equation:

$$\hat{L}\psi(\mathbf{q}) = \lambda\psi(\mathbf{q}) \quad (1.47)$$

For example, the operator $\hat{x}$ associated with the position variable x is the function x itself. The action of this operator on the wave function $\psi(x)$ is the multiplication of this function by x :

$$\hat{x}\psi(x) = x\psi(x). \quad (1.48)$$

As regards the operator $\hat{p}_x$ associated with the momentum variable $p_x = mv_x$, it is defined by $\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$, where $\hbar (= 1,054.10^{-34} \text{ J}\cdot\text{s})$ is Planck's constant divided by 2π and i the imaginary number such as $i^2 = -1$. In a one-dimensional problem, the action of the momentum operator on the wave function $\psi(x)$ reduces to the integration of the differential equation:

$$\hat{p}_x\psi(x) = \frac{\hbar}{i} \frac{d\psi(x)}{dx} = p_x\psi(x), \quad (1.49)$$

where the solution is $\psi(x) = A \exp(i \frac{p_x}{\hbar} x)$, with A the integration constant and $\psi(x)$ the wave function associated with the eigenvalue p_x .

When the energy E of the system must be calculated, it is required to apply the associated operator $\hat{H}$ to the wave function $\psi(q)$, i.e.:

$$\hat{H}\psi(\mathbf{q}) = E\psi(\mathbf{q}). \quad (1.50)$$

This relation corresponds to the Schrödinger equation, independent of time, in which the Hamiltonian operator $\hat{H}$ of a particle is expressed as:

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(x, y, z), \quad (1.51)$$

where m is the mass of the particle and $\nabla^2 (= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$ the Lapacian. The first term at the right hand side of the above equation

represents the kinetic energy operator and the second term the potential energy. Therefore, the knowledge of the Hamiltonian operator and boundary conditions of the system allows the determination of E and ψ .

Quantum particle in a rectangular box

By way of illustration and to clarify the concept of energy quantization, let us consider the problem of a quantum particle of mass μ in a rectangular box with sides a , b , c . If the particle is not subject to any external force, the potential energy is zero and the Schrödinger equation (Eq. 1.50) reduces to:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi = E\psi. \quad (1.52)$$

Let us seek a solution for this partial differential equation in the form of a product with three functions, each of them depending on a single variable, namely:

$$\psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z). \quad (1.53)$$

By substituting the expression of the wave function in equation (1.52), we obtain:

$$\begin{aligned} -\frac{\hbar^2}{2\mu} \left[\psi_2(y)\psi_3(z) \frac{\partial^2 \psi_1(x)}{\partial x^2} + \psi_1(x)\psi_3(z) \frac{\partial^2 \psi_2(y)}{\partial y^2} \right. \\ \left. + \psi_1(x)\psi_2(y) \frac{\partial^2 \psi_3(z)}{\partial z^2} \right] = E\psi_1(x)\psi_2(y)\psi_3(z), \end{aligned}$$

or

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{\psi_1(x)} \frac{\partial^2 \psi_1(x)}{\partial x^2} + \frac{1}{\psi_2(y)} \frac{\partial^2 \psi_2(y)}{\partial y^2} + \frac{1}{\psi_3(z)} \frac{\partial^2 \psi_3(z)}{\partial z^2} \right] = E. \quad (1.54)$$

As the sum of the three terms in square brackets is constant, we can write down $E = E_1 + E_2 + E_3$ and change the Schrödinger equation into three independent equations:

$$\frac{\partial^2 \psi_1(x)}{\partial x^2} = -\frac{2\mu E_1}{\hbar^2} \psi_1(x), \quad (1.55)$$

$$\frac{\partial^2 \psi_2(y)}{\partial y^2} = -\frac{2\mu E_2}{\hbar^2} \psi_2(y), \quad (1.56)$$

$$\frac{\partial^2 \psi_3(z)}{\partial z^2} = -\frac{2\mu E_3}{\hbar^2} \psi_3(z). \quad (1.57)$$

Solving these equations of the form $\ddot{X} = -k^2 X$ is immediate. The solutions are:

$$\psi_1(x) = A \sin k_1 x + A' \cos k_1 x, \quad (1.58)$$

$$\psi_2(y) = B \sin k_2 y + B' \cos k_2 y, \quad (1.59)$$

$$\psi_3(z) = C \sin k_3 z + C' \cos k_3 z, \quad (1.60)$$

where $k_1 = \sqrt{\frac{2\mu E_1}{\hbar^2}}$, $k_2 = \sqrt{\frac{2\mu E_2}{\hbar^2}}$ and $k_3 = \sqrt{\frac{2\mu E_3}{\hbar^2}}$. Now, to completely determine the solution of the problem, let us consider the boundary conditions imposed by the box walls which are:

$$\psi(0, y, z) = \psi(a, y, z) = 0, \quad (1.61)$$

$$\psi(x, 0, z) = \psi(x, b, z) = 0, \quad (1.62)$$

$$\psi(x, y, 0) = \psi(x, y, c) = 0. \quad (1.63)$$

The first of these boundary conditions requires that

$$\psi(0, y, z) = \psi_1(0)\psi_2(y)\psi_3(z) = 0 \quad (1.64)$$

in the x -direction, i.e. $A' = 0$ for all y and z . Likewise there is $B' = C' = 0$ in the directions y and z . Moreover, at $x = a$, the boundary condition reads:

$$\begin{aligned} \psi(a, y, z) &= \psi_1(a)\psi_2(y)\psi_3(z) = 0, \\ &= (A \sin k_1 a)(B \sin k_2 y)(C \sin k_3 z) = 0, \end{aligned} \quad (1.65)$$

that is to say $k_1 = \frac{l\pi}{a}$ irrespective of y and z . When repeating the calculation procedure in the directions y and z , we find the expressions of the parameters k_1 , k_2 and k_3 :

$$k_1 = \sqrt{\frac{2\mu E_1}{\hbar^2}} = \frac{l\pi}{a}, \quad (1.66)$$

$$k_2 = \sqrt{\frac{2\mu E_2}{\hbar^2}} = \frac{m\pi}{b}, \quad (1.67)$$

$$k_3 = \sqrt{\frac{2\mu E_3}{\hbar^2}} = \frac{n\pi}{c}, \quad (1.68)$$

where l , m and n are positive integers. Then, these values of k_1 , k_2 and k_3 make it possible to calculate the energy $E = E_1 + E_2 + E_3$:

$$E = \frac{\hbar^2}{2\mu}(k_1^2 + k_2^2 + k_3^2) = \frac{\hbar^2 \pi^2}{2\mu} \left(\frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2} \right), \quad (1.69)$$

as well as the wave function (Eq. 1.53):

$$\psi(x, y, z) = ABC \left(\sin \frac{l\pi}{a} x \right) \left(\sin \frac{m\pi}{b} y \right) \left(\sin \frac{n\pi}{c} z \right). \quad (1.70)$$

From then on all we have to do is determining the constant (ABC) by using the normalization condition for the wave function:

$$\iint \psi^*(x, y, z) \psi(x, y, z) dx dy dz = 1, \quad (1.71)$$

or:

$$(ABC)^2 \int \sin^2 \left(\frac{l\pi}{a} x \right) dx \times \int \sin^2 \left(\frac{m\pi}{b} y \right) dy \times \int \sin^2 \left(\frac{n\pi}{c} z \right) dz = 1. \quad (1.72)$$

As the three integrals are respectively $\frac{a}{2}$, $\frac{b}{2}$ and $\frac{c}{2}$, the resulting expression for the wave function is:

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \left(\sin \frac{l\pi}{a} x \right) \left(\sin \frac{m\pi}{b} y \right) \left(\sin \frac{n\pi}{c} z \right). \quad (1.73)$$

Degeneracy and density of states

Considering the expression of energy of the particle (Eq. 1.69), we see that it can take a succession of discrete values corresponding to the integers l , m and n . Being characterized by the three *quantum numbers* l , m , n , the energy of the particle is thus quantized. It may be noted in passing that quantification is a consequence of the boundary conditions of the wave function on the box walls and that the energy decreases as the particle mass and the box sizes are increasing, for given quantum numbers.

The fact that many wave functions may possess the same energy is an important aspect of the energy quantization. Assuming that $a = b = c$, the wave function and energy become respectively:

$$\psi(x, y, z) = \sqrt{\frac{8}{a^3}} \left(\sin \frac{l\pi}{a} x \right) \left(\sin \frac{m\pi}{a} y \right) \left(\sin \frac{n\pi}{a} z \right), \quad (1.74)$$

$$E = \frac{\hbar^2 \pi^2}{2\mu a^2} (l^2 + m^2 + n^2). \quad (1.75)$$

Therefore, for each triplet of values (l, m, n) , the permutation of two of them keeps the energy unchanged while giving different wave functions. The energy states are then said to be *degenerate*. For instance, if $l = m = 3$ and $n = 4$, the energy is:

$$E = \frac{\hbar^2 \pi^2}{2\mu a^2} [(3)^2 + (3)^2 + (4)^2] , \quad (1.76)$$

and does not vary by permutation of the integers l, m, n . Conversely, after permutation of the integers l, m and n , the wave function takes one of the three following forms:

$$\psi_{3,3,4} = \sqrt{\frac{8}{a^3}} \left(\sin \frac{3\pi}{a} x \right) \left(\sin \frac{3\pi}{a} y \right) \left(\sin \frac{4\pi}{a} z \right) , \quad (1.77)$$

$$\psi_{3,4,3} = \sqrt{\frac{8}{a^3}} \left(\sin \frac{3\pi}{a} x \right) \left(\sin \frac{4\pi}{a} y \right) \left(\sin \frac{3\pi}{a} z \right) , \quad (1.78)$$

$$\psi_{4,3,3} = \sqrt{\frac{8}{a^3}} \left(\sin \frac{4\pi}{a} x \right) \left(\sin \frac{3\pi}{a} y \right) \left(\sin \frac{3\pi}{a} z \right) . \quad (1.79)$$

In this case, the energy is three-fold degenerate. It should be noted that, if the three quantum numbers are equal, there is only one wave function so that the energy is non degenerate.

When the values of integers l, m and n are very high, the intervals between the energy levels become so low that a continuous variation of energy can be admitted. The relative energy difference reduces indeed with equation (1.75) to:

$$\begin{aligned} \frac{E_{l,m,n+1} - E_{l,m,n}}{E_{l,m,n}} &= \frac{[l^2 + m^2 + (n+1)^2] - (l^2 + m^2 + n^2)}{l^2 + m^2 + n^2} \\ &= \frac{2n + 1}{l^2 + m^2 + n^2} \ll 1. \end{aligned} \quad (1.80)$$

As a result, the *density of states* defined as the number of states per interval of energy at each energy level is usually evaluated as follows. For this purpose, each energy state, $E_{l,m,n}$, is depicted by a point of coordinates

$$\sqrt{\frac{\hbar^2 \pi^2}{2\mu a^2}} l, \quad \sqrt{\frac{\hbar^2 \pi^2}{2\mu a^2}} m, \quad \sqrt{\frac{\hbar^2 \pi^2}{2\mu a^2}} n. \quad (1.81)$$

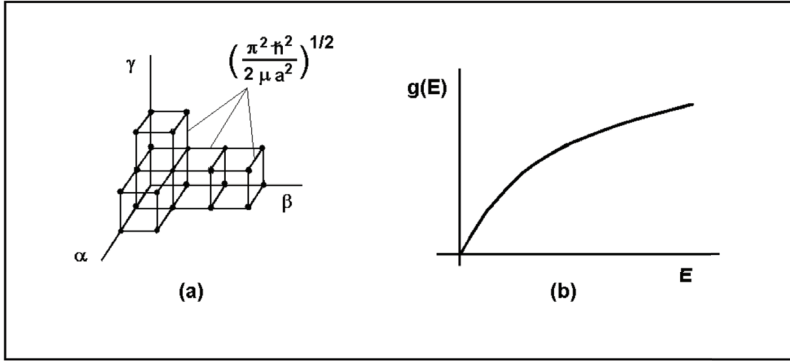


Figure 1.1: (a) Representative points of the energy states in the $\alpha\beta\gamma$ space. (b) Schematic representation of the variation of the density of states versus energy.

in the $(\alpha\beta\gamma)$ Cartesian coordinate system made of elementary cubes of side $\sqrt{\frac{\hbar^2 \pi^2}{2\mu a^2}}$ and volume $\left(\frac{\hbar^2 \pi^2}{2\mu a^2}\right)^{3/2}$ constituting a cubic lattice (Fig. 1.1).

As each elementary cube has 8 vertices and each vertex is shared by 8 cubes, the volume available for each point (state of energy) is the volume element $\left(\frac{\hbar^2 \pi^2}{2\mu a^2}\right)^{3/2}$. It could be noted that the square of the distance ρ from a point of the network to the origin is:

$$\rho^2 = \frac{\hbar^2 \pi^2}{2\mu a^2} [l^2 + m^2 + n^2] = E_{l,m,n}. \quad (1.82)$$

The higher the values of l, m, n the higher the number of points located on a sphere of equal energy. Therefore the number of energy states in the volume of a spherical ring, between ρ and $\rho + d\rho$, can be obtained by dividing the volume of the spherical ring $4\pi\rho^2 d\rho$ by the volume attributed to each point. As the numbers l, m, n are positive integers, only 1/8 of the spherical ring has to be considered, so that the number of energy states dG in the spherical ring is reduced to

$$dG = \frac{1}{8} \frac{4\pi\rho^2 d\rho}{\left(\frac{\hbar^2 \pi^2}{2\mu a^2}\right)^{3/2}} = \frac{\pi}{2} \left(\frac{2\mu a^2}{\hbar^2 \pi^2}\right)^{3/2} \rho^2 d\rho. \quad (1.83)$$

When it comes to calculating the density of states $g(E) = \frac{dG}{dE}$ as a function of energy, the variable ρ is substituted by the variable E by using equation (1.82) and by:

$$d\rho = \frac{1}{2E^{1/2}} dE. \quad (1.84)$$

Consequently, the density of states $g(E)$ is expressed as:

$$g(E) = \frac{dG}{dE} = \frac{a^3}{4\pi^2} \left(\frac{2\mu}{\hbar^2} \right)^{\frac{3}{2}} E^{1/2}. \quad (1.85)$$

The density of states is proportional to the square root of energy (Fig. 1.2c), that is to say to the square root of the sum of the squares of quantum numbers. Furthermore, it is an increasing function of the particle mass and box size and has the dimensions of inverse of energy. More importantly, it represents the number of wave functions per unit of energy between E and $E + dE$. For instance, let us calculate the density of states dG in the energy interval $E \pm \Delta E$ with $\Delta E = 0.01E$ for a classical particle (ion) of mass $\mu (= 2 \cdot 10^{-27} \text{ kg})$ in a cubic box of side $a = 10^{-2} \text{ m}$, at temperature $T = 300 \text{ K}$. The energy $E (= \frac{3}{2} k_B T)$, where $k_B = 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$, is $E \simeq 6 \cdot 10^{-21} \text{ J}$, and the number of energy states is:

$$\begin{aligned} dG &= \frac{a^3}{4\pi^2} \left(\frac{2\mu}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} dE \\ &= \frac{10^{-6}}{4\pi^2} \left[\frac{4 \cdot 10^{-27}}{(1.054 \cdot 10^{-34})^2} \right]^{\frac{3}{2}} (6 \cdot 10^{-21})^{\frac{1}{2}} \frac{6 \cdot 10^{-21}}{100} \simeq 2.5 \cdot 10^{22}. \end{aligned} \quad (1.86)$$

As a result, the degeneracy of a classical particle at room temperature is considerable. However, It should be stressed that the degeneracy of a quantum particle is just slightly lower than that of a classical particle. It is indeed easy to check whether the number of energy states of an electron of mass $\mu = 0.911 \cdot 10^{-30} \text{ kg}$ at the Fermi temperature of 50000 K and under the same conditions as those of the classical particle is a few hundred times lower. Moreover, if $N \simeq 10^{23}$ particles are considered in the cubic box in place of a unique particle, a calculation more complex than the previous one shows that the number of energy states is $dG \simeq 10^N$, i.e. considerably higher than it would be for a single particle.

Among the concepts of quantum mechanics that are useful to statistical mechanics, the size of the smallest volume of phase space available for each energy state should be mentioned too. To assess its dimensions, we associate the number of energy states dG to the volume of the phase space $d\Gamma$. The number of energy states dG is expressed first in terms of momentum p , by eliminating the energy in equation (1.86) with the relation $p^2 = 2\mu E$. It is easy to obtain:

$$dG = \frac{a^3}{4\pi^2\hbar^3} 2p^2 dp = \frac{4\pi a^3 p^2 dp}{h^3}. \quad (1.87)$$

In the case of one particle in a box of volume a^3 , the phase space is a 6-dimensional space, and the volume element $d\Gamma$ of the phase space containing dG energy states is:

$$d\Gamma = \iiint_{\mathbf{p}} d\mathbf{r} \iiint_{\mathbf{p}} d\mathbf{p}, \quad (1.88)$$

because the entire configuration space is occupied by the particle, whereas only the portion of momentum space between $\mathbf{p}$ and $\mathbf{p} + d\mathbf{p}$ is occupied. After integrating over the configuration space ($\iiint d\mathbf{r} = a^3$) and over the portion of momentum space between the spheres of radius p and $p + dp$, the volume of phase space $d\Gamma$ reduces to the expression:

$$d\Gamma = a^3 4\pi p^2 dp. \quad (1.89)$$

Therefore, the smallest volume of phase space available for each energy state has the following value:

$$\frac{d\Gamma}{dG} = \frac{a^3 4\pi p^2 dp}{\frac{4\pi a^3 p^2 dp}{h^3}} = h^3. \quad (1.90)$$

It will be assumed that this result, as demonstrated in the particular case of a particle in a box, is valid in all cases considered.

1.3 The concept of ensembles and probability density

The dynamic state applying to a unique particle with 3 generalized coordinates (r_1, r_2, r_3) and 3 generalized momenta (p_1, p_2, p_3) is represented by a point in the 6-dimensional phase space making it possible

to follow the evolution of the dynamic state of the system [1]. For a system constituted of N classical particles with no internal structure, the Hamiltonian is $H(\mathbf{r}^N, \mathbf{p}^N)$ where $\mathbf{r}^N$ is the $3N$ -dimensional coordinate vector $\mathbf{r}^N (= \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and $\mathbf{p}^N$ the $3N$ -dimensional momentum vector $\mathbf{p}^N (= \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$. As a consequence, the dynamic state of this system can be depicted by a cloud of N points in the 6 dimensional phase space called the *molecular phase space* or μ -space. It is worth noting should that, if only the positions of the particles are specified, the molecular configuration space corresponding to the 3-dimensional ordinary space should be employed. Contrary to this, if only the momenta of the particles are specified the momentum space in 3 dimensions must be used.

However, the dynamic state of a system of N particles can also be represented in the $6N$ -dimensional phase space. In this so-called *gas phase space* or γ -space, the dynamic state of the system is depicted by a single point with the $6N$ -dimensional vector:

$$(\mathbf{r}^N, \mathbf{p}^N) = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N ; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N). \quad (1.91)$$

In the γ -space, the trajectory described by the representative point makes it possible to follow up the evolution of the dynamic state of systems. Knowing the Hamiltonian $H(\mathbf{r}^N, \mathbf{p}^N)$ and the initial conditions (coordinates and momenta of all particles at a given time) can fully design the trajectory of the point that moves in the γ -space according to Hamilton's equations (Eq. 1.35):

$$\dot{r}_i = \frac{\partial H}{\partial p_i}, \quad (1.92)$$

$$\dot{p}_i = -\frac{\partial H}{\partial r_i}, \quad (1.93)$$

where $i = 1, 2, \dots, 3N$. Basically the integration of this system of $6N$ first order differential equations provides the $6N$ solutions $r_i(t)$ and $p_i(t)$ in which the $6N$ constants of integration are determined by the $6N$ initial conditions $r_i(0)$ and $p_i(0)$.

It is worthwhile to note that the point representing the state of the system in the γ -space describes an oriented trajectory which is never repeating the same point. If the trajectory had to be cut, there are two possible paths from the point of intersection, i.e. two separate outcomes for the system under identical initial conditions and this is

impossible. It should nevertheless be mentioned that, if the system consists of a bound particle in which the energy is conserved (as in the linear harmonic oscillator), the representative point in phase space follows the same path when describing a periodic closed curve as in figure (1.1).

It is also important to note the difference between the μ -space and the γ -space by the fact that the dynamic state of the system of N particles is represented by a cloud of N points in the μ -space and a single point in the γ -space. If the particles are *identical*, i.e. *indistinguishable*, it is easy to verify that the permutation of two particles does not change the representation in the μ -space (the cloud of N points remains unchanged) while it provides a different representation in the γ -space (the representative point changes of location) [2]. Since there are $N!$ permutations of the particles, the state of a system of N identical particles is described by a cloud of N points in the μ -space, whereas it is described by a cloud of $N!$ points in the γ -space. As the dimensions of the smaller volume of phase space in 6 dimensions available for each energy state is h^3 (Eq. 1.90), it seems evident that, in the $6N$ -dimensional γ -space, the smallest volume available for each energy state must be h^{3N} . These remarks are of great importance for subsequent applications.

To investigate the behaviour of a real system, Gibbs imagined using a great number of replicas of the system under study in the γ -space, assuming equiprobability and ergodicity¹. All replica of the system have the same volume, the same number of particles and the same type of particles. The replicas are independent of each other, meaning that the positions and momentum coordinates of particles differ from a replica to another at whatever moment. Nevertheless, they lead to the same thermodynamic state, i.e. same temperature, same pressure, same energy... All replicas of the collection, having different microstructures but the same macroscopic state, form a representative ensemble of the state of the system.

As each replica is depicted by a point in the γ -space, the number N_R of replicas form a cloud of N_R points describing their own path. As N_R can be as large as wanted, we can define a *point density* function depending on the positions and momentum coordinates of N particles as well as on time, noted $f(\mathbf{r}^N, \mathbf{p}^N, t)$. Therefore, the number of

¹For the property of ergodicity, see section 9.3.

points contained in the volume element $d\Gamma (= d\mathbf{r}^N d\mathbf{p}^N)$ of γ -space surrounding the point $(\mathbf{r}^N, \mathbf{p}^N)$ is:

$$dN_R = f(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}^N d\mathbf{p}^N. \quad (1.94)$$

Assuming that all the replicas have the same probability to find a given microstructure, the elementary probability of having a replica at random in the volume element $(d\mathbf{r}^N d\mathbf{p}^N)$ is obtained by taking the ratio of the number of replicas dN_R contained in $(d\mathbf{r}^N d\mathbf{p}^N)$ to the total number of replicas N_R :

$$\frac{dN_R}{N_R} = \frac{f(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}^N d\mathbf{p}^N}{\int \int_{6N} f(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}^N d\mathbf{p}^N} = P_N(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}^N d\mathbf{p}^N, \quad (1.95)$$

with $N_R = \int \int_{6N} f(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}^N d\mathbf{p}^N$. According to mathematical statistics, it amounts to define the function $P_N(\mathbf{r}^N, \mathbf{p}^N, t)$, which is a *probability density function* since it is normalized to unity.

1.4 The Liouville theorem

The purpose of this section is to show that the probability density function is conserved over the time, thus resulting in the mathematical form $\frac{d}{dt} P_N(\mathbf{r}^N, \mathbf{p}^N, t) = 0$, namely:

$$\begin{aligned} \frac{d}{dt} P_N(\mathbf{r}^N, \mathbf{p}^N, t) &= \frac{\partial}{\partial t} P_N(\mathbf{r}^N, \mathbf{p}^N, t) \\ &+ \sum_{i=1}^{3N} \left[\frac{\partial P_N(\mathbf{r}^N, \mathbf{p}^N, t)}{\partial r_i} \dot{r}_i + \frac{\partial P_N(\mathbf{r}^N, \mathbf{p}^N, t)}{\partial p_i} \dot{p}_i \right] = 0. \end{aligned} \quad (1.96)$$

The proof of this result – known as the *Liouville theorem* – can be provided by the points density function $f(\mathbf{r}^N, \mathbf{p}^N, t)$ in the γ -space, since, in agreement with equation (1.95), $P_N(\mathbf{r}^N, \mathbf{p}^N, t)$ is proportional to $f(\mathbf{r}^N, \mathbf{p}^N, t)$. To demonstrate that

$$\frac{d}{dt} f = \frac{\partial}{\partial t} f + \sum_{i=1}^{3N} \left[\frac{\partial f}{\partial r_i} \dot{r}_i + \frac{\partial f}{\partial p_i} \dot{p}_i \right] = 0, \quad (1.97)$$

we can call on the hydrodynamic analogy involving a comparison between the motion of points in the γ -space and a fluid in motion [3].

Let us consider an arbitrary volume Γ of the γ -space delimited by a closed hypersurface of area A . The number of points contained in the volume Γ is:

$$N_{\Gamma} = \int_{\Gamma} f(\mathbf{r}^N, \mathbf{p}^N, t) d\Gamma, \quad (1.98)$$

where $d\Gamma = d\mathbf{r}^N d\mathbf{p}^N$. The local variation of N_{Γ} over time (with $\mathbf{r}^N$ and $\mathbf{p}^N$ being given) is:

$$\frac{dN_{\Gamma}}{dt} = \int_{\Gamma} \frac{\partial}{\partial t} f(\mathbf{r}^N, \mathbf{p}^N, t) d\Gamma. \quad (1.99)$$

If there is neither well nor source in the volume Γ , this variation corresponds to the number of points passing through the area A during the time element dt . Now, with the conventional representation of figure (1.2) the number of points contained in the volume element $d\Gamma$ is written as:

$$d^2 N_{\Gamma} = -f \cdot (\mathbf{v} dt) \cdot (\mathbf{n} dA) > 0, \quad (1.100)$$

where $\mathbf{n}$ is the unit vector normal to dA and $\mathbf{v}$ the velocity vector of points in the hypervolume $d\Gamma$ whose components are:

$$\mathbf{v} = (\dot{\mathbf{r}}^N, \dot{\mathbf{p}}^N) = (\dot{r}_1, \dot{r}_2, \dots, \dot{r}_{3N}; \dot{p}_1, \dot{p}_2, \dots, \dot{p}_{3N}). \quad (1.101)$$

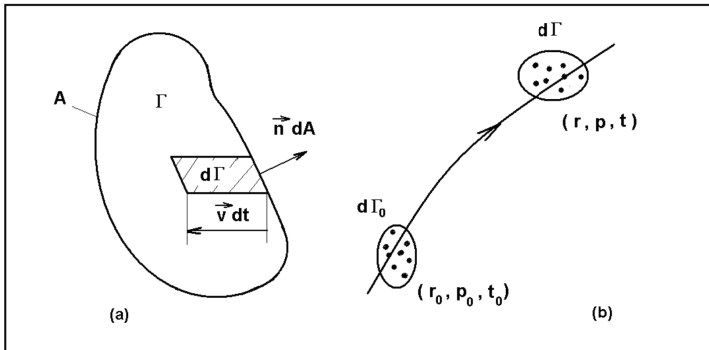


Figure 1.2: (a) Hydrodynamic analogy allowing us to assimilate the motion of points in the γ -space to that of a fluid in motion. (b) Conventional representation of two volume elements $d\Gamma$ and $d\Gamma_0$ of the phase space retained along a path.

Therefore, the number of points crossing the hypersurface of area A during the time dt is provided by the following integral over A :

$$\begin{aligned} dN_\Gamma &= - \oint_A f(\mathbf{v} dt) \cdot (\mathbf{n} dA), \\ \frac{dN_\Gamma}{dt} &= - \oint_A (f\mathbf{v}) \cdot (\mathbf{n} dA). \end{aligned} \quad (1.102)$$

With the theorem of Ostrogradski, the above expression can be transformed into:

$$\frac{dN_\Gamma}{dt} = - \oint_A (f\mathbf{v}) \cdot (\mathbf{n} dA) = - \int_\Gamma \text{div}(f\mathbf{v}) d\Gamma. \quad (1.103)$$

By identifying equations (1.99) and (1.103), we obtain directly:

$$\frac{\partial}{\partial t} f(\mathbf{r}^N, \mathbf{p}^N, t) = -\text{div}(f\mathbf{v}). \quad (1.104)$$

However, equation (1.101), the analytical expression of $\text{div}(f\mathbf{v})$ becomes:

$$\begin{aligned} \text{div}(f\mathbf{v}) &= \sum_{i=1}^{3N} \left[\frac{\partial}{\partial r_i} (f\dot{r}_i) + \frac{\partial}{\partial p_i} (f\dot{p}_i) \right] \\ &= f \sum_{i=1}^{3N} \left[\frac{\partial \dot{r}_i}{\partial r_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] + \sum_{i=1}^{3N} \left[\dot{r}_i \frac{\partial f}{\partial r_i} + \dot{p}_i \frac{\partial f}{\partial p_i} \right]. \end{aligned} \quad (1.105)$$

The expression in brackets in equation (1.105) can also be transformed in terms of the Hamiltonian H , using Hamilton's equations (Eqs. 1.92 and 1.93):

$$\dot{r}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \frac{\partial \dot{r}_i}{\partial r_i} = \frac{\partial^2 H}{\partial r_i \partial p_i}, \quad (1.106)$$

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} \quad \text{and} \quad \frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i \partial r_i}. \quad (1.107)$$

With these relations, the term in the first brackets of equation (1.105) is zero. Then the elimination of $\text{div}(f\mathbf{v})$ between equations (1.104) and (1.105) leads to:

$$\frac{\partial}{\partial t} f(\mathbf{r}^N, \mathbf{p}^N, t) = - \sum_{i=1}^{3N} \left[\dot{r}_i \frac{\partial f}{\partial r_i} + \dot{p}_i \frac{\partial f}{\partial p_i} \right], \quad (1.108)$$

or equivalently:

$$\frac{\partial}{\partial t} f(\mathbf{r}^N, \mathbf{p}^N, t) = - \sum_{i=1}^{3N} \left[\frac{\partial H}{\partial p_i} \frac{\partial f}{\partial r_i} - \frac{\partial H}{\partial r_i} \frac{\partial f}{\partial p_i} \right]. \quad (1.109)$$

When comparing equations (1.108) and (1.97), it appears that $\frac{d}{dt} f = 0$. Consequently, the Liouville theorem states that the points density function $f(\mathbf{r}^N, \mathbf{p}^N, t)$ in the vicinity of a point describing the trajectory in the γ -space does not vary over time. It can be seen in particular that:

$$f(\mathbf{r}^N, \mathbf{p}^N, t) = f(\mathbf{r}_0^N, \mathbf{p}_0^N, 0). \quad (1.110)$$

Another way to interpret the Liouville theorem is to define the *Liouville operator*:

$$\mathcal{L} = i[H,] = i \sum_{i=1}^{3N} \left[\frac{\partial H}{\partial r_i} \frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial}{\partial r_i} \right], \quad (1.111)$$

where i is the symbol of complex numbers and $[H,]$ the *Poisson bracket*, so that equation (1.109) is rewritten with the Liouville operator as:

$$\frac{\partial}{\partial t} f(\mathbf{r}^N, \mathbf{p}^N, t) = \sum_{i=1}^{3N} \left[\frac{\partial H}{\partial r_i} \frac{\partial f}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial f}{\partial r_i} \right] = -i\mathcal{L}f(\mathbf{r}^N, \mathbf{p}^N, t). \quad (1.112)$$

The integration of this equation leads to the formal solution:

$$f(\mathbf{r}^N, \mathbf{p}^N, t) = f(\mathbf{r}^N, \mathbf{p}^N, 0) \exp(-i\mathcal{L}t). \quad (1.113)$$

This expression shows explicitly how the points density function $f(\mathbf{r}^N, \mathbf{p}^N, t)$, i.e. the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N, t)$, evolves over time, for fixed values of $\mathbf{r}^N$ and $\mathbf{p}^N$.

That the Liouville theorem expresses the conservation of the points density function in the γ -space (Eq. 1.113) is not without consequence. Given the equations of motion, the point coordinates $(\mathbf{r}^N, \mathbf{p}^N)$ at the time t must indeed be expressed in terms of the point coordinates $(\mathbf{r}_0^N, \mathbf{p}_0^N)$ at the initial moment. However, the relations between the coordinates $(\mathbf{r}^N, \mathbf{p}^N)$ and $(\mathbf{r}_0^N, \mathbf{p}_0^N)$ require that the volume element $d\Gamma$ is preserved while undergoing a deformation (Fig. 1.3b), that is to say:

$$d\Gamma = d\mathbf{r}^N d\mathbf{p}^N = d\mathbf{r}_0^N d\mathbf{p}_0^N. \quad (1.114)$$

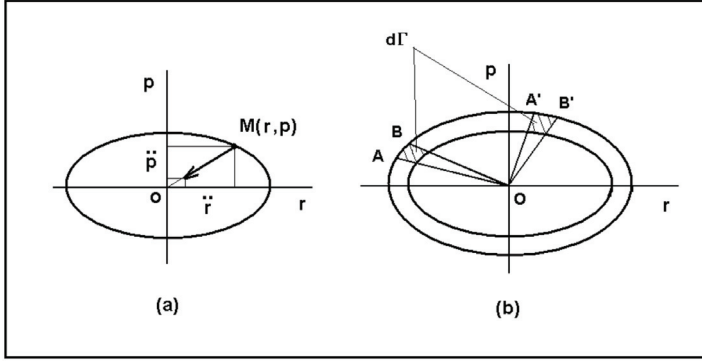


Figure 1.3: Illustration of the invariance of the element of phase extension. (a) Central acceleration motion of the point M , (b) Deformation of the volume element $d\Gamma$.

This finding can be accepted as convincing when considering the result of the linear harmonic oscillator and noting the analogy between the motion of a point M in the phase space and that of a particle describing an ellipse in the plane (r, p) .

Differentiating the equations of Hamilton (Eqs. 1.38 and 1.39) with respect to the time, we obtain $\dot{\vec{r}} = \frac{\dot{p}}{m}$ and $\dot{p} = -k\dot{r}$. Taking account of equation (1.2), the previous relations may be written as:

$$\ddot{r} = -\frac{k}{m}r, \quad (1.115)$$

$$\ddot{p} = -\frac{k}{m}p. \quad (1.116)$$

These relations show that the components of the acceleration of the point M are in the same ratio as its coordinates ($\frac{\ddot{r}}{\ddot{p}} = \frac{r}{p}$). It follows that the acceleration vector of the point M passes through the fixed point O and the movement of M is a central acceleration motion (Fig. 1.3). Such a motion is governed by the law of areas (Kepler's second law) which states that the areas swept by the radius vector is proportional to the time (Fig. 1.3). If Δt is the time taken for the radii OA and OA' to move to OB and OB' , respectively, the shaded regions have the same area resulting in the invariance of the volume element $d\Gamma$ of phase space in spite of being distorted.

The conservation of the volume element $d\Gamma$ can be demonstrated rigorously on the basis of the change of variables $(\mathbf{r}^N, \mathbf{p}^N)$ and $(\mathbf{r}_0^N, \mathbf{p}_0^N)$ noted symbolically:

$$r = r(r_0, p_0, t), \quad (1.117)$$

$$p = p(r_0, p_0, t). \quad (1.118)$$

The calculation (not reproduced here) shows that the Jacobian $J = \frac{D(r,p)}{D(r_0,p_0)}$ of the previous transformation is equal to unity and this certifies the invariance of the volume element $d\Gamma$. Actually, this property follows from the fact that space coordinates $\mathbf{r}^N$ and momentum coordinates $\mathbf{p}^N$ are conjugate to each other. It would not be true if the velocities were used instead of the momentum coordinates.

Note to illustrate this remark that the transformation of the volume element $dx dy dz$ (Cartesian coordinates) into $dr d\theta d\varphi$ (spherical coordinates) in ordinary space is made with the formula:

$$dx dy dz = |J| dr d\theta d\varphi, \quad (1.119)$$

where the Jacobian is equal to $|J| = r^2 \sin \theta$. This expression shows that the volume element in spherical coordinates is not equal to the volume element in Cartesian coordinates. If the dynamic state of one particle in the 6-dimensional phase space is taken into account, we note on the contrary that the volume element $d\Gamma$ is preserved during the transformation from the Cartesian coordinates into the spherical coordinates:

$$d\Gamma = dx dy dz dp_x dp_y dp_z = |J| dr d\theta d\varphi dp_r dp_\theta dp_\varphi, \quad (1.120)$$

because here $|J| = 1$, as it could be straightforwardly verified.

In summary, it has been shown that the points density function is conserved in the immediate vicinity of a point moving in the γ -space, $f(\mathbf{r}^N, \mathbf{p}^N, t) = f(\mathbf{r}_0^N, \mathbf{p}_0^N, t_0)$, and this also applies to the volume element $d\Gamma = d\Gamma_0$. Consequently, the dN_R points contained in the initial volume $d\Gamma_0$ are kept in the volume $d\Gamma$ during the evolution of the system, without any loss or gain, that is to say:

$$dN_R = f(\mathbf{r}^N, \mathbf{p}^N, t) d\Gamma = f(\mathbf{r}_0^N, \mathbf{p}_0^N, t_0) d\Gamma_0. \quad (1.121)$$

1.5 Postulates of statistical mechanics

The Liouville equation is a general equation appropriate to follow the behaviour of systems both in equilibrium and out-of-equilibrium considering that once the probability density function is known at the initial moment, it can be calculated at a later time by the equations of motion. However, if we are only interested in the properties of systems in equilibrium, the probability density function does not depend explicitly on the time, and the Liouville equation (Eq. 1.108) is reduced to:

$$\frac{\partial}{\partial t} P_N(\mathbf{r}^N, \mathbf{p}^N) = 0. \quad (1.122)$$

In practical applications, the issue is the calculation of thermodynamic quantities of systems based on the dynamical variables of particles. The property G can be written, in principle, in terms of $\mathbf{r}^N(t)$ and $\mathbf{p}^N(t)$, and its value calculated by using the *time average* between the initial time t_0 and time $t_0 + \tau$, namely:

$$G_t = \overline{G} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} G[\mathbf{r}^N(t), \mathbf{p}^N(t)] dt. \quad (1.123)$$

A priori, G_t depends on the dynamical variables $\mathbf{r}^N(t)$ and $\mathbf{p}^N(t)$ as well as the time interval τ over which the integration is performed. It is worth noting the essential difference existing between information contained in the dynamical (or microscopic) variables and those provided by the thermodynamic (or macroscopic) properties [4]. The dynamical variables are able to calculate the macroscopic state of the system whereas the knowledge of the thermodynamic properties does not permit the determination of the dynamical variables (positions and momentum coordinates of particles).

In the simplest case of a perfectly isolated system (constant energy), the integral in equation (1.123) can be evaluated from the law of variation of $G[\mathbf{r}^N(t), \mathbf{p}^N(t)]$ with the $6N$ solutions $\mathbf{r}^N(t)$ and $\mathbf{p}^N(t)$ obtained by solving Hamilton's equations owing to the given $6N$ initial conditions. However, a rapid calculation shows that the initial conditions are useless. Indeed, if the system contains $N \simeq 10^{23}$ particles and that we are able to afford to count the initial conditions at 1000 per second, it would take 10^{20} seconds or 10^{13} years, which is unimaginable. It seems that, even in the simple case where the system is perfectly isolated, the task is hopeless. The problem becomes more

complicated with a non-isolated system as the point $[\mathbf{r}^N(t), \mathbf{p}^N(t)]$ of the γ -space passes from a trajectory of constant energy to another, and the time necessary to perform the calculations is unthinkable.

A way to get out of the deadlock is to perform a numerical simulation of the actual experiment. For that purpose, a limited number of particles is considered and the equations of motion are separated in order to follow step by step the evolution of the system along the phase space trajectory by using a computer. With $N \sim 1000$ as a number of particles, the computer is able to count and calculate the positions and momenta of particles within about 10^{-13} seconds, making it possible to monitor the evolution of the system in a time record by solving the equations of motion by the finite difference method. In practice, the simulation begins with the *initialization phase* during which initial values to the positions and momenta of all particles are assigned. The calculation continues with the *thermalization phase* during which the system reaches the equilibrium. Then the simulation ends with the *production phase* of duration τ , during which the coordinates and moments of all particles are sampled and stored in computer files for subsequent statistical processing. For instance, the average of the pressure can be computed in this way, by using the formula of the kinetic theory of gases:

$$pV = \frac{N}{3m} \sum_{i=1}^N |\mathbf{p}_i(t)|^2. \quad (1.124)$$

The time average of the temperature can also be calculated with the integral on the time:

$$T_t = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} T[\mathbf{p}^N(t)] dt, \quad (1.125)$$

where $T[\mathbf{p}^N(t)]$ is provided by the law of equipartition of energy:

$$\frac{3}{2} k_B T[\mathbf{p}^N(t)] = \frac{1}{2Nm} \sum_{i=1}^N |\mathbf{p}_i(t)|^2. \quad (1.126)$$

The result is a function of the initial state $[\mathbf{r}_0^N(t), \mathbf{p}_0^N(t)]$ and its validity depends on the amplitude of temperature fluctuations. This is why the thermalization and production periods, as well as the time intervals useful to the numerical solution, have to be carefully chosen.

Apart from the numerical simulation, the macroscopic property G can also be calculated by using an indirect method proposed by Gibbs for very large systems where ergodicity is allowed. It is assumed in this method that the *time average* G_t is equal to the *ensemble average* G_e :

$$G_e = \langle G \rangle = \int \int_{6N} G [\mathbf{r}^N(t), \mathbf{p}^N(t)] P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N. \quad (1.127)$$

For example, the calculation of the mean energy is carried out with the Hamiltonian $H [\mathbf{r}^N(t), \mathbf{p}^N(t)]$ by using the expression:

$$E = \int \int_{6N} H [\mathbf{r}^N(t), \mathbf{p}^N(t)] P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N. \quad (1.128)$$

This constitutes the *first postulate of statistical mechanics*. It is of great importance as it shows that any macroscopic property can be calculated as soon as the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ is known. The equivalence between the time average and ensemble average, $G_t \equiv G_e$, does not flow naturally. Although few systems are truly ergodic, the principle of equivalence between the time average and ensemble average is applied without restriction as a consequence of the assumption of quasi-ergodicity [5].

For the calculations of statistics mechanics to be carried out, it is necessary to find an expression for the probability density function. The *second postulate* states that the probability density function depends on the Hamiltonian of the system, $P_N [H(\mathbf{r}^N, \mathbf{p}^N)]$. As regards its expression, it depends on the choice of the ensemble used to represent the state of the system. Three types of ensembles are generally used: the *microcanonical ensemble* for isolated systems tolerating no exchanges, the *canonical ensemble* permitting exchanges of energy but not of particles, and the *grand canonical ensemble* used for open systems making exchanges of energy and matter possible.

2 Derivation of the ensemble equations

As mentioned above, the *second postulate of statistic mechanics* states that the probability density function depends on the Hamiltonian of the system, $P_N [H(\mathbf{r}^N, \mathbf{p}^N)]$. The three types of ensembles presented in this chapter are commonly used. The *microcanonical ensemble* is applied to close isothermal systems, where no exchange of matter and energy are allowed. The *canonical ensemble* is applied to close isothermal systems where energy but not particles can be exchanged. The *grand canonical ensemble* is applied to open systems with exchanges of energy and matter while the chemical potential (energy per particle) is constant.

In this chapter, we are concerned primarily with the connection between the microscopic mechanical properties of molecules (molecular behaviour of the system) and macroscopic laws predicting simple equilibrium properties of any chemical system known over wide ranges of pressure and temperature. For the purpose, the molecular behaviour of systems is taken into account through the canonical ensemble used as reference system. This first general treatment to express the thermodynamic properties forms one of the most fascinating objects of the statistical mechanics developed by Gibbs. The chapter ends with the definition of the thermodynamic fluctuations, a topic not devoid of interest as the presence of fluctuations makes it possible to highlight the existence of some phenomena experimentally detected.

2.1 Probability density functions

The microcanonical ensemble

The microcanonical ensemble is used to examine the adiabatically isolated closed systems, where no exchange of matter and energy is permitted. The values of N and E are strictly defined. As the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ is a function of the Hamiltonian $H(\mathbf{r}^N, \mathbf{p}^N)$, it makes sense that $P_N(\mathbf{r}^N, \mathbf{p}^N)$ has a maximum value at the precise value of $H(\mathbf{r}^N, \mathbf{p}^N) = E$. This can lead formally to the mathematical expression:

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{C(E)} \delta [H(\mathbf{r}^N, \mathbf{p}^N) - E] , \quad (2.1)$$

where δ is the Dirac function¹ and $C(E)$ a normalization factor depending on the energy E and external parameters that are characteristics of the thermodynamic state of the system. The normalization condition of the probability density, $\int \int P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N = 1$, allows us to write:

$$C(E) = \int \int \delta [H(\mathbf{r}^N, \mathbf{p}^N) - E] d\mathbf{r}^N d\mathbf{p}^N. \quad (2.2)$$

Although the Dirac function is justified exclusively for an adiabatic system whose energy is exactly equal to E , the microcanonical ensemble can nevertheless be used for real systems whose energy fluctuates on a very narrow range ($E \pm \frac{\Delta E}{2}$). For such systems, the ensemble average (Eq. 1.127) of the thermodynamic property G is calculated with the relation:

¹The Dirac function $\delta(x)$ has an infinite value at $x = 0$ and zero value when $x \neq 0$. It is not defined by its form but by the following integrals:

$$\int_{-\infty}^{\infty} \delta(x) dx = 1$$

and

$$\int_{-\infty}^{\infty} \delta(x - a) f(x) dx = f(a).$$

The first property shows that the Dirac function is a distribution within the meaning of mathematical statistics.

$$G_e = \frac{1}{C(E)} \iint_{6N} G[\mathbf{r}^N(t), \mathbf{p}^N(t)] \delta[H(\mathbf{r}^N, \mathbf{p}^N) - E] d\mathbf{r}^N d\mathbf{p}^N. \quad (2.3)$$

To better understand the role of the normalization factor $C(E)$, we calculate the integral in equation (2.2) on the interval of energy between $(E - \frac{\Delta E}{2})$ and $(E + \frac{\Delta E}{2})$. This gives:

$$\int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} C(\varepsilon) d\varepsilon = \int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} \left[\iint_{6N} \delta[H(\mathbf{r}^N, \mathbf{p}^N) - \varepsilon] d\mathbf{r}^N d\mathbf{p}^N \right] d\varepsilon. \quad (2.4)$$

Since ΔE is small, the left side of the equation above is approximately equal to $C(E)\Delta E$. As far as the right side is concerned, it can again be written as follows after permutation of the integrals:

$$\begin{aligned} & \iint_{6N} \left[\int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} \delta[H(\mathbf{r}^N, \mathbf{p}^N) - \varepsilon] d\varepsilon \right] d\mathbf{r}^N d\mathbf{p}^N \\ &= \int \int_{\{H(\mathbf{r}^N, \mathbf{p}^N) \in [E - \frac{\Delta E}{2}, E + \frac{\Delta E}{2}]\}} d\mathbf{r}^N d\mathbf{p}^N, \end{aligned} \quad (2.5)$$

because $\int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} \delta[H(\mathbf{r}^N, \mathbf{p}^N) - \varepsilon] d\varepsilon = 1$ when $\varepsilon = H(\mathbf{r}^N, \mathbf{p}^N) \in [E - \frac{\Delta E}{2}, E + \frac{\Delta E}{2}]$. Therefore, equation (2.4) is reduced to:

$$C(E)\Delta E = \int \int_{\{H(\mathbf{r}^N, \mathbf{p}^N) \in [E - \frac{\Delta E}{2}, E + \frac{\Delta E}{2}]\}} d\mathbf{r}^N d\mathbf{p}^N. \quad (2.6)$$

The quantity $C(E)\Delta E$ corresponds to the volume portion of the γ -space between the hypersurfaces of energy $(E - \frac{\Delta E}{2})$ and $(E + \frac{\Delta E}{2})$.

Let us continue the discussion of the microcanonical ensemble in order to justify the equivalence between the time average and ensemble average. To this end, consider again the special case of the linear harmonic oscillator for which the Hamiltonian (Eq. 1.42) is:

$$H(r, p) = E = \frac{1}{2} \left(m\omega^2 r^2 + \frac{p^2}{m} \right), \quad (2.7)$$

where $r = \frac{1}{\omega} \sqrt{\frac{2E}{m}} \cos \omega t$ and $p = -\sqrt{2mE} \sin \omega t$. As the harmonic oscillator is an isolated system where the energy E is fixed, it is possible to calculate the ensemble average of any function G by using the probability density function for the microcanonical ensemble, namely:

$$G_e = \frac{1}{C(E)} \iint G[r(t), p(t)] \delta[H(r, p) - E] dr dp. \quad (2.8)$$

As has been done for equation (2.4), we calculate the following integral over the energy domain between $(E - \frac{\Delta E}{2})$ and $(E + \frac{\Delta E}{2})$. It yields:

$$\int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} G_e C(\varepsilon) d\varepsilon = \iint G[r(t), p(t)] \left[\int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} \delta[H(r, p) - \varepsilon] d\varepsilon \right] dr dp, \quad (2.9)$$

that is to say:

$$G_e = \lim_{\Delta E \rightarrow 0} \frac{1}{C(E)\Delta E} \iint_{\{H(r, p) \in [E - \frac{\Delta E}{2}, E + \frac{\Delta E}{2}]\}} G[r(t), p(t)] dr dp, \quad (2.10)$$

where the quantity $C(E)\Delta E$ corresponds to the area between the two ellipses of equations $H(r, p) = E - \frac{\Delta E}{2}$ and $H(r, p) = E + \frac{\Delta E}{2}$.

From Figure 2.1(a), where the semi-axes of the large ellipse are $a = \frac{1}{\omega} \sqrt{\frac{2(E + \frac{\Delta E}{2})}{m}}$ and $b = \sqrt{2m(E + \frac{\Delta E}{2})}$, and the semi-axes of the small ellipse are $a' = \frac{1}{\omega} \sqrt{\frac{2(E - \frac{\Delta E}{2})}{m}}$ and $b' = \sqrt{2m(E - \frac{\Delta E}{2})}$, we notice that the area of the shaded crown $\pi(ab - a'b')$ is written explicitly:

$$\begin{aligned} C(E)\Delta E &= \pi \left[\frac{1}{\omega} \sqrt{\frac{2(E + \frac{\Delta E}{2})}{m}} \sqrt{2m \left(E + \frac{\Delta E}{2} \right)} \right. \\ &\quad \left. - \frac{1}{\omega} \sqrt{\frac{2(E - \frac{\Delta E}{2})}{m}} \sqrt{2m \left(E - \frac{\Delta E}{2} \right)} \right] = \frac{2\pi}{\omega} \Delta E. \end{aligned} \quad (2.11)$$

By replacing the quantity $C(E)\Delta E$ by its expression in equation (2.10), we obtain:

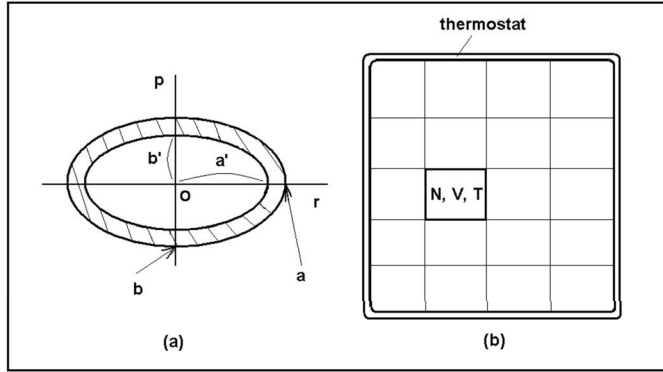


Figure 2.1: (a) Representation of the quantity $C(E)\Delta E$ in the γ -space of the linear harmonic oscillator. The meaning of the parameters a , a' , b and b' is given in the text. (b) Schematic representation of the canonical ensemble consisting of N_S identical subsystems, specified by the same values of N , V and T .

$$G_e = \lim_{\Delta E \rightarrow 0} \frac{\omega}{2\pi \Delta E} \int \int_{\{H(r,p) \in [E - \frac{\Delta E}{2}, E + \frac{\Delta E}{2}]\}} G[r(t), p(t)] dr dp. \quad (2.12)$$

As the harmonic oscillator has a periodic motion of period $T = \frac{2\pi}{\omega}$, it is possible to calculate the time average of $G[r(t), p(t)]$ with the relation:

$$G_t = \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} G[r(t), p(t)] dt. \quad (2.13)$$

Without changing the value of G_t , we evaluate its mean value over the energy domain between $(E - \frac{\Delta E}{2})$ and $(E + \frac{\Delta E}{2})$ according to the expression:

$$\int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} G_t d\varepsilon = \int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} \left[\frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} G[r(t), p(t)] dt \right] d\varepsilon, \quad (2.14)$$

hence:

$$G_t = \lim_{\Delta E \rightarrow 0} \frac{1}{\Delta E} \int_{E - \frac{\Delta E}{2}}^{E + \frac{\Delta E}{2}} \left[\frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} G[r(t), p(t)] dt \right] d\varepsilon. \quad (2.15)$$

Finally, we transform the integral over t and ε into an integral over r and p by the change of variables $r = \frac{1}{\omega} \sqrt{\frac{2E}{m}} \cos \omega t$ and $p = -\sqrt{2mE} \sin \omega t$ whose the Jacobian is:

$$\frac{\partial(r, p)}{\partial(E, t)} = \begin{vmatrix} -\sqrt{\frac{2E}{m}} \sin \omega t & \frac{1}{2\omega} \sqrt{\frac{2}{mE}} \cos \omega t. \\ -\omega \sqrt{2mE} \cos \omega t & -\frac{1}{2} \sqrt{\frac{2m}{E}} \sin \omega t \end{vmatrix} = 1. \quad (2.16)$$

After this change of variables, equation (2.15) takes the following form:

$$G_t = \lim_{\Delta E \rightarrow 0} \frac{1}{\Delta E} \frac{\omega}{2\pi} \int \int_{\{H(r, p) \in [E - \frac{\Delta E}{2}, E + \frac{\Delta E}{2}]\}} G[r(t), p(t)] dr dp, \quad (2.17)$$

where the integral is extended to the portion of the γ -space between the energy curves $(E - \frac{\Delta E}{2})$ and $(E + \frac{\Delta E}{2})$. By identifying equations (2.17) and (2.12), we find that the time average G_t coincides with the ensemble average G_e .

The canonical ensemble

In practice, the closed systems are more frequently isolated thermally than adiabatically. Concerning thermally isolated systems, the energy E is likely to vary and the microcanonical ensemble is not appropriate. In this case, the canonical ensemble should be used to be applied to closed systems where temperature T and particle number N remain constant while the energy E varies.

From the microscopic point of view, the canonical ensemble is defined by a collection of N_S systems with same volume V and same temperature T , each of them containing the same number of particles N . To ensure that the temperature is the same in all systems, we imagine that the N_S systems are placed in a thermostatic reservoir called the *supersystem*. The N_S systems with unknown internal structure are separated by walls that allow the transfers of heat but prevent the exchanges of matter (Fig. 2.1b). It is assumed that the supersystem is composed of the system studied (which is one of the N_S systems) and of the thermostat composed of the $(N_S - 1)$ other systems. Thus, for each system taken separately, the role of the thermostat is exercised by a set of systems that surround it.

The dynamic state of the system composed of N particles and currently under study is described in the γ -space by the vector $(\mathbf{r}^N, \mathbf{p}^N)$

whereas the thermostat composed of $M = (N_S - 1)N$ particles is described by the vector $(\mathbf{r}^M, \mathbf{p}^M)$. Logically, it can only be assumed that $M \gg N$ and $H_M(\mathbf{r}^M, \mathbf{p}^M) \gg H_N(\mathbf{r}^N, \mathbf{p}^N)$. Furthermore, it can be inferred that the supersystem is closed and isolated adiabatically, that is to say that the energy $E = H(\mathbf{r}^M, \mathbf{p}^M; \mathbf{r}^N, \mathbf{p}^N)$ is equal to the sum of the energies of the system studied and the thermostat, plus the interaction energy U_{int} between both entities. However, although the interaction energy is necessary to ensure the transfers of heat between the studied system and the thermostat, it is assumed to be considerably smaller than the energy of the supersystem so that $H_M(\mathbf{r}^M, \mathbf{p}^M) \gg H_N(\mathbf{r}^N, \mathbf{p}^N) \gg U_{int}$. This assumption is plausible because the energies of both entities are proportional to the volume, while the interaction energy is proportional to the surface of contact between the two entities. Therefore, one can approximately write:

$$H(\mathbf{r}^M, \mathbf{p}^M; \mathbf{r}^N, \mathbf{p}^N) \simeq H_M(\mathbf{r}^M, \mathbf{p}^M) + H_N(\mathbf{r}^N, \mathbf{p}^N). \quad (2.18)$$

If it is accepted that the supersystem is isolated adiabatically, the microcanonical distribution and its probability density function can be employed (Eq. 2.1), namely:

$$P_{M+N}(\mathbf{r}^M, \mathbf{p}^M; \mathbf{r}^N, \mathbf{p}^N) = \frac{1}{C(E)} \delta [H(\mathbf{r}^M, \mathbf{p}^M; \mathbf{r}^N, \mathbf{p}^N) - E] . \quad (2.19)$$

By evaluating the integral of the above relation over the domain of variation of variables $\mathbf{r}^M$ and $\mathbf{p}^M$, one obtains the probability density function for the system under study in the following form²:

$$\begin{aligned} P_N(\mathbf{r}^N, \mathbf{p}^N) &= \int \int_{6M} P_{M+N}(\mathbf{r}^M, \mathbf{p}^M; \mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^M d\mathbf{p}^M \\ &= \frac{1}{C(E)} \int \int_{6M} \delta [H(\mathbf{r}^M, \mathbf{p}^M; \mathbf{r}^N, \mathbf{p}^N) - E] d\mathbf{r}^M d\mathbf{p}^M , \end{aligned} \quad (2.20)$$

so that, after having replaced $H(\mathbf{r}^M, \mathbf{p}^M; \mathbf{r}^N, \mathbf{p}^N)$ by using equation (2.18), we arrive at:

²See the probability density function for random variables (Eq. 2.139).

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{C(E)} \iint_{6M} \delta [H_N(\mathbf{r}^N, \mathbf{p}^N) + E_M - E] d\mathbf{r}^M d\mathbf{p}^M, \quad (2.21)$$

with $E_M = H_M(\mathbf{r}^M, \mathbf{p}^M)$.

Naturally, the integral of equation (2.21) with the dynamical variables $(\mathbf{r}^M, \mathbf{p}^M)$ can be replaced by an integral over the energy E_M extended to the domain of the γ -space between the energy hypersurfaces $H_M(\mathbf{r}^M, \mathbf{p}^M) = E_M - \frac{\Delta E_M}{2}$ and $H_M(\mathbf{r}^M, \mathbf{p}^M) = E_M + \frac{\Delta E_M}{2}$. Before continuing the search for the expression of the probability density function for the canonical ensemble, return briefly to the relationship linking energy E_M with dynamical variables $(\mathbf{r}^M, \mathbf{p}^M)$ of the thermostat. When considering equation (2.6), we see that the domain of the γ -space containing the energy states between $(E_M - \frac{\Delta E_M}{2})$ and $(E_M + \frac{\Delta E_M}{2})$, and noted $\Gamma_M(E_M)$ reads equally:

$$\begin{aligned} \Gamma_M(E_M) &= \iint \left\{ H(\mathbf{r}^M, \mathbf{p}^M) \in \left[E_M - \frac{\Delta E_M}{2}, E_M + \frac{\Delta E_M}{2} \right] \right\} d\mathbf{r}^M d\mathbf{p}^M, \\ &= \int_{E_M - \frac{\Delta E_M}{2}}^{E_M + \frac{\Delta E_M}{2}} C_M(\varepsilon) d\varepsilon = C_M(E_M) \Delta E_M. \end{aligned} \quad (2.22)$$

By using equations (2.22) and (2.22), it is possible to transform the integral over the dynamical variables of the thermostat (Eq. 2.21) into an integral over the energy as follows:

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{C(E)} \int_{E_M - \frac{\Delta E_M}{2}}^{E_M + \frac{\Delta E_M}{2}} \delta [H_N(\mathbf{r}^N, \mathbf{p}^N) + \varepsilon - E] C_M(\varepsilon) d\varepsilon, \quad (2.23)$$

with $\varepsilon = E_M$.

Probability density function for the canonical ensemble

The last thing to be done is to obtain the function $C_M(\varepsilon)$ characterizing the thermostat. To calculate $C_M(\varepsilon)$, the thermostat is assigned to a system of $M = (N_S - 1)N$ identical particles of mass m , so that the energy of the thermostat is:

$$H_M(\mathbf{r}^M, \mathbf{p}^M) = E_M = \frac{1}{2m} \sum_{i=1}^M (p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2) + E_{pot}. \quad (2.24)$$

Without affecting the generality, suppose that the particles are free, in other words that the potential energy of interaction E_{pot} is zero and the energy E_M is formed alone by the kinetic energy $\frac{1}{2m} \sum_{i=1}^M (p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2)$. Then, if the reduced variables $P_x = \frac{p_x}{\sqrt{2m\varepsilon}}, \dots$ are used, the volume elements in the 3-dimensional μ -space and in the $3M$ -dimensional γ -space are respectively:

$$d\mathbf{P} = dP_x dP_y dP_z = \frac{dp_x}{\sqrt{2m\varepsilon}} \frac{dp_y}{\sqrt{2m\varepsilon}} \frac{dp_z}{\sqrt{2m\varepsilon}}, \quad (2.25)$$

or equivalently:

$$d\mathbf{P} = \frac{d\mathbf{p}}{(2m\varepsilon)^{\frac{3}{2}}} \quad \text{and} \quad d\mathbf{P}^M = \frac{d\mathbf{p}^M}{(2m\varepsilon)^{\frac{3M}{2}}}. \quad (2.26)$$

With these reduced variables, the expression of the energy is written:

$$E_M = \frac{2m\varepsilon}{2m} \sum_{i=1}^M (P_{x_i}^2 + P_{y_i}^2 + P_{z_i}^2), \quad (2.27)$$

and the volume $\Gamma_M(\varepsilon)$ defined by equation (2.22) becomes:

$$\Gamma_M(\varepsilon) = \int \int_{3M} d\mathbf{r}^M \int \int_{3M} (2m\varepsilon)^{\frac{3M}{2}} d\mathbf{P}^M. \quad (2.28)$$

In addition to that, if we pose $V^M = \int \int_{3M} d\mathbf{r}^M$, $C_M(\varepsilon)$ whose definition is given by equation (2.22) can be determined by taking the derivative of equation (2.28) with respect to ε . It yields:

$$C_M(\varepsilon) = \frac{d\Gamma_M(\varepsilon)}{d\varepsilon} = V^M \frac{3M}{2} (2m)^{\frac{3M}{2}} \varepsilon^{\frac{3M}{2}-1} \int \int_{3M} d\mathbf{P}^M = B\varepsilon^\sigma, \quad (2.29)$$

where $B = \frac{3M}{2} (2m)^{\frac{3M}{2}} V^M \int \int_{3M} d\mathbf{P}^M$ and $\sigma = \frac{3M}{2} - 1$ are two constants depending only on the thermostat.

By substituting $C_M(\varepsilon)$ in equation (2.23) and taking into account the property of the Dirac function, the probability density function for the system studied takes the following form:

$$\begin{aligned} P_N(\mathbf{r}^N, \mathbf{p}^N) &= \frac{1}{C(E)} \int_{E_M - \frac{\Delta E_M}{2}}^{E_M + \frac{\Delta E_M}{2}} \delta [H_N(\mathbf{r}^N, \mathbf{p}^N) + \varepsilon - E] B \varepsilon^\sigma d\varepsilon \\ &= \frac{B}{C(E)} [E - H_N(\mathbf{r}^N, \mathbf{p}^N)]^\sigma. \end{aligned} \quad (2.30)$$

It should be noted that an increase in the size of the thermostat ($M \rightarrow \infty$ and $E_M \rightarrow \infty$) implies that $\sigma \rightarrow \infty$. In relation to this, when the energy of the thermostat E_M tends to infinity, the same applies to the supersystem ($E \rightarrow \infty$). However, at this stage of the study, it can be assumed that the ratio $\frac{\sigma}{E}$ remains constant, i.e. the *thermodynamic limit* determined as $\lim_{E \rightarrow \infty} \frac{\sigma}{E} = \beta$ when σ and E tend to infinity. This assumption makes it possible to transform the probability density function for the canonical ensemble into:

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \lim_{\sigma \rightarrow \infty} \frac{B}{C(E)} E^\sigma \left[1 - \frac{\beta H_N(\mathbf{r}^N, \mathbf{p}^N)}{\sigma} \right]^\sigma. \quad (2.31)$$

Consequently, by using the Taylor expansion of the exponential³, the probability density function can be deduced as:

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \lim_{\sigma \rightarrow \infty} \frac{B}{C(E)} E^\sigma \exp [-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)]. \quad (2.32)$$

The probability density function for the canonical ensemble is traditionally called the *Gibbs distribution* when written as:

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{N! h^{3N} Q_N(V, T)} \exp [-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)]. \quad (2.33)$$

The term $N!$, introduced intuitively by Gibbs, refers to the need to take into account the indistinguishability of classical particles – see the difference between the μ -space and γ -space in section (1.3). We will see in the next chapter that the term $N!$ ensures the additivity of entropy and eliminates the Gibbs paradox. The term h^{3N} corresponds

³ $\exp(-\alpha) = \lim_{\sigma \rightarrow \infty} (1 - \frac{\alpha}{\sigma})^\sigma$.

to the smallest volume measurable of the γ -space. It is used because it is not necessary to list the dynamic states contained in cells of the γ -space whose dimensions are less than h^{3N} . Furthermore, its presence is necessary to ensure that the probability is a dimensionless function. As far as the so-called *partition function* $Q_N(V, T)$ is concerned, it is defined by the normalization condition of the probability density function $\int \int_{6N} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N = 1$ leading to:

$$Q_N(V, T) = \frac{1}{N!h^{3N}} \int \int_{6N} \exp [-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N. \quad (2.34)$$

The identification of equations (2.32) and (2.33) shows that the partition function $Q_N(V, T)$ is directly linked to the quantities B , $C(E)$ and E^σ by the following relation:

$$Q_N(V, T) = \frac{1}{N!h^{3N}} \lim_{\sigma \rightarrow \infty} \frac{C(E)}{B} \frac{1}{E^\sigma}. \quad (2.35)$$

As the quantities entering the partition function characterize mainly the thermostat, we understand why the partition function $Q_N(V, T)$ depends on the temperature T of the thermostat, in addition to the volume V and particle number N of the system under study. It can be noted in passing that, when ignoring the mutual interaction energy U_{int} between the system studied and the thermostat, the system is characterized by the canonical distribution, whereas the supersystem (consisting of the studied system and the thermostat) is characterized by the microcanonical distribution.

The grand canonical ensemble

To define the grand canonical ensemble we suppose that the system is in equilibrium with the thermostat and has a variable number of particles. Indeed, the particle number can vary, either because of the exchange of particles with other systems or because of the particles generated. As an example, the photon gas contained in an enclosure has a number of photons varying on the temperature (unlike conventional gas) due to the emission and absorption of radiations by the walls of the enclosure.

To simplify the calculations, let us suppose that it is composed of a single species of particles. In this case, the canonical distribution

(Eq. 2.33) can be used to examine the system in which the number of particles N could be fixed beforehand. Considering that the number of particles is varying, its dependence appears explicitly in the partition function. The usual way to write the probability density function for the grand canonical ensemble is:

$$P(N, \mathbf{r}^N, \mathbf{p}^N) = \frac{1}{N!h^{3N}\Xi} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N) + \beta\mu N], \quad (2.36)$$

where μ is the chemical potential and Ξ the partition function for the grand canonical ensemble replacing the partition function $Q_N(V, T)$ of the canonical ensemble. It is worth noticing that Ξ and $Q_N(V, T)$ are connected by a simple relationship obtained by applying the normalization condition to the probability density function. Given that the number of particles in the system can vary from zero to infinity, the normalization condition reads:

$$\sum_{N=0}^{\infty} \frac{1}{N!h^{3N}\Xi} \iint_{6N} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N) + \beta\mu N] d\mathbf{r}^N d\mathbf{p}^N = 1. \quad (2.37)$$

The previous relation makes it possible to express the partition function Ξ in terms of the partition function $Q_N(V, T)$ by using equation (2.34) as follows:

$$\begin{aligned} \Xi &= \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \exp(\beta\mu N) \iint_{6N} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N \\ &= \sum_{N=0}^{\infty} \exp(\beta\mu N) Q_N(V, T). \end{aligned} \quad (2.38)$$

As regards the probability of finding the system with exactly N particles, irrespective of their positions and momenta, it is determined by integrating the probability density function (Eq. 2.36) in relation to the positions and momenta:

$$\begin{aligned} P(N) &= \int \int_{6N} P(N, \mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \\ &= \frac{\exp(\beta\mu N)}{\Xi} \frac{1}{N!h^{3N}} \int \int_{6N} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N. \end{aligned} \quad (2.39)$$

When combined with equation (2.34), this relation reduces to:

$$P(N) = \frac{\exp(\beta\mu N)}{\Xi} Q_N(V, T). \quad (2.40)$$

2.2 The laws of thermodynamics

Thermodynamics is based on two laws. The first law establishes the equivalence between work and heat by means of the *internal energy* function. The second law of thermodynamics states the relationship between heat and temperature using the *entropy* function⁴. Among other things, an important issue of the classical thermodynamics is the equilibrium of systems. This requires using other functions to characterize the thermodynamic states such as the *enthalpy* and *free energy*. Another interesting question is the processes occurring in physicochemical systems with multiple constituents that involve the *partial molar* functions and *chemical potential*.

Preliminaries

Equilibrium, reversibility. A system is in *equilibrium* when its composition and thermodynamic properties do not vary over time. In a system in equilibrium, a slight variation of an equilibrium factor causes a change in the system with the same order of magnitude. Moreover, if the variation of the equilibrium factor changes sign, the modification of the system state changes direction. In contrast, if a slight variation of equilibrium factor triggers off a modification of the system state out of proportion to the intensity of the external perturbation, the system is in *non-equilibrium*. For instance, the introduction of a germ into a supercooled liquid launches the solidification that goes on, even if the germ is removed, and the heat production is out of proportion to the energy used to introduce the germ. Such a process introduces a character of irreversibility because a large amount of energy is required to bring back the system to its initial state.

First law. In a cyclic process, the *first law* of thermodynamics states that the ratio of work W to heat Q exchanged between the system and its environment is a universal constant J , irrespective of the shape of the cycle and the substance in the system. No experimental fact has ever been able to counter this law.

If it is agreed that what is absorbed by the system (work, heat, energy) is taken as positive and all that is produced by the system

⁴The two laws of thermodynamics have been formulated by the French scholar Sadi Carnot (1796 – 1832), the German doctor Robert Mayer (1814 – 1878) and the German physicist Rudolf Clausius (1822 – 1888).

as negative, the sign to put in the front of the universal constant J should be a minus sign ($\frac{W}{Q} = -J$). Now it is well known that to bring together two fields of physics, the *convention of coordination* consisting in identifying the universal constant to unity ($J = 1$) should be applied. In such a case, the two quantities W and Q are expressed in the same unit (joule) and the expression of the first law is reduced to:

$$W + Q = 0. \quad (2.41)$$

Equation (2.41) shows that a system cannot supply work ($W < 0$) – or heat ($Q < 0$) – during a cycle without compensation.

In an open process where the final state is different from the initial state, the first law takes a different form. We are indeed led intuitively to believe that the variation of the quantity ($W + Q$) between the initial state A and final state B should depend only on the states A and B , and not on the intermediate states. Otherwise, the condition $W + Q = 0$ should be not fulfilled in cyclic processes. Consequently, the first law for open processes is:

$$W + Q = E_B - E_A, \quad (2.42)$$

where E , called the *internal energy*, is a function defining the state of the system and not the path followed in the process. It results from equation (2.42) that an infinitesimal change of energy is an exact differential allowing to write the first law as:

$$\oint dE = 0 \quad \text{with} \quad dE = \delta W + \delta Q. \quad (2.43)$$

In the above equation, the symbol δ is used to indicate that the quantities δW and δQ taken separately are not, in general, exact differentials. If the work W is produced by forces of pressure, the expression of the infinitesimal amount of work is $\delta W = -p.dV$ and can be used both for compression and expansion. Substituting δW into equation (2.43), we obtain the specific expression of the first law:

$$dE = -pdV + \delta Q. \quad (2.44)$$

Second law. The first law of thermodynamics states the equivalence between thermal energy and mechanical energy, but gives no indication on the conditions of their mutual transformations. Whereas

all forms of energy can be transformed into thermal energy without limitation, the conversion of thermal energy (heat) into mechanical energy (work) requires particular conditions. Experiment shows that a system cannot provide work when it is in contact with a single heat source. This is the negation of the so-called *perpetual motion of the second kind*. In contrast, a system can produce work when it is in contact with two heat sources with different temperatures. The first studies to identify the most advantageous terms of transforming thermal energy into mechanical energy and calculate the energy *efficiency* of processes have been developed by Carnot. Incidentally, it is worth noting that the Carnot cycle is a purely theoretical cycle and has the major advantage of being reversible.

Generally, if Q_1 is the amount of heat taken from the hot source and Q_2 the amount of heat transferred, in vain, to the cold source, the logical form of the efficiency of the theoretical Carnot cycle is:

$$\eta = \frac{Q_1 + Q_2}{Q_1}, \quad (2.45)$$

where $Q_1 + Q_2$ is the amount of heat converted into work, with $Q_1 > 0$ and $Q_2 < 0$. Carnot showed in 1824 that the efficiency depends on temperatures T_1 and T_2 of the two heat sources, i.e. $\eta = f(T_1, T_2)$, and not on the nature of the fluid, but it was not until 1853 that Clausius clarified the relationship that binds efficiency η with T_1 and T_2 , written as:

$$\eta^{rev} = 1 + \frac{Q_2^{rev}}{Q_1^{rev}} = 1 - \frac{T_2}{T_1}. \quad (2.46)$$

This equation shows that the efficiency is strictly less than unity because it is practically impossible to have sources of heat where $T_1 = \infty$ and $T_2 = 0$. Furthermore, it should be recalled that equation (2.46) refers to a reversible cycle. However, in the real cycles, the temperature differences between the working fluid and the sources are never zero. Consequently, the successive steps of the cycle are not equilibrium states, so that the real cycles are irreversible cycles performed between temperatures $T_1^{irr} < T_1$ and $T_2^{irr} > T_2$. It ensues from it that the efficiency of an irreversible cycle is always lower than the efficiency of a reversible cycle:

$$\eta^{irr} = 1 + \frac{Q_2^{irr}}{Q_1^{irr}} = 1 - \frac{T_2^{irr}}{T_1^{irr}} < 1 - \frac{T_2}{T_1}. \quad (2.47)$$

Increase of entropy. From the expressions of the efficiency of a reversible cycle (Eq. 2.46) and of an irreversible cycle (Eq. 2.47), it follows:

$$\frac{Q_1^{rev}}{T_1} + \frac{Q_2^{rev}}{T_2} = 0 \quad \text{and} \quad \frac{Q_1^{irr}}{T_1} + \frac{Q_2^{irr}}{T_2} < 0. \quad (2.48)$$

These relationships indicate that the sum of the ratios of the amount of heat to the absolute temperature is zero or negative during the heat transfer in the whole cycle. Provided that it can be depicted in the Clapeyron diagram (reversible process), any cycle can be broken down into many infinitesimal cycles consisting of isothermal and adiabatic processes making it possible to transform equation (2.48) into the integral form:

$$\oint \frac{\delta Q}{T} \leq 0, \quad (2.49)$$

where the sign of equality applies to reversible cycles and the sign of inequality to irreversible cycles. Thus, there are no cycles for which the inequality $\oint \frac{\delta Q}{T} > 0$ is expected.

The mathematical expression $\oint \frac{\delta Q^{rev}}{T} = 0$ is formally analogous to the expression $\oint dE = 0$. According to equation (2.43), δQ is generally not an exact differential whereas dE is one. However the quantity $\frac{\delta Q^{rev}}{T}$ is an exact differential, although δQ^{rev} is not, because $\frac{1}{T}$ is the integrating factor of δQ^{rev} . This leads to the introduction of a state function, i.e. the *entropy* denoted S , which characterizes the state of systems and reads:

$$dS = \frac{\delta Q^{rev}}{T} \quad \text{and} \quad S_B - S_A = \int_A^B \frac{\delta Q^{rev}}{T}. \quad (2.50)$$

It should be noticed that the entropy is a quantity imperceptible to the senses and not directly measurable. The concept of entropy presented here is based on the historical method, but it is supported by a stricter mathematical construction. It also acquires a tangible meaning on the basis of atomistic considerations and using it provides the greatest value by fixing the direction of the spontaneous evolution of systems. With equation (2.49), we see that any cause of irreversibility leads to decreasing the value of the integral $\oint \frac{\delta Q}{T}$. If we consider a cycle in which the system passes from the state A to state B by an

irreversible path and returns to its initial state by a reversible path, this cycle is as a whole irreversible and equation (2.49) is reduced to:

$$\oint \frac{\delta Q^{irr}}{T} = \int_A^B \frac{\delta Q^{irr}}{T} + \int_B^A \frac{\delta Q^{rev}}{T} < 0. \quad (2.51)$$

Finally, owing to equation (2.50), the last integral can be used to find the following inequality:

$$\int_A^B \frac{\delta Q^{irr}}{T} < S_B - S_A. \quad (2.52)$$

This relationship is of particular interest when the process is adiabatic because $\delta Q^{irr} = 0$ and $S_A < S_B$. Thus, any process adiabatically irreversible and occurring spontaneously in an isolated system is always accompanied by an increase of entropy. The entropy function allows us to find the direction in which natural phenomena can evolve.

Thermodynamic equilibrium

Legendre transformation

It has just been said that any spontaneous process occurring in an isolated system is accompanied by an increase of entropy. However, when the entropy S has reached its maximum value, the system can no longer evolve because it is in equilibrium state. Moreover, it is also known that the equilibrium of any system is the one for which the energy E is minimum. Therefore, the trend toward thermodynamic equilibrium results from the combination of two factors: one is the tendency toward maximum entropy, the other one is the tendency toward minimum energy. Concerning these two changes, the functions of state used are not those of the internal energy E and entropy S .

In starting from the two laws of thermodynamics and combining equations (2.44) and (2.50), we obtain the following equation:

$$dE = -pdV + TdS, \quad (2.53)$$

which suggests that V and S are the natural variables for the state function E . Nevertheless, the entropy S is difficult to control experimentally and is obviously not the best independent variable to be used. It became apparent that the pairs of variables (V, T) and

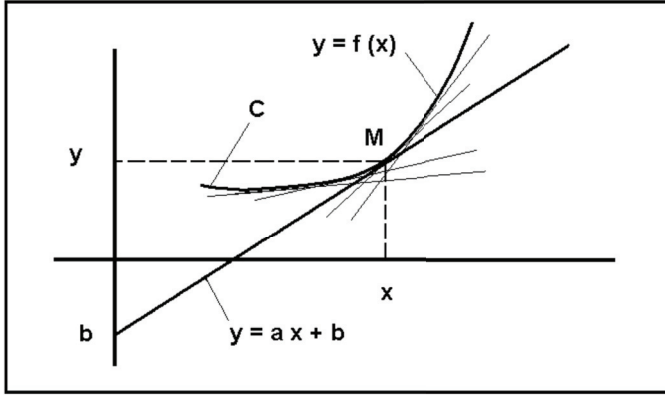


Figure 2.2: Explanatory diagram of the Legendre transform.

(T, p) , being more easily measured, are more advantageous choices. The search for functions of states associated with each of these pairs of variables is an important problem of thermodynamics solved by using the Legendre transformation.

To define the Legendre transformation, consider the function $y = f(x)$ which is traditionally represented by a curve C formed by the points M of coordinates (x, y) . However, it can also be shown in figure (2.2) with the family of tangents of equation $y = ax + b$, upon which the curve C is leaning. The transformation that substitutes the couple (a, b) to the couple (x, y) is called the *Legendre transformation*.

From the equation of tangents $y = ax + b$, we can deduce the variation of the y -intercept as a function of the slope a at any point $M(x, y)$, namely:

$$b = y - xa = g(a). \quad (2.54)$$

The function $b = g(a)$ is now equivalent to the function $y = f(x)$ because the knowledge of one leads to the knowledge of the other and, if $y = f(x)$ is known, $b = g(a)$ is determined by calculating $a = \frac{df}{dx}$ and $b = y - x \frac{df}{dx}$ as a function of x and y . Conversely, if $b = g(a)$ is known, we can deduce $y = f(x)$ by calculating $x = -\frac{dg}{da}$ and $y = b - \frac{dg}{da}$ in terms of a and b , with the aid of equation (2.54).

As an example, the Legendre transformation can be used to find the more suitable state function with the natural variables V and

T from the state function $E(V, S)$. Ignoring the variable V which is common to both the old and new state functions, we can calculate Legendre's transformation of $E(S)$. Given equation (2.53), we can see that the slope of the tangent to the curve $E(S)$ is $(\frac{\partial E}{\partial S})_V = T$. Therefore, the Legendre transformation calculated with equation (2.54), by identifying E to y , S to x and T to a , is $E - ST$. This new state function is called the *Helmholtz free energy*. It is a function of V and T denoted $F(V, T) = E - ST$ and its differential form is:

$$dF = -SdT - p dV. \quad (2.55)$$

By the same reasoning, it is easy to prove the existence of two other state functions: the *enthalpy*, denoted $H(S, p) = G + TS$, and the *Gibbs free energy*, denoted $G(p, T) = F + pV$, whose differential forms are:

$$dH = TdS + Vdp, \quad (2.56)$$

$$\text{and} \quad dG = -SdT + Vdp. \quad (2.57)$$

In summary, the four functions of states, as chosen according to the problem under treatment, are the internal energy $E(S, V)$, the Helmholtz free energy $F(T, V)$, the enthalpy $H(S, p)$ and the Gibbs free energy $G(T, p)$. Their differential forms are given by equations (2.53), (2.55), (2.56) and (2.57) respectively, and the transformations from one to another are performed by the following:

$$F = E - TS, \quad (2.58)$$

$$H = E + pV, \quad (2.59)$$

$$G = E - TS + pV. \quad (2.60)$$

Interpretation of free energy. The state functions E , F , H and G are very useful, not only to study the conditions for the equilibrium of thermodynamic systems but also to anticipate the direction of processes when the steady state is disrupted. Indeed, it has been said that the trend toward a maximum value of entropy is offset by a trend toward a minimum value of energy. However, imposing small variations ΔT , ΔV and Δp to the variables T and V or T and p , it appears that the state functions F and G play the most important role in studying the evolution of systems.

When a *spontaneous* (irreversible) process occurs in a system, the direction of evolution of the process can be predicted by considering the *fundamental law* of thermodynamics formed by equations (2.43) and (2.52), i.e.:

$$dE - TdS \leq \delta W, \quad (2.61)$$

which is verified for any process. Now, in a *reversible isothermal* process, it is easy to see with equation (2.58) that equation (2.61) is reduced to:

$$d(E - TS)_{T,V} = dF = \delta W. \quad (2.62)$$

It is only in this process, the work is strictly equal to the Helmholtz free energy variation ($W = \Delta F$) and can thus be considered as a state function. From the relationship $\Delta E - T\Delta S = \Delta F$, it follows that the internal energy variation ΔE is composed of two terms: the Helmholtz free energy variation ΔF , which is directly usable under the form of work, and the quantity $T\Delta S$ which is the amount of energy involved during heat exchanges.

Moreover, if the work is only due to a volume change ($\delta W = -pdV$), equation (2.61) becomes:

$$dE - TdS \leq -pdV, \quad (2.63)$$

so that, in a process at T and V constant, the work is zero ($\delta W = -pdV = 0$) and equation (2.63) is reduced to:

$$d(E - TS)_{T,V} \leq 0. \quad (2.64)$$

In contrast, if the process takes place at T and p constant, $\delta W = -pdV \neq 0$ and equation (2.63) is written:

$$d(E - TS + pV)_{T,p} \leq 0. \quad (2.65)$$

Given that $E - TS = F$ and $E - TS + pV = G$, it must be admitted, in accordance with equations (2.64) and (2.65), that the Helmholtz free energy F decreases in a spontaneous process, at constant T and V , and no further change is possible when the function F is minimum ($dF = 0$), whereas the Gibbs free energy G decreases in a spontaneous process, at T and p constant, and no change is possible when the function G is minimum ($dG = 0$).

The chemical potential

So far thermodynamics has been dealing with systems in which the processes took place without a change in the number and nature of the molecules. However there are systems where both the number and the nature of molecules are subject to variations. These multicomponent systems require a specific study.

Open systems. The functions of state E , F , H and G depend on their respective natural variables and the number of moles n_i of component i . For example, the Gibbs free energy $G(T, p, \dots, n_i, \dots)$ is a function of temperature, pressure and number of moles. However, the Gibbs free energy, like all state functions, is an *extensive quantity* leading to interesting properties highlighted by Lewis in 1900, allowing us to generate intensive functions called the *partial molar quantities*.

In order to define the partial molar quantities, let us consider an open homogeneous phase at constant T and p , whose state may be modified by increasing the number of moles of all components by a multiplicative constant λ . After transformation, the phase contains $\lambda n_1, \lambda n_2, \dots, \lambda n_i, \dots$ moles of each component and the Gibbs free energy, being an extensive quantity, behaves according to the relation $G(T, p, \dots, \lambda n_i, \dots) = \lambda \cdot G(T, p, \dots, n_i, \dots)$. This is the expression of a homogeneous function of the first degree of n_i . However, in accordance with Euler's theorem, the homogeneous function G satisfying the above equation is written down as follows (Eq. 1.28):

$$G(T, p, \dots, n_i, \dots) = \sum_i n_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} = \sum_i n_i \bar{G}_i, \quad (2.66)$$

where the partial derivatives of G with respect to n_i , noted $\bar{G}_i$, are called the *partial molar free energies*. Any partial molar function is formed by the partial derivative of an extensive quantity with respect to the number of moles of a component, while the number of moles of the other components remains constant. The partial molar functions are *intensive quantities* because they do not depend on the system size or the amount of material in the system, unlike functions from which they are derived. It should be stressed that the partial molar free energy $\bar{G}_i$ is exactly equal to the *chemical potential* $\mu_i (= \bar{G}_i)$ previously introduced by Gibbs. Therefore, the infinitesimal variation

of the Gibbs free energy obtained from equation (2.66) is written as a function of the chemical potential as follows:

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i. \quad (2.67)$$

However, in an elementary process where each variable undergoes an infinitesimal increase, the variation of the Gibbs free energy $G(T, p, \dots, n_i, \dots)$ is also:

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p, n_i} dT + \left(\frac{\partial G}{\partial p} \right)_{T, n_i} dp + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} dn_i. \quad (2.68)$$

Now, with equation (2.57) and the definition of the chemical potential, the partial derivatives in the above relation can be expressed in terms of entropy, volume and chemical potential as follows:

$$\left(\frac{\partial G}{\partial T} \right)_{p, n_i} = -S, \quad \left(\frac{\partial G}{\partial p} \right)_{T, n_i} = V, \quad \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}} = \mu_i, \quad (2.69)$$

and equation (2.68) be rewritten in the following compact formula:

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i. \quad (2.70)$$

By identifying equation (2.70) with equation (2.67), a new expression called the *Gibbs–Duhem relation* can be identically satisfied, namely:

$$SdT - Vdp + \sum_i n_i d\mu_i = 0. \quad (2.71)$$

For an infinitesimal process at T and p constant, this equation reduces to:

$$\sum_i n_i d\mu_i = 0. \quad (2.72)$$

Closed systems. After the open homogeneous systems (consisting of a single phase and of exchanging matter with the outside) have been investigated, we will consider the closed heterogeneous systems (consisting of several components distributed in two distinct phases). The total mass of the components is shared out among two phases, so that each phase is an open system in which the results of the preceding paragraph can be applied. The infinitesimal Gibbs free energy of

both phases α and β are then written in using equation (2.70) such as:

$$dG^\alpha = -S^\alpha dT + V^\alpha dp + \sum_i \mu_i^\alpha dn_i^\alpha, \quad (2.73)$$

$$dG^\beta = -S^\beta dT + V^\beta dp + \sum_i \mu_i^\beta dn_i^\beta. \quad (2.74)$$

Given the extensive property of the entropy ($S = S^\alpha + S^\beta$) and volume ($V = V^\alpha + V^\beta$), the infinitesimal Gibbs free energy of the heterogeneous system is:

$$dG = dG^\alpha + dG^\beta = -SdT + Vdp + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta. \quad (2.75)$$

However, when thermal equilibrium and mechanical equilibrium are achieved ($dT = 0$ and $dp = 0$), the condition of thermodynamic equilibrium ($dG = 0$) reduces to the expression:

$$\sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta = 0. \quad (2.76)$$

Since the number of each component in closed systems is constant ($n_i = n_i^\alpha + n_i^\beta = \text{constant}$), the following relation must be verified:

$$dn_i^\alpha + dn_i^\beta = 0. \quad (2.77)$$

To find the solution of the simultaneous equations (2.76) and (2.77), the method of Lagrange multipliers is used. This consists in multiplying equation (2.77) by an arbitrary coefficient λ and to subtract the result from equation (2.76), i.e.:

$$\sum_i (\mu_i^\alpha - \lambda) dn_i^\alpha + \sum_i (\mu_i^\beta - \lambda) dn_i^\beta = 0. \quad (2.78)$$

This relation is identically zero when the coefficient λ is equal to:

$$\lambda = \mu_i^\alpha = \mu_i^\beta. \quad (2.79)$$

Thus, a closed system made up of several components distributed between two (or more) phases is in thermal, mechanical and thermodynamical equilibrium when temperatures T , pressures p and chemical potentials μ_i , respectively, are the same in all present phases.

Formal expression for the chemical potential. After having presented the characteristics of closed heterogeneous systems and derived the conditions of equilibrium between the phases, we just have to evaluate the Gibbs free energy G given by equation (2.66):

$$G = \sum_i n_i^\alpha \mu_i^\alpha + \sum_i n_i^\beta \mu_i^\beta + \dots, \quad (2.80)$$

where μ_i are the chemical potentials of components in different phases. When studying the equilibrium of a thermodynamic system, it is useless, if not impossible, to know the absolute value of G . Being capable of finding its minimum value, the relative value of G is required.

The Gibbs free energy of a pure substance is a state function depending on the temperature, pressure and quantity of matter (Eq. 2.66). The Gibbs free energy of a mole of pure substance, which is also the chemical potential ($G = \mu$), have to be defined in a standard state of temperature and pressure arbitrarily chosen. This value of μ is a convenient reference against which the chemical potential can be calculated for other thermodynamic states. But, more than anything, it permits the calculation of the Gibbs free energy of a mixture made of different substances, with equation (2.80), when the chemical potential of each component is known. It is worth noting here that equation (2.80) applies when there is no interaction between the components. Otherwise, the interaction terms should be added because, in this case, the Gibbs free energy of mixing is not equal to the sum of the Gibbs free energies of its constituents.

When referring to the experimental studies of the chemical potential performed by various methods (vapor pressure, solubility, freezing point, chemical equilibrium...), we cannot claim that there is a universal law between the chemical potential and the composition of systems considering that each system has its own equation of state. The simplest form of the chemical potential is that of the ideal gas. To find its expression, consider a mole of ideal gas whose equation of state is $pV = RT$ and the elemental Gibbs free energy $dG = -SdT + Vdp$. By eliminating the volume between those two equations we have:

$$\left(\frac{\partial G}{\partial p} \right)_T = V = \frac{RT}{p}. \quad (2.81)$$

In an isothermal process of the mole of ideal gas from the initial pressure p^0 to final pressure p , the Gibbs free energy is:

$$G - G^0 = RT \ln \frac{p}{p^0}. \quad (2.82)$$

As the molar Gibbs free energy is equal to the chemical potential ($G = \mu$), the expression of the chemical potential for the ideal gas reduces to:

$$\mu(p, T) = \mu^0(T) + RT \ln p, \quad (2.83)$$

where $\mu^0(T)$ is the chemical potential at atmospheric pressure ($p^0 = 1$ atm) and temperature T , with p expressed in atmospheres.

This relation is rigorously applicable only to an ideal gas. For each real gas where interactions between molecules are not zero, the calculation of μ should be done with the adequate equation of state. However, the calculations are so complicated that it was decided to keep the same formal relationship (Eq. 2.83) for all systems by replacing the pressure by the *activity* a , i.e. the measure of the degree of interaction between molecules. When referring to one molecule of real gas, equation (2.83) becomes:

$$\frac{\mu(p, T)}{\mathbb{N}} = \frac{\mu^0(T)}{\mathbb{N}} + k_B T \ln a, \quad (2.84)$$

where $\mathbb{N} = \frac{R}{k_B}$ is the Avogadro number, with $R (= 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$ as the molar gas constant and $k_B (= 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1})$ the Boltzmann constant. The expression of the activity a as a function of the chemical potential per molecule $\frac{\mu(p, T)}{\mathbb{N}}$ is:

$$a = \frac{\exp\left(\frac{\mu}{\mathbb{N}k_B T}\right)}{\exp\left(\frac{\mu^0}{\mathbb{N}k_B T}\right)}. \quad (2.85)$$

It should be emphasized that activity closely related to the so-called *fugacity* – see section (3.1) – is one of the most important variables for the linking of the classical thermodynamics to the statistical mechanics.

2.3 The derivation of thermodynamic properties

In this section we show that the probability density function allows the deduction of all thermodynamic properties. For that purpose, we consider the canonical ensemble and start with the determination of the internal energy. Since the energy of a system is equal to the mean value of the Hamiltonian, the internal energy E of the system may be calculated by using the ensemble average (Eq. 1.128):

$$E = \frac{1}{N!h^{3N}Q_N(V,T)} \iint_{6N} H_N(\mathbf{r}^N, \mathbf{p}^N) \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N, \quad (2.86)$$

where equation (2.86) has been obtained by substituting the expression for the probability density function of the canonical ensemble given by equation (2.33) in (Eq. 1.128). However, the expression for the internal energy can also be obtained by differentiating the partition function (Eq. 2.34) with respect to the parameter β . Indeed, it is easy to check that

$$E = -\frac{1}{Q_N(V,T)} \frac{\partial}{\partial \beta} Q_N(V,T) = -\left[\frac{\partial}{\partial \beta} \ln Q_N(V,T) \right]. \quad (2.87)$$

This relation is of the utmost importance because, once the parameter β is known, it becomes possible to deduce the thermodynamic properties (macroscopic properties) from the partition function (microscopic properties). However, the determination of β is very delicate. The crucial question inherent to the statistical method arose for designers of statistical mechanics refers to the irreversibility of non-equilibrium thermodynamic processes. It is paradoxical that the statistical mechanics leads, as shown by Boltzmann, to reversible equations of the microscopic motions and to irreversible equations of the macroscopic motions. Indeed, by virtue of the reversibility of Hamilton's equations of the microscopic motions, the system can switch spontaneously from one microscopic state a to another b and vice versa, without any external action. From the macroscopic point of view, the system *should* easily and spontaneously pass either from the macroscopic state A to the state B or from the macroscopic state B to the state A . Nevertheless, the second law of thermodynamics (principle of increasing entropy) states that a spontaneous transformation

(macroscopic motion) is possible only in one direction, in contradiction with the above sentence.

This issue of the irreversibility of macroscopic processes is contained in the Boltzmann H-theorem whose mathematical expression is:

$$H(t) = \int \int_6 \rho_N^{(1)}(\mathbf{r}, \mathbf{p}, t) \ln \rho_N^{(1)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p}, \quad (2.88)$$

with

$$\frac{d}{dt} H(t) \leq 0, \quad (2.89)$$

where $\rho_N^{(1)}(\mathbf{r}, \mathbf{p}, t)$ is the generic distribution function for one particle that will be defined in section (3.3). Many objections have been made against the Boltzmann H-theorem. Among these, we can call on the Poincaré–Zermelo theorem stating that every single mechanical system, after a *sufficiently long* period of time, should return as close as possible towards the non-equilibrium initial state. According to the Poincaré–Zermelo theorem, a system should, not only pass from the non-equilibrium initial state to a steady state with decreasing quantity H , but also return to the non-equilibrium initial state with increasing quantity H , which is in contradiction with the Boltzmann H-theorem (Eq. 2.89). In fact, it seems that the theorem of Poincaré–Zermelo does not apply in this case. Without dwelling on this issue which is outside the scope of the book, we just remind of the recurrent explanation: “time long enough” mentioned in the theorem of Poincaré–Zermelo is of the order of $\exp(N)$ seconds [6] with $N \sim 10^{23}$. This corresponds to a long duration of $\exp(10^{23}) \sim 10^{0.43(10^{23})}$ seconds which has no physical meaning compared to the age of the universe of 10^{17} seconds. Therefore, the Poincaré–Zermelo theorem cannot be raised to challenge the validity of the Boltzmann H-theorem (i.e. the irreversibility of macroscopic processes) which is definitely acquired.

It is tempting to replace the distribution function $\rho_N^{(1)}(\mathbf{r}, \mathbf{p})$ – which was only available at the time of Boltzmann – in equation (2.88) by the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ and to consider the following integral on the γ -space:

$$S' = -k_B \int \int_{6N} P_N(\mathbf{r}^N, \mathbf{p}^N) \ln P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N, \quad (2.90)$$

where k_B is the Boltzmann constant, whose value is deduced by identifying thermodynamic properties obtained independently by the conventional method and the statistical method, as will be discussed later.

The relation between S' and H should be sought first, assuming that the system is composed of identical particles without interaction, thus independent. As a consequence, the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ is equal to the product of individual probability density functions⁵:

$$\begin{aligned} P_N(\mathbf{r}^N, \mathbf{p}^N) &= P_N^{(1)}(\mathbf{r}_1, \mathbf{p}_1) P_N^{(1)}(\mathbf{r}_2, \mathbf{p}_2) \dots P_N^{(1)}(\mathbf{r}_N, \mathbf{p}_N) \\ &= \prod_{i=1}^N P_N^{(1)}(\mathbf{r}_i, \mathbf{p}_i). \end{aligned} \quad (2.91)$$

Substituting the expression of the probability density function in equation (2.90) leads to S' , namely:

$$S' = -k_B \iint_{6N} \left[\prod_{i=1}^N P_N^{(1)}(\mathbf{r}_i, \mathbf{p}_i) \right] \left[\sum_{j=1}^N \ln P_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) \right] d\mathbf{r}^N d\mathbf{p}^N. \quad (2.92)$$

Then, we invert the integral and the discrete sum on j . After some transformations⁶, we obtain:

⁵See equation (2.140).

⁶The transformations are performed as follows:

$$\begin{aligned} S' &= -k_B \iint_{6N} [P_1 P_2 P_3 \dots P_N] \cdot [\ln P_1 + \ln P_2 + \ln P_3 + \dots + \ln P_N] d\mathbf{r}^N d\mathbf{p}^N \\ &= -k_B \iint_{6N} \{P_1 \ln P_1 \times (P_2 P_3 \dots P_N) + P_2 \ln P_2 \times (P_1 \cdot P_3 \dots P_N) \\ &\quad + P_3 \ln P_3 \times (P_1 P_2 \cdot P_4 \dots P_N) + \dots\} d\mathbf{r}^N d\mathbf{p}^N \\ &= -k_B \sum_{j=1}^N \iint_{6N} \left\{ P_j \ln P_j \prod_{i \neq j=1}^N P_i \right\} d\mathbf{r}^N d\mathbf{p}^N \\ &= -k_B \sum_{j=1}^N \left\{ \iint_6 P_j \ln P_j d\mathbf{r}_j d\mathbf{p}_j \int \prod_{i \neq j=1}^N P_i d\mathbf{r}^{N-1} d\mathbf{p}^{N-1} \right\}. \end{aligned}$$

$$S' = -k_B \sum_{j=1}^N \left\{ \left[\int \int_6 P_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) \ln P_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) d\mathbf{r}_j d\mathbf{p}_j \right] \right. \\ \left. \times \left[\int \int_6 \prod_{i \neq j=1}^N P_N^{(1)}(\mathbf{r}_i, \mathbf{p}_i) d\mathbf{r}^{N-1} d\mathbf{p}^{N-1} \right] \right\}. \quad (2.93)$$

Since the particles are independent, the integral in the second brackets is reduced to the product of $(N-1)$ integrals of the individual probability density functions, all of them being equal to the unity given the normalization condition of $P_N^{(1)}(\mathbf{r}, \mathbf{p})$:

$$\prod_{i \neq j=1}^N \int \int_6 P_N^{(1)}(\mathbf{r}_i, \mathbf{p}_i) d\mathbf{r}_i d\mathbf{p}_i = 1. \quad (2.94)$$

If, moreover, the probability density function $P_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j)$ is replaced by the generic distribution function $\rho_N^{(1)}(\mathbf{r}, \mathbf{p}) = N P_N^{(1)}(\mathbf{r}, \mathbf{p})$ according to equation (3.77), the expression of S' is reduced to:

$$S' = -k_B \sum_{j=1}^N \left\{ \int \int_6 \frac{1}{N} \rho_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) \left[\ln \rho_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) - \ln N \right] d\mathbf{r}_j d\mathbf{p}_j \right\} \\ = -k_B \sum_{j=1}^N \left\{ \left[\frac{1}{N} \int \int_6 \rho_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) \ln \rho_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) d\mathbf{r}_j d\mathbf{p}_j \right] \right. \\ \left. - \left[\ln N \int \int_6 \frac{1}{N} \rho_N^{(1)}(\mathbf{r}_j, \mathbf{p}_j) d\mathbf{r}_j d\mathbf{p}_j \right] \right\}. \quad (2.95)$$

After having simplified the terms bracketed with equations (2.88) and (2.94), we finally obtain:

$$S' = -k_B H + k_B N \ln N. \quad (2.96)$$

Concerning an equilibrium system of independent particles, we can see that the function S' identifies with the quantity $(-k_B H)$ plus the

constant $k_B \ln N^N$. The relation that connects S' to H and the inequality $\frac{dH(t)}{dt} \leq 0$ show that the inequality $\frac{dS'(t)}{dt} \geq 0$ holds for an isolated non-equilibrium system. This suggests that the function S' could correspond to the entropy of the system. To illustrate this, we calculate S' with equation (2.90) in which the probability density function for the canonical ensemble is used. The integral to be evaluated is:

$$S' = -k_B \frac{1}{N!h^{3N}Q_N(V,T)} \iint_{6N} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] \times \{-\beta H_N(\mathbf{r}^N, \mathbf{p}^N) - \ln N!h^{3N} - \ln Q_N(V,T)\} d\mathbf{r}^N d\mathbf{p}^N. \quad (2.97)$$

We proceed next with the averages of the three terms in brackets, with help from equations (2.86) and (2.34), and write S' in the analytical form:

$$S' = k_B [\beta E + \ln N!h^{3N} + \ln Q_N(V,T)]. \quad (2.98)$$

With $S_0 = k_B \ln N!h^{3N}$, which is a quantity independent of T and V , let us define the new function S as follows:

$$S = S' - S_0 = \beta k_B E + k_B \ln Q_N(V,T). \quad (2.99)$$

When this relation is identified with the classical thermodynamic entropy as defined in equation (2.58) by the formula:

$$S = \frac{E}{T} - \frac{F}{T}, \quad (2.100)$$

the result from it is the expressions of the parameter β and the Helmholtz free energy F :

$$\beta = \frac{1}{k_B T}, \quad (2.101)$$

$$F = -k_B T \ln Q_N(V,T). \quad (2.102)$$

The other thermodynamic properties can then be easily derived from the partition function $Q_N(V,T)$ with the following relations:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B \ln Q_N(V, T) + k_B T \left[\frac{\partial}{\partial T} \ln Q_N(V, T) \right]_V, \quad (2.103)$$

$$E = F - T \left(\frac{\partial F}{\partial T}\right)_V = k_B T^2 \left[\frac{\partial}{\partial T} \ln Q_N(V, T) \right]_V, \quad (2.104)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T \left[\frac{\partial}{\partial V} \ln Q_N(V, T) \right]_T, \quad (2.105)$$

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = 2k_B T \left[\frac{\partial}{\partial T} \ln Q_N(V, T) \right]_V + k_B T^2 \left[\frac{\partial^2}{\partial T^2} \ln Q_N(V, T) \right]_V. \quad (2.106)$$

The expressions of thermodynamic properties obtained by differentiating the Helmholtz free energy with respect to their conjugate variables are of great interest since they depend only on the partition function $Q_N(V, T)$.

It should be mentioned that the internal energy (Eq. 2.86) defined by the ensemble average of the Hamiltonian $H_N(\mathbf{r}^N, \mathbf{p}^N)$ is a mechanic property. By contrast, the entropy (Eq. 2.90), as defined by the ensemble average of the logarithm of the probability density function $\ln P_N(\mathbf{r}^N, \mathbf{p}^N)$, is a purely statistical property. Therefore, statistical mechanics gives new meaning to the concept of entropy. While it is considered in classical thermodynamics as a state function defining unambiguously the macroscopic state of systems, in statistical mechanics, entropy is a measure of the information on the microscopic state of systems supplied from the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$.

In addition, the chemical potential μ is another important thermodynamic property that can also be calculated. By definition, μ is equal to the work necessary to insert an N -th particle into a system that already contains $(N-1)$ particles. If N is large, μ corresponds to the Helmholtz free energy per particle:

$$\mu(V, T) = F(V, T, N) - F(V, T, N-1) = \left(\frac{\partial F}{\partial N}\right)_{V, T}. \quad (2.107)$$

Therefore, μ can also be written in terms of the partition function, with the help of equation (2.102), as:

$$\mu(V, T) = -k_B T \ln \frac{Q(V, T, N)}{Q(V, T, N-1)}, \quad (2.108)$$

or equivalently:

$$\exp(\beta\mu) = \frac{Q(V, T, N-1)}{Q(V, T, N)}. \quad (2.109)$$

2.4 Random events and random variables

In this section we briefly recall the concepts of probability theory and mathematical statistics essential to an understanding of statistical mechanics. Statistical methods are designed to study three classes of random phenomena. The first category refers to the simplest phenomena currently named *random events*. The second category deals with phenomena which are slightly more complex and represented by the *random variables*. The third category concerns phenomena which are definitely more complicated involving *random functions*.

Random events

A *random event* is an event resulting from an experiment which can be realized or not. The experiment set up to observe a random event is called the *test*. In practice, the ratio of the number m of tests carried out (successfully) to the total number M generated when M is high is traditionally defined as a probability of a random event A and reads:

$$P(A) = \lim_{M \rightarrow \infty} \frac{m}{M}. \quad (2.110)$$

This definition assumes that the results of the test (elementary events) are *equally likely*, that is to say that their probability of occurrence is the same. For example, in the test of throwing dice, the probability of occurrence of three (or any other face of the die) is $P(\{3\}) = 1/6$.

When calculating the probabilities, the events are treated as sets, with operations like union and intersection. Moreover, a real number $P(A)$ belonging to the interval $[0, 1]$ and called the *probability* (Fig. 2.3a) is associated with each event A . If Ω represents the universal set containing the total number of the events, Ω is the certain

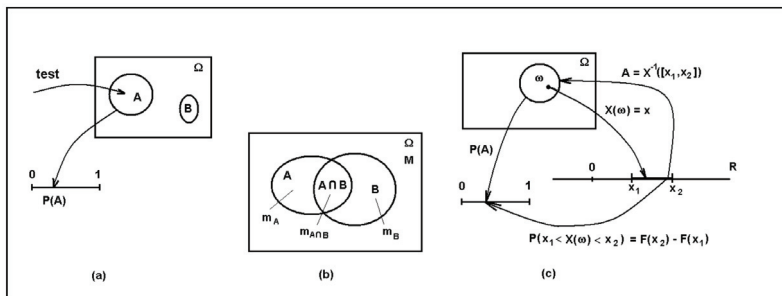


Figure 2.3: (a) Definition of the probability of occurrence of a random event: event A realized and event B unrealized. (b) Conditional probability of A under the condition B . (c) Definition of the probability of a random variable.

event for which the probability is $P(\Omega) = 1$. In turn, at the empty set Φ (impossible event) corresponds the probability $P(\Phi) = 0$.

In probability theory, the notions of *incompatible* events and *complete* system are also required. When two events cannot occur at the same time, their intersection is empty and they are said to be *incompatible*. If the events $A_1, A_2, \dots, A_n$ are incompatible with each other the probability of achieving at least one of them is:

$$P(A_1 \cup A_2 \cup \dots \cup A_n) = \sum_{i=1}^n P(A_i). \quad (2.111)$$

If it is certain that at least one event will happen during an experiment, the probability of achieving at least one of them is $\sum_{i=1}^n P(A_i) = 1$. For example, in the test of throwing dice, the probability of occurrence of at least one face is:

$$P(\{1\} \cup \{2\} \cup \{3\} \cup \{4\} \cup \{5\} \cup \{6\}) = \frac{1}{6} + \frac{1}{6} + \frac{1}{6} + \frac{1}{6} + \frac{1}{6} + \frac{1}{6} = 1. \quad (2.112)$$

Moreover, when the sum of probabilities of incompatible events is equal to unity, the events are said to form a *complete system*.

It is often necessary to use the concepts of *conditional probability* and *independent events*. When two random events A and B are not incompatible, then their intersection is non-zero (Fig. 2.3b). Among

the total number M of events generated, let us suppose that the number of occurrences of the event A is m_A , the number of occurrences of the event B is m_B and the number of simultaneous occurrences of the events A and B is $m_{A \cap B}$. The probability of occurrence of event A , given that event B has been realized, is called the *conditional probability* of A given B and is noted $P(A|B)$. Since it is certain that B was realized, it plays the role of a certain event for the event A that follows it. In this case, the conditional probability is expressed as:

$$\begin{aligned} P(A|B) &= \frac{m_{A \cap B}}{m_B} = \frac{m_{A \cap B}}{M} \frac{M}{m_B}, \\ &= \frac{P(A \cap B)}{P(B)}. \end{aligned} \quad (2.113)$$

Two events are said to be *independent* when the achievement of one does not influence the occurrence of the other one. In this case, the achievement of the event A does not depend on the event B , so that $P(A|B) = P(A)$ entailing that:

$$P(A \cap B) = P(A)P(B). \quad (2.114)$$

This relation means that the events A and B are independent of each other.

Random variables

A *random variable* is a function X that associates an element x of real numbers R (Fig. 2.3c) to the elementary event ω belonging to the set Ω . The definition of the random variable is just the mathematical translation of the concept of measuring apparatus combining the result ω of the experiment (information assimilated by the instrument) to the real number $x = X(\omega)$. The role of the random variable is to transpose the result of the observation onto the numerical line materialized by the reading dial. By misuse of language, the function X is often confused with the result x of the measure when considering the quantity taking values out of the set of real numbers as a random variable. Practically, the random variables will be denoted by capital letters to distinguish them from ordinary variables designated by lower case letters. By definition, the random variable $X(\omega)$ are incompatible and form a complete system.

Before performing an experiment, meaning before the needle moves on the reading dial, the experimenter implicitly wonders what the probability will be of the needle being located in a given interval $[x_1, x_2]$. The relationship establishing the correspondence between the probability $P(x_1 \leq X(\omega) < x_2)$ and the possible values of the random variable (Fig. 1.4c) is called the *distribution function* $F(x)$. The latter refers to the probability that the random variables $X(\omega)$ is below a predetermined threshold x :

$$F(x) = P(X(\omega) < x). \quad (2.115)$$

When the distribution function of the random variable $X(\omega)$ is known, it is easy to calculate the probability that this random variable falls in the interval $[x_1, x_2]$ by using the equation:

$$P(x_1 \leq X(\omega) < x_2) = F(x_2) - F(x_1). \quad (2.116)$$

If $F(x)$ is a continuous and differentiable function on the interval $]-\infty, \infty[$, the probability density function is defined by the function $f(x) = \frac{dF(x)}{dx}$ making it possible to calculate the elementary probability $P(x \leq X(\omega) < x + dx) = f(x)dx$ and the probability:

$$P(x_1 \leq X(\omega) < x_2) = F(x_2) - F(x_1) = \int_{x_1}^{x_2} f(x)dx. \quad (2.117)$$

Among the well-known laws of distribution, the *normal distribution* is of particular importance. Its probability density function is:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[-\frac{(x-\mu)^2}{2\sigma^2} \right], \quad (2.118)$$

where μ and σ are two parameters of the normal law. The study of the function $f(x)$, whose representation is a Gaussian, shows that the curve is symmetrical around $x = \mu$. It has two inflection points at $x = \mu \pm \sigma$, and the area under the curve is equal to unity (by definition of the probability density). The distribution function of the normal distribution is given by the formula:

$$\begin{aligned} F(x) &= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^x \exp \left[-\frac{(x-\mu)^2}{2\sigma^2} \right] dx, \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\frac{(x-\mu)}{\sigma}} \exp \left[-\frac{t^2}{2} \right] dt, \end{aligned} \quad (2.119)$$

after making the change of variables $t = \frac{x-\mu}{\sigma}$. This integral cannot be expressed in analytical form. Its calculation must be done by using the error function, $\text{erf}(u) = \frac{1}{\sqrt{2\pi}} \int_0^u \exp\left[-\frac{t^2}{2}\right] dt$, which is tabulated for all values of the upper bound u . With the following properties of the error function, namely $\text{erf}(-u) = -\text{erf}(u)$ and $\text{erf}(\infty) = 1/2$, equation (2.119) is reduced to⁷:

$$F(x) = \frac{1}{2} + \text{erf}\left(\frac{x-\mu}{\sigma}\right). \quad (2.120)$$

Numerical characteristics

It has been said that a random variable is completely described by its distribution function $F(x)$ or its probability density function $f(x)$. However, in practice, it is not always necessary to know $F(x)$ or $f(x)$. Knowing some numerical characteristics called the *moments* can be satisfactory as they provide a more or less rough indication of the distribution. When the random variable is discrete, the moments are usually calculated from observed data. But if the random variable is continuous, they can be expressed in the form of the probability density function $f(x)$.

⁷Integrals of the following form are rather frequent:

$$I(\beta) = \int_{-\infty}^{+\infty} \exp(-\beta u^2) du.$$

To perform the calculation, it is more convenient to start calculating the square of the integral:

$$I^2(\beta) = \int_{-\infty}^{+\infty} \exp(-\beta u^2) du \int_{-\infty}^{+\infty} \exp(-\beta v^2) dv.$$

However, after writing the product of integrals in the form of a double integral in the coordinates (u, v) and having adopted polar coordinates with the changes of variables $u = r \cos \theta$ and $v = r \sin \theta$, whose Jacobian is equal to r , the integral $I^2(\beta)$ is:

$$\begin{aligned} I^2(\beta) &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp[-\beta(u^2 + v^2)] dudv, \\ &= \int_0^{2\pi} \int_0^{+\infty} \exp(-\beta r^2) r dr d\theta = \frac{\pi}{\beta}. \end{aligned}$$

The *moment of order k* of the continuous random variable X is the number $\mu_k(X)$ given by the integral of the product of x^k by the probability density function $f(x)$:

$$\mu_k(X) = \int_{-\infty}^{\infty} x^k f(x) dx. \quad (2.121)$$

The *central moment of order k* of the continuous random variable X is the number $\alpha_k(X)$ defined by the following integral:

$$\alpha_k(X) = \int_{-\infty}^{\infty} [x - \mu_1(X)]^k f(x) dx. \quad (2.122)$$

It should be noted that the moments are ordinary numbers and not random variables. Among the numerical characteristics, the first-order moment $\mu_1(X)$ has a special importance because it allows the calculation of the central moments. It is also called the *mean value* of x - as it characterizes the central position of the distribution - and is denoted by $\mu_1(X) = \langle x \rangle$. From a purely mathematical point of view, equation (2.121) must be considered as an *operator* applied to the random variable. It is called the *mathematical expectation* or *expected value*, and is defined by:

$$E(X^k) = \mu_k(X) = \int_{-\infty}^{\infty} x^k f(x) dx, \quad \forall k. \quad (2.123)$$

Another important numerical characteristic is the second-order central moment $\alpha_2(X)$, called the *variance* of the random variable. It characterizes the dispersion of the distribution around the mean value $\langle x \rangle$ and is denoted by $\alpha_2(X) = V(X)$. It is easy to find the relationship between the variance $V(X)$ and the mean value $\langle x \rangle$ by using the mathematical expectation operator. Indeed:

$$\begin{aligned} V(X) &= E[(x - \langle x \rangle)^2] = E[x^2 - 2x\langle x \rangle + \langle x \rangle^2] \\ &= \langle x^2 \rangle - \langle x \rangle^2. \end{aligned} \quad (2.124)$$

Concerning the moments of higher orders, they are used to provide a more detailed description of distributions. As an example, the third-order central moment gives an indication on the degree of asymmetry of the distribution, and the fourth-order central moment on the degree of flattening. As a matter of fact, if all moments of the random

variable X are known, a perfect knowledge of the probability density function $f(x)$ would be acquired. To show this, compute the expected value of the function $\exp(itx)$:

$$E[\exp(itx)] = \int_{-\infty}^{\infty} [\exp(itx)] f(x) dx = \varphi_x(t). \quad (2.125)$$

The function $\varphi_x(t)$ is called the *characteristic function* of the random variable X . As it is also the Fourier transform of the probability density function $f(x)$, the inverse Fourier transform is:

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \varphi_x(t) \exp(-itx) dt. \quad (2.126)$$

The interest of the characteristic function lies in its successive derivatives with respect to t , for $t = 0$, which are proportional to the corresponding moments. We show this by using the Taylor expansion of exponential function:

$$\exp(itx) = 1 + itx + \frac{(it)^2}{2!} x^2 + \frac{(it)^3}{3!} x^3 + \dots, \quad (2.127)$$

for writing equation (2.125), that becomes:

$$\begin{aligned} \varphi_x(t) &= \int_{-\infty}^{\infty} f(x) dx + it \int_{-\infty}^{\infty} x f(x) dx + \frac{(it)^2}{2!} \int_{-\infty}^{\infty} x^2 f(x) dx \\ &+ \frac{(it)^3}{3!} \int_{-\infty}^{\infty} x^3 f(x) dx + \dots \end{aligned} \quad (2.128)$$

Owing to the properties of the probability density function and the definition of moments (Eq. 2.121), the above equation is simplified to:

$$\varphi_x(t) = 1 + it\mu_1 + \frac{(it)^2}{2!} \mu_2 + \frac{(it)^3}{3!} \mu_3 + \dots = \sum_{k=0}^{\infty} \frac{(it)^k}{k!} \mu_k. \quad (2.129)$$

However, when comparing this equation with the Maclaurin series for $\varphi_x(t)$, for $t = 0$, i.e.:

$$\begin{aligned} \varphi_x(t) &= \varphi_x(0) + t \left. \frac{d\varphi_x(t)}{dt} \right|_{t=0} + \frac{t^2}{2!} \left. \frac{d^2\varphi_x(t)}{dt^2} \right|_{t=0} \\ &+ \frac{t^3}{3!} \left. \frac{d^3\varphi_x(t)}{dt^3} \right|_{t=0} + \dots, \end{aligned} \quad (2.130)$$

we note that the moments μ_k identify with the quantities $i^{-k} \frac{d^k \varphi_x(t)}{dt^k} \Big|_{t=0}$. Therefore, if all the moments are known, the characteristic function $\varphi_x(t)$ and the probability density function $f(x)$ should also be deduced.

It should be noticed that the main relations linking the central moments α_k to the moments μ_k are:

$$\begin{aligned}\alpha_0 &= 1, \\ \alpha_1 &= 0, \\ \alpha_2 &= \mu_2 - \mu_1^2, \\ \alpha_3 &= \mu_3 - 3\mu_1\mu_2 + 2\mu_1^3, \\ \alpha_4 &= \mu_4 - 4\mu_1\mu_3 + 6\mu_1^2\mu_2 - 3\mu_1^4, \\ \dots &= \dots\end{aligned}\quad (2.131)$$

By way of illustration, we calculate the mean value and the variance of the Gaussian distribution (Eq. 2.118). The mean value is:

$$\langle x \rangle = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} x \exp \left[-\frac{(x-\mu)^2}{2\sigma^2} \right] dx. \quad (2.132)$$

To perform the integration, we use the reduced variable $t = \frac{x-\mu}{\sigma}$. It follows that:

$$\begin{aligned}\langle x \rangle &= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} (t\sigma + \mu) \exp \left(-\frac{t^2}{2} \right) d(\sigma t) \\ &= \frac{\sigma}{\sqrt{2\pi}} \int_{-\infty}^{\infty} t \exp \left(-\frac{t^2}{2} \right) dt + \frac{\mu}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp \left(-\frac{t^2}{2} \right) dt.\end{aligned}\quad (2.133)$$

The first integral is zero because the integrand is an odd function. Regarding the second integral, it is equal⁸ to $\sqrt{2\pi}$. Therefore, the mean value $\langle x \rangle$ corresponds to the parameter μ of the normal law. After rewriting the variance $V(X) = \alpha_2(X)$ with equations (2.122) and (2.118) in terms of reduced variable t , we obtain :

$$\begin{aligned}V(X) &= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} (x-\mu)^2 \exp \left[-\frac{(x-\mu)^2}{2\sigma^2} \right] dx, \\ &= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} (\sigma t)^2 \exp \left(-\frac{t^2}{2} \right) d(\sigma t).\end{aligned}\quad (2.134)$$

⁸see preceding footnote.

The integration by parts of the previous equation with $U = t$ and $V' = t \exp(-\frac{t^2}{2})$ leads to the following result:

$$V(X) = \frac{\sigma^2}{\sqrt{2\pi}} \left\{ \left[-t \exp\left(-\frac{t^2}{2}\right) \right]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \exp\left(-\frac{t^2}{2}\right) dt \right\}. \quad (2.135)$$

The term in square brackets is zero and the value of the integral is $\sqrt{2\pi}$. Therefore, the variance $V(X)$ is equal to σ^2 . With calculations similar to those just made, it is possible to obtain the following recurrence formula between the central moments of the normal law:

$$\alpha_k = (k-1)\sigma^2 \alpha_{k-2}, \quad (2.136)$$

with $\alpha_0 = 1$ and $\alpha_1 = 0$. It can be immediately checked that $\alpha_2 = \sigma^2$, $\alpha_3 = 0$ (meaning that the bell curve is symmetrical), $\alpha_4 = 3\sigma^4$, $\dots$. As far as the moments $\mu_k(X)$ are concerned, they are deduced from each other by the recurrence formulas (Eq. 2.131).

Sets of random variables

A set of random variables $X_1, X_2, \dots, X_n$ can be regarded as the components of the random vector $\mathbf{X} = (X_1, X_2, \dots, X_n)$ in a space of n dimensions whose probability density function is $f(x_1, x_2, \dots, x_n)$. Thus, the elementary probability dP of finding the extremity of the random vector $\mathbf{X}$ in the domain $d\Omega_A = dx_1 dx_2 \dots dx_n$ is calculated by the expression:

$$dP = f(x_1, x_2, \dots, x_n) dx_1 dx_2 \dots dx_n, \quad (2.137)$$

which generalizes equation (2.117). The probability by which the extremity of the random vector $\mathbf{X}$ will be on any point of the n -dimensional space is obviously:

$$\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} f(x_1, x_2, \dots, x_n) dx_1 dx_2, \dots, dx_n = 1. \quad (2.138)$$

Note in passing that the probability density function for a *random variable* is obtained by integrating $f(x_1, x_2, \dots, x_n)$ on the variation domain of the other variables. For example, the probability density function $f(x_1)$ of the variable X_1 is:

$$f(x_1) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} f(x_1, x_2, \dots, x_n) dx_2 \dots dx_n. \quad (2.139)$$

If the random variables $X_1, X_2, \dots, X_n$ are independent, the probability density function $f(x_1, x_2, \dots, x_n)$ is equal to the product of individual probability densities:

$$f(x_1, x_2, \dots, x_n) = f(x_1) \cdot f(x_2) \dots f(x_n). \quad (2.140)$$

This formula is equivalent to what has been obtained for the independent random events (Eq. 2.114). By contrast, if two random variables X and Y are dependent, the conditional probability that X lies in the interval $[x, x + dx]$, given that Y has the known value y , is $f(x|y)dx$, where $f(x|y)$ is the *conditional probability density*. According to equation (2.113), the joint probability is equal to $f(x, y)dxdy = f(x|y)dx \cdot f(y)dy$ and the density of the conditional probability is :

$$f(x|y) = \frac{f(x, y)}{f(y)}. \quad (2.141)$$

This formula can of course be generalized to random vectors $\mathbf{X} = (X_1, X_2, \dots, X_n)$ and $\mathbf{Y} = (Y_1, Y_2, \dots, Y_n)$.

It is also possible for a set of random variables to define moments by analogy with equations (2.121) and (2.122). The first-order moment of the random variable X_i is:

$$\mu_1(X_i) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} x_i \cdot f(x_1, x_2, \dots, x_n) dx_1 dx_2 \dots dx_n. \quad (2.142)$$

As regards the central moment of order two of the couple of random variables X_i and X_j , it is expressed as:

$$\begin{aligned} \alpha_2(X_i X_j) &= \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} [x_i - \mu_1(X_i)] [x_j - \mu_1(X_j)] \\ &\quad \times f(x_1, x_2, \dots, x_n) dx_1 dx_2 \dots dx_n. \end{aligned} \quad (2.143)$$

When $i = j$, the previous equation coincides with the variance of the random variable X_i . When $i \neq j$, the specific quantity $\alpha_2(X_i X_j)$ is called *covariance* measuring the degree of correlation between the random variables X_i and X_j . Thus, if the variables X_i and X_j are independent, the covariance is zero. In contrast, if the covariance of two random variables is zero, they are not necessarily independent.

2.5 Thermodynamic fluctuations

We found that the thermodynamic properties are obtained either by the ensemble average (Eq. 1.127) with the partition function $Q_N(V, T)$ or by the time average (Eq. 1.123), provided that the values of the quantity $G[\mathbf{r}^N(t), \mathbf{p}^N(t)]$ are never too far from the mean value $\overline{G} = \langle G \rangle$. In this case, the dispersion of values recorded is small and the mistake of confusing one of them with the mean value is low. In fact, as part of assessment of dispersion, the second-order central moment, i.e. variance (Eq. 2.124), is generally used because it is all the smaller as the dispersion is low.

The mean value of the thermodynamic quantity $G[\mathbf{r}^N(t), \mathbf{p}^N(t)]$ in the canonical ensemble is:

$$\begin{aligned} \langle G \rangle &= \frac{1}{N!h^{3N}Q_N(V, T)} \int \int_{6N} G[\mathbf{r}^N(t), \mathbf{p}^N(t)] \\ &\times \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N, \end{aligned} \quad (2.144)$$

and its variance is:

$$\begin{aligned} \langle (G - \langle G \rangle)^2 \rangle &= \frac{1}{N!h^{3N}Q_N(V, T)} \int \int_{6N} \{G[\mathbf{r}^N(t), \mathbf{p}^N(t)] - \langle G \rangle\}^2 \\ &\times \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N. \end{aligned} \quad (2.145)$$

In statistical mechanics, the square root of the variance of the quantity G is called *fluctuations* in G . From a practical standpoint, studying the fluctuations is very important as it enables us to understand some experimental phenomena such as the background noise in conductors (caused by fluctuations in the electric intensity), the capillary waves at the surface of liquids, the critical opalescence at the approach of the critical point, etc. (caused by fluctuations in the density), and all of them can be explained using statistical mechanics.

Energy fluctuations

In this subsection we will show that the energy fluctuations of a system containing a given number of particles N is expressed by means of the partition function and has a precise physical meaning. With the

usual notation (see Eq. 2.124), the square of the energy fluctuations is written:

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 - 2E \langle E \rangle + \langle E \rangle^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2, \quad (2.146)$$

where the expression of the mean value of the energy is given by equation (2.86) or equation (2.87), namely:

$$\begin{aligned} \langle E \rangle &= \frac{1}{N! h^{3N} Q_N(V, T)} \iint_{6N} H_N(\mathbf{r}^N, \mathbf{p}^N) \\ &\quad \times \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N \\ &= -\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta}, \end{aligned} \quad (2.147)$$

and the mean value of the square of the energy by:

$$\begin{aligned} \langle E^2 \rangle &= \frac{1}{N! h^{3N} Q_N(V, T)} \iint_{6N} H_N^2(\mathbf{r}^N, \mathbf{p}^N) \\ &\quad \times \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N \\ &= \frac{1}{Q_N} \frac{\partial^2 Q_N}{\partial \beta^2}. \end{aligned} \quad (2.148)$$

These two results allow us to rewrite equation (2.146) as follows:

$$\begin{aligned} \langle (E - \langle E \rangle)^2 \rangle &= \frac{1}{Q_N} \frac{\partial^2 Q_N}{\partial \beta^2} - \left(\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} \right)^2 \\ &= \frac{\partial}{\partial \beta} \left(\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} \right) = -\frac{\partial \langle E \rangle}{\partial \beta}. \end{aligned} \quad (2.149)$$

However, if equation (2.101) is used to write $\frac{\partial T}{\partial \beta} = -k_B T^2$, it is still possible to transform the expression of the square of the energy fluctuations as follows:

$$\langle (E - \langle E \rangle)^2 \rangle = -\frac{\partial \langle E \rangle}{\partial T} \frac{\partial T}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}. \quad (2.150)$$

For a system whose volume is kept constant, $\langle E \rangle$ and $\frac{\partial \langle E \rangle}{\partial T}$ represent, respectively, the internal energy and the specific heat at constant volume c_V . Therefore, the expression of the square of the energy fluctuations at constant volume reads:

$$\langle (E - \langle E \rangle)^2 \rangle_V = k_B T^2 c_V. \quad (2.151)$$

As a result, the energy fluctuations of a system described by the canonical ensemble is proportional to the square root of the specific heat. From a practical point of view, this relation is very important because it allows the calculation of the specific heat of liquids by numerical simulation methods that easily provide the mean values $\langle E \rangle$ and $\langle E^2 \rangle$ of the system. From the theoretical point of view, it is worthy to note that, when defining the temperature of a system by bringing it into contact with a thermostat, introduces an uncertainty into the value of energy. In fact, equation (2.151) has been established by considering the system at constant volume. However, if it is selected to maintain the pressure constant, the previous developments remain valid by replacing the internal energy E by the enthalpy $H (= E + pV)$, hence the following equation replaces equation (2.151):

$$\langle (H - \langle H \rangle)^2 \rangle_p = k_B T^2 c_p. \quad (2.152)$$

To evaluate the dispersion of energy, it is sometimes more advantageous to calculate the relative energy fluctuations, $\frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle}}{\langle E \rangle}$. To this end, we consider the canonical ensemble consisting of N identical systems in thermal contact. In fact, it amounts to assuming that each system is composed of a single particle and the supersystem consists of N particles. Since the specific heat of a thermodynamic system is proportional to the number of particles, we see from equation (2.151) that the energy fluctuations of the supersystem is proportional to $\sqrt{N}$. As a result, the energy is proportional to the number of particles N . On the other hand, the specific heat of a thermodynamic system is also proportional to N . Therefore, from equation (2.151), we see that the energy fluctuations of the supersystem are proportional to $\sqrt{N}$, and that the expression of the relative energy fluctuations is:

$$\frac{\sqrt{\langle (E - \langle E \rangle)^2 \rangle}}{\langle E \rangle} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}. \quad (2.153)$$

The relative fluctuations in the energy are inversely proportional to the square root of the number of particles in the system. It follows that the mean value of the energy $\langle E \rangle$ calculated from the partition function is more accurate when the system is the largest. This result

established for energy is generalized to all thermodynamic properties. It shows that, for a macroscopic system ($N \sim 10^{23}$ particles), the uncertainty of the thermodynamic properties is extremely low.

Volume fluctuations

To carry out the calculation of the volume fluctuations, we consider an enclosure where variations of volume are produced in applying an external pressure p^{ext} by a piston. One way to proceed is to isolate the *piston-particle* system whose state is determined by the generalized coordinates of the particles as well as by the position and velocity of the piston, so that the Hamiltonian of the piston-particle system is:

$$H_N^S(\mathbf{r}^N, \mathbf{p}^N, V, p) = H_N(\mathbf{r}^N, \mathbf{p}^N) + p^{ext}V + \frac{p^2}{2M}, \quad (2.154)$$

where $H_N(\mathbf{r}^N, \mathbf{p}^N)$ is the Hamiltonian of the particles, $p^{ext}V$ the potential energy of the piston and $\frac{p^2}{2M}$ its kinetic energy.

According to equation (2.145), the square of the volume fluctuations is:

$$\begin{aligned} \langle (V - \langle V \rangle)^2 \rangle &= \\ &= \frac{\iint_{6N+2} (V - \langle V \rangle)^2 \exp[-\beta H_N^S(\mathbf{r}^N, \mathbf{p}^N, V, p)] d\mathbf{r}^N d\mathbf{p}^N dV dp}{\iint_{6N+2} \exp[-\beta H_N^S(\mathbf{r}^N, \mathbf{p}^N, V, p)] d\mathbf{r}^N d\mathbf{p}^N dV dp}, \end{aligned} \quad (2.155)$$

where $\langle V \rangle$ is the mean value of the volume. Substituting the expression of the Hamiltonian of the piston-particle system in equation (2.155), the integral of the numerator can be divided into a product of three integrals, with the first one being written in the following form by using equations (2.34) and (2.102):

$$\begin{aligned} \iint_{6N} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N &= N! h^{3N} Q_N(V, T) \\ &= N! h^{3N} \exp(-\beta F), \end{aligned} \quad (2.156)$$

the second integral is:

$$\int_0^{+\infty} (V - \langle V \rangle)^2 \exp(-\beta p^{ext}V) dV, \quad (2.157)$$

and the third one is (see footnote 6 of this chapter):

$$\int_{-\infty}^{+\infty} \exp(-\beta \frac{p^2}{2M}) dp = \sqrt{\frac{2\pi M}{\beta}}. \quad (2.158)$$

Regarding the denominator in equation (2.155), it becomes:

$$\begin{aligned} \int \int_{6N+2} \exp[-\beta H_N^S(\mathbf{r}^N, \mathbf{p}^N, V, p)] d\mathbf{r}^N d\mathbf{p}^N dV dp &= N! h^{3N} Q'_N(V, T) \\ &= N! h^{3N} \exp(-\beta \Psi), \end{aligned} \quad (2.159)$$

where $Q'_N(V, T)$ and Ψ are two functions characterizing the piston-particle system.

After substituting the results of the integrals in equation (2.155), the square of the volume fluctuations is simplified to:

$$\begin{aligned} \langle (V - \langle V \rangle)^2 \rangle &= \frac{N! h^{3N} \exp(-\beta F)}{N! h^{3N} \exp(-\beta \Psi)} \sqrt{\frac{2\pi M}{\beta}} \\ &\quad \times \int_0^{+\infty} (V - \langle V \rangle)^2 \exp(-\beta p^{ext} V) dV \\ &= \exp(\beta \Psi) \sqrt{\frac{2\pi M}{\beta}} \int_0^{+\infty} (V - \langle V \rangle)^2 \exp[-\beta (F + p^{ext} V)] dV. \end{aligned} \quad (2.160)$$

However, if $\Phi (= F + p^{ext} V)$ denotes the free energy of the piston-particle system, it can be deduced that it has a minimum for the equilibrium volume $\langle V \rangle$ from the conditions:

$$\left. \frac{\partial \Phi}{\partial V} \right|_{V=\langle V \rangle} = \left. \frac{\partial F}{\partial V} \right|_{V=\langle V \rangle} + p^{ext} = 0 \quad \text{and} \quad \left. \frac{\partial^2 \Phi}{\partial V^2} \right|_{V=\langle V \rangle} = \left. \frac{\partial^2 F}{\partial V^2} \right|_{V=\langle V \rangle}. \quad (2.161)$$

Since $\frac{\partial \Phi}{\partial V} = 0$ and $\frac{\partial^2 \Phi}{\partial V^2} > 0$ when V is equal to the equilibrium volume $\langle V \rangle$, Φ has an increasing value when V deviates from both sides of the equilibrium value $\langle V \rangle$. Therefore, the term $\exp(-\beta \Phi)$ becomes significantly different from zero in the vicinity of $V = \langle V \rangle$ and tends to zero whereas V tends to zero or infinity. It is thus permissible to expand $\Phi(V)$ in Taylor series around $\langle V \rangle$ up to the second order, i.e.

$$\Phi(V) = \Phi(\langle V \rangle) + \frac{1}{2} (V - \langle V \rangle)^2 \left. \frac{\partial^2 \Phi}{\partial V^2} \right|_{V=\langle V \rangle}. \quad (2.162)$$

By substituting this expression in equation (2.160) and expanding the volume integration from $-\infty$ to $+\infty$, for the simple reason that the major contribution of the integral is located around $\langle V \rangle$, the expression of the square of the volume fluctuations becomes:

$$\begin{aligned} \langle (V - \langle V \rangle)^2 \rangle &= \sqrt{\frac{2\pi M}{\beta}} \exp \{ \beta [\Psi - \Phi(\langle V \rangle)] \} \\ &\times \int_{-\infty}^{+\infty} (V - \langle V \rangle)^2 \exp \left[-\frac{\beta}{2} (V - \langle V \rangle)^2 \frac{\partial^2 F}{\partial V^2} \Big|_{V=\langle V \rangle} \right] dV. \end{aligned} \quad (2.163)$$

Now, if we pose

$$\sigma^2 = \frac{1}{\beta \frac{\partial^2 F}{\partial V^2} \Big|_{V=\langle V \rangle}} \quad (2.164)$$

and

$$\sqrt{\frac{2\pi M}{\beta}} \exp [\beta (\Psi - \Phi)] = \frac{1}{\sigma \sqrt{2\pi}}, \quad (2.165)$$

we notice that the expression of the square of the volume fluctuations is nothing but the variance σ^2 of the Gaussian distribution (Eq. 2.134) for which:

$$\langle (V - \langle V \rangle)^2 \rangle = \sigma^2 = \frac{1}{\beta \frac{\partial^2 F}{\partial V^2} \Big|_{V=\langle V \rangle}}, \quad (2.166)$$

or still, according to equation (2.105) and the isothermal compressibility $\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$:

$$\langle (V - \langle V \rangle)^2 \rangle_T = -k_B T \left(\frac{\partial V}{\partial p} \right)_T = k_B T \cdot V \cdot \chi_T. \quad (2.167)$$

This relation shows that the square of the volume fluctuations of a system in equilibrium with the thermostat is proportional to the isothermal compressibility. The index $\langle V \rangle$ has been omitted in the partial derivative of V with respect to p , whereas the index T has been set to indicate that it is calculated at constant temperature of the thermostat. When the system is isolated adiabatically (constant entropy), the index T must be replaced by the index S :

$$\langle (V - \langle V \rangle)^2 \rangle_S = -k_B T \left(\frac{\partial V}{\partial p} \right)_S = k_B T \cdot V \cdot \chi_S. \quad (2.168)$$

Fluctuations in particle numbers

At first sight, we can think that fluctuations in the number of particles depends on the statistical ensemble used. This is not true because the results obtained with different expressions of the probability density function are equivalent to each other. In this section, we examine only fluctuations in the number of particles in a system without interaction. This case is not without interest because of the results apply to components in dilute solutions such as, for instance, the macroions in colloidal solutions.

Consider a volume V , occupied by N identical particles, in which a small volume v is observed. The mean number of particles in the volume v is $\langle n \rangle = N \frac{v}{V}$. The problem consists in calculating the fluctuations in the number of particles n in the volume v , as compared with the mean number $\langle n \rangle$. According to equation (2.124), the square of the fluctuations in the number of particles is expressed as:

$$\langle (n - \langle n \rangle)^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2. \quad (2.169)$$

In order to calculate the mean number of particles $\langle n \rangle$ and fluctuations $\sqrt{\langle (n - \langle n \rangle)^2 \rangle}$, we have first to determine the probability of finding n particles in the volume v that will be denoted $P(n)$. Then it just remains for us to apply the formulas of the average and variance:

$$\langle n \rangle = \sum_{n=0}^N n P(n), \quad (2.170)$$

$$\langle (n - \langle n \rangle)^2 \rangle = \sum_{n=0}^N (n - \langle n \rangle)^2 P(n). \quad (2.171)$$

These expressions differ from equations (2.121) and (2.122) by the nature of the random variable n that, here, is discrete. By replacing the integral by the discrete sum, the differential element of integration is removed and, consequently, $P(n)$ becomes a genuine probability and not a probability density function that makes sense only for continuous random variables. It is worth noting that $\langle n \rangle$ could be obtained without knowing $P(n)$ by direct calculation of the probability of finding a given particle in the volume v that is $p = \frac{v}{V}$ under the assumption of the equally likely events. It follows immediately that the mean number of particles is $\langle n \rangle = N \frac{v}{V} = Np$.

To perform a more detailed study, we calculate the probability $P(n)$ to place n particles chosen among N in the volume v . Note first that the probability of having simultaneously n particles in the volume v and the $(N - n)$ remaining particles outside this volume is $p^n(1 - p)^{N-n}$. Nevertheless, we must then multiply this quantity by the number of combinations of N particles taken n at a time, because there are $C_N^n = \frac{N!}{n!(N-n)!}$ different ways to choose those particles. Therefore, the expression of the probability $P(n)$ is:

$$P(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}. \quad (2.172)$$

This law of probability, known as the *binomial distribution*, is a function of three parameters n , N and p . It is easy to check that $P(n)$ is a genuine probability since $\sum P(n) = \sum C_N^n p^n (1-p)^{N-n} = 1$. The binomial distribution $P(n)$ has been plotted in figure 2.4 as a function of n , for $p = 0.4$ and $N = 30$. With three parameters, equation (2.172) is unsuitable for calculations when N is large, so that an approximate formula easier to be used was established. As the curve is symmetrical

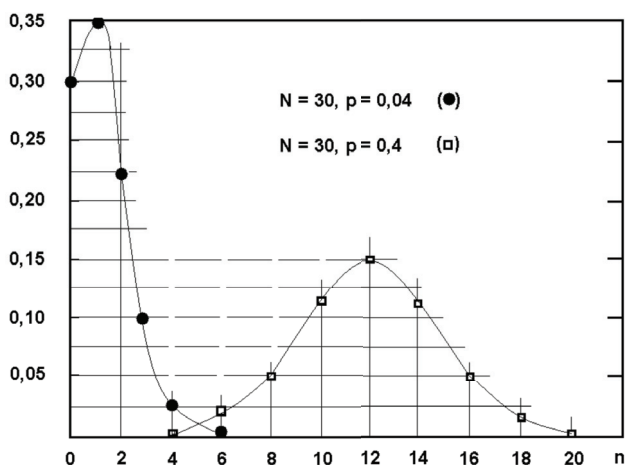


Figure 2.4: Representation of the binomial distribution as a function of n , for $N = 30$ with $p = 0.4$ and $p = 0.04$. When the probability p is close to 0.5, the binomial distribution tends to the Gauss distribution and when the probability p is very low, it tends to the Poisson distribution.

around $n = Np = 12$, it is worthwhile to consider this symmetry by changing the variables $n = (Np + x)$ and $N - n = (Nq - x)$ which lead to the relation $q = (1 - p)$ and permit us to rewrite equation (2.172) as follows:

$$P(x) = \frac{N!}{(Np+x)!(Nq-x)!} p^{Np+x} q^{Nq-x}. \quad (2.173)$$

However, if $N \rightarrow \infty$, the approximate formula of Stirling⁹ can be used to simplify the above equation that becomes:

$$P(x) = \frac{\left(1 + \frac{x}{Np}\right)^{-(Np+x)} \left(1 - \frac{x}{Nq}\right)^{-(Nq-x)}}{\sqrt{2\pi N \left(p + \frac{x}{N}\right) \left(q - \frac{x}{N}\right)}}. \quad (2.174)$$

This relation can be further simplified by taking the logarithm of the numerator and using its limited development¹⁰. After taking the sum of the two logarithms, we find:

$$\begin{aligned} \ln\left(1 + \frac{x}{Np}\right)^{-(Np+x)} + \ln\left(1 - \frac{x}{Nq}\right)^{-(Nq-x)} &= \\ &= -\frac{1}{2} \frac{x^2}{N} \left(\frac{1}{pq}\right) + \frac{1}{6} \frac{x^3}{N^2} \left(\frac{q^2 - p^2}{p^2 q^2}\right) + \dots \end{aligned} \quad (2.175)$$

Given these results and some simplifications, the probability $P(x)$ reduces to:

$$P(x) = \frac{\exp\left[-\frac{1}{2} \frac{x^2}{N} \left(\frac{1}{pq}\right) + \frac{1}{6} \frac{x^3}{N^2} \left(\frac{q^2 - p^2}{p^2 q^2}\right) + \dots\right]}{\sqrt{2\pi N \left(p + \frac{x}{N}\right) \left(q - \frac{x}{N}\right)}}. \quad (2.176)$$

⁹The Stirling approximation is used under the form:

$$N! \simeq N^N \exp(-N) \sqrt{2\pi N}.$$

¹⁰The logarithmic series expansions are:

$$\begin{aligned} \ln\left(1 + \frac{x}{Np}\right)^{-(Np+x)} &= -x - \frac{x^2}{Np} + \frac{1}{2} \frac{x^2}{Np} + \frac{1}{2} \frac{x^3}{(Np)^2} - \frac{1}{3} \frac{x^3}{(Np)^2} - \frac{1}{3} \frac{x^4}{(Np)^3} - \dots, \\ \ln\left(1 - \frac{x}{Nq}\right)^{-(Nq-x)} &= +x - \frac{x^2}{Nq} + \frac{1}{2} \frac{x^2}{Nq} - \frac{1}{2} \frac{x^3}{(Nq)^2} + \frac{1}{3} \frac{x^3}{(Nq)^2} - \frac{1}{3} \frac{x^4}{(Nq)^3} - \dots \end{aligned}$$

In addition, when the situation requires that $p \sim q \sim \frac{1}{2}$ with $N \rightarrow \infty$, the above expression is rewritten as a function of the old variables as:

$$P(n) \simeq \frac{1}{\sqrt{2\pi Np(1-p)}} \exp \left[-\frac{1}{2} \frac{(n - Np)^2}{Np(1-p)} \right]. \quad (2.177)$$

By comparing equation (2.177) with equation (2.118), we see that $P(n)$ is the Gaussian distribution where the mean value and variance are respectively:

$$\mu = \langle n \rangle = Np, \quad (2.178)$$

$$\sigma^2 = \langle (n - \langle n \rangle)^2 \rangle = Np(1-p). \quad (2.179)$$

The approximation consisting in replacing the binomial distribution by the Gaussian distribution is very important in many cases, but it is not suitable to calculate the fluctuations in the number of particles because $p = \frac{v}{V} \ll \frac{1}{2}$. Indeed, when the local fluctuations in the number of particles are investigated, the volume v is very small when compared to the volume V , so that the probability $p = \frac{v}{V} = \frac{\langle n \rangle}{N}$ is also very low. In these conditions ($N \rightarrow \infty$ and $p \rightarrow 0$), the approximation of binomial distribution does not lead to the Gaussian distribution but to the Poisson distribution (Fig. 2.4). To show this, we rewrite equation (2.172) as follows:

$$P(n) = \frac{N(N-1)(N-2)\dots(N-n+1)}{N^n} \frac{\langle n \rangle^n}{n!} \frac{\left(1 - \frac{\langle n \rangle}{N}\right)^N}{\left(1 - \frac{\langle n \rangle}{N}\right)^n}. \quad (2.180)$$

It is obvious that both the first fraction and the denominator of the third fraction of equation (2.180) tend to unity when $N \rightarrow \infty$. Furthermore, by using the remarkable limit of the exponential function¹¹, we obtain the Poisson distribution:

$$P(n) = \frac{\langle n \rangle^n}{n!} \exp(-\langle n \rangle), \quad (2.181)$$

¹¹The relation to use is:

$$\lim_{N \rightarrow \infty} \left(1 + \frac{x}{N}\right)^N \simeq \exp(x).$$

making possible the calculation of fluctuations in the number of particles when $p \rightarrow 0$. It is easy to check that the mean number of particles is $\langle n \rangle = Np$ as equation (2.170) transforms into:

$$\begin{aligned}\langle n \rangle &= \sum_{n=0}^N n \frac{\langle n \rangle^n}{n!} \exp(-\langle n \rangle) = \langle n \rangle \exp(-\langle n \rangle) \sum_{n=1}^N \frac{\langle n \rangle^{n-1}}{(n-1)!} \\ &= \langle n \rangle \exp(-\langle n \rangle) \left[1 + \frac{\langle n \rangle}{1} + \frac{\langle n \rangle^2}{2!} + \frac{\langle n \rangle^3}{3!} + \dots \right] = \langle n \rangle = Np. \quad (2.182)\end{aligned}$$

With respect to the fluctuations, they are obtained by a similar calculation from equation (2.171). Indeed, the expression of the mean value of n^2 is:

$$\begin{aligned}\langle n^2 \rangle &= \sum_{n=0}^N n^2 \frac{\langle n \rangle^n}{n!} \exp(-\langle n \rangle) = \langle n \rangle \exp(-\langle n \rangle) \sum_{n=1}^N n \frac{\langle n \rangle^{n-1}}{(n-1)!} \\ &= \langle n \rangle \exp(-\langle n \rangle) \left[\sum_{n=1}^N (n-1) \frac{\langle n \rangle^{n-1}}{(n-1)!} + \sum_{n=1}^N \frac{\langle n \rangle^{n-1}}{(n-1)!} \right], \\ &= \langle n \rangle \exp(-\langle n \rangle) [\langle n \rangle \exp\langle n \rangle + \exp\langle n \rangle] \\ &= \langle n \rangle [\langle n \rangle + 1] = Np(Np + 1). \quad (2.183)\end{aligned}$$

Therefore, the square of fluctuations in the number of particles is expressed as:

$$\langle (n - \langle n \rangle)^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2 = Np(Np + 1) - N^2 p^2 = Np. \quad (2.184)$$

Throughout this last subsection, we found the expression of the fluctuations in the number of particles in a system without interaction and we demonstrated the essential property of the Poisson distribution, namely that the variance $\langle (n - \langle n \rangle)^2 \rangle = Np$ is equal to the mean value $\langle n \rangle = Np$. This formula plays an essential role in the theory of

In what follows, the mathematical approximations will also be used:

$$\begin{aligned}\sum_{n=1}^N \frac{x^{n-1}}{(n-1)!} &\simeq \exp(x) \\ \text{and} \quad \sum_{n=2}^N (n-1) \frac{x^{n-1}}{(n-1)!} &\simeq x \exp(x).\end{aligned}$$

processes related to the presence of fluctuations when allowing us to evaluate the relative fluctuations in the number of particles:

$$\frac{\sqrt{\langle (n - \langle n \rangle)^2 \rangle}}{\langle n \rangle} = \frac{1}{\sqrt{Np}}. \quad (2.185)$$

The purpose of these calculations was to show that the fluctuations in the number of particles is very small when the number of particles in the system is large and the interactions between them are absent. It is worth noting that, when calculating the fluctuations in the number of particles, it is necessary to match the size of the volume element to the fluctuations. To clarify this remark, consider an enclosure of volume $V = 10^{-5} \text{ m}^3$ containing a number of molecules $N = 2.7 \cdot 10^{20}$ of ideal gas under normal pressure and temperature. If the volume considered is $v = V/10 = 10^{-6} \text{ m}^3$, the mean number of particles is $\langle n \rangle = N \frac{v}{V} = \frac{2.7 \cdot 10^{20}}{10}$, and the relative fluctuations are $\frac{1}{\sqrt{\langle n \rangle}} \sim 2 \cdot 10^{-10}$, which is practically negligible. But if the volume is much smaller, say $v = V/10^{15} = 10^{-20} \text{ m}^3$, the mean number of particles is $\langle n \rangle = N \frac{v}{V} = \frac{2.7 \cdot 10^{20}}{10^{15}}$, and the relative fluctuations $\frac{1}{\sqrt{\langle n \rangle}} \sim 2 \cdot 10^{-3}$ become much more important. This observation is crucial in certain phenomena related to light scattering such as the critical opalescence. This phenomenon occurs when the local fluctuations in the number of particles will disrupt the beam of visible light on a spot of the fluid.

Incidentally, note that the blue color of the sky is due to density fluctuations in the atmosphere because the scattered light is proportional to the fluctuations in the dielectric constant of air, which is itself proportional to the fluctuations in the number of particles and inversely proportional to the fourth power of wavelength. As a consequence, the blue wavelengths ($\sim 450 \text{ nm}$) are more widely spread than red wavelengths ($\sim 750 \text{ nm}$).

Finally, note that it is possible to calculate the mean and variance of the number of particles in an open system by using equations (2.170) and (2.171) together with the probability $P(N)$ of finding exactly N particles in the system (Eq. 2.40). It yields:

$$\langle N \rangle = \sum_{N=0}^{\infty} N P(N), \quad (2.186)$$

$$\langle (N - \langle N \rangle)^2 \rangle = \sum_{N=0}^{\infty} (N - \langle N \rangle)^2 P(N). \quad (2.187)$$

The expression of the mean number of particles is obtained using the partition function of the grand canonical ensemble as follows:

$$\begin{aligned}\langle N \rangle &= \sum_{N=0}^{\infty} N P(N) = \frac{\sum_{N=0}^{\infty} N \exp(\beta \mu N) Q_N(V, T)}{\Xi}, \\ &= k_B T \left(\frac{\partial}{\partial \mu} \ln \Xi \right)_{V, T}.\end{aligned}\quad (2.188)$$

It will be calculated in section (5.2) when studying of the compressibility equation of state whose result is decisive for the theory of liquids. Anticipating the result, it should be noticed that, for real gases and liquids in which the interactions between molecules cannot be neglected, the relative fluctuations in the number of particles becomes proportional to the square root of the temperature and the isothermal compressibility (Eq. 5.27).

Fluctuations in other properties

Considering the fluctuations in the way envisaged for energy (Eq. 2.151) and volume (Eq. 2.167), it may seem inappropriate to speak of temperature fluctuations since the value of T is imposed by the thermostat. It is true, provided that the system is assumed to be composed of many regions which are neither too small for the macroscopic properties to be defined inside nor too large for local fluctuations to be observed. Each region of the system is virtually in thermodynamic equilibrium. However, if the substance is homogeneous, every thermodynamic property is expressed in terms of two independent variables, so that the calculation of the fluctuations in a thermodynamic property reduces to the fluctuations in these two independent variables.

As an illustration, we calculate the temperature fluctuations of the system in considering T as a function of the independent variables V and E . Besides, we assume that the derivations in the volume and energy relatively to the mean values have the form:

$$\Delta V = V - \langle V \rangle, \quad (2.189)$$

$$\Delta E = E - \langle E \rangle, \quad (2.190)$$

where the averages of deviations and products of deviations are zero, $\langle \Delta V \rangle = \langle \Delta E \rangle = \langle \Delta E \Delta V \rangle = 0$ (because the variables E and V are independent of one another). It entails the following relation:

$$\Delta T = \left(\frac{\partial T}{\partial V} \right)_E \Delta V + \left(\frac{\partial T}{\partial E} \right)_V \Delta E. \quad (2.191)$$

By elevating this relation to the square and calculating the average, we find:

$$\begin{aligned} \langle \Delta T^2 \rangle &= \left(\frac{\partial T}{\partial V} \right)_E^2 \langle \Delta V^2 \rangle + 2 \left(\frac{\partial T}{\partial V} \right)_E \left(\frac{\partial T}{\partial E} \right)_V \langle \Delta E \Delta V \rangle \\ &\quad + \left(\frac{\partial T}{\partial E} \right)_V^2 \langle \Delta E^2 \rangle, \end{aligned} \quad (2.192)$$

where $\langle \Delta E \Delta V \rangle = 0$ and the quantities $\langle \Delta V^2 \rangle = \langle (V - \langle V \rangle)^2 \rangle$ and $\langle \Delta E^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle$ are given by equations (2.167) and (2.151), respectively. Therefore, the square of the temperature fluctuations, at constant volume, reduces to the expression:

$$\langle \Delta T^2 \rangle_V = \langle (T - \langle T \rangle)^2 \rangle_V = \left(\frac{\partial T}{\partial E} \right)_V^2 \langle (E - \langle E \rangle)^2 \rangle_V. \quad (2.193)$$

Since the partial derivative $\left(\frac{\partial T}{\partial E} \right)_V$ represents the specific heat at constant volume c_V , equation (2.193) turns with the aid of equation (2.151) into:

$$\langle (T - \langle T \rangle)^2 \rangle_V = \frac{k_B T^2}{c_V}. \quad (2.194)$$

It should be noted that the specific heat c_V appearing in this expression corresponds to the part of the system affected by energy fluctuations.

To calculate the square of the entropy fluctuations of the system, consider the function $S(V, E)$. By arguing what we have previously done, we obtain:

$$\langle \Delta S^2 \rangle_V = \langle (S - \langle S \rangle)^2 \rangle_V = \left(\frac{\partial S}{\partial E} \right)_V^2 \langle (E - \langle E \rangle)^2 \rangle_V, \quad (2.195)$$

and, given the fact that $\left(\frac{\partial S}{\partial E} \right)_V = \frac{1}{T}$, the square of the entropy fluctuations, at constant volume, reads:

$$\langle (S - \langle S \rangle)^2 \rangle_V = k_B c_V. \quad (2.196)$$

Moreover, by similar reasoning and considering the function $S(p, H)$, we obtain the square of the entropy fluctuations, at constant pressure, i.e.:

$$\langle \Delta S^2 \rangle_p = \langle (S - \langle S \rangle)^2 \rangle_p = \left(\frac{\partial S}{\partial H} \right)_p^2 \langle (H - \langle H \rangle)^2 \rangle_p, \quad (2.197)$$

which, owing to equation (2.152) and relation $\left(\frac{\partial S}{\partial H} \right)_p = \frac{1}{T}$, can also be transformed into the expression:

$$\langle (S - \langle S \rangle)^2 \rangle_p = k_B c_p. \quad (2.198)$$

The square of the pressure fluctuations, at constant temperature and constant entropy, can be calculated by following the process described above. In the first case, the function $p(V, T)$ is used for writing:

$$\langle \Delta p^2 \rangle_T = \langle (p - \langle p \rangle)^2 \rangle_T = \left(\frac{\partial p}{\partial V} \right)_T^2 \langle (V - \langle V \rangle)^2 \rangle_T. \quad (2.199)$$

Now, with the help of equation (2.167), the square of the pressure fluctuations, at constant temperature, leads to:

$$\langle (p - \langle p \rangle)^2 \rangle_T = -k_B T \left(\frac{\partial p}{\partial V} \right)_T. \quad (2.200)$$

In the second case, the function $p(V, S)$ is used, so that:

$$\langle \Delta p^2 \rangle_S = \langle (p - \langle p \rangle)^2 \rangle_S = \left(\frac{\partial p}{\partial V} \right)_S^2 \langle (V - \langle V \rangle)^2 \rangle_S. \quad (2.201)$$

And with equation (2.168), the square of the pressure fluctuations, at constant entropy, reduces to:

$$\langle (p - \langle p \rangle)^2 \rangle_S = -k_B T \left(\frac{\partial p}{\partial V} \right)_S. \quad (2.202)$$

Note in passing that the square of the pressure fluctuations can still be expressed as follows, owing to Reech's formula¹²:

$$\langle (p - \langle p \rangle)^2 \rangle_S = -\gamma k_B T \left(\frac{\partial p}{\partial V} \right)_T = \gamma \langle (p - \langle p \rangle)^2 \rangle_T. \quad (2.203)$$

¹²This formula yields the relation between the slopes at the intersection of a isothermal process ($pV = C$) and an isentropic process ($pV^\gamma = C$). One easily finds that $\left(\frac{\partial p}{\partial V} \right)_S = \gamma \left(\frac{\partial p}{\partial V} \right)_T$.

As a final example, consider the case of the product of fluctuations in volume and pressure, assuming that the pressure depends on the two independent variables T and V . This allows us to write the expression:

$$\Delta V \Delta p = \Delta V \left[\left(\frac{\partial p}{\partial T} \right)_V \Delta T + \left(\frac{\partial p}{\partial V} \right)_T \Delta V \right], \quad (2.204)$$

so that the mean value is:

$$\langle \Delta V \Delta p \rangle = \left(\frac{\partial p}{\partial T} \right)_V \langle \Delta T \Delta V \rangle + \left(\frac{\partial p}{\partial V} \right)_T \langle \Delta V^2 \rangle_T, \quad (2.205)$$

where $\langle \Delta T \Delta V \rangle = 0$, since T and V are independent variables. After the substitution of $\langle \Delta V^2 \rangle_T$ with the help of equation (2.167), we obtain:

$$\langle \Delta V \Delta p \rangle = - \left(\frac{\partial p}{\partial V} \right)_T k_B T \left(\frac{\partial V}{\partial p} \right)_T = -k_B T. \quad (2.206)$$

This relation shows that, within a homogeneous system, the fluctuations in volume and pressure are interdependent. As the result is negative, it follows that a volume increase in the portion of the system in question is accompanied by a pressure decrease, and vice versa.

3 Partition function and distribution functions

In this chapter we would like to draw the reader's attention on the difference between the *partition function* and the *distribution functions*. Because of the weak density of gases, their thermodynamic properties are expressed in terms of series expansions of the density (development of the virial expansion). But for liquids whose densities are much higher than those of gases, such expansions are put at fault. Therefore, the formalism of the partition function has to be replaced by that of the correlation functions. The latter allows more rigorous treatment for the interactions between particles in liquids which are stronger than in gases because of the high density that prevails there.

Among the correlation functions, the pair *correlation function* $g(r)$ is the central function of the microscopic theory of liquids. Interestingly, the pair correlation function can be obtained experimentally by X-ray diffraction or neutron scattering. However, calculations of the pair correlation function $g(r)$ and thermodynamic properties are made possible by means of total potential energy, provided that it can be written as a sum of pair potential $u(r)$ between the particles.

In fact, it is just after the interparticle potential is known that the task of statistical mechanics consisting in predicting the microscopic behaviour of any system does begin. The problem of determining interparticle potentials is ignored here, while our focus is on defining the pair correlation function.

3.1 The configurational partition function

If, for purposes of calculation, the canonical ensemble is used, the partition function $Q_N(V, T)$ of a system in equilibrium is written explicitly as a function of the particle number N , volume V , temperature T using the Hamiltonian $H_N(\mathbf{r}^N, \mathbf{p}^N)$ as (Eq. 2.34):

$$Q_N(V, T) = \frac{1}{N!h^{3N}} \int \int_{6N} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)] d\mathbf{r}^N d\mathbf{p}^N. \quad (3.1)$$

In real systems, it is essential to take into account the interactions between particles, so that the Hamiltonian is:

$$H_N(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\mathbf{r}^N), \quad (3.2)$$

where the first term of the right hand side of the above equation represents the kinetic energy of all the particles and the second term stands for the potential energy depending only on the coordinates. It is obvious that the partition function (Eq. 3.1) can be separated into an integral over the momenta and an integral over the positions, as follows:

$$Q_N(V, T) = \frac{1}{N!h^{3N}} \int \int_{3N} \exp\left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m}\right] d\mathbf{p}^N \times \int \int_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N. \quad (3.3)$$

The part of the partition function depending on the integral over the positions is called the *configurational partition function* (or *configuration integral*). It is usually denoted Z :

$$Z = \int \int_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N, \quad (3.4)$$

With this notation, the partition function reads:

$$Q_N(V, T) = \frac{Z}{N!h^{3N}} \prod_{i=1}^N \int \int \exp\left[-\frac{\beta}{2m}(p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2)\right] dp_{x_i} dp_{y_i} dp_{z_i}. \quad (3.5)$$

However, the momenta components in three orthogonal directions are independent of one another, so that the integral of the previous relation can be split into a product of three integrals:

$$I = \int \exp\left(-\frac{\beta p_{x_i}^2}{2m}\right) dp_{x_i} \times \int \exp\left(-\frac{\beta p_{y_i}^2}{2m}\right) dp_{y_i} \times \int \exp\left(-\frac{\beta p_{z_i}^2}{2m}\right) dp_{z_i}. \quad (3.6)$$

As each resultant integral¹ contained in the above expression is $\sqrt{\frac{2\pi m}{\beta}}$, the partition function is reduced to the expression:

$$Q_N(V, T) = \frac{Z}{N! h^{3N}} \left(\sqrt{\frac{2\pi m}{\beta}} \right)^{3N} = \frac{Z}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{3N}{2}}. \quad (3.7)$$

It is customary to write $Q_N(V, T)$ as a function of the parameter $\Lambda = \sqrt{\frac{h^2 \beta}{2\pi m}}$ called the *thermal wavelength* or *de Broglie wavelength*. This parameter is very important because it is related to the wavelength λ associated with the particle, and it indicates whether it is of classical or quantum nature. To set Λ , transform successively the expression of the wavelength λ as follows:

$$\lambda = \frac{2\pi\hbar}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2m\frac{3}{2}k_B T}} = \sqrt{\frac{2\pi}{3}} \Lambda, \quad (3.8)$$

where $h = 6.62 \cdot 10^{-34} \text{ J} \cdot \text{s}$ and $k_B = 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$. Therefore, if $\Lambda (\propto \lambda)$ is small compared to the average distance between particles, the particles are classical. Otherwise they are of a quantum nature.

To illustrate this feature, consider a gas of He atoms in normal conditions ($T = 293 \text{ K}$), with the density of particles $\frac{N}{V} = 10^{23} \text{ m}^{-3}$. The average distance between particles is $l \sim \left(\frac{V}{N}\right)^{1/3} \sim 2 \cdot 10^{-8} \text{ m}$. With the atomic mass for He of $m = 6.6 \cdot 10^{-27} \text{ kg}$, the thermal wavelength is:

$$\Lambda = \sqrt{\frac{h^2 \beta}{2\pi m}} = \frac{6.62 \times 10^{-34}}{(2\pi \times 6.6 \cdot 10^{-27} \times 1.38 \cdot 10^{-23} \times 273)^{1/2}} \sim 5.3 \cdot 10^{-11} \text{ m}. \quad (3.9)$$

¹The integrals are in the form:

$$\int_{-\infty}^{+\infty} \exp(-ap^2) dp = \sqrt{\frac{\pi}{a}}.$$

As the thermal wavelength is smaller than the average distance between particles, the system can be regarded as a classical system. By contrast, if the gas is at a temperature of 5 K with, for instance, the particle density of 10^{29} m^{-3} , the average distance is $l \sim 2 \cdot 10^{-10} \text{ m}$ while the thermal wavelength is:

$$\Lambda = \sqrt{\frac{\hbar^2 \beta}{2\pi m}} = \frac{6.62 \cdot 10^{-34}}{(2\pi \times 6.6 \cdot 10^{-27} \times 1.38 \cdot 10^{-23} \times 5)^{1/2}} \sim 4 \cdot 10^{-10} \text{ m}. \quad (3.10)$$

In this case, Λ is of the same order of magnitude as l so that the quantum effects cannot be ignored.

The general expression for the partition function of any system in equilibrium is:

$$Q_N(V, T) = \frac{Z}{N!} \left(\frac{2\pi m}{\beta \hbar^2} \right)^{\frac{3N}{2}} = \frac{Z}{N! \Lambda^{3N}}. \quad (3.11)$$

The two main contributions to the partition function are the thermal wavelength Λ , which depends only on temperature T , and the configuration integral Z , which depends on volume V , particle number N and possibly the temperature T when the potential energy depends on it. This shows that the expressions of thermodynamic quantities (Eqs. 2.102 to 2.106) are mainly functions of the potential energy through the configuration integral Z (Eq. 3.4).

The chemical potential (Eq. 2.107) is itself explicitly written as a function of Λ and Z , namely:

$$\begin{aligned} \exp(\beta\mu) &= \frac{Q(V, T, N-1)}{Q(V, T, N)} = \frac{Z_{N-1}(V, T)}{(N-1)! \Lambda^{3(N-1)}} \frac{N! \Lambda^{3N}}{Z_N(V, T)}, \\ &= N \Lambda^3 \frac{Z_{N-1}(V, T)}{Z_N(V, T)}. \end{aligned} \quad (3.12)$$

We will briefly digress about the relationship between the chemical potential μ and the fugacity z defined by the expression:

$$z = \frac{\exp(\beta\mu)}{\Lambda^3} = N \frac{Z_{N-1}(V, T)}{Z_N(V, T)}. \quad (3.13)$$

As usually prescribed by statistical mechanics, we split the chemical potential into the ideal gas contribution $\beta\mu^{id}$ and the excess contribution $\beta\mu^{ex}$:

$$\beta\mu = \beta\mu^{id} + \beta\mu^{ex}, \quad (3.14)$$

where the two contributions are given by:

$$\beta\mu^{id} = \ln [\rho\Lambda^3] , \quad (3.15)$$

$$\beta\mu^{ex} = \ln \left[\frac{z}{\rho} \right] . \quad (3.16)$$

The last two relations give us a precise meaning to the fugacity $z = \rho \frac{\exp(\beta\mu)}{\exp(\beta\mu^{id})}$ in close relation with Eq. (2.85). Note that the expression of chemical potential of the ideal gas, i.e. $\beta\mu^{id}$, will be calculated explicitly in section (4.1).

The purpose of this section is to define the expression of the partition function, regardless of the nature of the interparticle forces. However, even if our concern is not the determination of interactions, we would like to make some comments about the pair potential between two particles. It has been established that the character and magnitude of the interaction forces between two particles depend on their distance. They repel at short distances and attract at long distances according to a law of force, $F(r)$, which stipulates the simultaneous existence of (i) a repulsive force which decreases rapidly when the distance increases and (ii) an attractive force which also decreases with distance though less rapidly.

Consequently, when the distance r is larger than the equilibrium distance r_0 , the attractive force predominates and, when $r < r_0$, the repulsion overcomes on the attraction. These forces give rise to an oscillatory movement of the particles, which is not harmonic but rather of the form $F \propto 1/r^\alpha$, where α is taken to 12, for the repulsion, and 6 for the attraction within the Lennard-Jones potential. In fact, the oscillatory phenomenon is more complex because each particle interacts simultaneously with a large number of other particles inducing a disordered movement of the particles. The general shape of the potential of mutual interaction between two particles is depicted in figure (3.1). It is also modelled schematically by a square-well potential (dashed line) where ε is the cohesive energy of two particles, σ is the minimum distance of approach of two particles corresponding to the diameter of particles, and $\alpha\sigma$ is the action radius of the attractive force.

Assuming that the particles interact by pairs, the potential energy of the system can be written as a sum of pair potentials:

$$U(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j>i}^N u(r_{ij}) = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N u(r_{ij}) , \quad (3.17)$$

where the interatomic potential $u(r_{ij})$ between the particles i and j is a complicated function of the distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The sum is performed on all pairs of particles without omitting or counting the particles twice, hence the double sum and the factor $1/2$. To facilitate the counting of pair interactions, it is advisable to make a table with double entries where the subscripts i and j vary from 1 to N .

The simplest approximation, valid for the ideal gas, is to ignore the interaction potential posing $U(\mathbf{r}^N) = 0$. Sometimes, this approximation can be used for real gases without the error being too large. When the interactions between particles become appreciable, the approximation is inadequate. In this case, the method developed by Ursell and Mayer [7] is usually employed, allowing the calculation - at least formally - of the partition function of real gases.

In the method of Ursell and Mayer, the configuration integral is written by using the *Mayer function* f_{ij} defined by the following equation:

$$f_{ij} = \exp [-\beta u(r_{ij})] - 1. \quad (3.18)$$

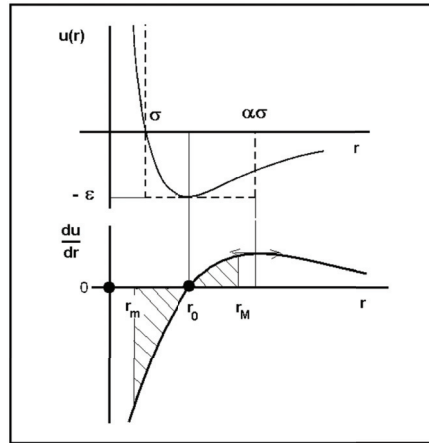


Figure 3.1: Representation of the interatomic potential modelled schematically by a square-well potential (dashed line in the upper panel).

With the function f_{ij} , the configuration integral (Eq. 3.4) is:

$$\begin{aligned} Z = \int \int_{3N} \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N &= \int \int_{3N} \prod_{j>i}^N \exp [-\beta u(r_{ij})] d\mathbf{r}^N \\ &= \int \int_{3N} \prod_{j>i}^N (1+f_{ij}) d\mathbf{r}^N. \end{aligned} \quad (3.19)$$

As a consequence, the partition function (Eq. 3.11) is given by the integral of a product of terms $(1+f_{ij})$, which once developed is:

$$\begin{aligned} Q_N(V, T) &= \frac{1}{N! \Lambda^{3N}} \int \int_{3N} \left[1 + \sum_i \sum_{j>i} f_{ij} \right. \\ &\quad \left. + \sum_i \sum_{j>i} \sum_{k>j>i} \sum_{l>k>j>i} f_{ij} f_{kl} + \dots \right] d\mathbf{r}^N. \end{aligned} \quad (3.20)$$

3.2 Cluster expansions for the partition function

A graph with N particles is a collection of N distinct circles numbered 1 to N and isolated or joined in pairs by a segment. Each segment represents a Mayer function, so that the use of graphs is a way of writing the integrals of the type specified in the partition function in a pictorial form. For example, figure (3.2) establishes the correspondence between a graph of 10 particles and its associated integral. With this convention, the partition function $Q_N(V, T)$ is simply:

$$Q_N(V, T) = \frac{1}{N! \Lambda^{3N}} \left[\begin{array}{c} \text{sum of all distinct} \\ \text{graphs to } N \text{ particles} \end{array} \right]. \quad (3.21)$$

To facilitate the counting of all graphs, it is useful to decompose each graph into a product of smaller units called *clusters*. A cluster is a graph in which no circle remains isolated. Thus, in a cluster of l particles, each circle is attached directly or indirectly to the $(l-1)$ other circles. For example, figure (3.3) displays a cluster of 6 particles and its associated integral.

With these definitions, it is clear that a graph can be separated into clusters. For example, the graph of 10 particles (Fig. 3.2) can be

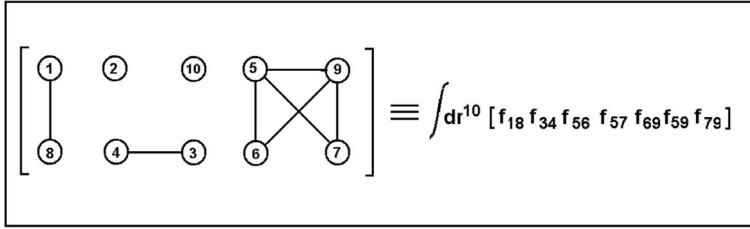


Figure 3.2: An example of a graph . The correspondence between the integral and its representative graph.

simplified, as shown in figure (3.4), into two clusters of $l = 1$ particle, two clusters of $l = 2$ particles and one cluster of $l = 4$ particles. More generally, any graph containing N particles reduces to a product of clusters whose configuration always satisfies the following equation:

$$\sum_l l m_l = N, \quad (3.22)$$

where m_l is the number of clusters with l particles. With the example of figure (3.4), we can immediately verify that $(1 \times 2) + (2 \times 2) + (4 \times 1) = 10$.

Before carrying out the enumeration of all terms of $Q_N(V, T)$, it is necessary to define the *reducible cluster integrals* $b_l(V, T)$ by the expression [8]:

$$b_l(V, T) = \frac{1}{l! V} \left[\begin{array}{c} \text{sum of all feasible clusters} \\ \text{with } l \text{ particles} \end{array} \right]. \quad (3.23)$$

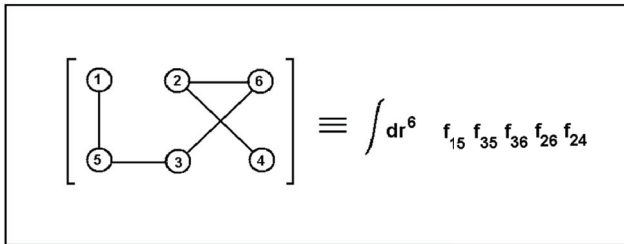


Figure 3.3: An example of cluster. The correspondence between the cluster and the integral it represents.

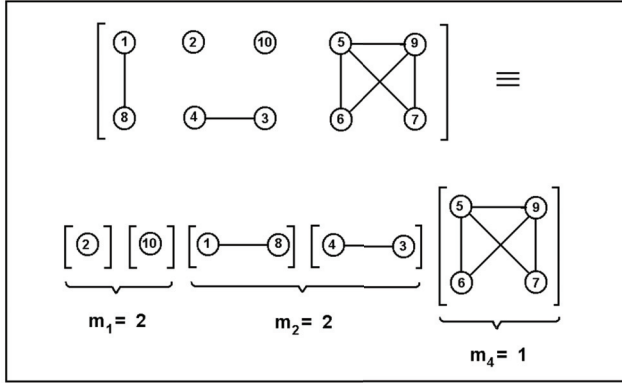


Figure 3.4: An example of decomposing a graph into clusters.

The first two reducible cluster integrals are:

$$b_1(V, T) = \frac{1}{V} [(1)] \equiv \frac{1}{V} \iint d\mathbf{r}_1 = 1$$

(1 cluster of 1 particle),

$$b_2(V, T) = \frac{1}{2V} [(1) - (2)] \equiv \frac{1}{2V} \iint f_{12} d\mathbf{r}_1 d\mathbf{r}_2$$

(1 cluster of 2 particles).

The pictorial representation of the reducible cluster integral of 3 particles, as shown in figure (3.5), reduces to a sum of 4 clusters of 3 particles. Its mathematical expression is:

$$b_3(V, T) \equiv \frac{1}{3!V} \iint \left[f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23} \right] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (3.24)$$

It is easy to see that $b_1(V, T)$ is a *reducible integral* by the fact that each of the terms can be factorized into a product of *irreducible integrals*, provided that the size of the enclosure containing the particles is large compared to the range of interaction forces. As examples, the calculation of $b_2(V, T)$ can be performed with equation (4.32) and the factorization of the first term of $b_3(V, T)$ carried out with the formula:

$$\iint [f_{12}f_{13}] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 = V \int f_{12} d\mathbf{r}_2 \int f_{13} d\mathbf{r}_3. \quad (3.25)$$

$$b_3 = \frac{1}{3!V} \left[\text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} \right]$$

$$b_3 = \frac{1}{6V} \int d\mathbf{r}^3 \left[f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23} + f_{12} f_{23} f_{13} \right]$$

Figure 3.5: An example of a cluster integral reducible to 4 clusters with 3 particles.

With the following definition of the *irreducible cluster integrals*²:

$$\beta_k = \frac{1}{k!V} \int \cdots \int S'_{1,2,\dots,k+1} d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_{k+1}, \quad (3.26)$$

where $S'_{1,2,\dots,k+1}$ is a product of Mayer functions which is obtained with cumbersome counting factors – see p. 136 of Ref. [3]. The first two irreducible cluster integrals have the expressions:

$$\beta_1 = \frac{1}{V} \iint f_{12} d\mathbf{r}_1 d\mathbf{r}_2, \quad (3.27)$$

$$\beta_2 = \frac{1}{2V} \iiint f_{12} f_{13} f_{23} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (3.28)$$

$$\dots = \dots$$

These formulas are used to write the reducible cluster integrals b_l in terms of the irreducible cluster integrals β_k . The first few expressions of $b_l = f(\beta_k)$ are:

$$b_2 = \frac{\beta_1}{2}, \quad (3.29)$$

$$b_3 = \frac{\beta_1^2}{2} + \frac{\beta_2}{3}, \quad (3.30)$$

$$b_4 = \frac{2\beta_1^3}{3} + \beta_1\beta_2 + \frac{\beta_3}{4}, \quad (3.31)$$

$$\dots = \dots$$

²Do not confuse the irreducible cluster integrals, denoted β_k , with the parameter $\beta = \frac{1}{k_B T}$.

and the first few expressions of $\beta_k = f(b_l)$ are:

$$\beta_1 = 2b_2, \quad (3.32)$$

$$\beta_2 = 3b_3 - 6b_2^2, \quad (3.33)$$

$$\beta_3 = 4b_4 - 24b_2b_3 + \frac{80}{3}b_2^3, \quad (3.34)$$

$$\dots = \dots$$

It is worth noticing that the cluster integrals b_l and β_k are temperature dependent, whereas they are almost independent of the volume when it is large compared to the action range of the forces. This can be seen, for instance, when noting that equation (4.32) coincides with the term $\beta_1 V$.

According to the previous considerations, it is possible to perform the enumeration of all distinct graphs with N particles present in the partition function. It is usually noted:

$$Q_N(V, T) = \frac{1}{N! \Lambda^{3N}} \sum_{\{m_l\}} S_{\{m_l\}}. \quad (3.35)$$

The notation $\sum_{\{m_l\}}$ stands for the sum of all graphs of N particles being formed with a set of N particles. Each of these graphs denoted $S_{\{m_l\}}$, contains m_1 clusters of 1 particle, m_2 clusters of 2 particles, m_3 clusters of 3 particles, and so on, with the condition $\sum_l l m_l = N$. The pictorial representation of such a graph is given in figure (3.6), and its corresponding algebraic form is:

$$\begin{aligned} S_{\{m_l\}} &= \sum_p \left[(1! V b_1)^{m_1} (2! V b_2)^{m_2} \dots (l! V b_l)^{m_l} \dots (N! V b_N)^{m_N} \right] \\ &= \sum_p \prod_{l=1}^N (l! V b_l)^{m_l}. \end{aligned} \quad (3.36)$$

In equation (3.36), the summation over p results from the need to consider all possible distributions of N particles among the clusters making the same contribution to the partition function. Since the N particles are numbered from 1 to N in an arbitrary manner, we could think that the summation over p gives rise to $N!$ permutations of the particles. But some of these permutations are ineffective because they do not produce new sets of clusters – see p. 468 of Ref. [7]. In fact, to

$$S_{\{m_l\}} = \sum_p \left[\text{diagram} \right]^{m_1} \left[\text{diagram} \right]^{m_2} \left[\text{diagram} \right]^{m_3} \left[\text{diagram} \right]^{m_4} \dots$$

Figure 3.6: Pictorial representation of the term $S_{\{m_l\}}$ of equation (3.35).

assess the number of terms in the summation over p , one must take into account the permutation of N particles, in considering that:

(1) the permutation of two particles in a group of m_l cluster integrals does not produce new configurations, so that $N!$ must be divided by the product of factorials $[(1!)^{m_1} (2!)^{m_2} \dots (l!)^{m_l} \dots (N!)^{m_N}]$,

(2) the permutation of two cluster integrals in a group of m_l cluster integrals does not lead to a new configuration³, so that $N!$ must be further divided by $(m_1! m_2! \dots m_l! \dots m_N!)$. It follows from these considerations that the number of terms in the sum over p is given by the expression:

$$\frac{N!}{m_1! (1!)^{m_1} m_2! (2!)^{m_2} \dots m_l! (l!)^{m_l} \dots m_N! (N!)^{m_N}} = \frac{N!}{\prod_{l=1}^N m_l! (l!)^{m_l}}. \quad (3.37)$$

By combining equations (3.36) and (3.37), $S_{\{m_l\}}$ is simplified to:

$$S_{\{m_l\}} = N! \prod_{l=1}^N \frac{(l! V b_l)^{m_l}}{m_l! (l!)^{m_l}} = N! \prod_{l=1}^N \frac{(V b_l)^{m_l}}{m_l!}. \quad (3.38)$$

Finally, the partition function (Eq. 3.35) is written by means of the reducible cluster integrals as follows:

$$Q_N(V, T) = \frac{1}{\Lambda^{3N}} \sum_{\{m_l\}} \prod_{l=1}^N \frac{(V b_l)^{m_l}}{m_l!}. \quad (3.39)$$

³This amounts to replacing the l particles of a group by the l particles of another group of the same order.

Simplified calculation of the partition function

Now that the purely statistical study has been achieved, we have to address the calculation of the partition function for real gases by replacing the sum of products of reducible cluster integrals b_l into equation (3.39). There are two ways to proceed. The simplest one, as described in this subsection, is meant to use only the term of the sum whose contribution is the most important. The second method is more rigorous and will be presented in the next subsection.

The simplified method assumes that the sum in equation (3.39) can be approximated by the term T_{Max} which gives the largest contribution, i.e.:

$$T_{Max} = \prod_{l=1}^N \frac{(Vb_l)^{m_l^*}}{m_l^*!}, \quad (3.40)$$

$$\text{or} \quad \ln T_{Max} = \sum_{l=1}^N [m_l^* \ln (Vb_l) - \ln m_l^*!], \quad (3.41)$$

where m_l^* is the number of clusters maximizing T_{Max} . First, we call on the Stirling's formula to evaluate $\ln m_l^*!$ that is in brackets of the previous relation:

$$\ln T_{Max} = \sum_{l=1}^N [m_l^* \ln (Vb_l) - m_l^* \ln m_l^* + m_l^*], \quad (3.42)$$

then we determine the value of m_l^* corresponding to $\ln T_{Max}$ by taking account of the condition $N = \sum_l l m_l$. To solve this problem, the method of Lagrange multipliers is implemented to find the maximum of a function subjected to constraints. The trick consists in combining the two previous relations in the X function constructed as follows:

$$X = \ln T_{Max} - \lambda N, \quad (3.43)$$

where λ is the so-called *Lagrange multiplier*. The extremum of X is obtained by canceling its derivative with respect to m_l :

$$\begin{aligned} \frac{\partial X}{\partial m_l} &= \frac{\partial}{\partial m_l} \left\{ \sum_{l=1}^N [m_l \ln (Vb_l) - m_l \ln m_l + m_l] - \lambda \sum_l l m_l \right\} \\ &= \sum_{l=1}^N \left(\ln \frac{Vb_l}{m_l} - \lambda l \right) = 0. \end{aligned} \quad (3.44)$$

The above relation yields the expression of m_l^* associated with T_{Max} . After simplification, it is found:

$$m_l^* = Vb_l \exp(-\lambda l). \quad (3.45)$$

As soon as the value of m_l^* is known, we are in a position to calculate the term T_{Max} and the partition function $Q_N(V, T)$:

$$Q_N(V, T) = \frac{1}{\Lambda^{3N}} T_{Max}, \quad (3.46)$$

as well as the free energy F and all other thermodynamic properties. But at this stage, the expression of m_l^* is still unknown because it depends on the Lagrange multiplier λ , which is also unknown. Before giving a physical interpretation to λ , an alternative method to calculate the partition function is presented in the next subsection which is not without academic interest.

Rigorous calculation of the partition function

In this subsection, use is made of the *steepest descent* method⁴, which is more rigorous than the method of Lagrange multipliers, because it takes into account all the terms of the sum in the partition function and not only the term having the largest contribution. For its implementation, introduce the generating function:

$$g(z) = \exp\left(\sum_{l=1}^{\infty} Vb_l z^l\right), \quad (3.47)$$

where z is a complex variable. In using the Taylor expansion of the exponential function, the generating function $g(z)$ is written as a series

⁴The steepest descent method that we owe to Darwin and Fowler was applied for the first time in the calculation of the partition function by M. Born and K. Fuchs, Proc. Roy. Soc. (London), A **166**, 391 (1938).

in ascending powers of z :

$$\begin{aligned}
 g(z) &= 1 + (Vb_1z + Vb_2z^2 + \dots + Vb_Nz^N + \dots) \\
 &\quad + \frac{1}{2!}(Vb_1z + Vb_2z^2 + \dots + Vb_Nz^N + \dots)^2 \\
 &\quad + \frac{1}{3!}(Vb_1z + Vb_2z^2 + \dots + Vb_Nz^N + \dots)^3 + \dots \\
 &= 1 + zVb_1 + z^2 \left[Vb_2 + \frac{1}{2!}(Vb_1)^2 \right] \\
 &\quad + z^3 \left[Vb_3 + \frac{1}{2!}2(Vb_1)(Vb_2) + \frac{1}{3!}(Vb_1)^3 \right] \\
 &\quad + z^4 [Vb_4 \dots] + z^5 [\dots] + \dots + z^N [\dots] + \dots \quad (3.48)
 \end{aligned}$$

It is worth noticing that the coefficient of z^N in equation (3.48) corresponds to the expression for the partition function $Q_N(V, T)$ (Eq. 3.39) apart from the constant Λ^{3N} . To check it, consider the following expression denoted R_N :

$$R_N = \Lambda^{3N} Q_N(V, T) = \sum_{\{m_l\}} \prod_{l=1}^N \frac{(Vb_l)^{m_l}}{m_l!}, \quad (3.49)$$

and, as an example, calculate the term R_3 by using the general formula. The condition $\sum_l l m_l = N$, which is still valid, reduces to the equation:

$$N = 3 = 1m_1 + 2m_2 + 3m_3, \quad (3.50)$$

with three possible combinations for m_l , i.e.:

$$(1) \quad m_1 = m_2 = 0 \quad \text{and} \quad m_3 = 1, \quad (3.51)$$

$$(2) \quad m_1 = m_2 = 1 \quad \text{and} \quad m_3 = 0, \quad (3.52)$$

$$(3) \quad m_1 = 3 \quad \text{and} \quad m_2 = m_3 = 0. \quad (3.53)$$

Then, we perform the calculation of R_3 making use of the equation (3.49) and the rules of combinations between l and m_l . It is found that:

$$\begin{aligned}
 R_3 &= \left[\frac{(Vb_1)^0}{0!} \frac{(Vb_2)^0}{0!} \frac{(Vb_3)^1}{1!} \right] + \left[\frac{(Vb_1)^1}{1!} \frac{(Vb_2)^1}{1!} \frac{(Vb_3)^0}{0!} \right] \\
 &\quad + \left[\frac{(Vb_1)^3}{3!} \frac{(Vb_2)^0}{0!} \frac{(Vb_3)^0}{0!} \right] = (Vb_3) + (Vb_1)(Vb_2) + \frac{(Vb_1)^3}{6}, \quad (3.54)
 \end{aligned}$$

which corresponds to the coefficient of z^3 in the generating function $g(z)$. It will be taken that it likewise applies to all the coefficients of $g(z)$.

When the generating function $g(z)$ is divided by z^{N+1} , the Laurent series follows:

$$\frac{g(z)}{z^{N+1}} = \frac{1}{z^{N+1}} + \frac{R_1}{z^N} + \frac{R_2}{z^{N-1}} + \dots + \frac{R_N}{z} + R_{N+1} + R_{N+2} \cdot z + R_{N+3} \cdot z^2 + \dots \quad (3.55)$$

The main part of this series expansion is composed of the terms that contain the powers of z in the denominator, and the coefficient R_N is the *residue* of the series related to the pole $z = 0$. According to the residue theorem, the integration of the series $g(z)z^{-(N+1)}$ around the pole removes all the terms of the series with the exception of the residue R_N . The application of this theorem leads immediately to:

$$R_N = \frac{1}{2\pi i} \oint \frac{g(z)}{z^{N+1}} dz = \frac{1}{2\pi i} \oint z^{-N-1} \exp\left(\sum_{l=1}^{\infty} Vb_l z^l\right) dz. \quad (3.56)$$

To calculate this integral, we choose the circle with centre O and radius r as a contour of integration. After the following change of variables:

$$\begin{aligned} z &= r \exp(i\phi) \\ \text{and} \quad dz &= ir \exp(i\phi) d\phi = iz d\phi \end{aligned} \quad (3.57)$$

in the expression of R_N , the partition function is then written:

$$Q_N(V, T) = \frac{R_N}{\Lambda^{3N}} = \frac{1}{2\pi \Lambda^{3N}} \int_{-\pi}^{+\pi} z^{-N} \exp\left(\sum_{l=1}^{\infty} Vb_l z^l\right) d\phi. \quad (3.58)$$

Before proceeding with the calculation of this integral, it is useful to examine carefully the integrand denoted $C(z)$ as a function of the complex variable $z = x + iy$. With the usual notations, the function $C(z)$ is:

$$C(z) = z^{-N} \exp\left(\sum_{l=1}^{\infty} Vb_l z^l\right) \equiv \text{Re}[C(x, y)] + i \text{Im}[C(x, y)]. \quad (3.59)$$

Let us consider first the variation of $C(z)$ along the real axis when z is a positive real variable ($\phi = 0$ and $z = x$). The first term,

x^{-N} , is a monotonically decreasing function of x , and the second term, $\exp(\sum_{l=1}^{\infty} V b_l x^l)$, is a monotonically increasing function of x , so that the product of these two functions presents a acute minimum (Fig. 3.7a) for the value $x = x_0$. Since the function $C(z)$ along the real axis can also be written as:

$$C(x, 0) = \exp \left[-N \ln x + \sum_{l=1}^{\infty} V b_l x^l \right], \quad (3.60)$$

the position x_0 of the minimum is given by the condition:

$$\left. \frac{\partial C}{\partial x} \right|_{x=x_0} = \left[-\frac{N}{x} + \sum_{l=1}^{\infty} l V b_l x^{l-1} \right] C(x, 0) = 0, \quad (3.61)$$

that is equivalent to:

$$N = \sum_{l=1}^{\infty} l V b_l x_0^l. \quad (3.62)$$

However, the function $C(z)$ is a *monogenic analytic* function which admits a unique derivative whatever the ratio between infinitesimal increments dx and dy , and meets the conditions of Cauchy-Riemann:

$$\frac{\partial \operatorname{Re} C}{\partial y} = -\frac{\partial \operatorname{Im} C}{\partial x} \quad \text{and} \quad \frac{\partial \operatorname{Im} C}{\partial y} = \frac{\partial \operatorname{Re} C}{\partial x}, \quad (3.63)$$

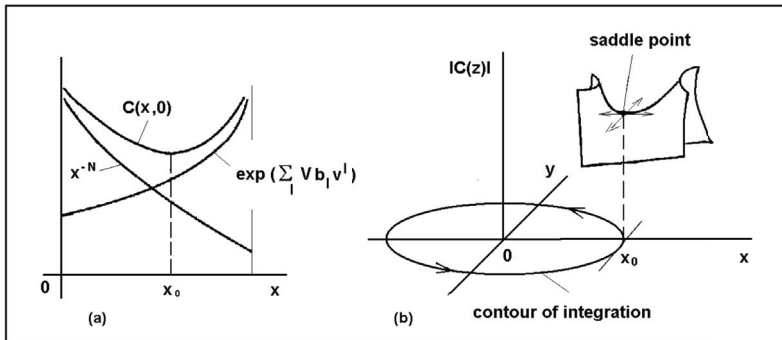


Figure 3.7: (a) Variation of the integrand $C(x, 0)$ along the real axis. (b) Schematic representation of the function $|C(x, y)|$ in the vicinity of the point $(x_0, 0)$.

simultaneously holding the condition:

$$\frac{\partial^2 \operatorname{Re} C}{\partial x^2} + \frac{\partial^2 \operatorname{Re} C}{\partial y^2} = 0 \quad \text{and} \quad \frac{\partial^2 \operatorname{Im} C}{\partial x^2} + \frac{\partial^2 \operatorname{Im} C}{\partial y^2} = 0. \quad (3.64)$$

It is easy with equation (3.59) to verify whether the Cauchy-Riemann conditions are reduced to:

$$\left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right] = 0. \quad (3.65)$$

As the curve in figure (3.7a) shows clearly that $\frac{dC}{dx}|_{x=x_0} = 0$ and $\frac{d^2 C}{dx^2}|_{x=x_0} > 0$, the inequality $\frac{d^2 C}{dy^2}|_{x=x_0} < 0$ is deduced from equation (3.65). This means that the function $C(z)$ has a minimum at $x = x_0$ on the real axis and a maximum along the axis parallel to the imaginary axis intersecting the real axis at $x = x_0$. The representation of the function $C(z)$ in the complex plane in figure (3.7b) shows a saddle point at $x = x_0$. Therefore, if the contour of integration is selected to be the circle of radius $r = x_0$, $|C(z)|$ has a very sharp maximum at $z = (x_0, 0)$ and the only significant contribution to the integral of $C(z)$, along the contour chosen, is found in the immediate vicinity of $x = x_0$. However, by choosing the circle of radius x_0 as a contour of integration, the argument of the exponential function in equation (3.59) can be expanded into a power series in ϕ , around $\phi = 0$, and stopped after the term ϕ^2 . This allows the transformation of $C(x, 0)$ as follows:

$$\begin{aligned} C(x, 0) &= \exp \left[-N \ln (r \exp i\phi) + \sum_{l=1}^{\infty} V b_l (r \exp i\phi)^l \right] \\ &\simeq \exp \left\{ -N \ln r - N i\phi + \sum_{l=1}^{\infty} V b_l r^l \left[1 + i l \phi + \frac{1}{2} (i l \phi)^2 \right] \right\} \\ &\simeq \exp \left\{ -N \ln r - N i\phi + \sum_{l=1}^{\infty} V b_l r^l \right. \\ &\quad \left. + \sum_{l=1}^{\infty} i l \phi V b_l r^l - \sum_{l=1}^{\infty} \frac{1}{2} (l \phi)^2 V b_l r^l \right\}. \end{aligned} \quad (3.66)$$

Given equation (3.62), the above relation for $z = r = x_0$ is simplified

to:

$$C(x, 0) \simeq \exp \left\{ -N \ln x_0 + \sum_{l=1}^{\infty} V b_l x_0^l - \frac{1}{2} \phi^2 \sum_{l=1}^{\infty} l^2 V b_l x_0^l \right\}. \quad (3.67)$$

With this expression, the partition function (Eq. 3.58) is written:

$$\begin{aligned} Q_N(V, T) &= \frac{1}{2\pi\Lambda^{3N}} \int_{-\pi}^{+\pi} \exp \left[-N \ln x_0 + \sum_{l=1}^{\infty} V b_l x_0^l - \frac{1}{2} \phi^2 \sum_{l=1}^{\infty} l^2 V b_l x_0^l \right] d\phi \\ &= \frac{1}{2\pi\Lambda^{3N}} \exp \left(-N \ln x_0 + \sum_{l=1}^{\infty} V b_l x_0^l \right) \int_{-\pi}^{+\pi} \exp \left(-\frac{1}{2} \phi^2 \sum_{l=1}^{\infty} l^2 V b_l x_0^l \right) d\phi. \end{aligned} \quad (3.68)$$

As regards the limits $-\pi$ and $+\pi$ of the integral over ϕ , they can be safely extended to $-\infty$ and to $+\infty$ because the main contribution of the integral is essentially in the vicinity of $\phi = 2k\pi$. The integral in the above equation being known⁵, the partition function finally takes the following analytical form:

$$\begin{aligned} Q_N(V, T) &= \frac{1}{2\pi\Lambda^{3N}} \frac{\exp \left(\sum_{l=1}^{\infty} V b_l x_0^l \right)}{x_0^N} \frac{\sqrt{\pi}}{\sqrt{\frac{1}{2} \sum_{l=1}^{\infty} l^2 V b_l x_0^l}}, \\ &= \frac{1}{\Lambda^{3N} x_0^N} \frac{\exp \left(\sum_{l=1}^{\infty} V b_l x_0^l \right)}{\sqrt{2\pi \sum_{l=1}^{\infty} l^2 V b_l x_0^l}}. \end{aligned} \quad (3.69)$$

3.3 Specific and generic distribution functions

To calculate the thermodynamic and structural properties of liquids, the method of *distribution functions* is commonly used. As it will be seen later, there are many distribution functions, but not all have the same importance. As an example, the probability of finding the system of N particles in a dynamic state defined by the volume element $(d\mathbf{r}^N d\mathbf{p}^N)$ at the extremity of the vector $(\mathbf{r}^N, \mathbf{p}^N)$ in the γ -space,

⁵see footnote 1 of this chapter.

is calculated with the probability density function for the canonical ensemble $P_N(\mathbf{r}^N, \mathbf{p}^N)$ as:

$$P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N. \quad (3.70)$$

However, other types of probabilities can also be calculated by using probability density functions of order less than $P_N(\mathbf{r}^N, \mathbf{p}^N)$ which are obtained by integrating $P_N(\mathbf{r}^N, \mathbf{p}^N)$ on a specific domain of the γ -space, as done with equation (2.139). Thus, the probability of finding the system of N particles in the volume element $d\mathbf{r}^N$ at the extremity of the vector $\mathbf{r}^N$ is:

$$\left[\iint_{3N} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{p}^N \right] d\mathbf{r}^N = P_N(\mathbf{r}^N) d\mathbf{r}^N. \quad (3.71)$$

Similarly, the probability of finding the system of N particles in a state defined by the volume element $d\mathbf{p}^N$ at the extremity of the vector $\mathbf{p}^N$ is:

$$\left[\iint_{3N} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N \right] d\mathbf{p}^N = P_N(\mathbf{p}^N) d\mathbf{p}^N. \quad (3.72)$$

It may also be advantageous to perform the integration of $P_N(\mathbf{r}^N, \mathbf{p}^N)$ over other parts of the γ -space. For instance, it may be useful to calculate the probability that a group of n *distinct* particles $\{\alpha_1, \alpha_2, \dots, \alpha_n\}$, taken at random in the system of N particles, will be in the dynamic state defined by the volume element $(d\mathbf{r}^n d\mathbf{p}^n)$ at the extremity of the vector $(\mathbf{r}^n, \mathbf{p}^n)$ in the γ -space. This probability is calculated with the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ through the relation:

$$\left[\iint_{6(N-n)} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{N-n} d\mathbf{p}^{N-n} \right] d\mathbf{r}^n d\mathbf{p}^n = P_N^{(n)}(\mathbf{r}^n, \mathbf{p}^n) d\mathbf{r}^n d\mathbf{p}^n. \quad (3.73)$$

The functions $P_N(\mathbf{r}^N)$, $P_N(\mathbf{p}^N)$ and $P_N^{(n)}(\mathbf{r}^n, \mathbf{p}^n)$ are probability density functions of order less than $P_N(\mathbf{r}^N, \mathbf{p}^N)$, known as *specific distribution functions*.

By contrast, if the particles are *identical*, a new class of functions called *generic distribution functions* are used. These functions do not have the characteristics of a probability density function, but are nevertheless interpreted in terms of probability. Recall first that, if the N particles are identical, their permutations do not affect the μ -space containing N points, but all the same generate a cloud of $N!$ points

in the γ -space – see section (1.3). Therefore, in order to calculate the probability of finding the system of N *identical* particles in the dynamic state defined by the volume $(d\mathbf{r}^N d\mathbf{p}^N)$ at the extremity of the vector $(\mathbf{r}^N, \mathbf{p}^N)$ in the γ -space, we are led to use a generic distribution function $N!$ times greater than $P_N(\mathbf{r}^N, \mathbf{p}^N)$. This distribution function is denoted:

$$\rho_N(\mathbf{r}^N, \mathbf{p}^N) = N!P_N(\mathbf{r}^N, \mathbf{p}^N). \quad (3.74)$$

The presence of $N!$ shows that the generic distribution function $\rho_N(\mathbf{r}^N, \mathbf{p}^N)$ is not a probability density function in the genuine sense because it is not normalized to unity.

Similarly, if we intend to calculate the probability that a group of n *identical* particles taken at random in the system of N particles will be in a dynamic state defined by the volume element $(d\mathbf{r}^n d\mathbf{p}^n)$ at the extremity of the vector $(\mathbf{r}^n, \mathbf{p}^n)$ in the γ -space, we have to replace the factor $N!$ by $\frac{N!}{(N-n)!}$, which corresponds to the number of ways n particles taken from the total system of N particles. In this case, the generic distribution function to use is:

$$\rho_N^{(n)}(\mathbf{r}^n, \mathbf{p}^n) = \frac{N!}{(N-n)!} P_N^{(n)}(\mathbf{r}^n, \mathbf{p}^n). \quad (3.75)$$

By combining equations (3.75) and (3.73), the opportunity arises to express each generic distribution function as a function of the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ which is the only function known. Thus Eq. (3.75) reads:

$$\begin{aligned} \rho_N^{(n)}(\mathbf{r}^n, \mathbf{p}^n) &= \frac{N!}{(N-n)!} P_N^{(n)}(\mathbf{r}^n, \mathbf{p}^n) \\ &= \frac{N!}{(N-n)!} \iint_{6(N-n)} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{N-n} d\mathbf{p}^{N-n}. \end{aligned} \quad (3.76)$$

It should be noted that the generic distribution function, for $n = 1$, is given by:

$$\rho_N^{(1)}(\mathbf{r}, \mathbf{p}) = \frac{N!}{(N-1)!} P_N^{(1)}(\mathbf{r}, \mathbf{p}) = NP_N^{(1)}(\mathbf{r}, \mathbf{p}). \quad (3.77)$$

We will see later that $P_N^{(1)}(\mathbf{r}, \mathbf{p})$ identifies with the distribution function of Maxwell-Boltzmann $f(\mathbf{r}, \mathbf{v})$ after a convenient change of variables is carried out. Further more, we must say that all the distribution functions have to depend explicitly on the time factor, when studying non-equilibrium processes.

3.4 The pair correlation function

In the canonical ensemble

The pair correlation function formalism is based on the generic distribution functions described in the previous section. If the canonical ensemble is used, the general expression for the generic distribution functions $\rho_N^{(n)}(\mathbf{r}^n)$ given by equation (3.76) is:

$$\rho_N^{(n)}(\mathbf{r}^n) = \frac{N!}{(N-n)!} \int \int_{6N-3n} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{N-n} d\mathbf{p}^N, \quad (3.78)$$

with

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{N! h^{3N} Q_N(V, T)} \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)]. \quad (3.79)$$

In addition, if the Hamiltonian of the system consists of the kinetic energy $\sum_i \frac{p_i^2}{2m}$ and the potential energy $U(\mathbf{r}^N)$, the partition function (Eq. 3.11) is expressed as:

$$\begin{aligned} Q_N(V, T) &= \frac{1}{N! h^{3N}} \int \int_{3N} \exp\left(-\beta \sum_i \frac{p_i^2}{2m}\right) d\mathbf{p}^N \int \int_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N \\ &= \frac{Z_N(V, T)}{N! \Lambda^{3N}}, \end{aligned} \quad (3.80)$$

where $Z_N(V, T)$ is the configuration integral and Λ the thermal wavelength, defined, respectively, by equations (3.4) and (3.9), i.e.:

$$Z_N(V, T) = \int \int \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N, \quad (3.81)$$

$$\text{and} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}. \quad (3.82)$$

Regarding the expression for the generic distribution functions, $\rho_N^{(n)}(\mathbf{r}^n)$, it can be transformed as:

$$\begin{aligned}\rho_N^{(n)}(\mathbf{r}^n) &= \frac{N!}{(N-n)!} \frac{1}{N!h^{3N}Q_N(V,T)} \times \\ &\quad \times \int \int_{3N} \exp\left(-\beta \sum_i \frac{p_i^2}{2m}\right) d\mathbf{p}^N \int \int_{3(N-n)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-n} \\ &= \frac{N!}{(N-n)!} \frac{1}{N!h^{3N}Q_N(V,T)} \left(\sqrt{\frac{2\pi m}{\beta}}\right)^{3N} \int \int_{3(N-n)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-n}\end{aligned}$$

and reduced to the following formula owing to equation (3.80):

$$\rho_N^{(n)}(\mathbf{r}^n) = \frac{N!}{(N-n)!} \frac{1}{Z_N(V,T)} \int \int_{3(N-n)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_{n+1} d\mathbf{r}_{n+2} \dots d\mathbf{r}_N. \quad (3.83)$$

With the normalization condition, the previous relation leads to:

$$\begin{aligned}\int \int_{3n} \rho_N^{(n)}(\mathbf{r}^n) d\mathbf{r}^n &= \frac{N!}{(N-n)!} \frac{1}{Z_N(V,T)} \int \int_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N \\ &= \frac{N!}{(N-n)!}.\end{aligned} \quad (3.84)$$

This formula shows that the generic distribution functions are not probability densities in the statistical sense because they are not normalized to unity. If $n = 1$, equation (3.84) becomes:

$$\int \rho_N^{(1)}(\mathbf{r}_1) d\mathbf{r}_1 = \frac{N!}{(N-1)!} = N, \quad (3.85)$$

and if the fluid is homogeneous and isotropic, $\rho_N^{(1)}(\mathbf{r}_1)$ does not depend on the positional coordinates of the particles, so that the generic distribution function to the first order $\rho_N^{(1)} = \frac{N}{\int d\mathbf{r}}$ is equal to the particle density ρ :

$$\rho_N^{(1)} = \frac{N}{V} = \rho. \quad (3.86)$$

It can be mentioned that, if the particles are independent, that is to say without mutual interaction ($U(\mathbf{r}^N) = 0$), the configuration

integral reduces to $Z_N(V, T) = V^N$ and the expression of the generic distribution functions (Eq. 3.83) is simplified to:

$$\begin{aligned}\rho_N^{(n)}(\mathbf{r}^n) &= \frac{N!}{(N-n)!} \frac{1}{Z_N(V, T)} \int \int_{3(N-n)} d\mathbf{r}^{N-n} = \frac{N!}{(N-n)!} \frac{V^{N-n}}{V^N} \\ &\simeq \left(\frac{N}{V}\right)^n = \rho^n.\end{aligned}\quad (3.87)$$

This expression is particularly advantageous for measuring the degree of interdependence of the particles, because of the reduced function:

$$g_N^{(n)}(\mathbf{r}^n) = \frac{\rho_N^{(n)}(\mathbf{r}^n)}{\rho^n} \quad (3.88)$$

tends towards unity when the particles are independent. In practice, the most important of these reduced functions is $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. It is called the *pair correlation function* and is expressed as:

$$\begin{aligned}g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2} \\ &= \frac{N!}{(N-2)!} \frac{1}{\rho^2} \frac{1}{Z_N(V, T)} \int \int_{3(N-2)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N.\end{aligned}\quad (3.89)$$

If the fluid is homogeneous and isotropic, the pair correlation function is denoted simply by $g_N^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) = g(r)$. In calculating the various thermodynamic properties, it will be seen that $g(r)$ acquires a great importance when the potential energy consists of a sum of pair potentials.

Finally, it should be noted that the pair correlation function $g(r)$ has a precise probabilistic sense. Indeed, if the integration of equation (3.89) is performed over the two variables of positions $\mathbf{r}_1$ and $\mathbf{r}_2$, the relation becomes:

$$\begin{aligned}\int \int_6 g_N^{(2)}(|\mathbf{r}_1 - \mathbf{r}_2|) d\mathbf{r}_1 d\mathbf{r}_2 &= \frac{N!}{(N-2)!} \frac{1}{\rho^2} \frac{1}{Z_N(V, T)} \times \\ &\times \int \int_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N.\end{aligned}\quad (3.90)$$

Since the integral in the above relation stands for the configuration integral $Z_N(V, T)$, the right hand side simplifies into $\frac{N(N-1)}{\rho^2}$. Concerning the integration of the left hand side of the above relation, it

can be carried out after performing the changes of variables $\mathbf{R} = \mathbf{r}_1$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, where $\mathbf{R}$ and $\mathbf{r}$ describe the volume of the system, and for which the Jacobian is equal to unity. Thus, after integration, the above relation reduces to:

$$\int_V d\mathbf{R} \int_V g(|\mathbf{r}|) d\mathbf{r} = \frac{N(N-1)}{\rho^2} \simeq \frac{N^2}{\rho^2}, \quad (3.91)$$

that is to say to:

$$\int_0^\infty 4\pi \rho r^2 g(r) dr \simeq N. \quad (3.92)$$

This relationship shows that the quantity $4\pi\rho r^2 g(r)dr$ represents the number of particles dN contained in the spherical crown between the radii r and $r+dr$ centered on a given particle. Therefore, the probability of finding a particle in the spherical crown of volume $dV = 4\pi r^2 dr$ at distance r from a given particle is:

$$\frac{dN}{N} = \frac{4\pi\rho r^2 g(r)dr}{N} = \rho g(r) \frac{dV}{N}. \quad (3.93)$$

The quantity $\rho g(r) = \frac{dN}{dV}$ represents the number of particles per unit volume at a specific position. If dV is large enough, $\frac{dN}{dV} = \frac{N}{V}$ tends to ρ and $g(r)$ tends to one. In fact, if there is no mutual interaction between the particles, $g(r) = 1$ for all distances greater than the contact distance of the two particles.

In the grand canonical ensemble

For open systems, the number of particles N is likely to change and the generic distribution functions of the grand canonical ensemble must be used rather than that of the canonical ensemble. It is therefore necessary to extend what has been done in the previous subsection. For this purpose, consider the expression of the generic distribution functions of open systems:

$$\rho^{(n)}(\mathbf{r}^n) = \sum_{N \geq n}^\infty \rho_N^{(n)}(\mathbf{r}^n) P(N), \quad (3.94)$$

where $P(N)$ is the probability that an open system contains exactly N particles (Eq. 2.40) and $\rho_N^{(n)}(\mathbf{r}^n)$ is the generic distribution function for n particles of the canonical ensemble. It is important to note

that, if both sides of equation (3.94) are multiplied by the volume element $(d\mathbf{r}_1 \dots d\mathbf{r}_n)$, the left hand side $\rho^{(n)}(\mathbf{r}^n) d\mathbf{r}_1 \dots d\mathbf{r}_n$ represents the probability of finding a group of n particles in the volume element $(d\mathbf{r}_1 \dots d\mathbf{r}_n)$ located at $\mathbf{r}_1, \dots, \mathbf{r}_n$, irrespective of the number N , while the term $\rho_N^{(n)}(\mathbf{r}^n) d\mathbf{r}_1 \dots d\mathbf{r}_n$ at right-hand side of the equation represents the probability of finding a group of n particles in the volume element $(d\mathbf{r}_1 \dots d\mathbf{r}_n)$, located at $\mathbf{r}_1, \dots, \mathbf{r}_n$, when the system contains exactly N particles. Moreover, as the generic distribution function $\rho_N^{(n)}(\mathbf{r}^n)$ exists only for N greater than n , the summation can start with $N=0$. It follows that the function $\rho^{(n)}(\mathbf{r}^n)$ is equal to the average value of the function $\rho_N^{(n)}(\mathbf{r}^n)$:

$$\rho^{(n)}(\mathbf{r}^n) = \sum_{N=0}^{\infty} \rho_N^{(n)}(\mathbf{r}^n) P(N) = \left\langle \rho_N^{(n)}(\mathbf{r}^n) \right\rangle. \quad (3.95)$$

As the probability $P(N)$ is given by equation (2.40) and $\rho_N^{(n)}(\mathbf{r}^n)$ by equation (3.83), it is found after various substitutions that:

$$\begin{aligned} \rho^{(n)}(\mathbf{r}^n) &= \sum_{N \geq n}^{\infty} \frac{\exp(\beta\mu N) Q_N(V, T)}{\Xi} \times \\ &\times \frac{N!}{(N-n)!} \frac{1}{Z_N(V, T)} \int \int_{3(N-n)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_{n+1} d\mathbf{r}_{n+2} \dots d\mathbf{r}_N \\ &= \sum_{N \geq n}^{\infty} \frac{\exp(\beta\mu N)}{\Xi} \times \\ &\times \frac{N!}{(N-n)!} \frac{1}{N! \Lambda^{3N}} \int \int_{3(N-n)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_{n+1} d\mathbf{r}_{n+2} \dots d\mathbf{r}_N, \quad (3.96) \end{aligned}$$

where Ξ is the partition function of the grand canonical ensemble (Eq. 2.38) independent of N , while $Q_N(V, T)$ is the partition function of the canonical ensemble (Eq. 3.80) which is a function of N . To simplify the integral, we usually introduce the fugacity $z = \frac{\exp(\beta\mu)}{\Lambda^3}$ defined by equation (3.13). This allows the writing of the generic distribution function $\rho^{(n)}(\mathbf{r}^n)$ under the standard form:

$$\rho^{(n)}(\mathbf{r}^n) = \frac{1}{\Xi} \sum_{N \geq n}^{\infty} \frac{z^N}{(N-n)!} \int \int_{3(N-n)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_{n+1} d\mathbf{r}_{n+2} \dots d\mathbf{r}_N. \quad (3.97)$$

It is worth noting that the generic distribution functions of the canonical and grand canonical ensembles give results which are virtually identical for large systems ($V \rightarrow \infty$ and $N \rightarrow \infty$) as long as $\rho = \frac{N}{V}$ is constant. This arises as to whether the contribution for which the index N equals $\langle N \rangle$ is much more important than all the other ones into the sum of equation (3.97).

Of course, the normalization condition can be applied to equation (3.95). Given equation (3.84), it follows:

$$\begin{aligned} \int \int_{3n} \rho^{(n)}(\mathbf{r}^n) d\mathbf{r}^n &= \int \int_{3n} \sum_{N=0}^{\infty} \rho_N^{(n)}(\mathbf{r}^n) P(N) d\mathbf{r}^n \\ &= \sum_{N=0}^{\infty} \left[\int \int_{3n} \rho_N^{(n)}(\mathbf{r}^n) d\mathbf{r}^n \right] P(N) = \left\langle \frac{N!}{(N-n)!} \right\rangle. \end{aligned} \quad (3.98)$$

If $n = 1$, the normalization condition reads:

$$\int_V \rho^{(1)}(\mathbf{r}_1) d\mathbf{r}_1 = \langle N \rangle, \quad (3.99)$$

and if $n = 2$ it becomes:

$$\int \int_6 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \langle N(N-1) \rangle = \langle N^2 \rangle - \langle N \rangle. \quad (3.100)$$

Besides, for a homogeneous and isotropic fluid, $\rho^{(1)}(\mathbf{r})$ does not depend on the coordinates of the particles, so that $\rho^{(1)} = \frac{\langle N \rangle}{V} = \rho$. Finally, as for the canonical ensemble, a reduced function can be employed for measuring the degree of interdependence of the particles. This is the quantity $g^{(n)}(\mathbf{r}^n) = \frac{\rho^{(n)}(\mathbf{r}^n)}{\rho^n}$ and, more specifically, the pair correlation function:

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho^2}. \quad (3.101)$$

3.5 Measurement of the pair correlation function

The pair correlation function $g(r)$ is determined from the measurement of the structure factor $S(q)$ by neutron scattering, X-ray or electron diffraction. Considering that the scatterers in liquids are essentially individual atoms, the diffraction experiments supply only

the structure of *monatomic liquids* such as rare gases and metals. By contrast, they do not provide any information on the structure of *molecular liquids*, unless they are formed of spherical molecules or monatomic ions as in some molten salts.

Furthermore, each type of radiation-matter interactions has its own particularities. While the electrons are diffracted by all the entities present in the atoms (electrons and nuclei), the X-rays are diffracted by the electrons localized on stable electron shells and the neutrons are scattered only by nuclei at the centre of the atoms. The electron diffraction is of practical use for low density fluids. In contrast, only the beams of neutrons and X-rays are suitable for studying the structure of liquids, with their respective advantages and disadvantages. For example, the radius of nuclei being 10,000 times smaller than that of the atoms, it is not surprising that the structure factor obtained with neutrons is not completely identical to that obtained with X-rays.

To perform an experiment using X-ray diffraction, the liquid sample must be irradiated with a monochromatic beam of X-rays having a wavelength close to the interatomic distance ($\lambda \sim 0,1$ nm). This radiation corresponds to a photon energy ($h\nu = \frac{hc}{\lambda} \sim 10^4$ eV) much larger than the average energy of an atom which is in the order of a few $k_B T$, i.e. $\sim 10^{-1}$ eV. The great differences of masses and energies between a photon and an atom make the photon-atom collision elastic (constant energy) and the matter transparent to radiations. Naturally, the dimensions of the sample should be sufficiently large compared with the wavelength λ of the radiation so that there are no side effects due to the walls of the enclosure - though not too large to avoid excessive absorption of the radiation. This would be particularly troublesome if the X-rays had to pass through metallic components with large atomic numbers.

The incident radiation is characterized by the wavelength λ and intensity I_0 , and the diffraction patterns observed depend on the structural properties of liquids as well as on the diffusional features of atoms. In neutron scattering, the atom is characterized by the *scattering cross section* $\sigma = 4\pi b^2$, where b is a parameter having approximately the value of the nucleus radius ($\sim 10^{-14}$ m). Note that the parameter b does not depend on the direction of observation but may vary slightly, even for pure elements, as a function of the isotope. For comparison, in the X-ray diffraction, the parameter corresponding to

b is the *atomic scattering factor* $A(q)$ which depends on the electron density in the isolated atom and the direction of observation. The structure factor $S(q)$ obtained with X-rays has, in general, a better accuracy at intermediate values of q . At the ends of the scale of q , it is less precise than the structure factor obtained with neutrons because the atomic scattering factor $A(q)$ is very small at high values of q , and it is poorly known for low values of q . The corrections to be brought to the experimental results are the concern of specialists and will not be discussed here.

Structure factor

When a photon of wave vector $\mathbf{k} = \frac{2\pi}{\lambda} \mathbf{u}$ interacts with an atom, it is deflected of an angle θ and the wave vector of the scattered photon is $\mathbf{k}' = \frac{2\pi}{\lambda} \mathbf{u}'$, where $\mathbf{u}$ and $\mathbf{u}'$ are unit vectors. Here, it is supposed that $|\mathbf{k}'| = |\mathbf{k}|$, so that the scattering is elastic ($E \propto k^2 = cte$) and the *scattering vector* (or transfer vector) $\mathbf{q}$ is defined (Fig. 3.8a) by the Bragg law:

$$\mathbf{q} = \mathbf{k}' - \mathbf{k}, \quad \text{and} \quad |\mathbf{q}| = 2 |\mathbf{k}| \sin \frac{\theta}{2} = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}. \quad (3.102)$$

When the interference is produced by two atoms (Fig. 3.8b) where the first one is placed in a position taken as origin and the other

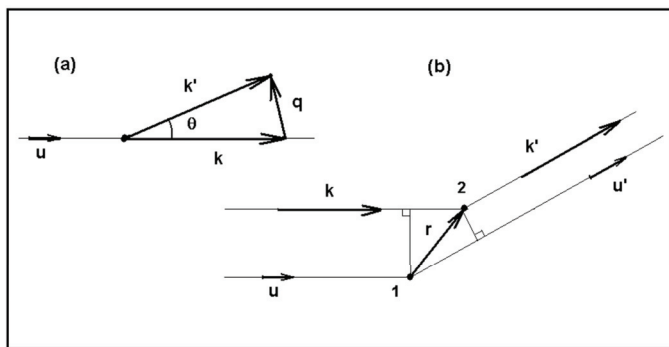


Figure 3.8: (a) Vectorial representation of the Bragg law. (b) Determination of the path difference $\delta = \mathbf{r} \cdot \mathbf{u}' - \mathbf{r} \cdot \mathbf{u}$ in the interference by two atoms.

at a distance $\mathbf{r}$, the amplitude of the scattered wave is given by the formula:

$$A = A_0 \exp\left(-i\frac{2\pi}{\lambda}\delta\right), \quad (3.103)$$

where δ is the path difference and A_0 the atomic scattering factor depending on the type of atom. According to figure (3.8b), the path difference is given by $\delta = \mathbf{r} \cdot \mathbf{u}' - \mathbf{r} \cdot \mathbf{u}$ and the expression for the scattering amplitude reduces to:

$$\begin{aligned} A &= A_0 \exp\left[-i\frac{2\pi}{\lambda}(\mathbf{r} \cdot \mathbf{u}' - \mathbf{r} \cdot \mathbf{u})\right] = A_0 \exp[-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}] \\ &= A_0 \exp(-i\mathbf{q} \cdot \mathbf{r}). \end{aligned} \quad (3.104)$$

Now, if an assembly of N identical atoms is considered (forming the liquid sample), the total scattering amplitude A_N is the sum of partial amplitudes:

$$A_N = \sum_{j=1}^N A_0 \exp(-i\mathbf{q} \cdot \mathbf{r}_j), \quad (3.105)$$

and the intensity scattered by the N atoms in direction θ (related to q , according to Bragg's law) is given by:

$$I(q) = A_N A_N^* = A_0 A_0^* \sum_{j=1}^N \sum_{l=1}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)]. \quad (3.106)$$

In a crystalline solid, the arrangement of atoms is known once and for all, and the scattered intensity I is represented by spots generating Laue or Debye-Scherrer patterns. In a liquid, the atoms are continuously in motion and the diffraction experiments supply only the average value of successive configurations during the experiment. Given the lack of translational symmetry in liquids, this average value provides no information on the long-range order. By contrast, it is a good measure of the short-range order around a given atom arbitrarily chosen. Thus, in a liquid, the intensity scattered by the atoms must be expressed in terms of q by the statistical average:

$$I(q) = I_0 \left\langle \sum_{j=1}^N \sum_{l=1}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \right\rangle. \quad (3.107)$$

To determine $I(q)$, the double sum is decomposed as follows:

$$I(q) = I_0 \left\langle \sum_{l=j=1}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \right\rangle + I_0 \left\langle \sum_{j=1}^N \sum_{l \neq j}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \right\rangle. \quad (3.108)$$

The first average value in this relation is equal to N because it contains the sum of N terms equal to unity when $l = j$. To evaluate the second average value, it should be possible to calculate the sum of exponential functions by considering all the pairs of atoms (j, l) in all the configurations occupied during the experiment, and then to perform the average of all the configurations. For systems containing a few particles, this calculation can be easily achieved through the numerical simulation. But for real systems, it proves unworkable: the method adopted consists in determining the average contribution of each pair of atoms (j, l) by using the probability of finding the atoms j and l in the positions $\mathbf{r}'$ and $\mathbf{r}$, respectively. To this end, the double sum is written by means of the Dirac function as:

$$\begin{aligned} & \sum_{j=1}^N \sum_{l \neq j}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] = \\ &= \sum_{j=1}^N \sum_{l \neq j}^N \iint d\mathbf{r} d\mathbf{r}' \exp[i\mathbf{q} \cdot (\mathbf{r}' - \mathbf{r})] \delta(\mathbf{r}_j - \mathbf{r}') \delta(\mathbf{r}_l - \mathbf{r}). \end{aligned} \quad (3.109)$$

The calculation of the ensemble average (Eq. 1.127) is done in using the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ of the canonical ensemble, as follows:

$$\begin{aligned} & \left\langle \sum_{j=1}^N \sum_{l \neq j}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \right\rangle = \iint d\mathbf{r} d\mathbf{r}' \exp[i\mathbf{q} \cdot (\mathbf{r}' - \mathbf{r})] \times \\ & \times \left\{ \sum_{j=1}^N \sum_{l \neq j}^N \iint_{6N} \delta(\mathbf{r}_j - \mathbf{r}') \delta(\mathbf{r}_l - \mathbf{r}) P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \right\}. \end{aligned} \quad (3.110)$$

The expression in brackets is formed by a double sum which contains $(N^2 - N) = N(N-1) = \frac{N!}{(N-2)!}$ identical terms. Indeed, each term of the sum is equal to the integral $\iint_{6(N-1)} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{N-2} d\mathbf{p}^N$ owing to the property of the Dirac function, because it is possible to perform

the integration directly over all the pairs $(\mathbf{r}_j, \mathbf{r}_l)$ formed with the N positional variables. Therefore, the expression in brackets reduces to:

$$\left\{ \frac{N!}{(N-2)!} \int \int_{6(N-1)} P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^{N-2} d\mathbf{p}^N \right\}, \quad (3.111)$$

and the ensemble average can be expressed in terms of the generic distribution function $\rho_N^{(2)}(\mathbf{r}^2)$, with the help of equation (3.78), as:

$$\left\langle \sum_{j=1}^N \sum_{l \neq j}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \right\rangle = \int \int_6 d\mathbf{r} d\mathbf{r}' \exp[i\mathbf{q} \cdot (\mathbf{r}' - \mathbf{r})] \rho_N^{(2)}(\mathbf{r}, \mathbf{r}'). \quad (3.112)$$

If it is assumed that the liquid is homogeneous and isotropic, and all the atoms have identical properties, the changes of variables $\mathbf{R} = \mathbf{r}$ and $\mathbf{X} = \mathbf{r}' - \mathbf{r}$ in the previous relation enable us to write explicitly the ensemble average with the pair correlation function $\rho_N^{(2)}(\mathbf{r}, \mathbf{r}') = \rho^2 g(|\mathbf{r}' - \mathbf{r}|)$, namely:

$$\begin{aligned} \left\langle \sum_{j=1}^N \sum_{l \neq j}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \right\rangle &= \int \int_6 d\mathbf{r} d\mathbf{r}' \exp[i\mathbf{q} \cdot (\mathbf{r}' - \mathbf{r})] \rho^2 g(|\mathbf{r}' - \mathbf{r}|) \\ &= \rho^2 \int_V d\mathbf{R} \int_V d\mathbf{X} \exp(i\mathbf{q} \cdot \mathbf{X}) g(X). \end{aligned} \quad (3.113)$$

After performing the integration over $\mathbf{R}$, giving rise to V , and the integration over $\mathbf{X}$, we finally obtain⁶:

$$\left\langle \sum_{j=1}^N \sum_{l \neq j}^N \exp[i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_l)] \right\rangle = 4\pi \rho^2 V \int_0^\infty \frac{\sin(qr)}{qr} g(r) r^2 dr. \quad (3.114)$$

⁶To evaluate the integral of the form $I = \int_V d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}) g(r)$, use is made of the spherical coordinates by placing the vector $\mathbf{q}$ alongside the z -axis so that $\theta = (\mathbf{q}, \mathbf{r})$. Thus, the integral reads:

$$I = \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \int_0^\infty \exp(iqr \cos \theta) g(r) r^2 dr$$

with $\mu = \cos \theta$ and $d\mu = -\sin \theta d\theta$. As a result the integral becomes:

$$\begin{aligned} I &= -2\pi \int_0^\infty \left[\int_{+1}^{-1} \exp(iqr\mu) d\mu \right] g(r) r^2 dr \\ &= -2\pi \int_0^\infty \frac{1}{iqr} [\exp(-iqr) - \exp(iqr)] g(r) r^2 dr = 4\pi \int_0^\infty \frac{\sin(qr)}{qr} g(r) r^2 dr. \end{aligned}$$

Since the integrand is increasing with r , the integral is diverging. This poses a problem because the scattered intensity has no physical meaning and seems not to have been measured. To overcome this difficulty, it is convenient to split the scattered intensity $I(q)$ defined by equation (3.108) in using equation (3.113) as:

$$I(q) = NI_0 + NI_0\rho \int_V \exp(i\mathbf{q} \cdot \mathbf{r})g(r)d\mathbf{r}, \quad (3.115)$$

or equivalently:

$$I(q) = NI_0 + NI_0\rho \int_V \exp(i\mathbf{q} \cdot \mathbf{r})[g(r)-1]d\mathbf{r} + NI_0\rho \int_V \exp(i\mathbf{q} \cdot \mathbf{r})d\mathbf{r}. \quad (3.116)$$

For large distances, $g(r)$ tends to unity and $[g(r)-1]$ tends towards zero, making the first integral of equation (3.116) convergent. As far as the second integral is concerned, it represents the Dirac function⁷, which is zero for all values of q , except for $q = 0$ where it is infinite. Thus, the expression of the scattered intensity $I(q)$ becomes:

$$I(q) = NI_0 + NI_0\rho \int_V \exp(i\mathbf{q} \cdot \mathbf{r})[g(r)-1]d\mathbf{r} + NI_0\rho(2\pi)^3\delta(\mathbf{q}). \quad (3.117)$$

From an experimental point of view, it is necessary to exclude the intensity measured in the direction of the incident beam ($q = 0$) which

⁷Fourier transform of the Dirac function is:

$$\delta(r_x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \delta(q_x) \exp(-iq_x r_x) dq_x = \frac{1}{2\pi},$$

and the inverse transform is:

$$\delta(q_x) = \int_{-\infty}^{+\infty} \delta(r_x) \exp(iq_x r_x) dr_x = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp(iq_x r_x) dr_x.$$

The three-dimensional generalization of the result is:

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3} \iiint_{-\infty}^{+\infty} \delta(\mathbf{q}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q} = \frac{1}{(2\pi)^3},$$

and the inverse transform is:

$$\delta(\mathbf{q}) = \iiint_{-\infty}^{+\infty} \delta(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = \frac{1}{(2\pi)^3} \iiint_{-\infty}^{+\infty} \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r},$$

with $\delta(\mathbf{q}) = \delta(q_x)\delta(q_y)\delta(q_z)$.

is not scattered at all. Therefore, the *structure factor* $S(q)$ of liquids is defined by the following normalized function:

$$\begin{aligned} S(q) &= \frac{I(q) - (2\pi)^3 N I_0 \rho \delta(\mathbf{q})}{N I_0} = 1 + \rho \int_V \exp(i\mathbf{q}\mathbf{r}) [g(r) - 1] d\mathbf{r} \\ &= 1 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} [g(r) - 1] r^2 dr. \end{aligned} \quad (3.118)$$

As a consequence, the pair correlation function $g(r)$ can be extracted from the experimental results of the structure factor $S(q)$ by performing the numerical Fourier transform:

$$\rho[g(r) - 1] = FT[S(q) - 1]. \quad (3.119)$$

Determination of the number of first neighbours

An accurate determination of the pair correlation function $g(r)$ presupposes a precise knowledge of the structure factor $S(q)$ for all values of q because the Fourier transform amplifies the imperfections altering $S(q)$ at low and high values of q . Figure (3.9) shows the general shapes of $S(q)$ and $g(r)$ of simple liquids. It can be noticed that they oscillate, similarly to each other, around unity for large values of q

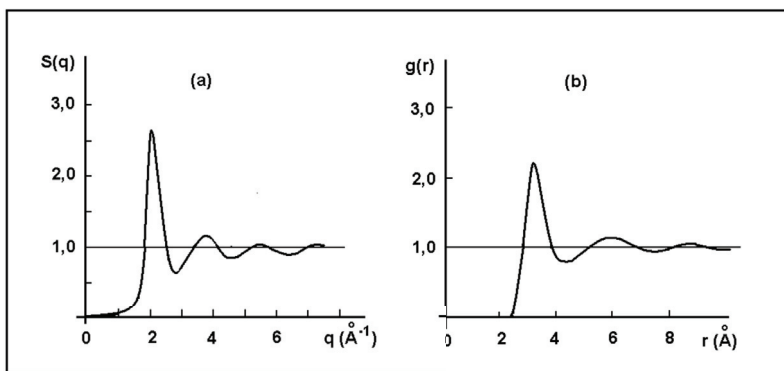


Figure 3.9: Typical representations of (a) the experimental structure factor $S(q)$ of a normal liquid metal and (b) the corresponding pair correlation function $g(r)$.

and r , respectively. Given that the atoms are impenetrable, the values of $g(r)$ are strictly zero for small distances. As regards the values of $S(q)$, they are very small – but nonzero – for small values of q . It should also be noted that the value of $S(0)$ is unreachable by the diffraction experiments because of the divergence of the integral into equation (3.114). It can nevertheless be obtained experimentally by measuring the isothermal compressibility χ_T via the speed of sound v_s because $S(0) \propto \chi_T \propto v_s^{-2}$.

When the pair correlation function $g(r)$ is extracted from $S(q)$, it can be used to determine various physical properties deriving directly from the structure, such as the *coordination number* in a monatomic liquid and all the other thermodynamic properties. In this paragraph, we show how to determine the coordination number Z (number of first neighbours) owing to the expression of the number of atoms $N(r)$ located around an atom taken at random which is proportional to the area under the curve $r^2g(r)$, namely,

$$N(r) = 4\pi \int_0^r \rho r^2 g(r) dr. \quad (3.120)$$

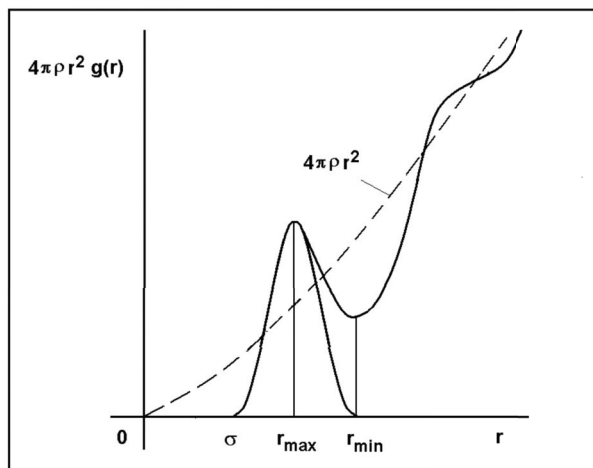


Figure 3.10: Determination of the coordination number Z from the pair correlation function $g(r)$.

If the upper limit of integration is less than or equal to the diameter σ of the atom, the number of neighbours is obviously zero, since $g(r)$ is zero inside the atom. As a result, the optimal upper limit of integration must be chosen to determine the number of nearest neighbours Z . Figure (3.10) depicts the two methods commonly used. The coordination number Z is either equal to the integral of $4\pi\rho r^2 g(r)$ from 0 to the first minimum ($r = r_{\min}$) of $g(r)$ or is equal to twice the integral from 0 to $r_{\max}$ where $r_{\max}$ is the location of the top of the first peak of $g(r)$, namely

$$Z = 4\pi \int_0^{r_{\min}} \rho r^2 g(r) dr \quad \text{or} \quad Z = 8\pi \int_0^{r_{\max}} \rho r^2 g(r) dr. \quad (3.121)$$

Each method has its advantages. In the second method $r_{\max}$ is easier to determine, but it should be assumed the peak symmetry of $g(r)$ which is not always the case as the atoms naturally tend to place themselves beyond $r_{\max}$. In contrast, in the first method, the value of $r_{\min}$ is more difficult to determine but the asymmetry of the peak is taken into account.

4 Equilibrium states of gases

In chapter 3, we have seen that the thermodynamic properties of gases can be deduced from the partition function developed in series expansions of the density containing all crucial information about the system. This chapter is devoted to presenting some examples of direct calculation of the partition function and thermodynamic properties derived therefrom for certain particular systems such as ideal gas, imperfect gas, real gas and ionized gas.

For imperfect and real gases, the method consists in calculating the free energy of the partition function (Eq. 2.102) and deriving the relevant thermodynamic properties. Concerning ionized gas composed of charged particles interacting with Coulomb forces, the partition function method cannot be used in the form originally prescribed because the slow variation of the long-range potential varying as r^{-1} causes a divergence of integrals in the calculations of the partition function.

To solve the problem, Debye and Hückel devised a specific method for processing systems where Coulomb forces are at work. The method involves replacing the current system with a system of independent charges on which a *mean electrostatic potential* is applied. The method uses the Boltzmann distribution with the Poisson equation to form a system of equations to be solved in a consistent way to determine the free energy of the real system. It should be noted that the set of equations can be solved analytically in the case of a diluted ionized gas, as will be shown in section (4.6).

4.1 Classical ideal gas

As a first example of applying the direct calculation of the partition function, consider the case of the monatomic ideal gas consisting of N atoms in an enclosure of volume V at temperature T , and with no interaction between each other. In such a system, the absence of interaction between the atoms amounts to saying that the potential energy $U(\mathbf{r}^N)$ is zero everywhere. Strictly speaking, $U(\mathbf{r}^N)$ is not totally zero because the atoms at the surface of the system are interacting with the walls of the enclosure. However, given the small number of atoms at the surface compared to the number of atoms in the volume, these interactions can be negligible and the Mayer functions considered to be zero. In this case, the configuration integral (Eq. 3.19) simplifies as:

$$Z = \int \int_{3N} d\mathbf{r}^N = V^N. \quad (4.1)$$

Calculation of thermodynamic properties

The partition function (Eq. 3.11) of a monatomic ideal gas is thus written as:

$$Q_N(V, T) = \frac{V^N}{N! \Lambda^{3N}}, \quad (4.2)$$

and, with equation (2.102) and Stirling's approximation¹, the free energy reduces to the expression:

$$\begin{aligned} F &= -k_B T \ln Q_N(V, T) = -k_B T \ln \frac{V^N}{N! \Lambda^{3N}}, \\ &= -N k_B T \left[\ln \frac{V}{N} - 3 \ln \Lambda + 1 \right]. \end{aligned} \quad (4.3)$$

Owing to equation (2.104), the internal energy E is:

$$E = k_B T^2 \left[\frac{\partial}{\partial T} \ln \frac{V^N}{N! \Lambda^{3N}} \right]_V = k_B T^2 \left[-3N \frac{\partial}{\partial T} \ln \Lambda \right]_V, \quad (4.4)$$

¹The Stirling approximation can be used here in the form:

$$\ln N! \simeq N \ln N - N.$$

and, since $\frac{\partial}{\partial T} \ln \Lambda = -\frac{1}{2T}$ (Eq. 3.9), it can be simplified to:

$$E = \frac{3}{2} N k_B T, \quad (4.5)$$

which is the correct result expected by the law of Joule.

Besides, with equation (2.105), the expression of the pressure is immediately obtained:

$$\begin{aligned} p &= - \left(\frac{\partial F}{\partial V} \right)_T = k_B T \left[\frac{\partial}{\partial V} \ln \frac{V^N}{N! \Lambda^{3N}} \right]_T, \\ &= \frac{N k_B T}{V} = \frac{2}{3} \frac{E}{V}. \end{aligned} \quad (4.6)$$

The chemical potential is another property which can be deduced with equations (2.107) and (4.3) accordingly:

$$\begin{aligned} \mu &= \left(\frac{\partial F}{\partial N} \right)_T = -k_B T [-\ln(\rho \Lambda^3) + 1] - N k_B T \left[-\frac{1}{N} \right] \\ &= k_B T \ln(\rho \Lambda^3). \end{aligned} \quad (4.7)$$

As expected, this result is the part of the chemical potential μ^{id} coming from the ideal gas (see equation 3.15).

With equation (2.106), we determine the specific heat at constant volume:

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} N k_B, \quad (4.8)$$

and the specific heat at constant pressure:

$$c_p = \left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_p + \left(p \frac{\partial V}{\partial T} \right)_p = \frac{5}{2} N k_B. \quad (4.9)$$

Incidentally, note that equation (4.6) makes it possible to calculate the pressure fluctuations:

$$\begin{aligned} \langle (p - \langle p \rangle)^2 \rangle &= \langle p^2 \rangle - \langle p \rangle^2 = \left\langle \left(\frac{2}{3} \frac{E}{V} \right)^2 \right\rangle - \left\langle \frac{2}{3} \frac{E}{V} \right\rangle^2 \\ &= \frac{4}{9V^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right) = \frac{4}{9V^2} k_B T^2 c_V. \end{aligned} \quad (4.10)$$

To write the last equality, equation (2.151) has been taken into account and this also applies to the fact that only the energy varies in the canonical ensemble. The relative fluctuations in the pressure is then expressed as:

$$\frac{\sqrt{\langle (p - \langle p \rangle)^2 \rangle}}{p} = \frac{2T}{3V} \sqrt{k_B c_V} \frac{V}{N k_B T} = \sqrt{\frac{2}{3N}}. \quad (4.11)$$

Similarly to the other thermodynamic properties, the relative fluctuations in the pressure is inversely proportional to the square root of the particle number in the system. The result can be extended to polyatomic ideal gases because the energy contributions of rotation and vibration are independent of the volume and disappear when calculating $p = -\left(\frac{\partial F}{\partial V}\right)_T$.

Expression of entropy

While the calculation of the entropy is easily done by using equation (2.103), the outcome deserves some comments which were not necessary for other thermodynamic properties. First, calculate the entropy with equation (2.103):

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = k_B \ln Q_N(V, T) + k_B T \left[\frac{\partial}{\partial T} \ln Q_N(V, T) \right]_V. \quad (4.12)$$

Since $\frac{\partial}{\partial T} \ln Q_N(V, T) = -3N \frac{\partial}{\partial T} \ln \Lambda = \frac{3N}{2T}$ (Eq. 4.2), the expression of the entropy becomes:

$$S = k_B \ln \frac{V^N}{N! \Lambda^{3N}} + k_B T \left[\frac{3N}{2T} \right]. \quad (4.13)$$

By using Stirling's formula to estimate $\ln N!$ and the expression of the thermal wavelength Λ to show the temperature dependence of S , we obtain:

$$\begin{aligned} S &= k_B \left[N \ln V - (N \ln N - N) - 3N \ln \Lambda \right] + \frac{3}{2} k_B N \\ &= k_B N \left[-\ln \frac{N}{V} \Lambda^3 + \frac{5}{2} \right] = k_B N \left[\ln \frac{V}{N} - \frac{3}{2} \ln \frac{h^2}{2\pi m k_B T} + \frac{5}{2} \right]. \end{aligned} \quad (4.14)$$

This formula, known as the *Sackur-Tetrode equation*, is historically important for two reasons.

The first reason is related to the Gibbs paradox. In the first calculation of the entropy performed by Gibbs, it was found that the partition function did not contain the term $N!$ at the denominator of the expression of S . Thus the entropy was not given by the Sackur–Tetrode equation (Eq. 4.14) but by the wrong formula:

$$S = k_B N \left[\ln V - \frac{3}{2} \ln \frac{h^2}{2\pi m k_B T} + \frac{3}{2} \right]. \quad (4.15)$$

As we shall see, this relation implies that the entropy is not an extensive function and does not exist as a function of state. Indeed, when two enclosures of volumes V_1 and V_2 contain N_1 and N_2 identical particles, respectively, at the same temperature T and pressure p , the entropy of the two separate systems are given by:

$$S_1 = k_B N_1 \left[\ln V_1 - \frac{3}{2} \ln \frac{h^2}{2\pi m k_B T} + \frac{3}{2} \right], \quad (4.16)$$

$$S_2 = k_B N_2 \left[\ln V_2 - \frac{3}{2} \ln \frac{h^2}{2\pi m k_B T} + \frac{3}{2} \right]. \quad (4.17)$$

When the two systems are adiabatically joined, the particles mix together and the entropy of mixing is not an extensive function because its expression is:

$$S_{\text{mix}} = k_B (N_1 + N_2) \left[\ln(V_1 + V_2) - \frac{3}{2} \ln \frac{h^2}{2\pi m k_B T} + \frac{3}{2} \right]. \quad (4.18)$$

In this adiabatic transformation – which should take place without a change of entropy – the calculation shows instead that the excess entropy is:

$$\begin{aligned} \Delta S &= S_{\text{mix}} - (S_1 + S_2) \\ &= k_B (N_1 + N_2) \ln(V_1 + V_2) - \left[k_B N_1 \ln V_1 + k_B N_2 \ln V_2 \right] \\ &= k_B (N_1 + N_2) \ln(V_1 + V_2) - k_B N_1 \ln V_1 - k_B N_2 \ln V_2. \end{aligned} \quad (4.19)$$

Nevertheless, in order that the entropy becomes an extensive function, Gibbs proposed, without particular justification, to divide the partition function by $N!$, thus leading to the Sackur–Tetrode equation (Eq. 4.14). Actually, with this correction, the entropy recovers an extensive character because the excess entropy is zero by force of

the above discussed modification. Equation (4.14) makes it easy to check that²:

$$\Delta S = k_B(N_1 + N_2) \ln \left(\frac{V_1 + V_2}{N_1 + N_2} \right) - k_B N_1 \ln \frac{V_1}{N_1} - k_B N_2 \ln \frac{V_2}{N_2} = 0. \quad (4.20)$$

The introduction of the term $N!$ was justified at a later time with the development of ideas about quantum mechanics after realizing that the microscopic particles are indistinguishable in contrast to objects of classical mechanics.

The second reason concerns the value of the entropy S at absolute zero. By observing equation (4.14), it is found that the entropy S tends to minus infinity when the temperature T tends to zero, which is contradictory with the third law of thermodynamics. This contradiction is caused by the fact that, in a state close to absolute zero, the quantum effects dominate and classical statistics does not apply. By contrast, at higher temperatures, quantum effects are negligible and classical statistics can be used. Therefore, equation (4.14) is valid only far from zero Kelvin and provides results in good agreement with experiments at high temperature. The calculation of the pressure in a gas phase in equilibrium with its liquid phase can serve as a validity test applied to the Sackur–Tetrode equation. If the equation of state of ideal gas (Eq. 4.6) is employed to write the entropy of the vapor phase S^{vap} as a function of pressure p , equation (4.14) is written:

$$S^{\text{vap}} = k_B N \left[\ln \frac{k_B T}{p} - \frac{3}{2} \ln \frac{h^2}{2\pi m k_B T} + \frac{5}{2} \right]. \quad (4.21)$$

On the other hand, since the entropy of the vapor S^{vap} is related to the entropy of the liquid S^{liq} and to the heat of vaporization L by the

²When the two enclosures are separated, the thermodynamic states are:

$$\begin{aligned} pV_1 &= N_1 k_B T, \\ pV_2 &= N_2 k_B T, \end{aligned}$$

and when they interact, we have:

$$p(V_1 + V_2) = (N_1 + N_2) k_B T.$$

By combining these relations, we find:

$$\ln \frac{V_1 + V_2}{N_1 + N_2} = \ln \frac{V_1}{N_1} = \ln \frac{V_2}{N_2},$$

which leads to $\Delta S = 0$.

following equation:

$$S^{\text{vap}} = S^{\text{liq}} + \frac{L}{T} \simeq \frac{L}{T}, \quad (4.22)$$

S^{vap} can be eliminated between the two previous relations in order to extract the pressure p :

$$\ln p \simeq -\frac{L}{k_{\text{B}}NT} - \frac{3}{2} \ln \frac{h^2}{2\pi m} + \frac{5}{2} + \frac{5}{2} \ln k_{\text{B}}T. \quad (4.23)$$

A good agreement between the value of p obtained with this formula and the experimental value is the best test of the Sackur-Tetrode equation, even if, in real systems, some additional terms have to be added into the previous relation coming from the internal structure of atoms. Historically, it is worth noting that this experiment enabled Tetrode (1912) to perform the first evaluation of the value of Planck's constant h .

Note finally that, with the expression of the entropy of the monatomic ideal gas, the relation linking volume and temperature in an adiabatic process is easily obtained. To do this, it just takes a calculation of $S_1 - S_2 = 0$ with:

$$S_1 = k_{\text{B}}N \left[\ln \frac{V_1}{N} - \frac{3}{2} \ln \frac{h^2}{2\pi m k_{\text{B}}T_1} + \frac{3}{2} \right], \quad (4.24)$$

$$S_2 = k_{\text{B}}N \left[\ln \frac{V_2}{N} - \frac{3}{2} \ln \frac{h^2}{2\pi m k_{\text{B}}T_2} + \frac{3}{2} \right]. \quad (4.25)$$

This directly leads to the adiabatic equation:

$$\ln V_1 + \frac{3}{2} \ln T_1 = \ln V_2 + \frac{3}{2} \ln T_2; \quad (4.26)$$

$$V_1 T_1^{\frac{3}{2}} = V_2 T_2^{\frac{3}{2}}, \quad (4.27)$$

which coincides with the classical equation $V_1^{\gamma-1} T_1 = V_2^{\gamma-1} T_2$, provided that the value $\gamma (= c_p/c_V = 5/3)$ for monatomic gases is used.

4.2 The imperfect gas

Partition Function

If the gas volume is very large and the atoms are spaced out in such a way that there is no chance of finding more than two atoms in

mutual interaction, the gas is said to be *slightly imperfect*. In this case, the terms of the sum in equation (3.20) beyond $\sum_i \sum_{j>i} f_{ij}$ can be neglected, and a crude calculation of the configuration integral can be done with the integrand $\left(1 + \sum_i \sum_{j>i} f_{ij}\right)$ assuming that the potential of the atom i with the $(N-1)$ other atoms is only equal to that of the atom i with its nearest neighbours j . This assumption holds because, around atom i , the atoms at distances greater than the range of action of the potential are without interaction with the atom i . In other words, $u(r_{ij}) \simeq 0$ between two atoms. This assumption holds because the atoms around the atom i at distances greater than the range of action of the potential are without interaction with the atom i . In other words, $u(r_{ij}) \simeq 0$ between two atoms sufficiently away from each other.

When writing the partition function:

$$\begin{aligned} Q_N(V, T) &= \frac{1}{N! \Lambda^{3N}} \iint_{3N} \left(1 + \sum_i \sum_{j>i} f_{ij}\right) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \\ &= \frac{1}{N! \Lambda^{3N}} \left[\iint_{3N} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N + \iint_{3N} \sum_i \sum_{j>i} f_{ij} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \right], \quad (4.28) \end{aligned}$$

we can see that the first integral is equal to V^N and, for the reason stated above, the second integral is a sum of terms of the type

$$\iint_6 f_{ij} d\mathbf{r}_i d\mathbf{r}_j \times \iint_{3(N-2)} d\mathbf{r}^{N-2}. \quad (4.29)$$

To assess the number of terms without leaving any of them out, we can enter all f_{ij} into a square table with N rows and N columns containing N^2 terms. However, the terms on the main diagonal should be removed in order to avoid counting the interaction of an atom with itself and then half of the remaining quantity is taken out to avoid double counting applied to the same interactions. The number of terms in the sum is therefore:

$$\frac{N^2 - N}{2} = \frac{1}{2} N(N-1), \quad (4.30)$$

and the partition function becomes:

$$Q_N(V, T) = \frac{1}{N! \Lambda^{3N}} \left[V^N + \frac{1}{2} N(N-1) V^{N-2} \iint_6 f_{ij} d\mathbf{r}_i d\mathbf{r}_j \right]. \quad (4.31)$$

The integral covers the positions of two neighbouring atoms i and j whose domain of integration extends to the whole volume V . Specifically, if the Cartesian coordinates of these two atoms are (x_i, y_i, z_i) and (x_j, y_j, z_j) , this is tantamount to performing the integration on the variables (x_i, y_i, z_i) and $(X = x_i - x_j, Y = y_i - y_j, Z = z_i - z_j)$. With respect to the Mayer function f_{ij} , it depends only on the distance r_{ij} between atoms i and j . As the Jacobian of the transformation is equal to unity and f_{ij} depends only on the coordinates (X, Y, Z) , the integral splits into two parts:

$$\begin{aligned} \int \int_6 f_{ij} d\mathbf{r}_i d\mathbf{r}_j &= \int \int dx_i dy_i dz_i \int \int f(X, Y, Z) dX dY dZ \\ &= V \int_0^\infty f(r) 4\pi r^2 dr. \end{aligned} \quad (4.32)$$

The last integration has been performed with the spherical coordinates assuming isotropy of the system. Equation (4.32) is crucial in the study of slightly imperfect gases. Once the pair potential $u(r)$ chosen, we are in position to calculate $f(r)$ with equation (3.18) and the partition function. Subject to the approximation $N(N-1) \sim N^2$, the partition function is finally written as:

$$Q_N(V, T) \simeq \frac{V^N}{N! \Lambda^{3N}} \left(1 + \frac{N^2}{2V} b \right), \quad (4.33)$$

$$\text{with} \quad b = \int_0^\infty f(r) 4\pi r^2 dr. \quad (4.34)$$

Thermodynamic properties

With the expression of the partition function (Eq. 4.33), it is easy to calculate the free energy by using equation (2.102):

$$\begin{aligned} F &= -k_B T \ln Q_N(V, T) \simeq -k_B T \ln \left[\frac{V^N}{N! \Lambda^{3N}} \left(1 + \frac{N^2}{2V} b \right) \right], \\ &\simeq -N k_B T \left[\ln \frac{V}{N} - 3 \ln \Lambda + 1 + \frac{N}{2V} b \right]. \end{aligned} \quad (4.35)$$

The last equality has been appropriately written with Stirling's approximation and the series expansion of $\ln(1 + \frac{N^2}{2V} b) \sim \frac{N^2}{2V} b$ because the inequality $Nb \ll \frac{V}{N}$ is true for a slightly imperfect gas. It should

be mentioned that the free energy of such a gas differs just from the free energy of the ideal gas (Eq. 4.3) by the term $\frac{N^2 k_B T}{2V} b$.

The other thermodynamic properties can then be deduced and compared to those of the ideal gas. For example, the calculation of the pressure with equation (2.105) is reduced to:

$$p = - \left(\frac{\partial F}{\partial V} \right)_T \simeq \frac{N k_B T}{V} \left[1 - \frac{N}{2V} b \right]. \quad (4.36)$$

Thus, the equation of state of a slightly imperfect gas differs from the equation of state of an ideal gas by the term $\frac{N^2 k_B T b}{2V^2}$. To learn more about this term, we calculate the expression of b with the Mayer function $f(r)$ for the *square-well* potential as portrayed schematically in figure (3.1) and defined by the parameters:

$$u(r) = \begin{cases} \infty & \text{if } r < \sigma, \\ -\varepsilon & \text{if } \sigma \leq r \leq \alpha\sigma, \\ 0 & \text{if } r > \alpha\sigma. \end{cases} \quad (4.37)$$

With equation (4.34), the integral b is:

$$\begin{aligned} b &= 4\pi \left\{ \int_0^\sigma [-1] r^2 dr + \int_\sigma^{\alpha\sigma} [\exp(\beta\varepsilon) - 1] r^2 dr \right\}, \\ &= -\frac{4\pi\sigma^3}{3} [\alpha^3 - (\alpha^3 - 1) \exp(\beta\varepsilon)]. \end{aligned} \quad (4.38)$$

Therefore, the equation of state of a slightly imperfect gas modeled by a square-well potential have the following analytical form:

$$p = \frac{N k_B T}{V} \left\{ 1 + \frac{N}{2V} \frac{4\pi\sigma^3}{3} \alpha^3 - \frac{N}{2V} \frac{4\pi\sigma^3}{3} (\alpha^3 - 1) \exp(\beta\varepsilon) \right\} \quad (4.39)$$

It can be seen that the expression of b results from the competition between two contributions (Eq. 4.38) depending on the two parameters α and ε . For instance, we find that the square well disappears, if $\varepsilon = 0$. This leaves a *hard-sphere* potential for which $b (= -\frac{4\pi\sigma^3}{3})$ is negative, whereas, when ε is significantly greater than $1/(\beta\alpha^3)$, b becomes positive. Consequently, at constant temperature and volume, the pressure of a slightly imperfect gas can be higher or lower than

that of the ideal gas. If the potential well ε is shallow, the Taylor expansion of the exponential allows us to write equation (4.39) as:

$$\begin{aligned} p &= \frac{Nk_B T}{V} \left\{ 1 + \frac{N}{2V} \frac{4\pi\sigma^3}{3} \alpha^3 - \frac{N}{2V} \frac{4\pi\sigma^3}{3} (\alpha^3 - 1) \left(1 + \frac{\varepsilon}{k_B T} \right) \right\}, \\ &= \frac{Nk_B T}{V} + \frac{N^2 k_B T}{V^2} \frac{4\pi\sigma^3}{6} - \frac{N^2}{V^2} \frac{4\pi\sigma^3}{6} (\alpha^3 - 1) \varepsilon. \end{aligned} \quad (4.40)$$

At this stage of the study, it is interesting to compare the equation of state given by equation (4.40) with the van der Waals equation of state:

$$\left(p + \frac{N}{V^2} A \right) (V - NB) = Nk_B T, \quad (4.41)$$

where A and B are two constants with specific physical significance. To find it, transform the van der Waals equation of state by assuming that the gas is slightly imperfect ($NB \ll V$). In this case, equation (4.41) reads:

$$p \simeq \frac{Nk_B T}{V} + \frac{N^2 k_B T}{V^2} B - \frac{N}{V^2} A, \quad (4.42)$$

so that its identification with equation (4.40) enables the constants A and B to be expressed as a function of the parameters σ , α and ε of the square-well potential. We find immediately:

$$B = \frac{4\pi\sigma^3}{6} = 4v_0, \quad (4.43)$$

$$A = \frac{4\pi\sigma^3 N}{6} (\alpha^3 - 1) \varepsilon = 4v_0 N (\alpha^3 - 1) \varepsilon. \quad (4.44)$$

Note that A is proportional to the depth of the potential well ε and B is equal to 4 times the volume v_0 of an atom of radius $\sigma/2$.

In addition, the entropy of a slightly imperfect gas is calculated with equation (2.103). It yields:

$$\begin{aligned} S &= - \left(\frac{\partial F}{\partial T} \right)_V \\ &\simeq Nk_B \left[\ln \frac{V}{N} - 3 \ln \Lambda + 1 + \frac{N}{2V} b \right] + Nk_B T \left[\frac{3}{2T} - \frac{N}{2V} \frac{\partial b}{\partial T} \right] \\ &\simeq Nk_B \left[\ln \frac{V}{N} - 3 \ln \Lambda + \frac{5}{2} + \frac{N}{2V} b - \frac{N}{2V} T \frac{\partial b}{\partial T} \right], \end{aligned} \quad (4.45)$$

where the thermal wavelength $\Lambda = \left(\frac{h^2\beta}{2\pi m}\right)^{\frac{1}{2}}$ is used to determine the relation $\frac{\partial}{\partial T} \ln \Lambda = -\frac{1}{2T}$. It is easy to see that the entropy of a slightly imperfect gas differs from that of an ideal gas (Eq. 4.14) only by the term $(\frac{N}{2V}b - \frac{N}{2V}T \frac{\partial b}{\partial T})$.

The expression of the internal energy E is obtained immediately by combining the expressions of the free energy (Eq. 4.35) and entropy (Eq. 4.45) in using equation (2.104). This provides:

$$\begin{aligned}
 E &= F - T \left(\frac{\partial F}{\partial T} \right)_V, \\
 &\simeq -Nk_B T \left[\ln \frac{V}{N} - 3 \ln \Lambda + 1 + \frac{N}{2V}b \right] \\
 &\quad + TNk_B \left[\ln \frac{V}{N} - 3 \ln \Lambda + \frac{5}{2} + \frac{N}{2V}b - \frac{N}{2V}T \frac{\partial b}{\partial T} \right] \\
 &\simeq Nk_B T \left(\frac{3}{2} - \frac{N}{2V}T \frac{\partial b}{\partial T} \right). \tag{4.46}
 \end{aligned}$$

4.3 The real gases

The partition function of the classical ideal gas has been determined in the preceding sections, thus enabling to deduce the main thermodynamic properties. In such a system, the atoms are subjected to no mutual interaction, so that we are led to take $U(\mathbf{r}^N) = 0$. When studying the imperfect gas, only the first two terms of the sum in brackets of equation (3.20) have been considered to calculate the configuration integral making it possible to deduce the thermodynamic properties and the equation of state. Studying the real gases as was undertaken in this section is more complicated because it implies having good knowledge of all the terms of the sum located in the configuration integral, bearing in mind that listing them is by far no easy matter. A convenient way to count the number of terms is to associate a graph to each integral.

The equation of state

The determination of the free energy F by means of the relation connecting statistical mechanics to classical thermodynamics reduces to the knowledge of the parameter x_0 and to calculating the reducible cluster integrals b_l in equation (3.69). It is easy to apply a physical meaning to the particular value x_0 of the real part of the complex variable z that has been arbitrarily introduced in the saddle point method. Since the denominator in equation (3.69) differs little from unity in the case of real gases, the free energy of the real gases is written [3]:

$$\begin{aligned} F &= -k_B T \ln Q_N(V, T) = -k_B T \ln \left[\frac{1}{\Lambda^{3N} x_0^N} \exp \left(\sum_{l=1}^{\infty} V b_l x_0^l \right) \right] \\ &= -k_B T \left[\sum_{l=1}^{\infty} V b_l x_0^l - N \ln (\Lambda^3 x_0) \right]. \end{aligned} \quad (4.47)$$

The physical meaning of the parameter x_0 is immediately apparent by calculating the chemical potential with equation (2.107). Since x_0 , in equation (4.47), is the only quantity depending on the number of particles N , the expression of chemical potential μ is:

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V, T} = -k_B T \left[\sum_{l=1}^{\infty} l V b_l x_0^{l-1} \frac{\partial x_0}{\partial N} - \ln (\Lambda^3 x_0) - N \frac{1}{x_0} \frac{\partial x_0}{\partial N} \right]. \quad (4.48)$$

However, the derivative of equation (3.62) with respect to N leads to the relation:

$$\sum_{l=1}^{\infty} l V b_l x_0^l \frac{1}{x_0} \frac{\partial x_0}{\partial N} = N \frac{1}{x_0} \frac{\partial x_0}{\partial N}, \quad (4.49)$$

which allows the simplification of the chemical potential in the form:

$$\beta \mu = \beta \left(\frac{\partial F}{\partial N} \right)_{V, T} = \ln (\Lambda^3 x_0). \quad (4.50)$$

By comparing this formula with equation (3.13), we see that the parameter x_0 identifies with the fugacity z (not to be confused with the complex variable z), namely:

$$x_0 = z = \frac{\exp(\beta \mu)}{\Lambda^3}. \quad (4.51)$$

With the physical meaning thus assigned to the parameter $x_0 = z$ (fugacity), it is possible to determine the thermodynamic properties of the real gases. Let us start with the calculation of the equation of state. After recalling that the reducible cluster integrals b_l are almost independent of the volume, we deduce the pressure from equations (2.105) and (4.47) as:

$$\frac{pV}{k_B T} = - \left(\frac{\partial F}{\partial V} \right)_{T,N} \frac{V}{k_B T} = \sum_{l=1}^{\infty} V b_l z^l. \quad (4.52)$$

Next, in combining equations (4.47), (4.50) and (4.52), we immediately obtain a very important relation between the free energy F , the chemical potential μ and the pressure p :

$$\frac{F}{k_B T} = \frac{\mu N}{k_B T} - \frac{pV}{k_B T}. \quad (4.53)$$

Incidentally, it should be noted that equation (4.52) has some resemblance to the virial equation of state in which the pressure is given in the form of an ascending power series of the density $\rho = N/V$, namely:

$$\frac{pV}{N k_B T} = 1 + B_2(T)\rho + B_3(T)\rho^2 + B_4(T)\rho^3 + \dots \quad (4.54)$$

In order to compare the two expressions of the equation of state (Eqs. 4.52 and 4.54), we express first the fugacity z as a function of the density ρ as:

$$z(\rho) = \rho + a_2 \rho^2 + a_3 \rho^3 + \dots, \quad (4.55)$$

then we obtain the number of particles N after having substituted this expression of the fugacity into equation (3.62). This gives:

$$N = \sum_{l=1}^{\infty} l V b_l z^l = V \sum_{l=1}^{\infty} l b_l (\rho + a_2 \rho^2 + a_3 \rho^3 + \dots)^l. \quad (4.56)$$

However, this relation allows us to extract the density $\rho = N/V$ under the following form:

$$\begin{aligned} \rho &= \frac{N}{V} = b_1 (\rho + a_2 \rho^2 + a_3 \rho^3 + \dots) + 2b_2 (\rho + a_2 \rho^2 + a_3 \rho^3 + \dots)^2 \\ &+ 3b_3 (\rho + a_2 \rho^2 + a_3 \rho^3 + \dots)^3 + \dots \end{aligned} \quad (4.57)$$

After the calculations have been developed, the identification of the coefficients of each power of ρ in the above relation leads to:

$$\rho b_1 \equiv \rho, \quad (4.58)$$

$$\rho^2(b_1 a_2 + 2b_2) \equiv 0, \quad (4.59)$$

$$\rho^3(b_1 a_3 + 4a_2 b_2 + 3b_3) \equiv 0, \quad (4.60)$$

$$\rho^4 [b_1 a_4 + 2b_2 (a_2^2 + 2a_3) + 9a_2 b_3 + 4b_4] \equiv 0, \quad (4.61)$$

$$\dots = \dots$$

These relations enable us to express easily the coefficients a_k in terms of the reducible cluster integrals b_l :

$$b_1 = 1, \quad (4.62)$$

$$a_2 = -2b_2, \quad (4.63)$$

$$a_3 = 8b_2^2 - 3b_3, \quad (4.64)$$

$$a_4 = -4b_4 - 40b_2^3 + 30b_2 b_3, \quad (4.65)$$

$$\dots = \dots$$

In addition, we can rewrite equation (4.52) in terms of the density, namely:

$$\frac{pV}{k_B T} = V \sum_{l=1}^{\infty} b_l (\rho + a_2 \rho^2 + a_3 \rho^3 + \dots)^l, \quad (4.66)$$

in which the coefficients a_k can be written as a function of the reducible cluster integrals b_l . With all calculations being done, we arrive at:

$$\begin{aligned} \frac{p}{k_B T} = & b_1 [\rho + (-2b_2) \rho^2 + (8b_2^2 - 3b_3) \rho^3 \\ & + (-4b_4 - 40b_2^3 + 30b_2 b_3) \rho^4 + \dots] \\ & + b_2 [\rho + (-2b_2) \rho^2 + (8b_2^2 - 3b_3) \rho^3 \\ & + (-4b_4 - 40b_2^3 + 30b_2 b_3) \rho^4 + \dots]^2 + \\ & + b_3 [\rho + (-2b_2) \rho^2 + (8b_2^2 - 3b_3) \rho^3 \\ & + (-4b_4 - 40b_2^3 + 30b_2 b_3) \rho^4 + \dots]^3 + \dots \quad (4.67) \end{aligned}$$

By gathering the terms of same degree of ρ , we obtain:

$$\frac{p}{k_{\text{B}}T} = \rho \left[1 - b_2\rho + (4b_2^2 - 2b_3)\rho^2 - (3b_4 - 18b_2b_3 + 20b_2^3)\rho^3 + \dots \right]. \quad (4.68)$$

But the coefficients of this polynomial arranged according to the increasing powers of ρ can also be expressed in terms of the irreducible cluster integrals β_k . The following expressions are indeed extracted from equation (3.33):

$$b_2 = \frac{1}{2}\beta_1, \quad (4.69)$$

$$(4b_2^2 - 2b_3) = -\frac{2}{3}\beta_2, \quad (4.70)$$

$$(3b_4 - 18b_2b_3 + 20b_2^3) = \frac{3}{4}\beta_3, \quad (4.71)$$

$$\dots = \dots,$$

on the basis of which equation (4.68) is rewritten as a function of the irreducible cluster integrals under the compact form:

$$\frac{p}{\rho k_{\text{B}}T} = 1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k \rho^k. \quad (4.72)$$

The comparison of this relation with equation (4.54) indicates that the virial coefficients can be calculated for each specific type of interaction, this being done in terms of the irreducible cluster integrals thanks to the formula:

$$B_k = \frac{1-k}{k} \beta_{k-1}. \quad (4.73)$$

This gives a clear physical meaning to the virial coefficients. Like for the irreducible cluster integrals, the coefficients B_k depend only on the temperature and interatomic potential, but are independent of the volume, hence of the density. They nevertheless provide an indication of the deviation between the real gases and the ideal gas.

Other pertinent thermodynamic properties

The investigation of the real gases goes on by calculating the internal energy. With equation (2.104), it is written:

$$\begin{aligned}
 E &= k_B T^2 \left[\frac{\partial}{\partial T} \ln Q_N(V, T) \right]_V \\
 &= k_B T^2 \frac{\partial}{\partial T} \ln \left[\frac{1}{\Lambda^{3N} z^N} \exp \left(\sum_{l=1}^{\infty} V b_l z^l \right) \right]_V \\
 &= k_B T^2 \left[-3N \frac{\partial}{\partial T} \ln \Lambda + \sum_{l=1}^{\infty} V \frac{\partial b_l}{\partial T} z^l \right] \\
 &= \frac{3}{2} N k_B T + k_B T^2 \sum_{l=1}^{\infty} V \frac{\partial b_l}{\partial T} z^l, \tag{4.74}
 \end{aligned}$$

where the last equality which leads to $\frac{\partial}{\partial T} \ln \Lambda = -\frac{1}{2T}$ has been obtained by using the thermal wavelength $\Lambda = \left(\frac{h^2 \beta}{2\pi m} \right)^{\frac{1}{2}}$. To express E as a function of the density, we use the following equality between equations (4.52) and (4.72):

$$\frac{pV}{k_B T} = \sum_{l=1}^{\infty} V b_l z^l = N \left(1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k \rho^k \right). \tag{4.75}$$

Then, we derive the above relation with respect to T :

$$\sum_{l=1}^{\infty} V \frac{\partial b_l}{\partial T} z^l = -N \sum_{k \geq 1} \frac{k}{k+1} \frac{\partial \beta_k}{\partial T} \rho^k \tag{4.76}$$

and use it to rewrite the expression of the internal energy E :

$$E = \frac{3}{2} N k_B T - N k_B T^2 \sum_{k \geq 1} \frac{k}{k+1} \frac{\partial \beta_k}{\partial T} \rho^k. \tag{4.77}$$

Neither is there much difficulty to express the free energy F , the entropy S and even the isothermal compressibility χ_T as a function of the density ρ by using the available formulas. Indeed, by combining equations (4.53), (4.50) and (4.72), the free energy takes the form of:

$$F = N k_B T \left[\ln (\Lambda^3 x_0) - 1 + \sum_{k \geq 1} \frac{k}{k+1} \beta_k \rho^k \right]. \tag{4.78}$$

When combining equations (4.77) and (4.78), it results the following expression of the entropy:

$$S = \frac{E-F}{T} = k_B N \left[-\ln(\Lambda^3 x_0) + \frac{5}{2} - \sum_{k \geq 1} \frac{k}{k+1} \frac{\partial(T\beta_k)}{\partial T} \rho^k \right]. \quad (4.79)$$

With regards to the isothermal compressibility, it is defined in terms of the density as:

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial \rho} \right)_T \left(\frac{\partial \rho}{\partial p} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T, \quad (4.80)$$

where the last equality has been obtained by considering the relation $\frac{\partial \rho}{\partial V} = -\frac{\rho}{V}$. Finally, the expression of the isothermal compressibility χ_T is written with equation (4.72) as follows:

$$\begin{aligned} \chi_T^{-1} &= \rho k_B T \left(1 - \sum_{k \geq 1} \frac{k}{k+1} \beta_k \rho^k \right) + \rho^2 k_B T \left(- \sum_{k \geq 1} \frac{k^2}{k+1} \beta_k \rho^{k-1} \right) \\ &= \rho k_B T \left[1 - \sum_{k \geq 1} k \beta_k \rho^k \right]. \end{aligned} \quad (4.81)$$

4.4 The Maxwell-Boltzmann distribution

Introduction

In this subsection, we propose to show that the probability density function for the canonical ensemble $P_N(\mathbf{r}^N, \mathbf{p}^N)$ of a system of independent particles simplifies to a form known as the Maxwell-Boltzmann distribution.

Let us write the probability density function (Eq. 2.33):

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{N! h^{3N} Q_N(V, T)} \exp[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N)]. \quad (4.82)$$

Since the particles are independent, the energy of the system is equal to the sum of the energies of individual particles. Therefore, the Hamiltonian (Eq. 3.2) is reduced to a sum of individual Hamiltonians

and the probability density function becomes a product of probability densities of the lowest order (Eq. 2.140):

$$H_N(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + u(\mathbf{r}_i) \right], \quad (4.83)$$

$$\text{and} \quad P_N(\mathbf{r}^N, \mathbf{p}^N) = \prod_{i=1}^N P_N^{(1)}(\mathbf{r}_i, \mathbf{p}_i), \quad (4.84)$$

$$\text{with} \quad P_N^{(1)}(\mathbf{r}, \mathbf{p}) = \frac{1}{h^3 Q(V, T)} \exp \left\{ -\beta \left[\frac{p^2}{2m} + u(\mathbf{r}) \right] \right\} \quad (4.85)$$

$$\text{and} \quad Q(V, T) = \frac{1}{h^3} \int \int \exp \left\{ -\beta \left[\frac{p^2}{2m} + u(\mathbf{r}) \right] \right\} d\mathbf{r} d\mathbf{p}. \quad (4.86)$$

Let us evaluate first the partition function $Q(V, T)$ by separating the integrals over the positions and momenta as:

$$Q(V, T) = \frac{1}{h^3} \int \int \exp \left\{ -\beta \frac{p^2}{2m} \right\} d\mathbf{p} \times \int \int \exp \{ -\beta u(\mathbf{r}) \} d\mathbf{r}, \quad (4.87)$$

where the integral over the momenta (Eq. 3.6) and the integral over the positions (Eq. 3.4) are respectively:

$$\int \int \exp \left\{ -\beta \frac{p^2}{2m} \right\} d\mathbf{p} = \left(\sqrt{\frac{2\pi m}{\beta}} \right)^3, \quad (4.88)$$

$$\int \int \exp \{ -\beta u(\mathbf{r}) \} d\mathbf{r} = Z. \quad (4.89)$$

As can be expected considering equation (3.7), the expression for the partition function is:

$$Q(V, T) = Z \left(\sqrt{\frac{2\pi m}{\beta h^2}} \right)^3. \quad (4.90)$$

Now, it should be stressed that the probability density function to the first order $P_N^{(1)}(\mathbf{r}, \mathbf{p})$ allows us to define the *Maxwell distribution* when the integration is performed over the positions:

$$P_N^{(1)}(\mathbf{p}) = \int \int P_N^{(1)}(\mathbf{r}, \mathbf{p}) d\mathbf{r} = \frac{1}{h^3 Q(V, T)} \int \int \exp \left\{ -\beta \left[\frac{p^2}{2m} + u(\mathbf{r}) \right] \right\} d\mathbf{r} \quad (4.91)$$

and the *Boltzmann distribution* when the integration is done on the momenta:

$$P_N^{(1)}(\mathbf{r}) = \iint P_N^{(1)}(\mathbf{r}, \mathbf{p}) d\mathbf{p} = \frac{1}{h^3 Q(V, T)} \iint \exp\left\{-\beta\left[\frac{p^2}{2m} + u(\mathbf{r})\right]\right\} d\mathbf{p}. \quad (4.92)$$

The Maxwell distribution

Considering the Maxwell distribution, we calculate the probability of finding the absolute value of the momentum of a particle between p and $p + dp$. This elementary probability has the expression $P_N^{(1)}(\mathbf{p})d\mathbf{p}$, where the volume element of momentum space is $d\mathbf{p} = 4\pi p^2 dp$, i.e. the spherical ring containing the points whose components p_x, p_y and p_z satisfy the inequality:

$$p < \sqrt{p_x^2 + p_y^2 + p_z^2} < p + dp. \quad (4.93)$$

The elementary probability in question is therefore:

$$\begin{aligned} P_N^{(1)}(\mathbf{p})d\mathbf{p} &= \frac{1}{h^3 Q(V, T)} \left\{ \iint \exp\left\{-\beta\left[\frac{p^2}{2m} + u(\mathbf{r})\right]\right\} d\mathbf{r} \right\} 4\pi p^2 dp \\ &= \frac{1}{h^3 Q(V, T)} \left\{ \iint \exp[-\beta u(\mathbf{r})] d\mathbf{r} \right\} 4\pi p^2 \exp\left(-\beta \frac{p^2}{2m}\right) dp. \end{aligned} \quad (4.94)$$

Use is made of equations (4.89) and (4.90) to evaluate the integral over $\mathbf{r}$ and simplify the above relation as follows:

$$\begin{aligned} P_N^{(1)}(\mathbf{p})d\mathbf{p} &= \frac{Z}{h^3 Z \left(\sqrt{\frac{2\pi m}{\beta h^2}}\right)^3} 4\pi p^2 \exp\left(-\beta \frac{p^2}{2m}\right) dp \\ &= 4\pi \left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} p^2 \exp\left(-\beta \frac{p^2}{2m}\right) dp. \end{aligned} \quad (4.95)$$

This expression gives the probability of finding the absolute value of the momentum between p and $p + dp$, but it also gives the probability that the absolute value of velocity of a given particle will be

between v and $v + dv$. To obtain an explicit form of the velocity distribution, the change of variables $p = mv$ is done in equation (4.95). The result of this probability, denoted $f(v)dv$, becomes:

$$\begin{aligned} f(v)dv &= 4\pi \left(\frac{\beta}{2\pi m} \right)^{3/2} (mv)^2 \exp \left[-\beta \frac{(mv)^2}{2m} \right] d(mv) \\ &= 4\pi \left(\frac{\beta m}{2\pi} \right)^{3/2} v^2 \exp \left(-\beta \frac{mv^2}{2} \right) dv. \end{aligned} \quad (4.96)$$

The function $f(v)$ is the *Maxwell velocity distribution*. It makes it possible to determine the probability of having the absolute value of the velocity of a particle in a given interval. The curve of $f(v)$, which passes through the origin, increases as the velocity increases reaching the maximum value for $v_M = \sqrt{\frac{2}{\beta m}}$, and then decreases to zero when the velocity tends to infinity (Fig. 4.1). The value v_M corresponding to the maximum of the curve is the most probable velocity.

It should be noted that the most probable velocity v_M should not be confused with the mean velocity which is equal to:

$$\langle v \rangle = \int_0^\infty v f(v) dv = 4\pi \left(\frac{\beta m}{2\pi} \right)^{3/2} \int_0^\infty v^3 \exp \left(-\beta \frac{mv^2}{2} \right) dv. \quad (4.97)$$

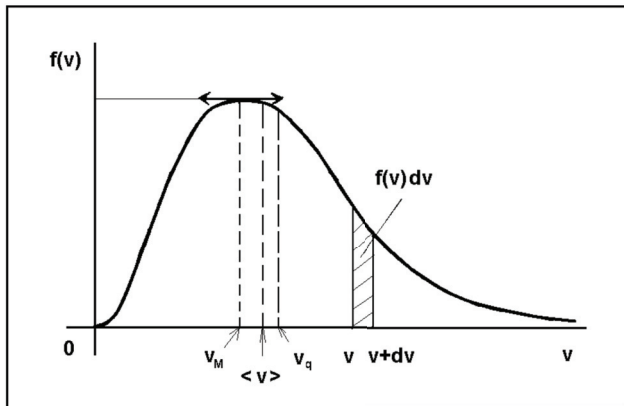


Figure 4.1: Schematic representation of the Maxwell velocity distribution.

The calculation of this integral becomes much easier if we remark that the integral:

$$I_n(a) = \int_0^{\infty} v^n \exp(-av^2) dv \quad (4.98)$$

results in³:

$$I_n(a) = \frac{1 \cdot 3 \cdot 5 \cdots (n-1)}{(2a)^{n/2}} \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2} \quad \text{if } n = 2, 4, 6, \dots, \quad (4.99)$$

$$= \frac{2 \cdot 4 \cdot 6 \cdots (n-1)}{(2a)^{(n+1)/2}} \quad \text{if } n = 3, 5, 7, \dots \quad (4.100)$$

By using the results of this integral for $n = 3$ and $a = \frac{\beta m}{2}$, we find $I_3(\frac{\beta m}{2}) = \frac{2}{(\beta m)^2}$ as well as the mean velocity:

$$\langle v \rangle = 4\pi \left(\frac{\beta m}{2\pi}\right)^{3/2} \frac{2}{(\beta m)^2} = \left(\frac{8}{\pi \beta m}\right)^{1/2}. \quad (4.101)$$

As regards the root-mean-square velocity $v_q = \sqrt{\langle v^2 \rangle}$, it is obtained with the standard formula:

$$\langle v^2 \rangle = \int_0^{\infty} v^2 f(v) dv = 4\pi \left(\frac{\beta m}{2\pi}\right)^{3/2} \int_0^{\infty} v^4 \exp\left(-\beta \frac{mv^2}{2}\right) dv. \quad (4.102)$$

The result of equation (4.98), for $n = 4$ and $a = \frac{\beta m}{2}$, being $I_4(\frac{\beta m}{2}) = \frac{3}{(\beta m)^2} \frac{1}{2} \left(\frac{2\pi}{\beta m}\right)^{\frac{1}{2}}$, it follows that the mean-square velocity is:

$$\langle v^2 \rangle = 4\pi \left(\frac{\beta m}{2\pi}\right)^{3/2} \frac{3}{2(\beta m)^2} \left(\frac{2\pi}{\beta m}\right)^{1/2} = \frac{3}{\beta m}. \quad (4.103)$$

This formula determines the average kinetic energy of a monatomic particle (with 3 degrees of freedom), namely $\langle E_c \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$.

³One obtains these recurrence formulas in considering the two following identities:

$$\begin{aligned} I_0(a) &= \int_0^{+\infty} \exp(-av^2) dv = \sqrt{\frac{\pi}{4a}}, \\ \text{and } I_1(a) &= \int_0^{+\infty} v \exp(-av^2) dv = \frac{1}{2a}, \end{aligned}$$

then calculating the successive derivatives of these identities with respect to a .

It also permits the calculation of the fluctuation of the velocity:

$$\langle (v - \langle v \rangle)^2 \rangle = \langle v^2 \rangle - \langle v \rangle^2 = \frac{1}{\beta m} \left(3 - \frac{8}{\pi} \right). \quad (4.104)$$

For the ideal gas, it is noticeable that the mean-square velocity $\langle v^2 \rangle$ is related to the speed of sound v_s . Indeed, as has been shown by Laplace, the speed of sound in fluids depends on the adiabatic compressibility χ_S and not on the isothermal compressibility χ_T . The reason is that the local variations of pressure produced by longitudinal waves propagate into the fluid too rapidly for the heat transfer to be observed. The classical Laplace formula giving the speed of sound is:

$$v_s^2 = \frac{c_p}{c_v} \frac{1}{m} \frac{V}{N} \frac{1}{\chi_T}. \quad (4.105)$$

Instead of that, for the ideal gas, the isothermal compressibility is equal to the inverse of the pressure, because:

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \frac{\partial}{\partial p} \left(\frac{Nk_B T}{p} \right)_T = \frac{1}{p}, \quad (4.106)$$

so that, after the substitution of the isothermal compressibility in equation (4.105), v_s^2 can be written as:

$$v_s^2 = \frac{c_p}{c_v} \frac{1}{\beta m} = \gamma \frac{\langle v^2 \rangle}{3}. \quad (4.107)$$

As the ratio of specific heats $\gamma = \frac{c_p}{c_v}$ of a monatomic ideal gas is $5/3$, it follows that the root-mean-square velocity is of the same order of magnitude as the speed of sound.

The Boltzmann distribution

Now we search for the expression of the Boltzmann distribution. For this purpose, we calculate the probability of finding a particle in a given position by using equation (4.92). The elementary probability that a particle will be in the given volume element $d\mathbf{r}$ of the configuration space is naturally $P_N^{(1)}(\mathbf{r})d\mathbf{r}$. However, it is also defined by the ratio of the number dN of particles contained in the volume element

$d\mathbf{r}$ to the total number N of particles. Therefore, identifying these two formulations of the probability combined with equation (4.92) gives:

$$\begin{aligned} \frac{dN}{N} &= P_N^{(1)}(\mathbf{r})d\mathbf{r} = \frac{1}{h^3 Q(V, T)} \left\{ \iint \exp\left\{-\beta\left[\frac{p^2}{2m} + u(\mathbf{r})\right]\right\} d\mathbf{p} \right\} d\mathbf{r} \\ &= \frac{1}{h^3 Q(V, T)} \left\{ \iint \exp\left(-\beta\frac{p^2}{2m}\right) d\mathbf{p} \right\} \exp[-\beta u(\mathbf{r})] d\mathbf{r}. \quad (4.108) \end{aligned}$$

Then, we use equation (4.88) to evaluate the integral over $\mathbf{p}$ and equation (4.90) to simplify the above expression. After transformations, this expression reads:

$$\frac{dN}{N} = \frac{1}{h^3 Z \left(\sqrt{\frac{2\pi m}{\beta h^2}}\right)^3} \left(\sqrt{\frac{2\pi m}{\beta}}\right)^3 \exp[-\beta u(\mathbf{r})] d\mathbf{r}, \quad (4.109)$$

hence:

$$n(\mathbf{r}) = \frac{dN}{d\mathbf{r}} = N \frac{\exp[-\beta u(\mathbf{r})]}{\iint \exp[-\beta u(\mathbf{r})] d\mathbf{r}}. \quad (4.110)$$

The function $n(\mathbf{r})$ corresponds to the *Boltzmann distribution*. It helps knowing the number of particles located in a given volume element. This is a very important function of classical physics, used whenever the potential energy of a system is equal to the sum of the energies of individual particles.

As a direct application of the Boltzmann distribution, we consider the ideal gas subjected to the gravity field. Assuming that the z -axis is vertical and oriented upwards, the volume element $d\mathbf{r} = Sdz$ is considered as a slice of section S and thickness dz . In addition, the potential energy acting on each particle is $u(z) = mgz$ and the number of particles dN in the volume Sdz is given by equation (4.110). Therefore, the probability of finding a particle at the altitude z should be:

$$\frac{dN}{Sdz} = \frac{N}{S} \frac{\exp(-\beta mgz)}{\int_0^\infty \exp(-\beta mgz) dz} = \frac{N}{S} \frac{mg}{k_B T} \exp\left(-\frac{mgz}{k_B T}\right). \quad (4.111)$$

If the concentration of particles at the altitude $z = 0$ is $n_0 = \frac{N}{S} \frac{mg}{k_B T}$, the concentration at the altitude z is expressed as:

$$n(z) = n_0 \exp\left(-\frac{mgz}{k_B T}\right). \quad (4.112)$$

This is the *barometric formula* usually found in the books on hydrostatics.

4.5 The mean electrostatic potential

An ionized gas is a gas composed of anions and cations, or ions and electrons, in equilibrium and electrically neutral. The charged particles constituting the ionized gas interact via a Coulomb potential, which renders the method of the partition function inapplicable if performed under the form described in the previous sections. Indeed, the Coulomb potential is a long-range potential varying as r^{-1} and causing a divergence of the cluster integrals entering the calculation of the partition function. Therefore, a specific method must be implemented to directly calculate the free energy of ionized gases.

This method was applied by Debye and Hückel [9] to the treatment of electrolytes as typical specimens of ionized gases. It has also been employed by Thomas [10] and Fermi [11] within the quantum formalism to examine the inhomogeneous degenerate electron gas, and by Mott [12] to address the problem of the electronic screening of an impurity in the metal.

Before presenting the method, recall first that the free energy of a system of uncharged particles is:

$$F_0 = -k_B T \ln Q_N(V, T) = -k_B T \ln \left[\frac{1}{N! \Lambda^{3N}} \iint_{3N} \exp[-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N \right], \quad (4.113)$$

where $U_0(\mathbf{r}^N)$ is the potential energy composed of the sum of pair potentials:

$$U_0(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j>i}^N u(r_{ij}). \quad (4.114)$$

If the system is composed of particles carrying charges q_i , all Coulomb interactions have to be added to $U_0(\mathbf{r}^N)$, so that the potential energy of the system is:

$$U(\mathbf{r}^N) = \sum_i \sum_{j>i} u(r_{ij}) + \sum_i \sum_{j>i} \frac{q_i q_j}{\varepsilon |\mathbf{r}_{ij}|}. \quad (4.115)$$

It should be stressed that the pair potential $u(r)$ has a very strong repulsion at short distances - possibly represented by a hard-sphere potential - and a weak attraction at long distances due to dispersion forces. At large distances, this attractive potential varying as r^{-6}

is negligible as compared to the attractive Coulomb potential arising between two particles of opposite charges and varying as r^{-1} .

Generally, the expression for the free energy F of a system of charged particles is written as a function of the potential energy $U(\mathbf{r}^N)$ as:

$$F = -k_B T \ln \left\{ \frac{1}{N! \Lambda^{3N}} \int \int_{3N} \exp \left[-\beta U_0(\mathbf{r}^N) - \beta \sum_i \sum_{j>i} \frac{q_i q_j}{\varepsilon |\mathbf{r}_{ij}|} \right] d\mathbf{r}^N \right\}. \quad (4.116)$$

The Coulomb potential determines the configuration and motion of the charges. However, it has a specific characteristic insofar as, in turn, the charges exert a feedback on the potential, thus making the calculation of F impossible with equation (4.116). To determine the free energy F , Debye and Hückel conceived an elegant method meant to replace the real system by a system of *independent charges* on which an "external electrostatic field" would be applied. The role of this field is to produce, at the location of each charge q_i , a field identical to the one which is actually generated by all the other charges. Assuming that such a field can be created, the electrostatic interaction energy of the system would be written:

$$\sum_i \sum_{j>i} \frac{q_i q_j}{\varepsilon |\mathbf{r}_{ij}|} \rightarrow \sum_{i=1}^N q_i \Phi(\mathbf{r}_i), \quad (4.117)$$

where $\Phi(\mathbf{r}_i)$ is the external electrostatic potential acting on the charge q_i localized at $\mathbf{r}_i$. The potential energy $q_i \Phi(\mathbf{r}_i)$ is a self-consistent field as it determines the motion of the charge q_i which act retroactively upon the potential energy.

With this new expression for the potential energy, the free energy of the system becomes:

$$F = -k_B T \ln \left\{ \frac{1}{N! \Lambda^{3N}} \int \int_{3N} \exp \left[-\beta U_0(\mathbf{r}^N) - \beta \sum_{i=1}^N q_i \Phi(\mathbf{r}_i) \right] d\mathbf{r}^N \right\}. \quad (4.118)$$

At first glance, the equation (4.118) does not seem to be easy for use. However, in calculating the partial derivative of the free energy with respect to the charge q_i located at $\mathbf{r}_i$, there is a means to calculate

F and justify the existence of the electrostatic potential $\Phi(\mathbf{r}_i)$. The calculation of the partial derivative of F with respect to q_i gives:

$$\begin{aligned} \frac{\partial F}{\partial q_i} &= -k_{\text{B}}T \frac{\iint_{3N} [-\beta\Phi(\mathbf{r}_i)] \exp \left[-\beta U_0(\mathbf{r}^N) - \beta \sum_{i=1}^N q_i \Phi(\mathbf{r}_i) \right] d\mathbf{r}^N}{\iint_{3N} \exp \left[-\beta U_0(\mathbf{r}^N) - \beta \sum_{i=1}^N q_i \Phi(\mathbf{r}_i) \right] d\mathbf{r}^N} \\ &= \langle \Phi(\mathbf{r}_i) \rangle. \end{aligned} \quad (4.119)$$

Since the partial derivative of the free energy with respect to q_i is nothing else than the mean value $\langle \Phi(\mathbf{r}_i) \rangle$ of the electrostatic potential on the site $\mathbf{r}_i$, the total differential of the free energy at T and V constant is:

$$dF = \sum_{i=1}^N \frac{\partial F}{\partial q_i} dq_i = \sum_{i=1}^N \langle \Phi(\mathbf{r}_i) \rangle dq_i. \quad (4.120)$$

The free energy of the system corresponds to the integral over q_i in the above equation. To perform this integration, it is more convenient to carry out the integration over the *charge parameter* $\lambda \in [0, 1]$ defined by the relation $dq_i = q_i d\lambda$. This setting allows us to vary virtually the charge q_i continuously - from 0 (uncharged particles) to q_i (fully charged particles) - and write the total differential of the free energy under the form:

$$dF = \sum_{i=1}^N \langle \Phi(\mathbf{r}_i, \lambda) \rangle q_i d\lambda. \quad (4.121)$$

The free energy F of the system is therefore determined with the following equation:

$$F = F_0 + \sum_{i=1}^N q_i \int_0^1 \langle \Phi(\mathbf{r}_i, \lambda) \rangle d\lambda, \quad (4.122)$$

where F_0 is the free energy of the system of uncharged particles ($\lambda = 0$) and $\langle \Phi(\mathbf{r}_i, \lambda) \rangle$ the *mean electrostatic potential* acting on particle i located at $\mathbf{r}_i$, when all the particles have the same individual charge λq_i .

Thus, the calculation of the free energy of the system is subordinate to that of the mean electrostatic potential $\langle \Phi(\mathbf{r}_i, \lambda) \rangle$. To briefly explain the method of calculating the electrostatic potential $\Phi(r)$, we suppose that the system is composed of n_{s_0} particles of species s per

unit volume bearing the charge q_s . As the system has to be electrically neutral, the positive total charge equals the negative total charge, namely:

$$\sum_s q_s n_{s0} = 0. \quad (4.123)$$

However, each charge creates an electrostatic potential $\Phi(r)$ in its environment that produces a cloud of charges symmetrically spheric, but not uniformly charged. If $n_s(\mathbf{r})$ denotes the number of charges of species s in the volume element $d\mathbf{r}$ at the position $\mathbf{r}$, it is quite appropriate to assume that the charge distribution in the electrostatic potential $\Phi(r)$ is given by the Boltzmann distribution (Eq. 4.110) because the charges are considered as independent. The charge distribution $n_s(\mathbf{r})$ writes:

$$n_s(\mathbf{r}) = n_{s0} \exp[-\beta q_s \Phi(\mathbf{r})]. \quad (4.124)$$

The Boltzmann distribution linking the local charge density $n_s(\mathbf{r})$ to the electrostatic potential $\Phi(r)$ is not sufficient to solve the problem because the two functions $n_s(\mathbf{r})$ and $\Phi(r)$ are unknown. A second relation should be used to combine $n_s(\mathbf{r})$ with $\Phi(r)$. This relation is the Poisson equation⁴:

$$\nabla^2 \Phi(\mathbf{r}) = -\frac{\sum_s q_s n_s(\mathbf{r})}{\varepsilon_0 \varepsilon}, \quad (4.125)$$

where the summation is made on all the charges and $\varepsilon_0 \varepsilon$ is the dielectric constant of the medium. The Boltzmann distribution and the Poisson equation thus form a system of equations that is generally solved by a self-consistent method in taking first a trial function $\Phi(\mathbf{r})$ to calculate $n_s(\mathbf{r})$, then in substituting $n_s(\mathbf{r})$ in Poisson's equation to determine a new function $\Phi(\mathbf{r})$, and so on, until obtaining stable functions. However, in some cases, the system of simultaneous equations can be solved analytically with the Debye-Hückel theory, as we shall see in the next section.

⁴Here the Poisson equation and the Coulomb equation will be written in the rationalized M.K.S. unit system (SI units), such as $\nabla^2 \Phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\varepsilon_0}$, where $\rho(\mathbf{r})$ is the density of charges, and $F(\mathbf{r}) = \frac{qq'}{4\pi\varepsilon_0 r^2}$ respectively. But, these equations can also be written in the unrationalized Gaussian unit system, such as $\nabla^2 \Phi(\mathbf{r}) = -4\pi\rho(\mathbf{r})$ and $F(\mathbf{r}) = \frac{qq'}{r^2}$. The difference between the two unit systems is in the respective positions of the factors 4π and ε_0 in the formulas.

4.6 The ionized gas

Formulation of the problem

Consider a strong, but very dilute, electrolyte (where the ionization is complete) in which the ion density of type s is n_{s0} . If the ions are distributed randomly, the probabilities of finding an anion or a cation at a given place would be the same. In reality, the ions are not randomly distributed because, around an anion, there is more chance to find a cation rather than another anion. In the Debye-Hückel theory [9], the issue is to calculate the electrostatic potential $\Phi(\mathbf{r})$ on an ion located at $\mathbf{r}$ arising from the action of all the other ions. For this purpose, we consider an ion i of type s , with the charge $q_{s,i}$, located at a spot taken as the origin. The charge distribution around this ion is given by equation (4.124), the electrostatic potential produced at point $\mathbf{r}$ by equation (4.125) and the condition of neutrality of the system by equation (4.123). Now, in combining equations (4.124) and (4.125), we eliminate $n_s(\mathbf{r})$ and write:

$$\nabla^2 \Phi(\mathbf{r}) = -\frac{1}{\varepsilon_0 \varepsilon} \sum_s q_s n_{s0} \exp[-\beta q_s \Phi(\mathbf{r})] . \quad (4.126)$$

Assuming, moreover, that the interaction energy $q_s \Phi(\mathbf{r})$ is small compared to the thermal energy $\beta^{-1} = k_B T$ (this is true when the electrolyte is very dilute), we make the first-order Taylor expansion of the exponential function and write the above equation by taking into account the condition of neutrality (Eq. 4.123):

$$\begin{aligned} \nabla^2 \Phi(\mathbf{r}) &= -\frac{1}{\varepsilon_0 \varepsilon} \sum_s q_s n_{s0} [1 - \beta q_s \Phi(\mathbf{r})] \\ &= \frac{1}{\varepsilon_0 \varepsilon} \beta \sum_s n_{s0} q_s^2 \Phi(\mathbf{r}) . \end{aligned} \quad (4.127)$$

The last equality is the Poisson-Boltzmann linearized equation. In the original theory, Debye and Hückel assumed that the ions are point charges. But it is more realistic to consider the ions as spherical rigid particles of radius a , containing no charge other than the charge q_s concentrated at the sphere centre. As the spheres of radius a are

impenetrable, the Poisson–Boltzmann equation can be split into two partial differential equations:

$$\nabla^2\Phi(\mathbf{r}) = 0 \quad \text{if } 0 < r < a; \quad (4.128)$$

$$= \kappa_D^2\Phi(\mathbf{r}) \quad \text{if } r \geq a, \quad (4.129)$$

where:

$$\kappa_D^2 = \frac{1}{\varepsilon_0 \varepsilon k_B T} \sum_s n_{s0} q_s^2. \quad (4.130)$$

The parameter κ_D has been introduced to simplify the writing. The inverse parameter κ_D has the dimension of length and it is called the *Debye length*. The value of this length is roughly equal to the thickness of the ionic atmosphere beyond which the electrostatic potential around an ion has no appreciable value. For an electrolyte solution with a density of anions $n_{-0} = \frac{N_{-0}}{V}$ and a density of cations $n_{+0} = \frac{N_{+0}}{V}$, the parameter κ_D is written explicitly as:

$$\kappa_D^2 = \frac{1}{\varepsilon_0 \varepsilon k_B T} [n_{-0} q_-^2 + n_{+0} q_+^2]. \quad (4.131)$$

To solve the Poisson–Boltzmann equation, the spherical symmetry of the system suggests using the Laplacian in spherical coordinates:

$$\nabla^2\Phi(\mathbf{r}) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \varphi^2}, \quad (4.132)$$

in which the radial part is only retained. From the change of variables $u = r\Phi$, it results:

$$\frac{d\Phi}{dr} = -\frac{u}{r^2} + \frac{1}{r} \frac{du}{dr}, \quad (4.133)$$

that enables us to write the radial part of the Laplacian in the form:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Phi}{dr} \right) = \frac{1}{r} \frac{d^2 u}{dr^2}. \quad (4.134)$$

It is then easy to solve the following system of differential equations:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Phi}{dr} \right) = \frac{1}{r} \frac{d^2 u}{dr^2} = 0, \quad 0 < r < a, \quad (4.135)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Phi}{dr} \right) = \frac{1}{r} \frac{d^2 u}{dr^2} = \kappa_D^2 \frac{u}{r}, \quad r \geq a, \quad (4.136)$$

whose solutions are:

$$\Phi = \frac{u}{r} = C_1 + \frac{C_2}{r}, \quad 0 < r < a, \quad (4.137)$$

$$= \frac{u}{r} = \frac{C_3}{r} \exp(-\kappa_D r) + \frac{C_4}{r} \exp(\kappa_D r), \quad r \geq a, \quad (4.138)$$

where C_1 , C_2 , C_3 and C_4 are four constants of integration to be determined with the boundary conditions. The value of the constant $C_4 = 0$ is imposed by the fact that the electrostatic potential Φ tends to zero as r tends to infinity. Concerning the constant C_2 , it comes from the Gauss theorem $\iint \mathbf{E} \cdot d\mathbf{S} = 1/(\varepsilon_0 \varepsilon) \sum q_s$ by calculating the flux produced by the point charge $q_{s,i}$ – located at the ion centre – through a small sphere of radius $r < a$. As $\mathbf{E} = -\mathbf{grad} \Phi$, the Gauss theorem is expressed under the differential form as:

$$-\frac{d\Phi}{dr} 4\pi r^2 = \frac{q_{s,i}}{\varepsilon_0 \varepsilon}. \quad (4.139)$$

By identifying the electrostatic field on the sphere of radius r , i.e. $-\frac{d\Phi}{dr} = \frac{q_{s,i}}{\varepsilon_0 \varepsilon} \frac{1}{4\pi r^2}$, with its expression issued from equation (4.137), i.e. $-\frac{d\Phi}{dr} = \frac{C_2}{r^2}$, we immediately obtain the integration constant $C_2 = \frac{q_{s,i}}{4\pi \varepsilon_0 \varepsilon}$. To determine the two remaining constants C_1 and C_3 , we write the conditions of continuity of the electrostatic potential and its first derivative at $r = a$, i.e. $\Phi_{in}(a) = \Phi_{ex}(a)$ and $\frac{d\Phi_{in}}{dr}|_a = \frac{d\Phi_{ex}}{dr}|_a$. Thus, the following system of algebraic equations is deduced:

$$C_1 + \frac{q_{s,i}}{4\pi \varepsilon_0 \varepsilon a} = \frac{C_3}{a} \exp(-\kappa_D a), \quad (4.140)$$

$$\frac{q_{s,i}}{4\pi \varepsilon_0 \varepsilon a^2} = \frac{\kappa_D C_3}{a} \exp(-\kappa_D a) + \frac{C_3}{a^2} \exp(-\kappa_D a), \quad (4.141)$$

from which the two integration constants C_3 and C_1 are drawn:

$$C_3 = \frac{q_{s,i}}{4\pi \varepsilon_0 \varepsilon} \left[\frac{\exp(\kappa_D a)}{1 + \kappa_D a} \right], \quad (4.142)$$

$$C_1 = -\frac{q_{s,i}}{4\pi \varepsilon_0 \varepsilon} \left(\frac{\kappa_D}{1 + \kappa_D a} \right). \quad (4.143)$$

Finally, the electrostatic potential acting on an ion taken as the

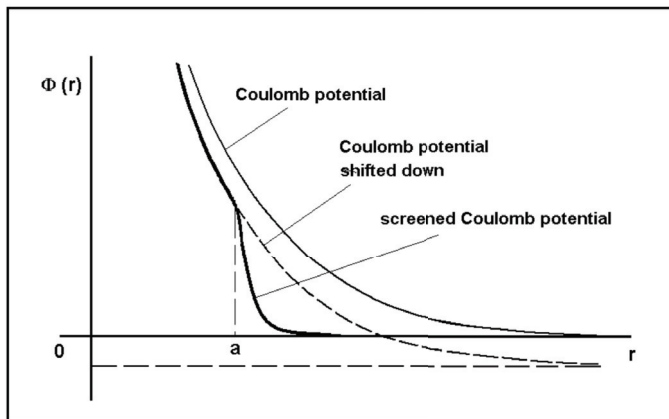


Figure 4.2: Schematic representation of the electrostatic potential around an ion whose charge is concentrated at the center of the ionic sphere of radius a .

origin is expressed as:

$$\Phi(r) = \frac{q_{s,i}}{4\pi\epsilon_0\epsilon r} - \frac{q_{s,i}}{4\pi\epsilon_0\epsilon} \left(\frac{\kappa_D}{1 + \kappa_D a} \right), \quad 0 < r < a, \quad (4.144)$$

$$= \frac{q_{s,i}}{4\pi\epsilon_0\epsilon} \left[\frac{\exp(\kappa_D a)}{1 + \kappa_D a} \right] \frac{\exp(-\kappa_D r)}{r}, \quad r \geq a. \quad (4.145)$$

It is found that the electrostatic potential in the sphere of radius a is a Coulomb potential slightly shifted downwards (Fig. 4.2) while, beyond the radius a , it is a screened Coulomb potential decaying faster than the Coulomb potential.

Thermodynamic properties and density of ionic charges

To calculate the free energy of the electrolytes with equation (4.122), it is first necessary to determine the expression for the mean electrostatic potential $\langle \Phi(\mathbf{r}_i, \lambda) \rangle$. As stated above, this is the electrostatic potential acting on the particle i when all the particles have the same individual charge λq . It should be recalled that the quantity:

$$\Phi(r) = \frac{q_{s,i}}{4\pi\epsilon_0\epsilon r} - \frac{q_{s,i}}{4\pi\epsilon_0\epsilon} \left(\frac{\kappa_D}{1 + \kappa_D a} \right), \quad (4.146)$$

represents the total electrostatic potential produced by *all* the charges, including the particle i itself by means of its contribution $\frac{q_{s,i}}{4\pi\epsilon_0\epsilon r}$. However, the mean electrostatic potential $\langle\Phi(\mathbf{r}_i, \lambda)\rangle$ is a constant potential which does not contain the contribution of the particle i . Therefore, the expression of the mean electrostatic potential is:

$$\langle\Phi(\mathbf{r}_i, \lambda)\rangle = \Phi(r) - \frac{q_{s,i}}{4\pi\epsilon_0\epsilon r} = -\frac{q_{s,i}}{4\pi\epsilon_0\epsilon} \left[\frac{\kappa_D(\lambda)}{1 + \kappa_D(\lambda)a} \right]. \quad (4.147)$$

To calculate the integral in equation (4.122), it remains to explicitly write $\langle\Phi(\mathbf{r}_i, \lambda)\rangle$ in terms of the charge parameter λ , in replacing q_s by λq_s and transforming $\kappa_D(\lambda)$ as follows:

$$\kappa_D^2(\lambda) = \frac{1}{\epsilon_0\epsilon k_B T} \sum_s n_{s0} \lambda^2 q_s^2 = \lambda^2 \kappa_D^2. \quad (4.148)$$

Whereupon, the mean electrostatic potential $\langle\Phi(\mathbf{r}_i, \lambda)\rangle$ takes the analytical form:

$$\langle\Phi(\mathbf{r}_i, \lambda)\rangle = -\frac{q_{s,i}}{4\pi\epsilon_0\epsilon} \left[\frac{\lambda^2 \kappa_D}{1 + \lambda \kappa_D a} \right]. \quad (4.149)$$

Substituting the expression of the mean electrostatic potential into equation (4.122) allows to determine the free energy of the electrolyte:

$$F = F_0 - \sum_{i=1}^N \frac{q_{s,i}^2 \kappa_D}{4\pi\epsilon_0\epsilon} \int_0^1 \frac{\lambda^2}{1 + \lambda \kappa_D a} d\lambda. \quad (4.150)$$

It is possible to simplify the previous relation after performing the integration⁵ over λ and converting the discrete sum $\sum_{i=1}^N q_{s,i}^2$ over individual charges into a discrete sum over the type of charges, with all this amounting to expressing it as a function of the parameter κ_D (Eq. 4.130). Since $n_{s0} = \frac{N_{s0}}{V}$ is the number of particles of species s per unit volume, it results:

$$\begin{aligned} \sum_{i=1}^N q_{s,i}^2 &= \sum_s N_{s0} q_s^2 = V \sum_s n_{s0} q_s^2 \\ &= V \epsilon_0 \epsilon k_B T \kappa_D^2. \end{aligned} \quad (4.151)$$

⁵The result of the integral over λ is:

$$\int_0^1 \frac{\lambda^2}{1 + \lambda \kappa_D a} d\lambda = \frac{1}{\kappa_D^3 a^3} \left[\ln(1 + \kappa_D a) - \kappa_D a + \frac{1}{2} \kappa_D^2 a^2 \right].$$

When these transformations have been achieved, the free energy of the electrolyte per unit volume is reduced to:

$$\beta \left(\frac{F - F_0}{V} \right) = -\frac{1}{4\pi a^3} \left[\ln(1 + \kappa_D a) - \kappa_D a + \frac{1}{2} \kappa_D^2 a^2 \right]. \quad (4.152)$$

Having knowledge of the free energy makes it possible to calculate the other thermodynamic properties. Instead of reproducing these calculations that can be found in the book by McQuarrie [13], we had rather determine the distribution of the ionic charges around an ion in a dilute electrolytic solution. Recall that the charge of an ion is concentrated at the sphere centre of radius a . In addition, the charge density $\rho(\mathbf{r})$ is zero into the sphere whereas, outside the sphere of radius a , it is calculated by using equation (4.124):

$$\rho(r) = \sum_s q_s n_s(r) = \sum_s q_s n_{s0} \exp[-\beta q_s \Phi(r)]. \quad (4.153)$$

Now we linearize the above equation by expanding the exponential function in a Taylor series:

$$\rho(r) = \sum_s q_s n_{s0} - \sum_s \beta n_{s0} q_s^2 \Phi(r), \quad (4.154)$$

then, simplify the relation by using the neutrality condition of the system (Eq. 4.123) and considering the electrostatic potential beyond $r = a$ (Eq. 4.145). One thus obtains:

$$\rho(r) = -\frac{q_{s,i}}{4\pi\epsilon_0\epsilon} \left[\frac{\exp(\kappa_D a)}{1 + \kappa_D a} \right] \frac{\exp(-\kappa_D r)}{r} \sum_s \beta n_{s0} q_s^2 \quad r \geq a. \quad (4.155)$$

Finally, we use equation (4.130) to transform the term $\sum_s \beta n_{s0} q_s^2$ as a function of the parameter κ_D . It follows that:

$$\rho(r) = -\frac{q_{s,i} \kappa_D^2}{4\pi} \left[\frac{\exp(\kappa_D a)}{1 + \kappa_D a} \right] \frac{\exp(-\kappa_D r)}{r} \quad r \geq a. \quad (4.156)$$

As could be expected, the charge density $\rho(r)$ has a sign opposite to the central charge $q_{s,i}$.

Equation (4.156) permits the calculation of the total charge in a spherical ring located between r and $r + dr$ by evaluating the quantity:

$$X(r) = |\rho(r) 4\pi r^2| = q_{s,i} \kappa_D^2 \left[\frac{\exp(\kappa_D a)}{1 + \kappa_D a} \right] r \exp(-\kappa_D r). \quad (4.157)$$

This function offers a clear indication on the shape and extent of the ionic atmosphere surrounding any ion of the electrolytic solution. By calculating the derivative of $X(r)$, it is found that the function passes through a maximum for the value $r_{\max} = \frac{1}{\kappa_D}$ corresponding to the densest region of the ionic atmosphere, and producing a screen around the ion in that way. Besides, the maximum of the curve $X(r)$ shifts towards large values of r when κ_D decreases, i.e. when the electrolyte becomes more dilute.

5 Theory of the liquid state

We saw that the determination of thermodynamic properties of gases can be made either by the method of partition function or by the method of correlation functions. The former is a very elegant and efficient method giving the partition function by a direct calculation as compared with the correlation function method that uses the pair correlation function $g(r)$. The latter is a powerful method necessary to investigating the liquid state. Interestingly, both methods are equivalent, though the correlation function method which is slightly more complicated to implement than the partition function belongs to a more general theory enabling us to study the systems in equilibrium and out-of-equilibrium.

In this chapter, we present the formalism required to determine the pertinent thermodynamic properties of liquids in terms of the pair correlation function $g(r)$ and the effective pair potential $u(r)$ likely to contain the two-body and three-body potentials. One of the major issues of microscopic liquid theory is the search for the genuine pair potential describing interactions in different types of liquids such as atomic liquids, molecular liquids, ionic liquids, colloidal suspensions (see for instance [14, 15, 16]). It should be emphasized that the lack of knowledge about actual interactions can be compensated by simplified potential models capable of describing the properties of model liquids rather than those of real liquids. Among these potentials are the hard-sphere, square-well, Lennard–Jones, Yukawa, Kac potentials, etc.

We also provide a brief review of the thermodynamic perturbation theory proposed by Zwanzig [17], and we mention the square-gradient theory of van der Waals to investigate the inhomogeneous systems at equilibrium. It will be seen that, to implement the perturbation theory, it is necessary to use, in addition to the weak perturbative

potential, a reference system whose structure looks like that of the real liquid.

5.1 Thermodynamic properties of liquids

Internal energy

The internal energy of a liquid is calculated with the equation (2.104):

$$E = k_B T^2 \frac{\partial}{\partial T} \ln Q_N(V, T), \quad (5.1)$$

where the partition function $Q_N(V, T)$ depends on the configuration integral $Z_N(V, T)$ and the thermal wavelength Λ is in accordance with the classical expression (Eq. 3.11):

$$Q_N(V, T) = \frac{Z_N(V, T)}{N! \Lambda^{3N}}, \quad (5.2)$$

with:

$$Z_N(V, T) = \int \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N \quad (5.3)$$

$$\text{and} \quad \Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}. \quad (5.4)$$

The derivative of $\ln Q_N(V, T)$ with respect to T is written:

$$\frac{\partial}{\partial T} \ln Q_N(V, T) = \frac{\partial}{\partial T} \ln Z_N(V, T) - 3N \frac{\partial}{\partial T} \ln \Lambda, \quad (5.5)$$

with

$$\frac{\partial}{\partial T} \ln Z_N(V, T) = \frac{1}{Z_N(V, T)} \iint \left[\frac{1}{k_B T^2} U(\mathbf{r}^N) \right] e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}^N \quad (5.6)$$

$$\text{and} \quad \frac{\partial}{\partial T} \ln \Lambda = \frac{1}{\Lambda} \left(-\frac{1}{2T^{3/2}} \sqrt{\frac{h^2}{2\pi m k_B}} \right) = -\frac{1}{2T}. \quad (5.7)$$

To go on with the calculation, the potential energy $U(\mathbf{r}^N) = \sum_i \sum_{j>i} u(r_{ij})$ is explicitly written as a sum of pair potentials (Eq. 3.17), so that the internal energy reads:

$$E = \frac{3}{2} N k_B T + \frac{1}{Z_N(V, T)} \iint \left[\sum_i \sum_{j>i} u(r_{ij}) \right] \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N. \quad (5.8)$$

The first term on the right hand side of this equation is the kinetic energy of the ideal gas, and the second term represents the potential energy of interaction. Given the additivity assumption of the pair potentials, it is reasonable to accept that the sum is composed of $N(N-1)/2$ equal terms and to write:

$$\sum_i \sum_{j>i} \frac{1}{Z_N(V, T)} \iint u(r_{ij}) \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N = \frac{N(N-1)}{2} \langle u(r_{ij}) \rangle, \quad (5.9)$$

with:

$$\langle u(r_{ij}) \rangle = \frac{\iint u(r_{ij}) \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N}{\iint \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N}. \quad (5.10)$$

If the values of the couple (i, j) are chosen to be, for example, $i = 1$ and $j = 2$, the integral in the numerator of equation (5.10) is written by isolating the elements of integration $d\mathbf{r}_1$ and $d\mathbf{r}_2$ as follows:

$$\langle u(r_{12}) \rangle = \frac{1}{Z_N(V, T)} \iint_6 u(r_{12}) \left\{ \iint_{3(N-2)} e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N \right\} d\mathbf{r}_1 d\mathbf{r}_2. \quad (5.11)$$

Then, with equation (3.89), the term in brackets can be expressed as a function of the pair correlation function as:

$$\begin{aligned} \langle u(r_{12}) \rangle &= \frac{1}{Z_N(V, T)} \iint_6 u(r_{12}) \left[g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rho^2 \frac{(N-2)!}{N!} Z_N(V, T) \right] d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \rho^2 \frac{(N-2)!}{N!} \iint_6 u(r_{12}) \left[g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5.12)$$

For a homogeneous and isotropic fluid, it is convenient to make the changes of variables $\mathbf{R} = \mathbf{r}_1$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, where $\mathbf{R}$ and $\mathbf{r}$ describe the volume of the system. That allows us to write the expression for

the internal energy under the integral form:

$$\begin{aligned} E &= \frac{3}{2}Nk_{\text{B}}T + \frac{N(N-1)}{2}\rho^2 \frac{(N-2)!}{N!} \iint_6 u(r_{12}) \left[g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{3}{2}Nk_{\text{B}}T + \frac{\rho^2}{2} \int_V d\mathbf{R} \int_V u(r)g(r)d\mathbf{r}, \end{aligned} \quad (5.13)$$

or equivalently:

$$E = \frac{3}{2}Nk_{\text{B}}T + 2\pi\rho N \int_0^\infty u(r)g(r)r^2 dr. \quad (5.14)$$

Consequently, the calculation of the internal energy of liquids requires appropriate knowledge of the pair potential $u(r)$ and the pair correlation function $g(r)$. As regards the latter, the choice is to use, either the experimental values, or the values calculated from the microscopic theory of liquids which will be outlined in the following chapter. It can be noted that the integral in equation (5.14) is the product of the pair potential by the pair correlation function weighted by r^2 . It should also be mentioned that the calculation of E can be made by taking account of the three-body potential $u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and three-body correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. In this case, the three-body correlation function has to be determined by the theory of liquids because it is not accessible by experiment.

Pressure equation of state

The expression for the pressure is obtained in the same manner as the internal energy, i.e. by considering equation (2.105):

$$p = k_{\text{B}}T \frac{\partial}{\partial V} \ln Q_N(V, T) = k_{\text{B}}T \frac{\partial}{\partial V} \ln Z_N(V, T). \quad (5.15)$$

The derivative of the configuration integral with respect to the volume in the above relation requires using the reduced variable $\mathbf{X} = \frac{\mathbf{r}}{V^{1/3}}$ that enables us to find the dependence of the potential energy $U(\mathbf{r}^N)$ on volume. Indeed, if the volume element is $d\mathbf{r} = Vd\mathbf{X}$, the scalar variable r simplifies as $r = V^{1/3}X$, leading to $dr = V^{1/3}dX$, and the derivative of r with respect to V becomes:

$$\frac{dr}{dV} = \frac{1}{3}V^{-2/3}X = \frac{1}{3V}r. \quad (5.16)$$

The configuration integral and its derivative with respect to the volume are written with the reduced variables in the following forms:

$$Z_N(V, T) = V^N \iint_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{X}_1 \dots d\mathbf{X}_N, \quad (5.17)$$

and

$$\begin{aligned} \frac{\partial}{\partial V} \ln Z_N(V, T) &= \frac{N}{V} \\ &+ \frac{V^N}{Z_N(V, T)} \frac{\partial}{\partial V} \left[\iint_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{X}_1 \dots d\mathbf{X}_N \right] \\ &= \frac{N}{V} + \frac{V^N}{Z_N(V, T)} \iint_{3N} \left[-\beta \frac{\partial U(\mathbf{r}^N)}{\partial V} \right] \exp[-\beta U(\mathbf{r}^N)] d\mathbf{X}_1 \dots d\mathbf{X}_N. \end{aligned} \quad (5.18)$$

Assuming that the potential energy is decomposed into a sum of pair potentials, and with the help of equation (5.16), the derivation of the potential energy versus volume is achieved as follows:

$$\begin{aligned} \frac{\partial U(\mathbf{r}^N)}{\partial V} &= \frac{\partial}{\partial V} \sum_i \sum_{j>i} u(r_{ij}) = \sum_i \sum_{j>i} \frac{\partial u(r_{ij})}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial V} \\ &= \frac{1}{3V} \sum_i \sum_{j>i} r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}}, \end{aligned} \quad (5.19)$$

and the derivative of the configuration integral reduces to

$$\begin{aligned} \frac{\partial}{\partial V} \ln Z_N(V, T) &= \frac{N}{V} - \frac{\beta}{3V} \frac{V^N}{Z_N(V, T)} \times \\ &\times \iint_{3N} \left[\sum_i \sum_{j>i} r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right] \exp[-\beta U(\mathbf{r}^N)] d\mathbf{X}_1 \dots d\mathbf{X}_N. \end{aligned} \quad (5.20)$$

In returning to the old position variables, the expression of the pressure is:

$$\begin{aligned} p &= k_B T \frac{N}{V} - \frac{1}{3V} \frac{1}{Z_N(V, T)} \times \\ &\times \sum_i \sum_{j>i} \iint_{3N} \left[r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right] \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_1 \dots d\mathbf{r}_N. \end{aligned} \quad (5.21)$$

As for the calculation of the internal energy, the assumption of additivity of the pair potentials permits writing the sum of integrals in the previous relation as follows:

$$\begin{aligned} \sum_i \sum_{j>i} \frac{1}{Z_N(V, T)} \iint \left[r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right] \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N \\ = \frac{N(N-1)}{2} \left\langle r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right\rangle, \end{aligned} \quad (5.22)$$

with

$$\left\langle r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right\rangle = \frac{\iint \left[r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right] \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N}{\iint \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}^N}. \quad (5.23)$$

If the indices $i=1$ and $j=2$ are chosen for the couple of particles (i, j) , equation (5.23) can be written by isolating the elements of integration $d\mathbf{r}_1$ and $d\mathbf{r}_2$ in the integral of the numerator:

$$\begin{aligned} \left\langle r_{12} \frac{\partial u(r_{12})}{\partial r_{12}} \right\rangle &= \frac{1}{Z_N(V, T)} \times \\ &\times \iint_6 r_{12} \frac{\partial u(r_{12})}{\partial r_{12}} \left[\iint_{3(N-2)} \exp [-\beta U(\mathbf{r}^N)] d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N \right] d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5.24)$$

Then, with equation (3.89), the pair correlation function appears explicitly in the term in square brackets, so that the above relation reads:

$$\begin{aligned} \left\langle r_{12} \frac{\partial u(r_{12})}{\partial r_{12}} \right\rangle &= \frac{1}{Z_N(V, T)} \times \\ &\times \iint_6 r_{12} \frac{\partial u(r_{12})}{\partial r_{12}} \left[g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rho^2 \frac{(N-2)!}{N!} Z_N(V, T) \right] d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \rho^2 \frac{(N-2)!}{N!} \iint_6 r_{12} \frac{\partial u(r_{12})}{\partial r_{12}} \left[g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5.25)$$

For a homogeneous and isotropic fluid, the standard transformations of variables $\mathbf{R} = \mathbf{r}_1$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ permit the writing of the

expression for pressure (Eq. 5.21) as follows:

$$\begin{aligned}
 p &= k_{\text{B}}T \frac{N}{V} - \frac{1}{3V} \frac{N(N-1)}{2} \rho^2 \frac{(N-2)!}{N!} \times \\
 &\quad \times \iint_6 r_{12} \frac{\partial u(r_{12})}{\partial r_{12}} \left[g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= k_{\text{B}}T \frac{N}{V} - \frac{1}{6V} \rho^2 \int_V d\mathbf{R} \int_V r \frac{\partial u(r)}{\partial r} g(r) d\mathbf{r}, \quad (5.26)
 \end{aligned}$$

or equivalently:

$$p = k_{\text{B}}T \frac{N}{V} - \frac{2\pi}{3} \rho^2 \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} g(r) dr. \quad (5.27)$$

Equation (5.27) gives the pressure of liquids as a function of the pair potential and the pair correlation function. It represents the equation of state of liquids, called the *pressure equation of state*. As for the internal energy, it can be written with additional terms containing the three-body potential $u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and the three-body correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. Furthermore, it is important to note that, beside the pressure equation of state, another equation of state can be deduced which is based on different considerations as it will be discussed in section (5.2).

Chemical potential

With equations (5.14) and (5.27), the internal energy E and pressure p are obtainable for any system, provided that the potential energy is decomposable into a sum of pair potentials $u(r)$ and the pair correlation function $g(r)$ is known. The two functions E and p occurring in the mechanics and thermodynamics are not sufficient to deduce the other thermodynamic properties. Useful results are the expressions for the chemical potential μ and the entropy S as a function of $g(r)$. Traditionally, the expression of the chemical potential [18] is obtained by integrating the partition function with respect to a parameter to be defined, as we shall see in what follows.

First recall the formal expression for the chemical potential (Eq. 2.107):

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} = F(V, T, N) - F(V, T, N-1). \quad (5.28)$$

According to equations (2.102) and (3.11), the free energy F is written:

$$\begin{aligned} F(V, T, N) &= -k_B T \ln Q_N(V, T) \\ &= -k_B T [\ln Z_N(V, T) - \ln N! - N \ln \Lambda^3], \end{aligned} \quad (5.29)$$

so that the expression for the chemical potential can be simplified to the form:

$$\begin{aligned} \mu &= -k_B T [\ln Z_N(V, T) - \ln N! - N \ln \Lambda^3] \\ &\quad + k_B T [\ln Z_{N-1}(V, T) - \ln(N-1) - (N-1) \ln \Lambda^3], \end{aligned} \quad (5.30)$$

or:

$$\mu = k_B T \left[-\ln \frac{Z_N(V, T)}{Z_{N-1}(V, T)} + \ln N + \ln \Lambda^3 \right]. \quad (5.31)$$

To obtain the argument of the logarithm in the above relation, we are asked to proceed and write the potential energy as a function of the *coupling parameter* λ , according to reference [13] (p. 262):

$$U(\mathbf{r}^N, \lambda) = \lambda \sum_{j=2}^N u(r_{1j}) + \sum_{i,j>i \geq 2}^N \sum_{i,j>i \geq 2}^N u(r_{ij}). \quad (5.32)$$

The coupling parameter λ has the same meaning as the charge parameter introduced in the model of Debye–Hückel (Eq. 4.121). Varying from 0 to 1, it indicates the degree of coupling of the particle to which it is assigned with the rest of the system. In the above relation, $\lambda = 1$ means that the particle 1 is completely coupled with the other particles, while $\lambda = 0$ indicates a zero coupling, i.e. the absence of the particle 1 in the system. This allows us to write the very important relations:

$$\begin{aligned} U(\mathbf{r}^N, 1) &= \sum_{j=2}^N u(r_{1j}) + \sum_{i,j>i \geq 2}^N \sum_{i,j>i \geq 2}^N u(r_{ij}) \\ &= \sum_{i,j>i \geq 1}^N \sum_{i,j>i \geq 1}^N u(r_{ij}) = U(\mathbf{r}^N) \end{aligned} \quad (5.33)$$

$$\text{and} \quad U(\mathbf{r}^N, 0) = \sum_{i,j>i \geq 2}^N \sum_{i,j>i \geq 2}^N u(r_{ij}) = U(\mathbf{r}^{N-1}). \quad (5.34)$$

With these relations in mind, the configuration integrals (Eq. 3.4) are written respectively:

$$Z_N(V, T, \lambda=1) = \iint_{3N} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N = Z_N(V, T) \quad (5.35)$$

and

$$Z_N(V, T, \lambda=0) = \int_V d\mathbf{r}_1 \iint_{3(N-1)} \exp[-\beta U(\mathbf{r}^{N-1})] d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (5.36)$$

so that they are joined together by the formula:

$$Z_N(V, T, \lambda=0) = V Z_{N-1}(V, T). \quad (5.37)$$

These relations can now be used to calculate the logarithm of the ratio of configuration integrals contained in equation (5.31):

$$\begin{aligned} \ln \frac{Z_N(V, T)}{Z_{N-1}(V, T)} &= \ln \frac{Z_N(V, T, \lambda=1)}{Z_N(V, T, \lambda=0)} + \ln V, \\ &= \ln V + \int_0^1 \frac{\partial \ln Z_N}{\partial \lambda} d\lambda. \end{aligned} \quad (5.38)$$

With the general expression for the configuration integral:

$$Z_N(V, T, \lambda) = \iint_{3N} \exp[-\beta U(\mathbf{r}^N, \lambda)] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (5.39)$$

where the potential energy is given by equation (5.32), we are in a position to evaluate the partial derivative $\frac{\partial Z_N}{\partial \lambda}$:

$$\frac{\partial Z_N(V, T, \lambda)}{\partial \lambda} = -\beta \iint_{3N} \left[\sum_{j=2}^N u(r_{1j}) \right] \exp[-\beta U(\mathbf{r}^N, \lambda)] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (5.40)$$

as well as $\frac{\partial \ln Z_N}{\partial \lambda}$, namely:

$$\frac{\partial \ln Z_N(V, T, \lambda)}{\partial \lambda} = -\frac{\beta}{Z_N} \sum_{j=2}^N \iint_{3N} u(r_{1j}) \exp[-\beta U(\mathbf{r}^N, \lambda)] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (5.41)$$

Since the above equation includes $(N-1)$ identical terms, it can be written:

$$\frac{\partial \ln Z_N(V, T, \lambda)}{\partial \lambda} = -\frac{\beta(N-1)}{Z_N} \iint_{3N} u(r_{1j}) \exp[-\beta U(\mathbf{r}^N, \lambda)] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (5.42)$$

With the index value $j=2$, the elements of integration $d\mathbf{r}_1$ and $d\mathbf{r}_2$ can be isolated, as done for the internal energy and pressure, to transform the above equation into:

$$\begin{aligned} \frac{\partial \ln Z_N(V, T, \lambda)}{\partial \lambda} &= -\frac{\beta(N-1)}{Z_N(V, T)} \times \\ &\times \iint_6 u(r_{12}) \left\{ \iint_{3(N-2)} \exp[-\beta U(\mathbf{r}^N, \lambda)] d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N \right\} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5.43)$$

Owing to equation (3.89), the previous relation can be explicitly written in terms of the pair correlation function as:

$$\begin{aligned} \frac{\partial \ln Z_N(V, T, \lambda)}{\partial \lambda} &= -\frac{\beta(N-1)}{Z_N(V, T)} \times \\ &\times \iint_6 u(r_{12}) \left\{ g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \lambda) \rho^2 \frac{(N-2)!}{N!} Z_N(V, T) \right\} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= -\beta \rho^2 \frac{(N-1)(N-2)!}{N!} \iint_6 u(r_{12}) \left\{ g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \lambda) \right\} d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5.44)$$

If the fluid is homogeneous and isotropic, the above relation is simplified by using the changes of variables $\mathbf{R} = \mathbf{r}_1$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. After all simplifications have been done, $\frac{\partial \ln Z_N(\lambda)}{\partial \lambda}$ is reduced to:

$$\frac{\partial \ln Z_N(V, T, \lambda)}{\partial \lambda} = -\frac{\beta \rho^2}{N} V \int_0^\infty u(r) g(r, \lambda) 4\pi r^2 dr. \quad (5.45)$$

It only remains for us to combine equation (5.45) with equation (5.38) to find the logarithm of the ratio of configuration integrals. We obtain:

$$\begin{aligned} \ln \frac{Z_N(V, T)}{Z_{N-1}(V, T)} &= \ln V + \int_0^1 \frac{\partial \ln Z_N}{\partial \lambda} d\lambda \\ &= \ln V - \beta \rho \int_0^1 d\lambda \int_0^\infty u(r) g(r, \lambda) 4\pi r^2 dr. \end{aligned} \quad (5.46)$$

Finally, by carrying forward this result in equation (5.31), the useful expression for the chemical potential is obtained in the form:

$$\mu = k_B T \left[-\ln V + \beta \rho \int_0^1 \int_0^\infty u(r) g(r, \lambda) 4\pi r^2 dr d\lambda + \ln N + \ln \Lambda^3 \right], \quad (5.47)$$

or equivalently:

$$\mu = k_B T \ln \rho \Lambda^3 + 4\pi \rho \int_0^1 \int_0^\infty u(r) g(r, \lambda) r^2 dr d\lambda. \quad (5.48)$$

Thus, like the internal energy (Eq. 5.14) and pressure (Eq. 5.27), the chemical potential (Eq. 5.48) can be calculated in terms of the pair potential and the pair correlation function.

Entropy

With the expressions of the internal energy E , pressure P and chemical potential μ , it is possible to deduce the entropy S by combining equations (2.100) and (4.53) as:

$$S = \frac{E - F}{T} = \frac{E}{T} - \frac{\mu N}{T} + \frac{pV}{T}, \quad (5.49)$$

where E , μ and p are given by equations (5.14), (5.48) and (5.27), respectively. Obviously, the calculation of the entropy with equation (5.49) implies adequate understanding of the pair potential. However, it should be stressed that the entropy can also be evaluated by using the pair correlation function $g(r)$ alone, without resorting to the pair potential. The demonstration is outside the scope of this presentation. The interested reader should refer to the original articles of Nettleton and Green [19] and Raveché [20]. We simply indicate the outline of the proof from equation (2.90):

$$S = -k_B \iint_{6N} P_N(\mathbf{r}^N, \mathbf{p}^N) \ln P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N. \quad (5.50)$$

This roughly follows the same approach as in section (2.3), assuming that the particles are identical and interacting, i.e. not independent.

As a consequence, equation (2.91) cannot be used. Here, the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ is split into a part depending on the momenta $\mathbf{p}$ and another one depending on the positions $\mathbf{r}$:

$$P_N(\mathbf{r}^N, \mathbf{p}^N) = \prod_{i=1}^N P_N^{(1)}(\mathbf{p}_i) \cdot P_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (5.51)$$

where each term $P_N^{(1)}(\mathbf{p}_i)$ corresponds to the Maxwell distribution function (Eq. 4.95). As far as $P_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is concerned, it is factorized into a sequence of the multiparticle correlation functions $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, $g_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, etc. After transformations and term by term integrations of equation (5.50), we find an expansion in series written in the following form, when stopped at the pair correlation function $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$:

$$\begin{aligned} S \simeq S^{id} - \frac{1}{2} k_B \rho^2 \int \int g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \ln g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ + \frac{1}{2} k_B \rho^2 \int \int [g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 1] d\mathbf{r}_1 d\mathbf{r}_2, \end{aligned} \quad (5.52)$$

where S^{id} is the entropy of the ideal gas (Eq. 4.14). With the classical changes of variables for the homogeneous and isotropic systems, we finally obtain the expression for the entropy as a function of $g(r)$ without explicit dependence on the pair potential, namely:

$$S \simeq k_B N \left(-\ln \rho \Lambda^3 + \frac{5}{2} \right) - 2\pi k_B \rho N \int_0^\infty [g(r) \ln g(r) - g(r) + 1] r^2 dr. \quad (5.53)$$

Expansion of $g(r)$ in powers of the density

So far, little is known about the pair correlation function $g(r)$, except that it measures the degree of dependence between the particles. The development of theoretical methods for its calculation will be the object of the next chapter. Nevertheless, at this stage, it is possible to have a primary indication of the form of the pair correlation function $g(r, \rho, T)$ that, a priori, must depend on the position r , density ρ and temperature T .

As the equation of state (Eq. 5.27), intended to be applied to liquids, is also valid for gases, it is interesting to compare it to the virial equation of state (Eq. 4.54):

$$\frac{p}{\rho k_B T} = 1 + \rho B_2(T) + \rho^2 B_3(T) + \rho^3 B_4(T) + \dots \quad (5.54)$$

Considering equations (4.73), (3.32) and (3.2) the second term of the expansion in the above equation, is expressed by means of the irreducible cluster integral β_1 as:

$$\rho B_2(T) = -\frac{1}{2} \beta_1 \rho = -b_2 \rho, \quad (5.55)$$

that is to say as:

$$\rho B_2(T) = -\frac{\rho}{2V} \iint f_{12} d\mathbf{r}_1 d\mathbf{r}_2. \quad (5.56)$$

After using the Mayer function (Eq. 3.18) and the changes of variables $\mathbf{R} = \mathbf{r}_1$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, the above relation reads:

$$\begin{aligned} \rho B_2(T) &= -\frac{\rho}{2V} \int d\mathbf{R} \int \{\exp[-\beta u(r)] - 1\} d\mathbf{r} \\ &= -2\pi \rho \int_0^\infty \{\exp[-\beta u(r)] - 1\} r^2 dr, \end{aligned} \quad (5.57)$$

and since $u(r)$ tends to zero when r goes to infinity, the integration by parts of the integral leads to the expression:

$$\rho B_2(T) = -\frac{2\pi}{3} \frac{\rho}{k_B T} \int_0^\infty r^3 \frac{\partial u}{\partial r} \exp[-\beta u(r)] dr, \quad (5.58)$$

which can be replaced in the virial equation of state (Eq. 5.54):

$$\frac{p}{\rho k_B T} = 1 - \frac{2\pi}{3} \frac{\rho}{k_B T} \int_0^\infty r^3 \frac{\partial u}{\partial r} \exp[-\beta u(r)] dr + \rho^2 B_3(T) + \dots \quad (5.59)$$

However, in comparing the first two terms of the right hand member of the previous relation with the equation of state (Eq. 5.27), we note that the pair correlation function $g(r)$ identifies with the Boltzmann factor $\exp[-\beta u(r)]$. This finding suggests using the following

expansion in powers of the density as an approximative form for the pair correlation function:

$$g(r, \rho, T) = g_0(r, T) + \rho g_1(r, T) + \rho^2 g_2(r, T) + \dots, \quad (5.60)$$

with

$$g_0(r, T) = \exp[-\beta u(r)]. \quad (5.61)$$

If this approximate form is adopted for the pair correlation function, equation (5.27) can be written with the expansion in powers of the density as:

$$\frac{p}{\rho k_B T} = 1 - \frac{2\pi}{3} \frac{\rho}{k_B T} \sum_{k=0}^{\infty} \rho^k \int_0^{\infty} r^3 \frac{\partial u(r)}{\partial r} g_k(r) dr. \quad (5.62)$$

By identifying the terms of equation (5.62) one by one with those of the virial equation of state (Eq. 5.54), we obtain the virial coefficients:

$$B_3(T) = -\frac{2\pi}{3} \frac{1}{k_B T} \int_0^{\infty} r^3 \frac{\partial u(r)}{\partial r} g_1(r) dr, \quad (5.63)$$

$$B_4(T) = -\frac{2\pi}{3} \frac{1}{k_B T} \int_0^{\infty} r^3 \frac{\partial u(r)}{\partial r} g_2(r) dr, \quad (5.64)$$

$$\dots = \dots$$

These expressions give the opportunity to test the approximate forms of the first contributions $g_1(r, T)$, $g_2(r, T)$, ... to the expansion of the pair correlation function because the first virial coefficients $B_3(T)$, $B_4(T)$, ... are known for the most common pair potentials.

It should be stressed that, when the pair correlation function is replaced by the Boltzmann factor in the expression for the energy (Eq. 5.14), the second term of the expansion of the energy of real gases (Eq. 4.77) is not recovered. This is due to the fact that the expression for the pair correlation function is solely an approximate function.

5.2 Compressibility equation of state

Relation between $g(r)$ and particle number fluctuations

To find the relation between the pair correlation function $g(r)$ and the fluctuations of particle number, consider the expression:

$$\int \int_6 \left[\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2, \quad (5.65)$$

in which the generic distribution functions $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ and $\rho^{(1)}(\mathbf{r}_1)$ have been defined in section (3.3). With equations (3.99) and (3.100), it is possible to transform the above relation into:

$$\int \int_6 \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \int_V \rho^{(1)}(\mathbf{r}_1) d\mathbf{r}_1 \int_V \rho^{(1)}(\mathbf{r}_2) d\mathbf{r}_2 = [\langle N^2 \rangle - \langle N \rangle^2] - \langle N \rangle^2. \quad (5.66)$$

But it is also possible to express it in terms of the pair correlation function $g(r)$:

$$\begin{aligned} \int \int_6 \left[\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2 = \\ = \int \int_6 \left[\rho^2 g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^2 \right] d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (5.67)$$

As usual, if the fluid is homogeneous and isotropic, the changes of variables $\mathbf{R} = \mathbf{r}_1$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ allow to simplify the above relation as:

$$\int \int_6 \left[\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2) \right] d\mathbf{r}_1 d\mathbf{r}_2 = 4\pi\rho^2 V \int_0^\infty [g(r) - 1] r^2 dr. \quad (5.68)$$

Now, by identifying equations (5.66) and (5.68), we obtain a very important relation that links the pair correlation function $g(r)$ to the fluctuations of the particle number, i.e.:

$$\begin{aligned} 4\pi\rho^2 V \int_0^\infty [g(r) - 1] r^2 dr &= \langle N \rangle \left[\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} - 1 \right]; \\ 1 + 4\pi\rho \int_0^\infty [g(r) - 1] r^2 dr &= \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \end{aligned} \quad (5.69)$$

A glance at equation (3.118) shows that the left-hand side of the above relation is nothing else than the structure factor at $q = 0$, so that equation (5.69) is still written:

$$S(0) = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \quad (5.70)$$

Therefore, the value of the structure factor $S(0)$ stands for a measure of the fluctuations of the particle number in liquids.

Compressibility equation of state

In this subsection, we derive an expression for a new equation of state for liquids based on the relationship between the isothermal compressibility χ_T and the fluctuations of the particle number. For this, the quantity $\frac{\partial \langle N \rangle}{\partial \mu}$ is evaluated by two different routes and then identified.

The first calculation comes under statistical mechanics. It begins with the expression for the mean number of particles $\langle N \rangle$ in the grand canonical ensemble (Eq. 2.188):

$$\langle N \rangle = \sum_{N=0}^{\infty} NP(N), \quad (5.71)$$

where $P(N)$ is the probability of having exactly N particles in the system. It is given by equation (2.40):

$$P(N) = \frac{\exp(\beta N \mu)}{\Xi} Q(V, T). \quad (5.72)$$

According to equations (3.11) and (4.51), it can also be written in the following forms:

$$P(N) = \frac{\exp(\beta N \mu)}{\Xi} \frac{Z_N}{N! \Lambda^{3N}} = \frac{z^N}{N!} \frac{Z_N}{\Xi}, \quad (5.73)$$

and, as $\sum_{N=0}^{\infty} P(N) = 1$, the partition function Ξ of the grand canonical ensemble (see Eq. 2.38) is:

$$\Xi = \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N. \quad (5.74)$$

As a result, the mean number of particles becomes:

$$\langle N \rangle = \sum_{N=0}^{\infty} N \frac{z^N}{N!} \frac{Z_N}{\Xi}, \quad (5.75)$$

and its derivative with respect to the chemical potential is calculated as follows. Firstly, let us evaluate the first derivative of the fugacity (Eq. 4.51) with respect to the chemical potential, i.e. $\frac{\partial z}{\partial \mu} = \beta z$, which allows writing the derivative of $\langle N \rangle$ with respect to μ as follows:

$$\begin{aligned} \frac{\partial \langle N \rangle}{\beta \partial \mu} &= \frac{\partial \langle N \rangle}{\beta \partial z} \frac{\partial z}{\partial \mu} = \beta z \frac{\partial}{\beta \partial z} \left[\sum_{N=0}^{\infty} N \frac{z^N}{N!} \frac{Z_N}{\Xi} \right] \\ &= z \left[\sum_{N=0}^{\infty} N^2 \frac{z^{N-1}}{N!} \frac{Z_N}{\Xi} + \sum_{N=0}^{\infty} N \frac{z^N}{N!} Z_N \left(-\frac{1}{\Xi^2} \frac{\partial \Xi}{\partial z} \right) \right], \end{aligned} \quad (5.76)$$

or equivalently:

$$\frac{\partial \langle N \rangle}{\beta \partial \mu} = \sum_{N=0}^{\infty} N^2 \frac{z^N}{N!} \frac{Z_N}{\Xi} - z \sum_{N=0}^{\infty} N \frac{z^N}{N!} \frac{Z_N}{\Xi^2} \left(\sum_{N=0}^{\infty} N \frac{z^{N-1}}{N!} Z_N \right). \quad (5.77)$$

Then, expressing the terms contained in the sums as a function of $P(N)$, with the help of equation (5.72), it results:

$$\frac{\partial \langle N \rangle}{\beta \partial \mu} = \sum_{N=0}^{\infty} N^2 P(N) - \sum_{N=0}^{\infty} N P(N) \sum_{N=0}^{\infty} N P(N) = \langle N^2 \rangle - \langle N \rangle^2. \quad (5.78)$$

The second calculation of $\frac{\partial \langle N \rangle}{\beta \partial \mu}$ comes under classical thermodynamics. In the grand canonical ensemble, where T and V are constant, the Gibbs–Duhem relation (Eq. 2.71) reduces to $Nd\mu = Vdp$, hence the expression¹:

$$N \left(\frac{\partial \mu}{\partial N} \right)_{T,V} = V \left(\frac{\partial p}{\partial N} \right)_{T,V} = V \left[- \left(\frac{\partial p}{\partial V} \right)_{T,N} \left(\frac{\partial V}{\partial N} \right)_{T,p} \right], \quad (5.79)$$

¹Simply use the relation:

$$\left(\frac{\partial p}{\partial V} \right)_N \left(\frac{\partial V}{\partial N} \right)_p \left(\frac{\partial N}{\partial p} \right)_V = -1.$$

and, with the definition of the isothermal compressibility χ_T and within the thermodynamic limit ($N \rightarrow \infty$ and $V \rightarrow \infty$, with $\rho = N/V$), it follows:

$$-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \chi_T \quad (5.80)$$

$$\text{and} \quad \left(\frac{\partial N}{\partial V} \right)_{T,p} = \rho, \quad (5.81)$$

that enables us to rewrite equation (5.79) as:

$$N \left(\frac{\partial \mu}{\partial N} \right)_{T,V} = \frac{1}{\chi_T} \frac{1}{\rho}. \quad (5.82)$$

Thus, in the grand canonical ensemble, the derivative of the mean number of particles $\langle N \rangle$ with respect to the chemical potential μ leads to more relevant relation:

$$\frac{\partial \langle N \rangle}{\beta \partial \mu} = \langle N \rangle \rho k_B T \chi_T. \quad (5.83)$$

Now, by identifying equations (5.78) and (5.83), we note that the fluctuations of the particle number depend explicitly on the isothermal compressibility through the relation:

$$\rho k_B T \chi_T = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \quad (5.84)$$

Finally, the comparison of equation (5.84) with equation (5.69) shows that the structure factor at $q = 0$ is also expressed in terms of the isothermal compressibility:

$$S(0) = 1 + 4\pi\rho \int_0^\infty [g(r) - 1] r^2 dr = \rho k_B T \chi_T. \quad (5.85)$$

Therefore, the value of the structure factor at $q=0$, while inaccessible by X-ray diffraction or neutron scattering, becomes a thermodynamic property directly related to the isothermal compressibility. In addition, the integration of the second equality of equation (5.85) provides a new equation of state for liquids named *compressibility equation of state*. Note that equation (5.85) is an exact relation and that the equation of state resulting from it does not contain the pair potential $u(r)$, unlike the pressure equation of state given by equation (5.27).

Thermodynamic consistency

It is clear that the pressure equation of state (Eq. 5.27) yields a method of determining an expression for the isothermal compressibility χ_T different from that of equation (5.85) which, moreover, depends on the pair potential. Indeed, if it is assumed that the pair correlation function depends on ρ and T , whereas the pair potential does not, one can calculate the isothermal compressibility with equation (5.27) as:

$$\begin{aligned}\chi_T^{-1} &= -V \left(\frac{\partial p}{\partial V} \right)_T = \rho \left(\frac{\partial p}{\partial \rho} \right)_T \\ &= k_B T \rho - \frac{2\pi\rho}{3} \left[2\rho \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} g(r, T, \rho) dr \right. \\ &\quad \left. + \rho^2 \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} \frac{\partial g(r, T, \rho)}{\partial \rho} dr \right], \quad (5.86)\end{aligned}$$

or equivalently:

$$\chi_T^{-1} = k_B T \rho - \frac{2\pi\rho^2}{3} \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} \left[2g(r, T, \rho) + \rho \frac{\partial g(r, T, \rho)}{\partial \rho} \right] dr. \quad (5.87)$$

When the pair potential $u(r)$ is properly chosen and the pair correlation function $g(r)$ accurately determined for a given liquid, equations (5.85) and (5.87) must provide the same value of the isothermal compressibility χ_T . As the pair correlation function is known as being approximate, the two isothermal compressibility values coincide seldom, if ever.

All the information collected from the comparison of the two results of the isothermal compressibility can be understood as a test of the microscopic theory of liquids. By forcing the equality between χ_T (pressure) (Eq. 5.87) and χ_T (compressibility) (Eq. 5.85), the *thermodynamic consistency* is imposed in the simplest possible way. Consequently, the equality between χ_T (pressure) and χ_T (compressibility) is a guarantee that the thermodynamic consistency is reached, thus making possible the determination of a most accurate pair correlation function $g(r)$.

It should be noticed that it is possible to impose the thermodynamic consistency with properties other than the isothermal compressibility. For example, with equation (5.83), a relation between the derivative of the chemical potential μ with respect to the density

ρ ($= N/V$) and the isothermal compressibility χ_T can be derived, and the relation will read:

$$\frac{\beta \partial \mu}{\partial \rho} = \frac{\beta}{\partial N} \frac{\partial \mu}{\partial \rho} = V \frac{\beta \partial \mu}{\partial N} = \frac{1}{\rho^2 k_B T \chi_T}. \quad (5.88)$$

The thermodynamic consistency may also be imposed by means of the expressions of internal energy (Eq. 5.14) and pressure (Eq. 5.27). For the purpose, we combine the fundamental law of thermodynamics $dE = TdS - pdV$ with the Maxwell relation $(\frac{\partial S}{\partial V})_T = (\frac{\partial p}{\partial T})_V$ as:

$$\begin{aligned} \left(\frac{\partial E}{\partial V} \right)_T &= T \left(\frac{\partial S}{\partial V} \right)_T - p \\ &= T \left(\frac{\partial p}{\partial T} \right)_V - p = T^2 \frac{\partial}{\partial T} \left(\frac{p}{T} \right)_V. \end{aligned} \quad (5.89)$$

If equation (5.89) is transformed as:

$$\left(\frac{\partial E}{\partial \rho} \right)_T \frac{\partial \rho}{\partial V} = T^2 \frac{\partial}{\partial \beta} \left(\frac{p}{T} \right)_V \frac{\partial \beta}{\partial T}, \quad (5.90)$$

it is possible to continue the mathematical processing by using the equations:

$$\frac{\partial \rho}{\partial V} = -\frac{\rho}{V} \quad \text{and} \quad \frac{\partial \beta}{\partial T} = -\frac{\beta}{T}. \quad (5.91)$$

Indeed, it follows:

$$-\frac{\rho}{V} \left(\frac{\partial E}{\partial \rho} \right)_T = -\frac{\beta}{T} T^2 \frac{\partial}{\partial \beta} \left(\frac{p}{T} \right)_V, \quad (5.92)$$

$$\frac{\rho^2}{N} \left(\frac{\partial E}{\partial \rho} \right)_T = \frac{1}{k_B} \frac{\partial}{\partial \beta} \left(\frac{p}{T} \right)_V, \quad (5.93)$$

$$\rho^2 \frac{\partial}{\partial \rho} \left(\frac{E}{N} \right)_T = \frac{\partial}{\partial \beta} \left(\frac{p}{k_B T} \right)_V, \quad (5.94)$$

or equivalently:

$$\rho \frac{\partial}{\partial \rho} \left(\frac{\beta E}{N} \right)_T = \beta \frac{\partial}{\partial \beta} \left(\frac{\beta p}{\rho} \right)_V. \quad (5.95)$$

Nevertheless, if the expressions for the internal energy (Eq. 5.14) and pressure (Eq. 5.27) are considered, namely:

$$\frac{\beta E}{N} = \frac{3}{2} + 2\pi\beta\rho \int_0^\infty u(r)g(r)r^2 dr \quad (5.96)$$

$$\text{and} \quad \frac{\beta p}{\rho} = 1 - \frac{2\pi}{3}\beta\rho \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} g(r) dr, \quad (5.97)$$

their derivatives with respect to ρ and β lead respectively to:

$$\begin{aligned} \rho \frac{\partial}{\partial \rho} \left(\frac{\beta E}{N} \right)_T &= \rho \left\{ 2\pi\beta \int_0^\infty u(r)g(r)r^2 dr \right. \\ &\quad \left. + 2\pi\beta\rho \int_0^\infty u(r) \frac{\partial g(r)}{\partial \rho} r^2 dr \right\}, \end{aligned} \quad (5.98)$$

$$\begin{aligned} \beta \frac{\partial}{\partial \beta} \left(\frac{\beta p}{\rho} \right)_V &= \beta \left\{ -\frac{2\pi}{3}\rho \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} g(r) dr \right. \\ &\quad \left. - \frac{2\pi}{3}\beta\rho \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} \left[-\frac{T}{\beta} \frac{\partial g(r)}{\partial T} \right] dr \right\}, \end{aligned} \quad (5.99)$$

so that the thermodynamic consistency (Eq. 5.95) is finally achieved with the following equation:

$$\int_0^\infty u(r) \left[g(r) + \rho \frac{\partial g(r)}{\partial \rho} \right] r^2 dr = -\frac{1}{3} \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} \left[g(r) - T \frac{\partial g(r)}{\partial T} \right] dr. \quad (5.100)$$

5.3 Treatment of three-body potentials

Determination of thermodynamic properties

It has been stated previously that the potential energy of a liquid is depicted as a sum of pair potentials. However, it turns out that for some systems, such as some rare gas liquids, the three-body potentials cannot be ignored [21]. If this happens, equations (5.14) for the internal energy, (5.27) for the pressure, (5.48) for the chemical potential and (5.53) for the entropy can no longer be used because they

only take account of the pair potentials. For a liquid with the total potential energy:

$$U(\mathbf{r}^N) = \sum_{i < j}^N u_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k), \quad (5.101)$$

the thermodynamic properties should be evaluated with relations that contain an additional contribution combining the three-body potential $u_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$ and the three-body correlation function $g^{(3)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$. As we do not want to slow down the study with mathematical developments based on those made for the pair potential, we will give only the general formulas for E , p , μ and S without comment (see [22]).

The considerations of section (5.1) can be used to generalize the expression for the internal energy E as:

$$\begin{aligned} E = & \frac{3}{2} N k_B T + \frac{\rho^2}{2!} \iint u_2(\mathbf{r}_1, \mathbf{r}_2) g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ & + \frac{\rho^3}{3!} \iiint u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \end{aligned} \quad (5.102)$$

This also applied to the pressure p and the chemical potential μ written respectively:

$$\begin{aligned} p = & k_B T \frac{N}{V} - \frac{1}{2!} \frac{\rho^2}{3V} \iint r_{12} \frac{\partial u_2(r_{12})}{\partial r_{12}} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ & - \frac{1}{3!} \frac{\rho^3}{3V} \iiint \left[r_{12} \frac{\partial}{\partial r_{12}} + r_{13} \frac{\partial}{\partial r_{13}} + r_{23} \frac{\partial}{\partial r_{23}} \right] \times \\ & \times u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \end{aligned} \quad (5.103)$$

and

$$\begin{aligned} \mu = & k_B T \ln \rho \Lambda^3 + \frac{\rho^2}{N} \int_0^1 d\lambda \iint u(\mathbf{r}_1, \mathbf{r}_2) g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \lambda) d\mathbf{r}_1 d\mathbf{r}_2 \\ & + \frac{1}{2!} \frac{\rho^3}{N} \int_0^1 d\lambda \iiint u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \lambda) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \end{aligned} \quad (5.104)$$

The general implementation is more complicated for the entropy S .

The appropriate expression is [20], [23]:

$$\begin{aligned}
 S = & S^{id} - \frac{1}{2}k_B\rho^2 \iint g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \ln g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
 & + \frac{1}{2}k_B\rho^2 \iint \left[g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 1 \right] d\mathbf{r}_1 d\mathbf{r}_2 \\
 & - \frac{1}{2}k_B\rho^3 \iiint g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \ln \left[\delta g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\
 & + \frac{1}{6}k_B\rho^3 \iiint \left[g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(2)}(\mathbf{r}_1, \mathbf{r}_3) \right. \\
 & \quad - g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\
 & \quad \left. + g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) + g^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - 1 \right] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (5.105)
 \end{aligned}$$

where $S^{id} = -k_B N (\ln \rho \Lambda^3 - \frac{5}{2})$ and the quantity $\delta g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is defined by the ratio:

$$\delta g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)g^{(2)}(\mathbf{r}_2, \mathbf{r}_3)}. \quad (5.106)$$

It should be mentioned that these expressions for the thermodynamic properties contain the three-body potential $u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ as well as the three-body correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ whose measurement by diffraction experiments is impossible and the theoretical determination extremely difficult. Performing calculations on them is one of the challenges of the liquid theory and conducting an estimate at present implies using the superposition approximation of Kirkwood [18], [24] whose easiest form is:

$$g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \simeq g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)g^{(2)}(\mathbf{r}_2, \mathbf{r}_3). \quad (5.107)$$

Calculation of two-centre integrals in thermodynamic properties

In practice, it is important to simplify the calculation of integrals of the type $\iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3$ in the expressions for the thermodynamic properties. If the fluid is homogeneous and isotropic, the integrals over $\mathbf{r}_1$ and $\mathbf{r}_2$ are usually calculated with the changes of variables $\mathbf{R} = \mathbf{r}_1$ and $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$, where $\mathbf{R}$ and $\mathbf{r}_{12}$ describe the volume of

the system. When such changes of variables have already been used, the differential element $d\mathbf{r}_1 d\mathbf{r}_2$ is:

$$d\mathbf{r}_1 d\mathbf{r}_2 = d\mathbf{R} 4\pi r_{12}^2 dr_{12}, \quad (5.108)$$

with $\int d\mathbf{R} = V$.

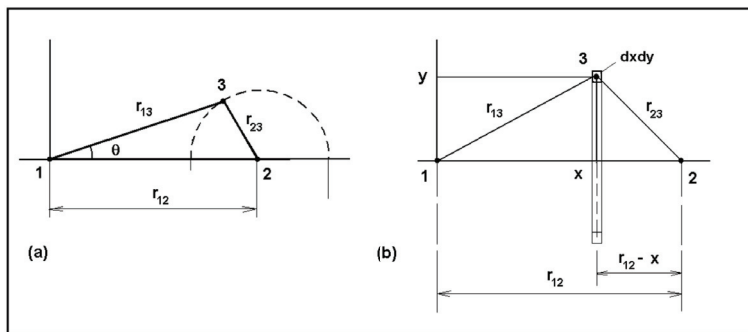


Figure 5.1: Use of bipolar coordinates to determine the volume element $d\mathbf{r}_3$.

For given values of $\mathbf{r}_1$ and $\mathbf{r}_2$, the integral over $\mathbf{r}_3$ should be examined more carefully because of the interdependence between the three variables $\mathbf{r}_1, \mathbf{r}_2$ and $\mathbf{r}_3$. To assess the volume element $d\mathbf{r}_3$, it is convenient [3] to use the bipolar coordinates r_{13} and r_{23} with r_{12} constant (Fig. 5.1a) which are linked by the relation:

$$r_{23}^2 = r_{12}^2 + r_{13}^2 - 2r_{12}r_{13} \cos \theta. \quad (5.109)$$

The volume element $d\mathbf{r}_3$ corresponds to the circular ring (Fig. 5.1b) of radius y and section $dx dy$ centered on the axis joining the atoms 1 and 2, namely:

$$d\mathbf{r}_3 = 2\pi y dx dy. \quad (5.110)$$

It is clear that the bipolar coordinates r_{13} and r_{23} can be expressed in terms of the auxiliary variables x and y by using the following equations:

$$r_{13}^2 = x^2 + y^2 \quad \text{and} \quad r_{23}^2 = (r_{12} - x)^2 + y^2, \quad (5.111)$$

where the Jacobian of the transformation is:

$$J = \begin{vmatrix} \frac{\partial r_{13}}{\partial x} & \frac{\partial r_{13}}{\partial y} \\ \frac{\partial r_{23}}{\partial x} & \frac{\partial r_{23}}{\partial y} \end{vmatrix} = \begin{vmatrix} \frac{x}{r_{13}} & \frac{y}{r_{13}} \\ -\frac{(r_{12}-x)}{r_{23}} & \frac{y}{r_{23}} \end{vmatrix} = \frac{y r_{12}}{r_{13} r_{23}}. \quad (5.112)$$

Then, the surface elements $dr_{13}dr_{23}$ and $dx dy$ are related by the formula:

$$dr_{13}dr_{23} = |J| dx dy = \frac{y r_{12}}{r_{13} r_{23}} dx dy, \quad (5.113)$$

and the volume element $d\mathbf{r}_3$ can be written in terms of the bipolar coordinates within the relation:

$$d\mathbf{r}_3 = 2\pi \frac{r_{13} r_{23}}{r_{12}} dr_{13} dr_{23}. \quad (5.114)$$

As seen in figure (5.1a), the integration limits of the variables r_{13} and r_{23} are respectively:

$$|r_{12} - r_{23}| \leq r_{13} \leq r_{12} + r_{23} \quad \text{and} \quad 0 \leq r_{23} \leq \infty. \quad (5.115)$$

With these changes of variables, and considering the superposition approximation of Kirkwood, the contribution E_3 to the internal energy stemming from the three-body potential transforms as follows:

$$\begin{aligned} E_3 &= \frac{\rho^3}{3!} \iiint u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ &= \frac{\rho^3}{3!} \iiint u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \times \\ &\quad \times (d\mathbf{R} 4\pi r_{12}^2 dr_{12}) \left(2\pi \frac{r_{13} r_{23}}{r_{12}} dr_{13} dr_{23} \right), \quad (5.116) \end{aligned}$$

or:

$$\begin{aligned} E_3 &= \frac{4\pi^2}{3} \rho^2 N \int_0^\infty g^{(2)}(r_{12}) r_{12} dr_{12} \int_0^\infty g^{(2)}(r_{23}) r_{23} dr_{23} \times \\ &\quad \times \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} u_3(r_{12}, r_{13}, r_{23}) g^{(2)}(r_{13}) r_{13} dr_{13}. \quad (5.117) \end{aligned}$$

The contributions of the three-body potential to the chemical potential μ and entropy S are similarly obtained. By contrast, the contribution p_3 to the pressure is significantly more complicated, except in the case where the three-body potential is that of Axilrod–Teller

[21] because p_3 is directly proportional to E_3 . Indeed, the Axilrod–Teller potential is an homogeneous function of variables r_{12} , r_{13} and r_{23} of degree (-9) . Thus, in virtue of Euler’s theorem (Eq. 1.28), we can write:

$$\left[r_{12} \frac{\partial}{\partial r_{12}} + r_{13} \frac{\partial}{\partial r_{13}} + r_{23} \frac{\partial}{\partial r_{23}} \right] u_3(r_{12}, r_{13}, r_{23}) = -9u_3(r_{12}, r_{13}, r_{23}), \quad (5.118)$$

so that the contribution p_3 reads:

$$p_3 = -\frac{1}{3!} \frac{\rho^3}{3V} \iiint \left[-9u_3(r_{12}, r_{13}, r_{23}) \right] g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3, \quad (5.119)$$

or:

$$p_3 = \frac{3}{3!} \frac{\rho^3}{V} \iiint u_3(r_{12}, r_{13}, r_{23}) g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (5.120)$$

As a consequence, comparing equations (5.120) and (5.116) reveals that

$$p_3 = \frac{3}{V} E_3. \quad (5.121)$$

These expressions for the thermodynamic properties are formally correct. They contain explicitly the binary and ternary potentials of the liquid under study as well as the pair and triplet correlation functions. The triplet correlation function is written via the Kirkwood superposition approximation in terms of the pair correlation function, which is the only function to be calculated in advance by the liquid theory.

5.4 Effective pair potential

From the 1960s, good quality measurements of the structure factor $S(q)$, by X-ray diffraction or neutron scattering gave the opportunity to extract an *effective pair potential* composed of the pair potential and N -body interactions. Simultaneously, the liquid theory has been extensively developed to determine the effective pair potential $u_{eff}(r)$ by using the pair potential $u_2(r)$ and three-body potential [25, 26]. It turns out that the evaluation of $u_{eff}(r)$ is possible with equation (5.102) or equation (5.103).

a) If the internal energy is chosen, equation (5.102) is written as:

$$E = \frac{3}{2}Nk_B T + \frac{\rho^2}{2!} \iint g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \left[u_2(\mathbf{r}_1, \mathbf{r}_2) + \frac{\rho}{3} \int_V u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r}_3 \right] d\mathbf{r}_1 d\mathbf{r}_2, \quad (5.122)$$

where the effective potential is defined by the expression in brackets:

$$u_{\text{eff}}^{(E)}(r_{12}) = u_2(\mathbf{r}_1, \mathbf{r}_2) + \frac{\rho}{3} \int_V u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r}_3. \quad (5.123)$$

By using equation (5.114) to express the volume element $d\mathbf{r}_3$ and equation (5.107) for the triplet correlation function, the integrand of the above equation simplifies and the effective pair potential results in:

$$u_{\text{eff}}^{(E)}(r_{12}) = u_2(r_{12}) + \frac{\rho}{3} \int_0^\infty \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} u_3(r_{12}, r_{23}, r_{13}) \times \\ \times g^{(2)}(r_{13}) g^{(2)}(r_{23}) \left(2\pi \frac{r_{13} r_{23}}{r_{12}} dr_{13} dr_{23} \right). \quad (5.124)$$

b) If the pressure is chosen to determine the effective pair potential, equation (5.103) is transformed into:

$$p = k_B T \frac{N}{V} - \frac{1}{2!} \frac{\rho^2}{3V} \iint g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \left\{ r_{12} \frac{\partial u_2(r_{12})}{\partial r_{12}} + \right. \\ \left. + \frac{\rho}{3} \int \left[r_{12} \frac{\partial}{\partial r_{12}} + r_{13} \frac{\partial}{\partial r_{13}} + r_{23} \frac{\partial}{\partial r_{23}} \right] u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \times \right. \\ \left. \times \frac{g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r}_3 \right\} d\mathbf{r}_1 d\mathbf{r}_2. \quad (5.125)$$

Assuming that the liquid is homogeneous and isotropic, the virial operator can be simplified owing to the formula:

$$r_{12} \frac{\partial}{\partial r_{12}} + r_{13} \frac{\partial}{\partial r_{13}} + r_{23} \frac{\partial}{\partial r_{23}} = 3r_{12} \frac{\partial}{\partial r_{12}}, \quad (5.126)$$

to provide the following expression for the pressure:

$$p = k_B T \frac{N}{V} - \frac{1}{2!} \frac{\rho^2}{3V} \iint g^{(2)}(r_{12}) \left[r_{12} \frac{\partial u_2(r_{12})}{\partial r_{12}} + \right. \\ \left. + \frac{\rho}{3} \int 3r_{12} \frac{\partial u_3(r_{12}, r_{23}, r_{13})}{\partial r_{12}} \frac{g^{(3)}(r_{12}, r_{23}, r_{13})}{g^{(2)}(r_{12})} d\mathbf{r}_3 \right] d\mathbf{r}_1 d\mathbf{r}_2, \quad (5.127)$$

or equivalently:

$$\begin{aligned}
 p = & k_B T \frac{N}{V} - \frac{1}{2!} \frac{\rho^2}{3V} \iint g^{(2)}(r_{12}) r_{12} \frac{\partial}{\partial r_{12}} \left[u_2(r_{12}) \right. \\
 & + \frac{\rho}{3} \int_0^\infty \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} 3u_3(r_{12}, r_{23}, r_{13}) \times \\
 & \left. \times \frac{g^{(3)}(r_{12}, r_{23}, r_{13})}{g^{(2)}(r_{12})} \left(2\pi \frac{r_{13} r_{23}}{r_{12}} dr_{13} dr_{23} \right) \right] d\mathbf{r}_1 d\mathbf{r}_2. \quad (5.128)
 \end{aligned}$$

Within the Kirkwood approximation, it therefore seems possible to define an effective pair potential with the expression in square brackets that reads:

$$\begin{aligned}
 u_{\text{eff}}^{(p)}(r_{12}) = & u_2(r_{12}) + \rho \int_0^\infty \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} u_3(r_{12}, r_{23}, r_{13}) \times \\
 & \times g^{(2)}(r_{13}) g^{(2)}(r_{23}) \left(2\pi \frac{r_{13} r_{23}}{r_{12}} dr_{13} dr_{23} \right). \quad (5.129)
 \end{aligned}$$

It should be mentioned that the expressions $u_{\text{eff}}^{(p)}(r)$ and $u_{\text{eff}}^{(E)}(r)$ are not equivalent as equations (5.124) and (5.129) differ by the factor 1/3 outside the integral. This is not surprising because equation (5.129) requires the derivation of the pair and three-body potentials with respect to r_{12} , and omits the derivation of the correlation functions in obtaining the pressure. It is worth noting that some authors [27, 28] have advocated the use of the factor 2/3 ahead the integral of equation (5.124) as a compromise.

That the expressions for the effective potential differ according to the choice of the energy and the pressure raises a commentary on the nature of the interaction potentials in liquids in terms of *uniqueness*, *representatively* and *transferability* [29]. It is quite unusual that a system is investigated by using a unique potential; most of time the same liquid can be studied by different potentials. As regards the representatively, which is the ability of a potential to describe, at best, a large number of physical properties of the system, it is quite unlikely that the same potential predicts correctly all properties. As for the transferability, which reflects the ability to use the same potential in different environments, i.e. for different thermodynamic states, it occurs quite infrequently. As an exception, the Lennard–Jones potential is transferable for rare gases as the same parameters (ε and σ) are usually used at all temperatures and densities.

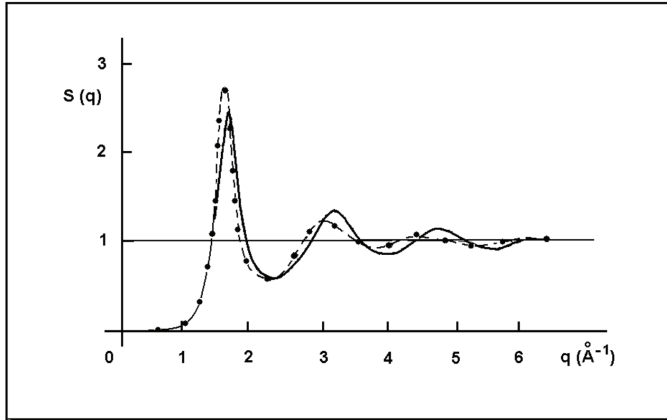


Figure 5.2: Experimental structure factor of liquid sodium at 373 K (points) and structure factor of the hard-sphere model (solid line) with $\eta = 0.45$.

5.5 Expansion of the free energy

Formulation of the problem

All theoretical and experimental studies have shown that the structure factor $S(q)$ of liquids closely resembles that of the fluid of hard spheres (HS). To be convinced, it suffices to look at figure (5.2) depicting the experimental structure factor [30] of liquid sodium at 373 K, as compared with the structure factor of the HS model [31] for a packing fraction η of 0.45. The agreement is not too bad, even though the peak amplitudes differ perceptibly and the oscillations are slightly shifted. Beside the experimental results, numerical calculations [32] showed that the structure factor, being obtained with the Lennard-Jones potential and capable of describing the structure of simple fluids to high densities, strongly resembles the structure factor of the HS fluid whose diameter is correctly chosen.

Such a qualitative agreement emphasizes the important role played by the repulsive part of the potential to describe the structure factor of liquids, while the long-range attractive part has a lesser effect. It can be said for the sake of simplicity that the repulsive part of the

potential determines the structure of liquids (atomic stacking or steric effect) and the attractive part insures the cohesion of liquids.

It is important to recall that the thermodynamic properties of the HS fluid (Eqs. 5.176 to 5.192) and the HS structure factor $S_{HS}(q)$ can be calculated with a high degree of accuracy (see Eq. 6.181). This suggests to replace the repulsive part of potentials of liquids by the HS potential – which becomes the *reference system* – and then compare the structural and thermodynamic properties of liquids with those of the HS fluid by making necessary corrections. Thus, to perform these corrections, the long-range attractive part of potential must be considered as a perturbation to the reference system.

The rest of the section is devoted to a succinct presentation of the thermodynamic perturbation theory [33]. It should be stressed that the calculation of the thermodynamic properties by means of the thermodynamic perturbation theory requires the knowledge of the pair correlation function $g_{HS}(r)$ of the HS fluid, and not that of the actual liquid.

The Zwanzig method

In the perturbation theory developed by Zwanzig [17] it is assumed that the total potential energy $U(\mathbf{r}^N)$ of the system can be decomposed into two parts. The first part, $U_0(\mathbf{r}^N)$, is the energy of the unperturbed system considered as the reference system and the second part, $U_1(\mathbf{r}^N)$, is the small energy perturbation. Historically, Zwanzig made the potential energy dependent on the coupling parameter λ by the relation:

$$U(\mathbf{r}^N) = U_0(\mathbf{r}^N) + \lambda U_1(\mathbf{r}^N), \quad (5.130)$$

in order to vary continuously the potential energy from $U_0(\mathbf{r}^N)$ to $U(\mathbf{r}^N)$, by changing λ from 0 to 1, and expand the free energy F of the real system in Taylor series as:

$$F = F_0 + \lambda \left(\frac{\partial F}{\partial \lambda} \right) + \frac{\lambda^2}{2} \left(\frac{\partial^2 F}{\partial \lambda^2} \right) + \dots \quad (5.131)$$

By replacing the potential energy $U(\mathbf{r}^N)$ in the expression of the configuration integral (Eq. 3.4), we obtain:

$$\begin{aligned} Z_N(V, T) &= \int \int_{3N} \exp \{ -\beta [U_0(\mathbf{r}^N) + \lambda U_1(\mathbf{r}^N)] \} d\mathbf{r}^N \\ &= \int \int_{3N} \exp [-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N \times \\ &\quad \times \frac{\int \int_{3N} \{ \exp [-\beta \lambda U_1(\mathbf{r}^N)] \} \exp [-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N}{\int \int_{3N} \exp [-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N}. \end{aligned} \quad (5.132)$$

The first integral represents the configuration integral $Z_N^{(0)}(V, T)$ of the reference system, and the remaining expression can be regarded as the average value of the quantity $\exp [-\beta \lambda U_1(\mathbf{r}^N)]$, so that the above relation can be put in the form:

$$Z_N(V, T) = Z_N^{(0)}(V, T) \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0, \quad (5.133)$$

where $\langle \dots \rangle_0$ stands for the ensemble average calculated in the canonical ensemble of the reference system.

To calculate the thermodynamic properties, we determine first the free energy F of the real system with equations (2.102) and (3.80):

$$F = -k_B T \ln Q_N(V, T) = -k_B T \ln \frac{Z_N(V, T)}{N! \Lambda^{3N}}. \quad (5.134)$$

After replacing the configuration integral (Eq. 5.133) in the expression of free energy, it follows:

$$-\beta F = \ln \frac{Z_N^{(0)}(V, T)}{N! \Lambda^{3N}} + \ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0. \quad (5.135)$$

The first term on the right hand side of this relation corresponds to the free energy of the reference system, which will be denoted $(-\beta F_0)$, and the second term represents the free energy of the perturbation:

$$-\beta F_1 = \ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0. \quad (5.136)$$

Since the perturbation $U_1(\mathbf{r}^N)$ is small, $\exp (-\beta \lambda U_1)$ can be expanded in a series as:

$$\exp (-\beta \lambda U_1) = 1 - \beta \lambda U_1 + \frac{1}{2!} \beta^2 \lambda^2 U_1^2 - \frac{1}{3!} \beta^3 \lambda^3 U_1^3 + \dots, \quad (5.137)$$

so that the ensemble average $\langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0$, calculated by the definition:

$$\langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 = \frac{\int \int_{3N} \{ \exp [-\beta \lambda U_1(\mathbf{r}^N)] \} \exp [-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N}{\int \int_{3N} \exp [-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N}, \quad (5.138)$$

is expressed as:

$$\langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 = 1 - \beta \lambda \langle U_1 \rangle_0 + \frac{1}{2!} \beta^2 \lambda^2 \langle U_1^2 \rangle_0 - \frac{1}{3!} \beta^3 \lambda^3 \langle U_1^3 \rangle_0 + \dots \quad (5.139)$$

In passing, we can note that the coefficients β in this expansion are the moments within the meaning of equation (2.129). Given the form of equation (5.139), it is still possible to write equation (5.136) by using the Taylor series of the logarithm of $\langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0$, namely² :

$$\begin{aligned} \ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 &= \\ &= -\beta \lambda \langle U_1 \rangle_0 + \frac{1}{2!} \beta^2 \lambda^2 \langle U_1^2 \rangle_0 - \frac{1}{3!} \beta^3 \lambda^3 \langle U_1^3 \rangle_0 + \dots \\ &\quad - \frac{1}{2} \left\{ \beta^2 \lambda^2 \langle U_1 \rangle_0^2 - \beta^3 \lambda^3 \langle U_1 \rangle_0 \langle U_1^2 \rangle_0 + \beta^4 \lambda^4 [\dots] + \dots \right\} \\ &\quad + \frac{1}{3} \left\{ -\beta^3 \lambda^3 \langle U_1 \rangle_0^3 + \frac{3}{2} \beta^4 \lambda^4 \langle U_1 \rangle_0^2 \langle U_1^2 \rangle_0 \right. \\ &\quad \left. - \frac{1}{2} \beta^5 \lambda^5 [\dots] + \dots \right\} - \dots \quad (5.140) \end{aligned}$$

²The calculation is carried out by writing equation (5.139) as follows:

$$\langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 = 1 + x,$$

$$\text{with} \quad x = -\beta \lambda \langle U_1 \rangle_0 + \frac{1}{2!} \beta^2 \lambda^2 \langle U_1^2 \rangle_0 - \frac{1}{3!} \beta^3 \lambda^3 \langle U_1^3 \rangle_0 + \dots$$

and using the Taylor series of $\ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0$:

$$\ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 = \ln(1 + x) = x - \frac{1}{2} x^2 + \frac{1}{3} x^3 - \dots \quad \text{if } |x| < 1,$$

where

$$\begin{aligned} x &= -\beta \lambda \langle U_1 \rangle_0 + \frac{1}{2!} \beta^2 \lambda^2 \langle U_1^2 \rangle_0 - \frac{1}{3!} \beta^3 \lambda^3 \langle U_1^3 \rangle_0 + \dots \\ x^2 &= \beta^2 \lambda^2 \langle U_1 \rangle_0^2 - \beta^3 \lambda^3 \langle U_1 \rangle_0 \langle U_1^2 \rangle_0 + \beta^4 \lambda^4 \left[\frac{1}{4} \langle U_1^2 \rangle_0^2 + \frac{1}{3} \langle U_1 \rangle_0 \langle U_1^3 \rangle_0 \right] + \dots \\ x^3 &= -\beta^3 \lambda^3 \langle U_1 \rangle_0^3 + \frac{3}{2} \beta^4 \lambda^4 \langle U_1 \rangle_0^2 \langle U_1^2 \rangle_0 - \frac{1}{2} \beta^5 \lambda^5 \left[\langle U_1 \rangle_0^2 \langle U_1^3 \rangle_0 \right. \\ &\quad \left. + \frac{3}{2} \langle U_1 \rangle_0 \langle U_1^2 \rangle_0^2 \right] + \dots \end{aligned}$$

After simplifications, the series expansion in power of β is reduced to:

$$\begin{aligned} \ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 &= -\beta \lambda \langle U_1 \rangle_0 + \frac{1}{2!} \beta^2 \lambda^2 \left[\langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2 \right] \\ &\quad - \beta^3 \lambda^3 \left[\frac{1}{3!} \langle U_1^3 \rangle_0 - \frac{1}{2} \langle U_1 \rangle_0 \langle U_1^2 \rangle_0 + \frac{1}{3} \langle U_1 \rangle_0^3 \right] \\ &\quad + \beta^4 \lambda^4 [\dots] - \dots \end{aligned} \quad (5.141)$$

Now, denoting:

$$c_1 = \langle U_1 \rangle_0, \quad (5.142)$$

$$c_2 = \frac{1}{2!} \left[\langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2 \right], \quad (5.143)$$

$$c_3 = \frac{1}{3!} \left[\langle U_1^3 \rangle_0 - 3 \langle U_1 \rangle_0 \langle U_1^2 \rangle_0 + 2 \langle U_1 \rangle_0^3 \right], \quad \text{etc.} \quad (5.144)$$

we find that:

$$\ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 = -\lambda \beta c_1 + \lambda^2 \beta^2 c_2 - \lambda^3 \beta^3 c_3 + \dots \quad (5.145)$$

The contribution of the perturbation (Eq. 5.136) to the free energy is then written in compact form as:

$$-\beta F_1 = \ln \langle \exp [-\beta \lambda U_1(\mathbf{r}^N)] \rangle_0 = -\lambda \beta \sum_{n=1}^{\infty} c_n (-\lambda \beta)^{n-1}, \quad (5.146)$$

and the expression for the free energy F of the real system is obtainable by substituting equation (5.146) into equation (5.135):

$$-\beta F = -\beta F_0 - \beta F_1 = -\beta F_0 - \lambda \beta c_1 + \lambda^2 \beta^2 c_2 - \lambda^3 \beta^3 c_3 + \dots,$$

or:

$$F = F_0 + \lambda c_1 - \lambda^2 \beta c_2 + \lambda^3 \beta^2 c_3 - \dots, \quad (5.147)$$

in which the free energy of the real system is deduced by putting $\lambda = 1$. This development of the free energy in powers of β constitutes the *high temperature approximation*. Note that the technique used to obtain the coefficients c_n is the *cumulant expansion method* [34].

The van der Waals equation

As a first application of the thermodynamic perturbation theory, we search the phenomenological equation of state of van der Waals. For

that purpose, consider equation (5.147) at zero order in β . The simplest assumption to be made to calculate the coefficient c_1 is to decompose the total potential energy into a sum of pair potentials split as :

$$U(\mathbf{r}^N) = U_0(\mathbf{r}^N) + U_1(\mathbf{r}^N) = \sum_i \sum_{j>i} u_0(r_{ij}) + \sum_i \sum_{j>i} u_1(r_{ij}). \quad (5.148)$$

Therefore, the free energy of the perturbation to the zero order in β is given by equation (5.142), i.e.:

$$c_1 = \langle U_1 \rangle_0 = \frac{\int \int_{3N} \left[\sum_i \sum_{j>i} u_1(r_{ij}) \right] \exp[-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N}{\int \int_{3N} \exp[-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N}. \quad (5.149)$$

To simplify the above relation, we proceed as for the calculation of the internal energy of liquids (Eq. 5.8) by making appear the pair correlation function of the reference system in the integral of the numerator. If the sum of pair potentials is assumed to be made of terms equal to $\sum_i \sum_{j>i} u_1(r_{ij}) = \frac{N(N-1)}{2} u_1(r_{12})$, the coefficient c_1 reduces to:

$$c_1 = \frac{1}{Z_0(V, T)} \iint \frac{N(N-1)}{2} u_1(r_{12}) \times \\ \times \left\{ \iint_{3(N-2)} \exp[-\beta U_0(\mathbf{r}^N)] d\mathbf{r}_3 \dots d\mathbf{r}_N \right\} d\mathbf{r}_1 d\mathbf{r}_2. \quad (5.150)$$

The integral between the brackets is expressed in terms of the pair correlation function (Eq. 3.89), and the coefficient c_1 is put in the alternative form:

$$c_1 = \frac{N(N-1)}{2Z_0(V, T)} \frac{(N-2)! \rho^2 Z_0(V, T)}{N!} \iint u_1(r_{12}) g_0(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \\ = \frac{\rho^2}{2} \int d\mathbf{R} \int u_1(r) g_0(r) d\mathbf{r}. \quad (5.151)$$

Yet, to find the van der Waals equation, we choose the HS potential of diameter σ as reference system and suppose that the perturbation is a weakly attractive potential whose form need not be specified (Fig. 5.3a). At the time when the model was developed by van der Waals, we were unaware of the existence of the pair correlation function; accordingly it was reasonable to estimate $g_0(r)$ by a function

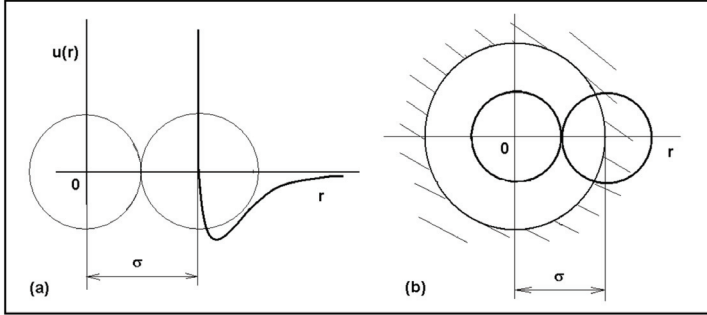


Figure 5.3: (a) Schematic representation of the interparticle potential by a hard-sphere potential plus a perturbation . (b) Definition of the covolume by the quantity $b = \frac{1}{2} \left(\frac{4}{3} \pi \sigma^3 \right)$.

equal to zero inside the particle and equal to one outside. Following van der Waals, suppose further that the available volume per particle³ is $b = \frac{2}{3} \pi \sigma^3$ and the unoccupied volume is $(V - Nb)$.

With these simplifications in mind, the configuration integral (Eq. 4.1) and the free energy of the reference system (Eq. 4.3) are written respectively:

$$Z_0(V, T) = \int \int_{3N} \exp [-\beta U_0(\mathbf{r}^N)] d\mathbf{r}^N = (V - Nb)^N \quad (5.152)$$

and:

$$\begin{aligned} F_0 &= -k_B T \ln \left[\frac{(V - Nb)^N}{N! \Lambda^{3N}} \right] \\ &= -N k_B T \left[\ln \frac{(V - Nb)}{N} - 3 \ln \Lambda + 1 \right]. \end{aligned} \quad (5.153)$$

As far as the coefficient c_1 (Eq. 5.151) is concerned, it simplifies to:

$$c_1 = 2\pi \rho^2 V \int_{\sigma}^{\infty} u_1(r) r^2 dr = -a \rho N, \quad (5.154)$$

$$\text{with} \quad a = -2\pi \int_{\sigma}^{\infty} u_1(r) r^2 dr. \quad (5.155)$$

³The parameter b introduced by van der Waals is the covolume. Its expression results from the fact that, if two particles are in contact, half of the excluded volume $\frac{4}{3} \pi \sigma^3$ must be assigned to each particle.

Therefore, the expression for the free energy (Eq. 5.147) of the van der Waals model is:

$$F = F_0 + c_1 = -Nk_{\text{B}}T \left[\ln \frac{(V-Nb)}{N} - 3 \ln \Lambda + 1 \right] - a\rho N, \quad (5.156)$$

and the van der Waals equation of state reduces to:

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{Nk_{\text{B}}T}{V-Nb} - a \frac{N^2}{V^2}, \quad (5.157)$$

or equivalently:

$$\left(p + a \frac{N^2}{V^2} \right) (V-Nb) = Nk_{\text{B}}T. \quad (5.158)$$

It is obvious that the equation of state of the ideal gas is recovered by putting $b = a = 0$ in the above relation. In order to improve the quality of the van der Waals equation of state, the expression for the HS free energy (see Eq. 5.186) can be used as reference system to calculate F_0 in equation (5.156), and the HS pair correlation function $g_{\text{HS}}(r)$ can be employed to calculate c_1 in equation (5.151). Another way to improve the results is yet to calculate the term c_2 to be put in equation (5.147).

To evaluate the mean values of the perturbation $U_1(\mathbf{r}^N)$ in equations (5.143) and (5.144), Barker and Henderson [35] have suggested to divide the domain of interatomic distances within sufficiently small intervals (r_1, r_2) , (r_2, r_3) , $\dots$, (r_i, r_{i+1}) , $\dots$, and to consider the perturbation as a constant value in each interval. Assuming that the perturbation in the interval (r_i, r_{i+1}) is $u_1(r_i)$, and the number of atoms subjected to this potential is N_i , the total perturbation can be written as a sum of disturbing potentials as:

$$U_1(\mathbf{r}^N) = \sum_i N_i u_1(r_i), \quad (5.159)$$

before inserting into the configuration integral. The advantage of this assumption is to calculate the coefficients c_n and the free energy (Eq. 5.147), not with the mean values of the perturbation but rather with the fluctuations of the particle number. In fact, each disturbing potential $u_1(r_i)$ being constant in the interval to which it belongs, it

can be written $\langle U_1 \rangle_0^2 = \sum_i \sum_j \langle N_i \rangle_0 \langle N_j \rangle_0 u_1(r_i) u_1(r_j)$. For instance, the coefficient c_2 defined by equation (5.143) becomes:

$$c_2 = \frac{1}{2!} \sum_i \sum_j [\langle N_i N_j \rangle_0 - \langle N_i \rangle_0 \langle N_j \rangle_0] u_1(r_i) u_1(r_j). \quad (5.160)$$

In the following, we present two expressions of c_2 obtained by Barker and Henderson according to the method described above without giving the intermediate mathematical developments. The first expression uses the *macroscopic approximation* of the compressibility (MC), where ρ is assumed to be dependent on p , and the second expression uses the *local approximation* of the compressibility (LC), where ρ and g_0 depend on p . They are written respectively:

$$c_2(MC) = \frac{\pi N \rho}{\beta} \left(\frac{\partial \rho}{\partial p} \right)_0 \int u_1^2(r) g_0(r) r^2 dr \quad (5.161)$$

and

$$\begin{aligned} c_2(LC) &= \frac{\pi N \rho}{\beta} \int u_1^2(r) \frac{\partial [\rho g_0(r)]}{\partial p} r^2 dr \\ &= \frac{\pi N \rho}{\beta} \left(\frac{\partial \rho}{\partial p} \right)_0 \frac{\partial}{\partial \rho} \left[\int \rho u_1^2(r) g_0(\rho; r) r^2 dr \right]. \end{aligned} \quad (5.162)$$

These authors tested these two approximations of c_2 for the HS reference system with the square-well potential as perturbation. At low and high densities, the results of both approximations are comparable, whereas, at intermediate densities, the results obtained with the LC approximation are in better agreement with the simulation results than that of the MC approximation. Note also that the coefficient c_3 has been calculated by Mansoori and Canfield [36] with the MC approximation. Its expression is:

$$c_3(MC) = \frac{\pi N \rho}{6 \beta^2} \left(\frac{\partial^2 \rho^2}{\partial p^2} \right)_0 \int u_1^3(r) g_0(r) r^2 dr. \quad (5.163)$$

It is then possible to calculate the first few terms of the expansion of the free energy F (Eq. 5.147) by using the HS system as reference system. But there is no criterion yet for choosing the diameter of hard spheres. This is an important issue because the repulsive part of all the potentials has to be replaced by a HS potential of diameter

properly chosen. Decisive progress has been made to solve this problem according to three separate approaches: the variational method [37], the Barker–Henderson method [38] and the Weeks–Chandler–Andersen method [39].

5.6 The hard-sphere reference potential

By way of illustration, we calculate the equation of state of the HS fluid for which the pair potential is:

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma; \\ 0 & \text{if } r > \sigma, \end{cases} \quad (5.164)$$

where σ is the HS diameter. The Boltzmann factor associated with this potential has a significant property that allows deducing the thermodynamic properties under particularly simple forms. Indeed, the representation of the Boltzmann factor:

$$\exp[-\beta u(r)] = \begin{cases} 0 & \text{if } r \leq \sigma; \\ 1 & \text{if } r > \sigma, \end{cases} \quad (5.165)$$

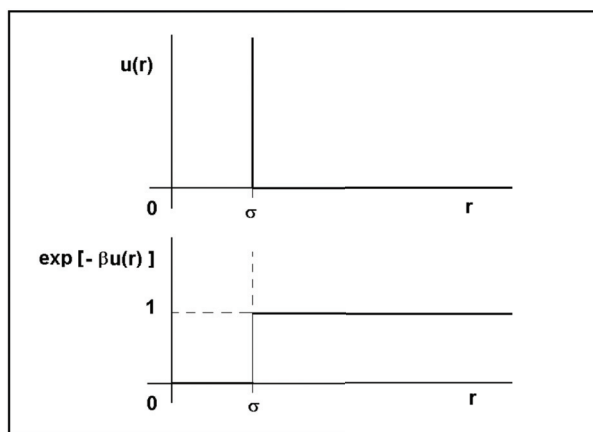


Figure 5.4: Representation of the HS potential and its Boltzmann factor.

corresponds to a step function (Fig. 5.4) whose derivative with respect to r is the Dirac function:

$$\frac{\partial}{\partial r} \exp[-\beta u(r)] = -\beta \frac{\partial u}{\partial r} \exp[-\beta u(r)] = \delta(r - \sigma). \quad (5.166)$$

Substituting $\frac{\partial u}{\partial r}$ from the previous relation into equation (5.27) yields the pressure:

$$\begin{aligned} p &= k_B T \frac{N}{V} - \frac{2\pi}{3} \rho^2 \int_0^\infty r^3 \left\{ -\frac{1}{\beta} \frac{\delta(r - \sigma)}{\exp[-\beta u(r)]} \right\} g(r) dr, \\ &= k_B T \frac{N}{V} + \frac{2\pi}{3} k_B T \rho^2 \sigma^3 g(\sigma) \exp[\beta u(\sigma)]. \end{aligned} \quad (5.167)$$

However, $\frac{\partial u}{\partial r}$ can also be carried forward into equation (5.59), thus leading to the virial equation:

$$\frac{p}{\rho k_B T} = 1 + \frac{2\pi}{3} \rho \sigma^3 + \rho^2 B_3(T) + \rho^3 B_4(T) + \dots \quad (5.168)$$

For the HS fluid, the dimensionless parameter η , called the *packing fraction*, is extensively used. It is defined by the ratio of the volume occupied by the N spheres to the total volume V of the system, that is to say:

$$\eta = \frac{1}{V} \frac{4\pi}{3} \left(\frac{\sigma}{2} \right)^3 N = \frac{\pi}{6} \rho \sigma^3. \quad (5.169)$$

The virial equation is then expressed in terms of the packing fraction as:

$$\frac{p}{\rho k_B T} = \frac{p^{\text{id}}}{\rho k_B T} + \frac{p^{\text{ex}}}{\rho k_B T}, \quad (5.170)$$

where p^{id} represents the contribution of the ideal gas (Eq. 4.6) and p^{ex} the excess pressure coming from the interactions between the particles:

$$\frac{p^{\text{id}}}{\rho k_B T} = 1 \quad \text{and} \quad \frac{p^{\text{ex}}}{\rho k_B T} = 4\eta + \eta^2 B'_3(T) + \eta^3 B'_4(T) + \dots \quad (5.171)$$

Note that the first 6 coefficients $B'_3(T)$, $B'_4(T)$, ... have been calculated analytically [40] and by molecular dynamics [41] with great precision. In addition, by rounding off the numerical values of coefficients $B'_3(T)$, $B'_4(T)$, ... to the nearest integer values, Carnahan

and Starling [42] have shown that the excess pressure can be approximately written as:

$$\frac{p^{\text{ex}}}{\rho k_B T} \simeq 4\eta + 10\eta^2 + 18\eta^3 + 28\eta^4 + 40\eta^5 + 54\eta^6 \dots = \sum_{k=1}^{\infty} (k^2 + 3k)\eta^k. \quad (5.172)$$

It is only by combining judiciously the first derivative and second derivative of the geometric series $\sum_{k=1}^{\infty} \eta^k$ that equation (5.172) transforms as rational fraction. Indeed, the sum:

$$\sum_{k=1}^{\infty} (k^2 + 3k)\eta^k = \sum_{k=1}^{\infty} (k^2 - k)\eta^k + \sum_{k=1}^{\infty} 4k\eta^k \quad (5.173)$$

is written as⁴:

$$\sum_{k=1}^{\infty} (k^2 + 3k)\eta^k = \frac{2\eta^2}{(1-\eta)^3} + \frac{4\eta}{(1-\eta)^2}, \quad (5.174)$$

so that the excess pressure is reduced to:

$$\frac{p^{\text{ex}}}{\rho k_B T} \simeq \sum_{k=1}^{\infty} (k^2 + 3k)\eta^k = \frac{4\eta - 2\eta^2}{(1-\eta)^3}. \quad (5.175)$$

Therefore, the equation of state of the HS fluid is given with a high degree of accuracy by:

$$\frac{p}{\rho k_B T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}. \quad (5.176)$$

It is also possible to calculate the internal energy of the HS fluid by substituting $u(r)$ into equation (5.14). Since $u(r)$ is zero when $r > \sigma$

⁴For obtaining the rational fraction, consider the geometric series:

$$\sum_{k=1}^{\infty} \eta^k = \eta + \eta^2 + \eta^3 + \dots = \frac{\eta}{1-\eta}$$

and its first and second derivatives:

$$\sum_{k=1}^{\infty} k\eta^{k-1} = \frac{1}{(1-\eta)^2} \quad \text{and} \quad \sum_{k=1}^{\infty} k(k-1)\eta^{k-2} = \frac{2}{(1-\eta)^3}.$$

and $g(r)$ is zero when $r < \sigma$, it follows that the integral is always zero and the internal energy is equal to that of the ideal gas (Eq. 4.5):

$$E = \frac{3}{2} N k_B T. \quad (5.177)$$

As far as the free energy F is concerned, it is determined by integrating the pressure over the volume with the relation:

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = - \left(\frac{\partial F^{\text{id}}}{\partial V} \right)_T - \left(\frac{\partial F^{\text{ex}}}{\partial V} \right)_T, \quad (5.178)$$

where F^{id} is the free energy of the ideal gas (Eq. 4.3) :

$$F^{\text{id}} = N k_B T (\ln \rho \Lambda^3 - 1), \quad (5.179)$$

and F^{ex} the excess free energy calculated by integrating equation (5.172):

$$\begin{aligned} F^{\text{ex}} &= - \int p^{\text{ex}} dV \\ &= - \int \frac{N k_B T}{V} \left(4\eta + 10\eta^2 + 18\eta^3 + 28\eta^4 \right. \\ &\quad \left. + 40\eta^5 + 54\eta^6 \dots \right) \frac{dV}{d\eta} d\eta. \end{aligned} \quad (5.180)$$

With the relation $\frac{dV}{d\eta} = -\frac{V}{\eta}$ and equation (5.169), F^{ex} reduces to the series:

$$F^{\text{ex}} = N k_B T \int (4 + 10\eta + 18\eta^2 + 28\eta^3 + 40\eta^4 + 54\eta^5 \dots) d\eta, \quad (5.181)$$

namely:

$$\frac{F^{\text{ex}}}{N k_B T} = 4\eta + 5\eta^2 + 6\eta^3 + 7\eta^4 + 8\eta^5 + 9\eta^6 \dots = \sum_{k=1}^{\infty} (k+3)\eta^k. \quad (5.182)$$

As for the pressure, this series can be put in the form of a rational fraction by combining the geometric series $\sum_{k=1}^{\infty} \eta^k$ with its first derivative. Indeed, the identity

$$\sum_{k=1}^{\infty} (k+3)\eta^k = \sum_{k=1}^{\infty} k\eta^k + \sum_{k=1}^{\infty} 3\eta^k \quad (5.183)$$

is still written as:

$$\sum_{k=1}^{\infty} (k+3)\eta^k = \frac{\eta}{(1-\eta)^2} + \frac{3\eta}{(1-\eta)}, \quad (5.184)$$

allowing us to find the expression for the excess free energy:

$$\frac{F^{ex}}{Nk_B T} = \sum_{k=1}^{\infty} (k+3)\eta^k = \frac{4\eta - 3\eta^2}{(1-\eta)^2}. \quad (5.185)$$

Consequently, the expression for the free energy of the HS fluid is:

$$\begin{aligned} F &= F^{id} + F^{ex}, \\ \text{or} \quad \frac{F}{Nk_B T} &= \ln \rho \Lambda^3 - 1 + \frac{4\eta - 3\eta^2}{(1-\eta)^2}. \end{aligned} \quad (5.186)$$

The entropy is obtained by using a similar method of calculation based on deriving the free energy with respect to the temperature:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = - \left(\frac{\partial F^{id}}{\partial T} \right)_V - \left(\frac{\partial F^{ex}}{\partial T} \right)_V, \quad (5.187)$$

where S^{id} is the entropy of the ideal gas⁵:

$$S^{id} = -Nk_B (\ln \rho \Lambda^3 - 1), \quad (5.188)$$

and the excess entropy S^{ex} arises from the relation:

$$S^{ex} = - \left(\frac{\partial F^{ex}}{\partial T} \right)_V = -Nk_B \frac{4\eta - 3\eta^2}{(1-\eta)^2}, \quad (5.189)$$

so that the expression for the entropy of the HS fluid is given by:

$$\frac{S}{Nk_B} = -\ln \rho \Lambda^3 + 1 - \frac{4\eta - 3\eta^2}{(1-\eta)^2}. \quad (5.190)$$

⁵The HS fluid has zero potential energy. As a consequence, it is fully driven by entropy, and temperature is just a scaling factor leading to the expression for the ideal gas (Eq. 4.14).

Finally, in combining equations (5.186) and (5.176) with the help of equation (4.53), the chemical potential of the HS fluid is given under the form:

$$\begin{aligned}\frac{\mu}{k_B T} &= \frac{F}{N k_B T} + \frac{p}{\rho k_B T} \\ &= \ln \rho \Lambda^3 - 1 + \frac{4\eta - 3\eta^2}{(1 - \eta)^2} + \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (5.191)\end{aligned}$$

or equivalently:

$$\frac{\mu}{k_B T} = \ln \rho \Lambda^3 - 1 + \frac{1 + 5\eta - 6\eta^2 + 2\eta^3}{(1 - \eta)^3}. \quad (5.192)$$

As they all stem from equation (5.172), the expressions of thermodynamic properties (p , F , S and μ) of the HS fluid make up a homogeneous group of relations specific to the Carnahan and Starling equation of state. Otherwise, other expressions for the thermodynamic properties can also be derived by using the pressure equation of state (Eq. 5.27), on the one hand, and the compressibility equation of state (Eq. 5.85), on the other hand. Unlike the Carnahan and Starling equation of state, these two equations of state require good knowledge of the HS pair correlation function, $g_{HS}(r)$.

The methods for calculating the pair correlation function $g(r)$ and structure factor $S(q)$ of liquids will be presented in the next chapter. Note that it is generally not possible to express $g(r)$ and $S(q)$ of liquids by means of elementary functions. Only the structure factor of the HS fluid, $S_{HS}(q)$, is available in an analytical form. Besides, the thermodynamic properties (p , F , S and μ) of the HS fluid, obtained with the equations of state of pressure and compressibility, have analytic expressions very similar to those deduced from the Carnahan and Starling equation of state, and they provide results whose differences are indistinguishable at low density.

5.7 The variational method

It is found that, even if the pair interactions are attractive over some domains of the interparticle separation, the structure is essentially dominated by the repulsive forces. So the HS reference system yields an excellent basis for a perturbative extension to more realistic pair

potentials. There have been several attempts to predict the thermodynamic properties of liquids in terms of the HS system and a perturbative expansion of the interaction potential. In this section, we present the important variational method based on the Gibbs–Bogoliubov inequality [43].

This method consists in finding a strict limit to the free energy by an upper bound which gives a good approximation for the free energy of the real system. This has been proved by showing that the sum of the terms beyond c_1 in equation (5.147), when expanded to first order in β , is always negative [37]. The way to do it is by considering the expression for the free energy (Eq. 5.135):

$$-\beta F = \ln \frac{Z_N^{(0)}(V, T)}{N! \Lambda^{3N}} + \ln \langle \exp[-\beta U_1(\mathbf{r}^N)] \rangle_0, \quad (5.193)$$

and to write the perturbation $U_1(\mathbf{r}^N)$ around its mean value $\langle U_1 \rangle_0$ as:

$$U_1 = \langle U_1 \rangle_0 + \Delta U_1. \quad (5.194)$$

After the insertion of U_1 in equation (5.193), we obtain:

$$\begin{aligned} -\beta F &= -\beta F_0 + \ln \left\langle \exp[-\beta \langle U_1 \rangle_0] \cdot \exp[-\beta \Delta U_1] \right\rangle_0 \\ &= -\beta F_0 + \ln \left\{ \exp[-\beta \langle U_1 \rangle_0] \cdot \langle \exp[-\beta \Delta U_1] \rangle_0 \right\} \\ &= -\beta F_0 - \beta \langle U_1 \rangle_0 + \ln \langle \exp[-\beta \Delta U_1] \rangle_0. \end{aligned} \quad (5.195)$$

However, considering the series expansion of exponential function, we get the following inequality⁶:

$$-\beta F \geq -\beta F_0 - \beta \langle U_1 \rangle_0 + \ln \left\langle \sum_{k=0}^{2n+1} \frac{(-\beta \Delta U_1)^k}{k!} \right\rangle_0 \quad (5.196)$$

$$\text{or} \quad F \leq F_0 + \langle U_1 \rangle_0 - \frac{1}{\beta} \ln \left\langle \sum_{k=0}^{2n+1} \frac{(-\beta \Delta U_1)^k}{k!} \right\rangle_0. \quad (5.197)$$

⁶The Maclaurin formula of the exponential function naturally leads to the inequality:

$$\exp(x) \geq \sum_{k=0}^{2n+1} \frac{x^k}{k!} \quad (n = 0, 1, 2, \dots).$$

For $n = 0$, the last term of the previous relation is:

$$\ln \left\langle \sum_{k=0}^1 \frac{(-\beta \Delta U_1)^k}{k!} \right\rangle_0 = \ln \langle 1 - \beta \Delta U_1 \rangle_0 \simeq -\beta \langle \Delta U_1 \rangle_0, \quad (5.198)$$

but as the mean value of the deviation $\langle \Delta U_1 \rangle_0$ is zero, equation (5.197) is reduced to the inequality:

$$F \leq F_0 + \langle U_1 \rangle_0, \quad (5.199)$$

usually called the *Gibbs-Bogoliubov inequality*. A thorough study of this inequality shows that it is always valid and unnecessary to consider the values of n greater than zero. Equation (5.199), at the base of the variational method, allows us to find the value of the parameter d making the *free energy* F *minimum*. If the reference system is that of the hard spheres, the value of free energy obtained with this particular value of d (or $\eta = \frac{\pi}{6} \rho d^3$) is considered as the best estimate of the free energy of the real system. Its expression is:

$$F \leq F_{HS} + \frac{\rho N}{2} \int u_1(r) g_{HS}(\eta; r) dr, \quad (5.200)$$

where $F_0 = F_{HS}$ is given by equation (5.186) and $\langle U_1 \rangle_0 = c_1$ by equation (5.151). As $g_{HS}(\eta; r) = 0$ when $r < d$ and $u_1(r) = u(r) - u_{HS}(r) = u(r)$ when $r \geq d$, the equation (5.200) can be written as:

$$F \leq F_{HS} + 2\pi\rho N \int_0^\infty u(r) g_{HS}(\eta; r) r^2 dr. \quad (5.201)$$

Being given that there is no analytical expression for the pair correlation function $g_{HS}(\eta; r)$ - whereas there exists one for the structure factor $S_{HS}(\eta; q)$ - it is interesting to calculate the integral of the previous equation in reciprocal space. For this, consider the expression of the structure factor (Eq. 3.118):

$$S_{HS}(\eta; q) - 1 = \rho \int [g_{HS}(\eta; r) - 1] \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \quad (5.202)$$

as well as the Fourier transform of the perturbation:

$$u_1(q) = \int u_1(r) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \quad (5.203)$$

$$\text{with } u_1(r) = \frac{1}{(2\pi)^3} \int u_1(q) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q}, \quad (5.204)$$

in order to write the Gibbs–Bogolyubov inequality (Eq. 5.200) in the form:

$$\begin{aligned}
 F &\leq F_{HS} + \frac{\rho N}{2} \int \left[\frac{1}{(2\pi)^3} \int u_1(q) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q} \right] g_{HS}(\eta; r) d\mathbf{r} \\
 &\leq F_{HS} + \frac{N}{16\pi^3} \int \left[\rho \int g_{HS}(\eta; r) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \right] u_1(q) d\mathbf{q} \\
 &\leq F_{HS} + \frac{N}{16\pi^3} \int \left\{ \rho \int [g_{HS}(\eta; r) - 1] \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \right. \\
 &\quad \left. + \rho \int \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \right\} u_1(q) d\mathbf{q}. \quad (5.205)
 \end{aligned}$$

After equation (5.202) is used and the term $\int \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = 8\pi^3 \delta(\mathbf{q})$ omitted that is zero except at $q = 0$ (Eq. 3.118), the Gibbs–Bogolyubov inequality becomes:

$$F \leq F_{HS} + \frac{N}{16\pi^3} \int \{[S_{HS}(\eta; q) - 1]\} u_1(q) d\mathbf{q}. \quad (5.206)$$

Practically, to implement the variational method, the value of η (or d) is changed until the result of the integral is minimum. Therefore, it yields simultaneously the optimal value of the HS diameter d and a good estimate of the free energy F of the real system.

5.8 The square-gradient theory of van der Waals

Introduction

The key to success in determining the properties of thermodynamic systems at equilibrium lies in the knowledge of the free energy. For example, the thermodynamic perturbation theory, briefly described in previous sections, aims to build an expression for the free energy of *homogeneous* systems which is used to derive other thermodynamic properties, whereas it does not envisage the study of *inhomogeneous* systems. Yet, the general treatment of inhomogeneous systems has been proposed long before the perturbation theory by van der Waals (1893) who was first to establish the variational principle of thermodynamic equilibrium by considering the inhomogeneity of the density of particles in an interfacial phase.

The original work of van der Waals [44] concerns the weakly inhomogeneous systems such as planar liquid-vapour interfaces at equilibrium. It is based on the square-gradient theory in which the inhomogeneity between two phases is studied by using the gradient of the particle density. This is achieved with the inclusion of an additional term depending on the square of the density gradient in the expression of the free energy. In addition, it is required that the free energy is minimum in the closed system (temperature, volume and number of particles constant). It results that the model predicts a nonzero interfacial tension and a density profile varying in a non-zero thickness interface.

Although it was decisive, the work of van der Waals has long been ignored until Cahn and Hilliard [45] rediscovered the theory by studying the structure of liquid-liquid interface in the context of nucleation. Successive versions of the square-gradient theory have evolved considerably all along that time and are at the basis of the density functional theory which is used to obtain an accurate description of the behaviour of the confined fluid phases.

Square-gradient model

Van der Waals considered the planar interface between the homogeneous liquid phase of particle density ρ_L constant and the homogeneous vapour phase of particle density ρ_V constant. In the interfacial region⁷, the particle density varies continuously between the two extreme values ρ_L and ρ_V . It constitutes a one-component fluid at equilibrium, wherein the total number of particles, volume and temperature are fixed. In addition, the forces of gravity are assumed to be negligible, so that the z -axis perpendicular to the interface is chosen in any direction of space.

According to the theory of van der Waals, the Helmholtz free energies of liquid and vapour phases, per particle and in units of $k_B T$, are given by equation (5.156) under the respective forms:

$$\beta f_L = \beta \frac{F_L}{N} = \ln \left(\frac{\Lambda^3 \rho_L}{1 - b \rho_L} \right) - 1 - \beta a \rho_L, \quad (5.207)$$

⁷This representation of the interface is different from that of Laplace, for which the interface is a membrane without thickness. By contrast, it is closer to the representation given by Gibbs, where the interface is defined by an imaginary surface - called the *dividing surface* - optimally positioned in the interfacial region.

(Eq. 5.154), but by evaluating the reversible work necessary to move a particle from the liquid phase ($z = -\infty$) to the interfacial region. To evaluate this reversible work we draw a perpendicular to the interface and place a particle P on this axis, at a distance z from an origin located in the liquid where the particle density is constant. Then, we consider a layer of thickness dl in the interfacial region, taken at the distance l of P (Fig. 5.5a), wherein the particle density is $\rho(z)$. After calling $\frac{\partial u_1(r)}{\partial r} \rho(z-l)$ the force exerted on the particle P by the particles contained in the volume element located at a distance $r (= \sqrt{l^2 + s^2})$, we note that the z -component of the force exerted on P by all the other particles is reduced to the integral of $\frac{\partial u_1(r)}{\partial r} \frac{l}{r} \rho(z-l)$ over the volume. However, when using the cylindrical coordinates, the component $\Gamma(z)$ of this force is:

$$\Gamma(z) = \int_{-\infty}^{+\infty} \left[\int_0^{+\infty} \frac{\partial u_1(r)}{\partial r} \frac{l}{r} \rho(z-l) 2\pi s ds \right] dl. \quad (5.210)$$

From l constant, it follows that $s ds = r dr$ and $u_1(\infty) = 0$, so that the integral in square brackets in the above equation is equal to $-2\pi l \rho(z-l) u_1(|l|)$, and the force $\Gamma(z)$ is expressed as:

$$\Gamma(z) = - \int_{-\infty}^{+\infty} \rho(z-l) 2\pi l u_1(|l|) dl. \quad (5.211)$$

With this expression of the force, it becomes possible to calculate the reversible work to move a particle from the liquid phase to the interfacial region:

$$\begin{aligned} W(z) &= \int_{-\infty}^z \Gamma(z) dz \\ &= \int_{-\infty}^z \left[- \int_{-\infty}^{+\infty} \rho(z-l) 2\pi l u_1(|l|) dl \right] dz. \end{aligned} \quad (5.212)$$

The calculation of the integral in brackets is facilitated by setting $d\psi(l) = 2\pi l u_1(|l|) dl$, with $\psi(\pm\infty) = 0$, because the perturbation is an attractive dispersion force derived from the potential $u_1(l) \sim \frac{1}{l^6}$ and $\psi(l) \sim \frac{1}{l^4}$. Since $\psi(l)$ is an even function, the integration by parts of the term in square brackets representative of the force $\Gamma(z)$ reduces

to:

$$\begin{aligned}\Gamma(z) &= -\rho(z-l)\psi(l)\Big|_{l=-\infty}^{l=+\infty} + \int_{-\infty}^{+\infty} \psi(l) \frac{\partial \rho(z-l)}{\partial l} dl \\ &= \int_{-\infty}^{+\infty} \psi(l) \frac{\partial \rho(z-l)}{\partial l} dl.\end{aligned}\quad (5.213)$$

In order to proceed to the second integration, van der Waals suggested to use the Taylor series expansion of the local particle density $\rho(z-l)$ around l :

$$\rho(z-l) = \rho(z) - \rho'(z)l + \frac{1}{2!}\rho''(z)l^2 - \frac{1}{3!}\rho'''(z)l^3 + \dots, \quad (5.214)$$

for which the partial derivative with respect to l is:

$$\frac{\partial \rho(z-l)}{\partial l} = -\rho'(z) + \rho''(z)l - \frac{1}{2}\rho'''(z)l^2 + \dots \quad (5.215)$$

Substituting this expression in equation (5.213) leads to the following form for the force $\Gamma(z)$:

$$\begin{aligned}\Gamma(z) &= -\int_{-\infty}^{+\infty} \psi(l)\rho'(z)dl + \int_{-\infty}^{+\infty} \psi(l)\rho''(z)ldl \\ &\quad - \frac{1}{2}\int_{-\infty}^{+\infty} \psi(l)\rho'''(z)l^2dl + \dots,\end{aligned}\quad (5.216)$$

and the substitution of $\Gamma(z)$ into equation (5.212) provides the reversible work for a particle to pass from the liquid to the interfacial region:

$$\begin{aligned}W(z) &= -\int_{-\infty}^z \left[\int_{-\infty}^{+\infty} \psi(l)dl \right] \rho'(z)dz + \int_{-\infty}^z \left[\int_{-\infty}^{+\infty} \psi(l)ldl \right] \rho''(z)dz \\ &\quad - \frac{1}{2}\int_{-\infty}^z \left[\int_{-\infty}^{+\infty} \psi(l)l^2dl \right] \rho'''(z)dz + \dots\end{aligned}\quad (5.217)$$

As $\psi(l)$ is an even function, the integral in brackets of the second term on the right hand side is cancelled and the expression for the work $W(z)$ is reduced to:

$$W(z) = [\rho_L - \rho(z)] \int_{-\infty}^{+\infty} \psi(l)dl - \frac{1}{2}\rho''(z) \int_{-\infty}^{+\infty} \psi(l)l^2dl + \dots, \quad (5.218)$$

because $\rho(-\infty) = \rho_L$ and $\rho'(-\infty) = \rho''(-\infty) = 0$.

Now, simplification is made on the two integrals in the above relation. By integrating by parts, the first one becomes:

$$\int_{-\infty}^{+\infty} \psi(l) dl = l\psi(l) \Big|_{l=-\infty}^{l=+\infty} - \int_{-\infty}^{+\infty} l d\psi = -2\pi \int_{-\infty}^{+\infty} l^2 u_1(|l|) dl = 2a. \quad (5.219)$$

It is remarkable that this integral, equal to $2a$, is the same as that calculated with equation (5.155). As far as the second integral is concerned, it simplifies as:

$$\begin{aligned} \int_{-\infty}^{+\infty} \psi(l) l^2 dl &= \frac{l^3}{3} \psi(l) \Big|_{l=-\infty}^{l=+\infty} - \int_{-\infty}^{+\infty} \frac{l^3}{3} d\psi \\ &= -\frac{2\pi}{3} \int_{-\infty}^{+\infty} l^4 u_1(|l|) dl = 2c. \end{aligned} \quad (5.220)$$

Ultimately, the reversible work required to move a particle from the liquid phase into the interfacial region is:

$$W(z) = 2a [\rho_L - \rho(z)] - c\rho''(z) + \dots \quad (5.221)$$

This expression of the work makes it possible to calculate the reduced free energy $\beta f_P(z)$, per particle, of the perturbation. As was stressed by van der Waals in his original work, $f_P(z)$ is only half the work $W(z)$ (because the force used for it to be calculated is derived from a pair potential) from which the free energy per particle, $a\rho_L$, must be subtracted as it represents the transport of the particle through the liquid phase. Therefore, the free energy of the perturbation $f_P(z)$ is:

$$\begin{aligned} f_P(z) &= \frac{W(z)}{2} - a\rho_L = a[\rho_L - \rho(z)] - \frac{c}{2}\rho''(z) - a\rho_L + \dots \\ &= -a\rho(z) - \frac{c}{2}\rho''(z) + \dots, \end{aligned} \quad (5.222)$$

and the general expression of the reduced Helmholtz free energy, per particle, for the interfacial region (inhomogeneous phase) is:

$$\begin{aligned} \beta f_I(z) &= \beta f_R(z) + \beta f_P(z) \\ &= \ln \left(\frac{\Lambda^3 \rho(z)}{1 - b\rho(z)} \right) - 1 - \beta a\rho(z) - \beta \frac{c}{2}\rho''(z) + \dots \end{aligned} \quad (5.223)$$

The first three terms of the right hand side of this expression are the same as those of an homogeneous phase (with the local particle density), whereas the last term is due to the inhomogeneity of the interfacial region: it disappears in the liquid or vapour phases where the density is constant. Note that this series expansion is not restrictive, and the next term, if it proved useful, is proportional to the fourth derivative of the particle density $\frac{d^4\rho(z)}{dz^4}$.

For the practical examination of the liquid-vapour interface, it is necessary to determine the total reduced free energy, per unit area, by performing the following integration of $\beta f_I(z)$:

$$\begin{aligned}\beta \frac{F}{A} &= \int \beta f_I(z) \rho(z) dz \\ &= \int \left[\rho(z) \ln \left(\frac{\Lambda^3 \rho(z)}{1 - b\rho(z)} \right) - \rho(z) - \beta a \rho^2(z) - \beta \frac{c}{2} \rho''(z) \rho(z) \right] dz, \quad (5.224)\end{aligned}$$

where A is the area of the interface and $f_I(z)\rho(z)$ the free energy per unit volume. After the integration by parts of the last term in brackets, in the above relation, is done, it is also written as:

$$-\beta \frac{c}{2} \int \rho''(z) \rho(z) dz = \beta \frac{c}{2} \int [\rho'(z)]^2 dz, \quad (5.225)$$

given that $\rho'(\pm\infty) = 0$. The expression for the interfacial Helmholtz free energy per unit area is finally:

$$\beta \frac{F}{A} = \int \left[\rho(z) \ln \left(\frac{\Lambda^3 \rho(z)}{1 - b\rho(z)} \right) - \rho(z) - \beta a \rho^2(z) + \beta \frac{c}{2} [\rho'(z)]^2 \right] dz. \quad (5.226)$$

It should be stressed that equation (5.226) has been generalized to investigate the inhomogeneous bulk systems and the phase transitions [4] under the form:

$$F[\rho(\mathbf{r})] = \int \left[f_0[\rho(\mathbf{r})] - a\rho^2(\mathbf{r}) + \frac{c}{2} [\nabla\rho(\mathbf{r})]^2 \right] d\mathbf{r}, \quad (5.227)$$

where $f_0[\rho(\mathbf{r})]$ is the free energy depending on the equation of state. Equation (5.227) clearly shows that the free energy is a density functional⁹ of the particle density.

⁹A functional is a law of correspondence which associates a real number (the free energy $\frac{F}{A}$) to a function (the local particle density $\rho(z)$).

Liquid-vapour interface at equilibrium

The principle of equilibrium established in classical thermodynamics stipulates that the spontaneous evolution of a closed system stops when the free energy F is minimum (section 2.2). In addition, a closed system consisting of several phases is in thermal, mechanical and thermodynamical equilibrium when temperature T , pressure P and chemical potential μ are identical in all present phases. It should be remembered that the interfaces between different phases are surfaces without thickness, imposing a sudden discontinuity on the particle density in crossing from one phase to another. This representation of the interface is legitimate when we are only interested in bulk properties of systems. By contrast, for studying interfacial properties, we have to treat the interface as a phase in its own right, with a specific thickness in which the particle density $\rho(z)$ varies continuously.

In the problem raised here, van der Waals stated the principle of equilibrium by saying that the matter distribution in the interfacial phase is optimal when the profile of particle density $\rho(z)$ minimizes the Helmholtz free energy $\frac{F}{A}$ given by equation (5.226). As the liquid-vapour system is a closed system where temperature T , volume V and total number of particles N are constant, the minimization of free energy is subject to the condition:

$$\int \rho(\mathbf{r}) d\mathbf{r} = N \quad \text{or} \quad \int \rho(z) dz = \frac{N}{A}, \quad (5.228)$$

where $A = \int dx dy$ represents the area of the interface. The search for the minimum of the integral $\frac{F}{A}$ under the constraint of equation (5.228) implies using the method of Lagrange multipliers and the method of variations developed by Euler, i.e. by forming a linear combination of the variations $\frac{F}{A}$ and $\frac{N}{A}$ in the form:

$$\delta \left(\frac{F}{A} \right) - \lambda \delta \left(\frac{N}{A} \right) = 0, \quad (5.229)$$

where λ is an arbitrary coefficient, and both $\delta \left(\frac{F}{A} \right)$ and $\delta \left(\frac{N}{A} \right)$ are the variations of integrals provided respectively by equations (5.226) and (5.228) with respect to the variation $\delta \rho(z)$ of the local particle density.

Before exploring the result of equation (5.229), we extract the terms in the brackets of equation (5.224) which are specific to the equation of state. By noting $\beta f_0(z)$ the sum of terms that depend on

the equation of state (in this case, it is the van der Waals equation of state):

$$\beta f_0(z) = \ln \left(\frac{\Lambda^3 \rho(z)}{1 - b\rho(z)} \right) - 1 - \beta a\rho(z), \quad (5.230)$$

the equation (5.224) is written:

$$\frac{F}{A} = \int \rho(z) \left[f_0(z) - \frac{c}{2} \rho''(z) \right] dz. \quad (5.231)$$

As regards equation (5.229), it is reduced to:

$$\delta \int \rho(z) \left[f_0(z) - \frac{c}{2} \rho''(z) - \lambda \right] dz = 0. \quad (5.232)$$

However, the variation of this integral is equal to:

$$\begin{aligned} & \int \delta \rho(z) \left[f_0(z) - \frac{c}{2} \rho''(z) - \lambda \right] dz \\ & + \int \rho(z) \left[\frac{\partial f_0(z)}{\partial \rho} \delta \rho(z) - \frac{c}{2} \delta \rho''(z) \right] dz = 0, \end{aligned} \quad (5.233)$$

that reads:

$$\begin{aligned} & \int \delta \rho(z) \left[f_0(z) + \rho(z) \frac{\partial f_0(z)}{\partial \rho} - \frac{c}{2} \rho''(z) - \lambda \right] dz \\ & - \frac{c}{2} \int \rho(z) \delta \rho''(z) dz = 0. \end{aligned} \quad (5.234)$$

In order to calculate the second integral in the above equation, we integrate it twice by parts to make appear explicitly $\delta \rho(z)$ in the integrand¹⁰. The result is :

$$-\frac{c}{2} \int \rho(z) \delta \rho''(z) dz = -\frac{c}{2} \int \delta \rho(z) \rho''(z) dz, \quad (5.235)$$

¹⁰The first integration by parts, with $U = \rho(z)$, hence $dU = \rho'(z)dz$, and $dV = \delta \rho''(z)dz$, hence $V = \int \delta \left(\frac{d^2 \rho}{dz^2} \right) dz = \delta \rho'(z)$, provides the expression:

$$\int \rho(z) \delta \rho''(z) dz = \rho(z) \delta \rho'(z) \Big|_{-\infty}^{+\infty} - \int \rho'(z) \delta \rho'(z) dz,$$

and the second integration by parts, with $U = \rho'(z)$, hence $dU = \rho''(z)dz$, and

allowing us to simplify the expression of the variation of the integral (Eq. 5.234) under the form:

$$\int \delta \rho(z) \left[f_0(z) + \rho(z) \frac{\partial f_0(z)}{\partial \rho} - c \rho''(z) - \lambda \right] dz = 0. \quad (5.236)$$

As this relation has to be verified at any point in the system, the equilibrium condition is written:

$$f_0(z) + \rho(z) \frac{\partial f_0(z)}{\partial \rho} - c \rho''(z) - \lambda = 0. \quad (5.237)$$

The density profile $\rho(z)$ in the liquid-vapour system at equilibrium is obtained by integrating the above equation after choosing the equation of state and setting the coefficient λ .

To give a physical meaning to the coefficient λ , we apply the equilibrium condition (Eq. 5.237) to the liquid phase in which $\rho(z) = \rho_L$ and $\rho'(z) = \rho''(z) = 0$, and where the free energy of the liquid phase per particle, $f_0(z) = f_L$, is given by equation (5.207). Due to the fact that $\left(\frac{\partial f}{\partial v}\right)_T = -p$ and $\frac{\partial \rho}{\partial v} = -\frac{p}{v}$, the term $\rho \left(\frac{\partial f}{\partial \rho}\right)_T$ is equal to $p v$, and equation (5.237) applied to the liquid phase reduces to:

$$F_L + p_L V_L = N_L \lambda, \quad (5.238)$$

where $F_L = N_L f_L$ is the free energy of the liquid phase and $V_L = N_L v_L$ the volume of the liquid phase. However, if this relation is compared with equation (5.49), we see that the coefficient λ is nothing else than the chemical potential of liquid, i.e. $\lambda = \mu_L$. By the same reasoning, a similar relation to equation (5.238) is obtained for the vapour phase, i.e. $\lambda = \mu_V$. Consequently, according to the square-gradient theory of van der Waals, it results that the coefficient λ is equal to the chemical potentials of the liquid and vapour phases in

$dV = \delta \rho'(z) dz$, hence $V = \int \delta \left(\frac{d\rho}{dz}\right) dz = \delta \rho(z)$, yields:

$$\begin{aligned} \int \rho(z) \delta \rho''(z) dz &= \rho(z) \delta \rho'(z) \Big|_{-\infty}^{+\infty} - \rho'(z) \delta \rho(z) \Big|_{-\infty}^{+\infty} + \int \delta \rho(z) \rho''(z) dz, \\ \int \rho(z) \delta \rho''(z) dz &= \int \delta \rho(z) \rho''(z) dz, \end{aligned}$$

because $\rho'(\pm\infty) = 0$. With the above relation, we demonstrate an interesting feature of the functional derivative.

agreement with the thermodynamic equilibrium condition derived by Gibbs (Eq. 2.79), namely:

$$\lambda = \mu_L = \mu_V = \mu. \quad (5.239)$$

Incidentally, the equality of pressures in liquid and vapour phases can also be proved. For this, we write equation (5.237) as:

$$\frac{\partial}{\partial \rho} [\rho(z)f_0(z) - \rho(z)\mu] = c\rho''(z). \quad (5.240)$$

Then, we pose $\omega(\rho) = [\rho(z)f_0(z) - \rho(z)\mu]$ in the previous equation allowing to write¹¹:

$$d\omega = \frac{1}{2}cd[\rho'(z)]^2; \quad (5.241)$$

$$\omega = \frac{1}{2}c[\rho'(z)]^2 - p. \quad (5.242)$$

It is easy to see that $\omega(\rho)$ is identified with the pressure in the liquid¹²: $\omega(\rho_L) = -p_L$ and $\omega(\rho_V) = -p_V$. Thus, as $d\omega$ is equal to zero in the liquid and vapour phases, with $\rho'(\pm\infty) = 0$, it results that:

$$\omega(\rho_L) = \omega(\rho_V), \quad (5.243)$$

therefore

$$p_L = p_V = p. \quad (5.244)$$

This shows that the equilibrium conditions, as derived by van der Waals, are consistent with the thermal, mechanical and thermodynamical equilibrium conditions in inhomogeneous closed systems, as previously set up by Gibbs.

¹¹With the relation $\omega(\rho)$, equation (5.240) is written as:

$$\frac{\partial \omega}{\partial \rho} = c\rho''(z),$$

and in multiplying each side of it by $\rho'(z)dz$, it is simplified as:

$$\frac{\partial \omega}{\partial \rho} \rho'(z)dz = c\rho''(z)\rho'(z)dz, \quad d\omega = \frac{1}{2}cd[\rho'(z)]^2.$$

¹²Indeed, in comparing the function $\omega(\rho) = [\rho(z)f_0(z) - \rho(z)\mu]$, namely $\omega = \rho \frac{F}{N} - \rho\mu$, with equation (5.49), i.e. $F = \mu N - pV$, it follows merely $\omega = -p$.

The first property that arises from the square-gradient model is the particle density profile $\rho(z)$ obtained by integration of equation (5.240). The theory is appealing for its contribution to the description of interfacial phases in terms of local particle density. However, the square-gradient approximation is actually applicable to systems where the density profile varies slowly, as in liquid-vapour interfaces near the critical point. For inhomogeneous systems with a sheer density profile, an additional term should be added in the development of the particle density. Moreover, the square-gradient approximation applies only to systems where long range interactions allow the convergence of the integral in equation (5.220).

Interfacial tension

With the density profile in hand, it becomes possible to calculate the interfacial tension γ defined by the formula:

$$\gamma = \frac{F - (N\mu - pV)}{A}, \quad (5.245)$$

where $(N\mu - pV)$ represents the free energy of bulk phases, with A the area of the interface and F the Helmholtz free energy of the system given by equation (5.226):

$$\frac{F}{A} = \int_{-\infty}^{+\infty} \left[\rho(z) f_0(z) + \frac{c}{2} [\rho'(z)]^2 \right] dz, \quad (5.246)$$

where $f_0(z)$ is defined by equation (5.230). With the relations $\omega = \frac{1}{2} c [\rho'(z)]^2 - p$ (Eq. 5.242) and $\omega = \rho f_0 - \rho\mu$, the above integral reduces to:

$$\frac{F}{A} = \int_{-\infty}^{+\infty} \left[\frac{c}{2} [\rho'(z)]^2 - p + \rho\mu + \frac{c}{2} [\rho'(z)]^2 \right] dz. \quad (5.247)$$

As the bulk free energy is $F_L + F_V = N\mu - pV$, the previous equation simplifies to the form:

$$\frac{F}{A} = \frac{N\mu - pV}{A} + \int_{-\infty}^{+\infty} c [\rho'(z)]^2 dz. \quad (5.248)$$

Consequently, the interfacial tension (Eq. 5.245) takes the simple form:

$$\gamma = \int_{-\infty}^{+\infty} c [\rho'(z)]^2 dz, \quad (5.249)$$

and, if c does not depend on the density, it is also written as:

$$\gamma = c \int_{-\infty}^{+\infty} [\rho'(z)]^2 dz = c \int_{\rho_L}^{\rho_V} \rho'(z) d\rho. \quad (5.250)$$

The interfacial tension can thus be deduced with the van der Waals square-gradient model provided that the density profile $\rho(z)$ and the coefficient c are known. The accuracy of the calculations relies on the limitations imposed by the square-gradient theory, which requires a slow variation of the density profile. For this reason, the results are better in the inhomogeneous systems near the critical point – where the interfacial region is thick and the density profile varies slowly – than in a thin interface region and steep gradient. To improve the results, more terms in the density expansion of the free energy (Eq. 5.224) can be used, with the series truncated after the quartic terms. In practice, the density profile $\rho(z)$ is often used in an empirical form such as hyperbolic tangent (Fig. 5.5b).

It should be stressed that there are harmful consequences when the model is used for fluids with power-law decaying pair potentials preventing the rapid convergence of the coefficient c of the square-gradient (Eq. 5.220). A gradient expansion does not exist for such potentials. One way to obtain more satisfactory results is to consider the coefficient c as an adjustable parameter that can possibly depend on the density [46], [47]. Another possibility is to calculate the coefficient, in terms of the direct correlation function, with the formula [48]:

$$c = \frac{1}{12\beta} \int r^2 c^{(2)}(\rho, \mathbf{r}) d\mathbf{r}, \quad (5.251)$$

where $c^{(2)}(\rho, \mathbf{r})$ is the direct correlation function (see Eq. 6.109).

In spite of the foregoing drawbacks, the square-gradient model remains useful for describing the thermodynamics of inhomogeneous systems, including, not only interfacial tension, but also a variety of interfacial phenomena such as nucleation, wetting transitions [45, 49], as well as the behaviour of many complex liquids [50, 51]. The results are also good for oscillatory density profiles, as in liquid metals [52]. Lastly note that the square-gradient model is to be seen as the former development of the density functional theory for classic systems [48], as it is indeed a very powerful tool in the statistical physics.

6 Equilibrium structure of liquids

In the previous chapter, we have defined the spatial correlation functions and indicated how the thermodynamic properties of liquids are deduced from their microscopic properties. In particular, it has been shown that internal energy (Eq. 5.14), pressure (Eq. 5.27) and chemical potential (Eq. 5.48) are expressed in terms of the pair correlation function $g(r)$ and the pair potential $u(r)$. By contrast, entropy (Eq. 5.53) and isothermal compressibility (Eq. 5.85) can only be determined with the pair correlation function, without resorting to the pair potential. This is not surprising since the pair correlation function $g(r)$ itself is derived from the pair potential $u(r)$. It has also been mentioned that the thermodynamic properties of liquids are obtainable more adequately by including the three-body potential $u_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and the three-body correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. Anyway, even if an effective potential is generated by gathering the pair and three-body potentials, there is no way to escape the need to estimate the three-body correlation function with the Kirkwood superposition approximation (Eq. 5.107) for an evaluation of the thermodynamic properties.

This chapter is devoted to the theories enabling the calculation of the pair correlation function $g(r)$ from the pair potential $u(r)$. These theories can be divided into two categories. The first category is based on equation (3.89) connecting the pair correlation function $g(r)$ to the partition function $Z_N(V, T)$ and the potential energy $U(\mathbf{r}^N)$. The method consists in expressing the pair correlation function $g(r)$ as a function of the pair potential $u(r)$ and the three-body correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. As the latter is unknown, it is necessary to resort to the Kirkwood approximation to carry out the calculation of $g(r)$ as a function of $u(r)$. The relation obtained is an integro-differential equation to be solved numerically by an iterative method.

The second category of these theories is based on a function of another type, i.e. the *direct correlation function* $c(r)$ as defined by the Ornstein–Zernike (OZ) relation. However, this approach requires to use an additional independent equation, combined with the Ornstein–Zernike relation, to deduce $g(r)$ as a function of $u(r)$. One of the difficulties of the liquid theory is precisely to develop this additional equation.

Although based on very different concepts, the two approaches to calculate $g(r)$ (Kirkwood approximation and the additional equation supplementing the OZ equation) are similar in the sense that they both require an additional equation which remains an approximate relation. To test these approximations, we can compare the theoretical results of thermodynamic properties (the most sensitive ones towards the details of the pair correlation function) together with the experimental results. In any case, the best way to judge the quality of an approximation is to compare the pair correlation function obtained from the theory with that one provided by numerical simulation for a given pair potential. Being free of experimental errors, the numerical simulation is the genuine test for the approximations of the liquid theory as it provides virtually exact results¹.

In this chapter, we first deduce the integro-differential equation of Yvon–Born–Green (YBG) corresponding to the first approach of liquid theory. Then we present the Percus–Yevick (PY) equation as a representative of the integral equations. For that purpose, we chose to introduce the PY equation in terms of the density functional theory which is very useful to justify the Ornstein–Zernike relation and the linear density response of a system to an external perturbation. The final part of the chapter is dedicated to the description of the bridge function required to determine the thermodynamic and structural properties of liquids in a self-consistent way.

¹When implementing the Monte Carlo (MC) and molecular dynamics (MD) simulations, which are considered as numerical experiments, excluding statistical and systematic errors resulting from the exploitation of results is impossible.

6.1 The Yvon-Born-Green equation

Obtaining the Yvon-Born-Green equation

The YBG equation [54, 55] is inseparable from the Kirkwood equation [18] which was established at the same time. Both equations are based on the expression of the pair correlation function (Eq. 3.89). The YBG equation is obtained by deriving the pair correlation function with respect to the coordinates of a given particle, whereas that of Kirkwood is established by deriving the pair correlation function with respect to the coupling parameter λ defined in equation (5.32). Here we will focus on the YBG equation.

We consider the expression of the pair correlation function (Eq. 3.89) of the canonical ensemble:

$$\begin{aligned}\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \rho^2 g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{N!}{(N-2)!} \frac{1}{Z_N(V, T)} \int \int_{3(N-2)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2}.\end{aligned}\quad (6.1)$$

Then, we perform its differentiation with respect to the variable $\mathbf{r}_1$, by maintaining $\mathbf{r}_2$ constant. We obtain:

$$\begin{aligned}\frac{\partial \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} &= \frac{N!}{(N-2)!} \frac{1}{Z_N(V, T)} \times \\ &\times \int \int_{3(N-2)} \left[-\beta \frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_1} \right] \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2}.\end{aligned}\quad (6.2)$$

If it is assumed that the potential energy $U(\mathbf{r}^N)$ reduces to a sum of pair potentials explicitly written as:

$$\begin{aligned}U(\mathbf{r}^N) &= \sum_{i=1}^{N-1} \sum_{j>i}^N u(r_{ij}) \\ &= u(r_{12}) + u(r_{13}) + u(r_{14}) + u(r_{15}) + \dots + u(r_{1N}) \\ &\quad + u(r_{23}) + u(r_{24}) + \dots + u(r_{2N}) \\ &\quad + u(r_{34}) + u(r_{35}) + \dots + u(r_{3N}) + \dots,\end{aligned}\quad (6.3)$$

all the terms with index i greater than or equal to 2 are independent of $\mathbf{r}_1$, so that the derivative of $U(\mathbf{r}^N)$ with respect to $\mathbf{r}_1$ is split into:

$$\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_1} = \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} + \sum_{j=3}^N \frac{\partial u(r_{1j})}{\partial \mathbf{r}_1}, \quad (6.4)$$

where $\frac{\partial u(r_{12})}{\partial \mathbf{r}_1}$ represents the force exerted by particle 2 on particle

1. After substituting this expression of $\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_1}$ in equation (6.2), it follows:

$$\begin{aligned} \frac{\partial \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} = & -\frac{N!}{(N-2)!} \frac{\beta}{Z_N(V, T)} \left\{ \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} \iint_{3(N-2)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2} \right. \\ & \left. + \sum_{j=3}^N \iint_{3(N-2)} \frac{\partial u(r_{1j})}{\partial \mathbf{r}_1} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2} \right\}. \end{aligned} \quad (6.5)$$

The first integral in the above equation can easily be written in terms of $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ in using equation (6.1). Its expression reduces to:

$$\begin{aligned} -\frac{N!}{(N-2)!} \frac{\beta}{Z_N(V, T)} \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} \iint_{3(N-2)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2} = \\ = -\beta \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (6.6)$$

As regards the second integral, it can be estimated by the sum of $(N-2)$ integrals identical to that where j takes any value greater than or equal to 3. For example, if $j = 3$, the integral becomes:

$$\begin{aligned} \sum_{j=3}^N \iint \frac{\partial u(r_{1j})}{\partial \mathbf{r}_1} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2} = \\ = (N-2) \iint \frac{\partial u(r_{13})}{\partial \mathbf{r}_1} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2} \end{aligned} \quad (6.7)$$

and simplifies to:

$$\dots = (N-2) \iint_3 \frac{\partial u(r_{13})}{\partial \mathbf{r}_1} \left\{ \iint_{3(N-3)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_4 d\mathbf{r}_5 \dots d\mathbf{r}_N \right\} d\mathbf{r}_3. \quad (6.8)$$

Given the general expression of the generic distribution functions (Eq. 3.83), the integral in the brackets of equation (6.8) is expressed in terms of the generic third-order distribution function $\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$:

$$\iint_{3(N-3)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_4 d\mathbf{r}_5 \dots d\mathbf{r}_N = \rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{(N-3)!}{N!} Z_N(V, T). \quad (6.9)$$

With the expressions of the integrals just defined, equation (6.5) is transformed as:

$$\begin{aligned} \frac{\partial \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} &= -\beta \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \frac{N!}{(N-2)!} \frac{\beta}{Z_N(V, T)} \times \\ &\quad \times (N-2) \iint \frac{\partial u(r_{13})}{\partial \mathbf{r}_1} \left\{ \rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{(N-3)!}{N!} Z_N(V, T) \right\} d\mathbf{r}_3 \\ &= -\beta \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \beta \iint \frac{\partial u(r_{13})}{\partial \mathbf{r}_1} \rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3, \quad (6.10) \end{aligned}$$

or:

$$\frac{\partial}{\partial \mathbf{r}_1} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} - \beta \iint \frac{\partial u(r_{13})}{\partial \mathbf{r}_1} \frac{\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r}_3. \quad (6.11)$$

This relation is the *Yvon-Born-Green equation*. It is an integro-differential equation which does not make it possible to calculate the pair correlation function, under its present form, because it contains the unknown generic third-order distribution function $\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. One way to solve the problem is in using the superposition approximation of Kirkwood.

The Kirkwood superposition approximation

The origin of the Kirkwood approximation [18] is based on the concept of *potential of average force*. First evaluate the logarithmic derivative

of $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ with respect to $\mathbf{r}_1$ from equations (6.1) and (6.2), to obtain:

$$\begin{aligned} \frac{\partial}{\partial \mathbf{r}_1} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \beta \frac{\iint_{3(N-2)} \left[-\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_1} \right] \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2}}{\int \int_{3(N-2)} \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^{N-2}} \\ &= \beta \mathbf{F}_1(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (6.12)$$

The two integrals in the above relation, where the element of integration is $d\mathbf{r}^{N-2} = d\mathbf{r}_3 \dots d\mathbf{r}_N$, depend only on the variables $\mathbf{r}_1$ and $\mathbf{r}_2$, so that the function denoted $\mathbf{F}_1(\mathbf{r}_1, \mathbf{r}_2)$, which has the dimensions of force, is the mean value of $-\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_1}$. This function is called *average force* and this name refers to the force exerted by particle 2 on particle 1. It should not be confused with the total force exerted by all the particles of the system on particle 1 whose expression is:

$$\mathbf{F}_1(\mathbf{r}^N) = -\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_1}. \quad (6.13)$$

Consequently, it can be thought that the average force $\mathbf{F}_1(\mathbf{r}_1, \mathbf{r}_2)$ is derived from the *potential of average force* $w(\mathbf{r}_1, \mathbf{r}_2)$ by the equation:

$$\mathbf{F}_1(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\partial w(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1}, \quad (6.14)$$

and that equation (6.12) is simplified to:

$$\frac{\partial}{\partial \mathbf{r}_1} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\beta \frac{\partial w(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1}. \quad (6.15)$$

Integrating the above equation yields:

$$\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = A \exp[-\beta w(\mathbf{r}_1, \mathbf{r}_2)] = \rho^2 g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \quad (6.16)$$

Assuming now that the two particles are far apart from each other (independent particles), it results that $\lim_{r_{12} \rightarrow \infty} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 1$ and $\lim_{r_{12} \rightarrow \infty} w(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 0$. Accordingly, the equation (6.16) reduces to:

$$\lim_{r_{12} \rightarrow \infty} \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 = A, \quad (6.17)$$

$$\text{therefore} \quad g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \exp[-\beta w(\mathbf{r}_1, \mathbf{r}_2)]. \quad (6.18)$$

The last relation is a new definition of the pair correlation function in terms of the potential of average force . As regards the superposition approximation, it consists in considering that the potentials of average force are additive, just like the pair potentials. For the three-body potential, it corresponds to:

$$w(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \simeq w(\mathbf{r}_1, \mathbf{r}_2) + w(\mathbf{r}_1, \mathbf{r}_3) + w(\mathbf{r}_2, \mathbf{r}_3). \quad (6.19)$$

If, however, equation (6.16) extends to the generic third-order distribution function, namely:

$$\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \rho^3 \exp[-\beta w(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)], \quad (6.20)$$

the superposition approximation enables us to write $\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ as:

$$\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \simeq \rho^3 \exp[-\beta w(\mathbf{r}_1, \mathbf{r}_2)] \exp[-\beta w(\mathbf{r}_1, \mathbf{r}_3)] \exp[-\beta w(\mathbf{r}_2, \mathbf{r}_3)]. \quad (6.21)$$

Making use of equations (6.16) and (6.18), the above relation becomes:

$$\frac{\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{\rho^3} = g_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \simeq g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3) g_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3), \quad (6.22)$$

or equivalently:

$$\frac{\rho_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)} \simeq \rho g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3) g_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3). \quad (6.23)$$

This is the simplest form of the *superposition approximation* of Kirkwood [18]. It is valid only for low densities, when the particles are far away from each other. Indeed, if the particles 1 and 2 are distant from the particle 3, both functions $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3)$ and $g_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3)$ tend to unity and $g_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ tends to $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. Although inappropriate for high densities, the Kirkwood approximation is still used for want of anything better. Note that the three-body correlation function $g_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is not accessible by direct measurement, but it can be calculated by numerical simulation within a specific configuration of particles. Surprisingly, in an equilateral triangle [56, 57], the gap between $g_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ and $g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ does not exceed 10% for HS and Lennard-Jones potentials. Also note that substantial improvements have been implemented to the superposition approximation [58] subsequently, but they will not be considered in the following to solve the YBG equation.

Solving the Yvon–Born–Green equation

After replacing the generic third-order distribution function (Eq. 6.23) in equation (6.11), the YBG equation reads:

$$\begin{aligned} \frac{\partial}{\partial \mathbf{r}_1} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= -\beta \frac{\partial u(r_{12})}{\partial \mathbf{r}_1} \\ &- \beta \rho \iiint_3 \frac{\partial u(r_{13})}{\partial \mathbf{r}_1} g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3) g_N^{(2)}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3. \end{aligned} \quad (6.24)$$

If the liquid is homogeneous and isotropic, it is advisable to transform the differential elements $d\mathbf{r}_1$ and $d\mathbf{r}_3$ in the above equation in order to facilitate the numerical integration. We focus first on the left hand side of the previous relation, namely the differentiation with respect to $\mathbf{r}_1$ by performing the following changes of variables (Fig. 6.1):

$$\mathbf{r}_1 = x_1 \mathbf{i} + y_1 \mathbf{j} + z_1 \mathbf{k}, \quad (6.25)$$

$$\mathbf{r}_2 = x_2 \mathbf{i} + y_2 \mathbf{j} + z_2 \mathbf{k}, \quad (6.26)$$

$$\mathbf{r}_{12} = (x_2 - x_1) \mathbf{i} + (y_2 - y_1) \mathbf{j} + (z_2 - z_1) \mathbf{k}, \quad (6.27)$$

$$r_{12} = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}. \quad (6.28)$$

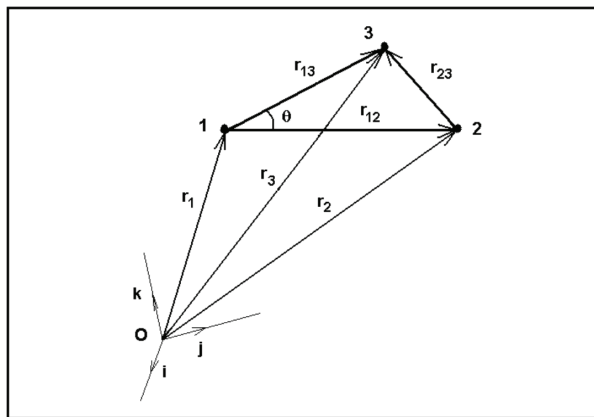


Figure 6.1: Respective positions of the three particles 1, 2 and 3 in the system.

With these new variables, the derivatives of $\ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ and $u(r_{12})$ with respect to $\mathbf{r}_1$ transform as:

$$\frac{\partial}{\partial \mathbf{r}_1} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\partial}{\partial r_{12}} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial r_{12}}{\partial \mathbf{r}_1}, \quad (6.29)$$

$$\frac{\partial u(r_{12})}{\partial \mathbf{r}_1} = \frac{\partial u(r_{12})}{\partial r_{12}} \frac{\partial r_{12}}{\partial \mathbf{r}_1}, \quad (6.30)$$

with:

$$\frac{\partial r_{12}}{\partial \mathbf{r}_1} = \frac{\partial r_{12}}{\partial x_1} \mathbf{i} + \frac{\partial r_{12}}{\partial y_1} \mathbf{j} + \frac{\partial r_{12}}{\partial z_1} \mathbf{k} = \mathbf{grad}_{\mathbf{r}_1} r_{12}. \quad (6.31)$$

Considering that we also have:

$$\frac{\partial r_{12}}{\partial x_1} = -\frac{(x_2 - x_1)}{r_{12}}, \quad (6.32)$$

$$\frac{\partial r_{12}}{\partial y_1} = -\frac{(y_2 - y_1)}{r_{12}}, \quad (6.33)$$

$$\frac{\partial r_{12}}{\partial z_1} = -\frac{(z_2 - z_1)}{r_{12}}, \quad (6.34)$$

it results in the relation:

$$\frac{\partial r_{12}}{\partial \mathbf{r}_1} = -\frac{\mathbf{r}_{12}}{r_{12}}, \quad (6.35)$$

which allows us to write the derivatives of $\ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, $u(r_{12})$ and, by analogy, $u(r_{13})$ as:

$$\frac{\partial}{\partial \mathbf{r}_1} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial}{\partial r_{12}} \ln \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2), \quad (6.36)$$

$$\frac{\partial u(r_{12})}{\partial \mathbf{r}_1} = -\frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial u(r_{12})}{\partial r_{12}}, \quad (6.37)$$

$$\frac{\partial u(r_{13})}{\partial \mathbf{r}_1} = -\frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial u(r_{13})}{\partial r_{13}}. \quad (6.38)$$

Consequently, these early changes of variables yield the following simplified expression for the YBG equation:

$$-\frac{\mathbf{r}_{12}}{r_{12}} \frac{\partial}{\partial r_{12}} \left[k_B T \ln g(r_{12}) + u(r_{12}) \right] = \rho \iint \frac{\mathbf{r}_{13}}{r_{13}} \frac{\partial u(r_{13})}{\partial r_{13}} g(r_{13}) g(r_{23}) d\mathbf{r}_3. \quad (6.39)$$

However, to allow the numerical integration of this equation, it is necessary to remove its vectorial character by considering figure (6.1). Indeed, in this figure we can see that:

$$r_{23}^2 = r_{12}^2 + r_{13}^2 - 2r_{12}r_{13} \cos \theta, \quad (6.40)$$

$$\frac{\mathbf{r}_{12}}{r_{12}} \cdot \frac{\mathbf{r}_{12}}{r_{12}} = 1, \quad (6.41)$$

$$\frac{\mathbf{r}_{13}}{r_{13}} \cdot \frac{\mathbf{r}_{12}}{r_{12}} = \cos \theta = \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}r_{13}}. \quad (6.42)$$

Therefore, the multiplication of equation (6.39) by the unit vector $\frac{\mathbf{r}_{12}}{r_{12}}$ leads directly to the scalar integro-differential equation:

$$\begin{aligned} \frac{\partial}{\partial r_{12}} [k_B T \ln g(r_{12}) + u(r_{12})] = \\ = -\rho \int \int \frac{\partial u(r_{13})}{\partial r_{13}} \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}r_{13}} \right) g(r_{13})g(r_{23})d\mathbf{r}_3. \end{aligned} \quad (6.43)$$

Thus, from the symmetrical form of the integral kernel in equation (6.39), it can be noted that only the projection of the vectorial equation on the axis joining particles 1 and 2 contributes to the result. The integral over $\mathbf{r}_3$ in equation (6.43) is a two-centre integral calculated by using the bipolar coordinates r_{13} and r_{23} . This transformation has already been made in section (5.3). Accordingly, the volume element $d\mathbf{r}_3$ is expressed (Eq. 5.114) as:

$$d\mathbf{r}_3 = 2\pi \frac{r_{13}r_{23}}{r_{12}} dr_{13}dr_{23}, \quad (6.44)$$

and, as regards the limits of integration of r_{13} and r_{23} , it is recommended to choose them as follows:

$$|r_{12} - r_{13}| \leq r_{23} \leq r_{12} + r_{13} \quad \text{and} \quad 0 \leq r_{13} \leq \infty. \quad (6.45)$$

With these new transformations taken into account, the equation (6.43) becomes:

$$\begin{aligned} \frac{\partial}{\partial r_{12}} [k_B T \ln g(r_{12}) + u(r_{12})] = -\pi\rho \int_{r_{13}=0}^{\infty} \frac{\partial u(r_{13})}{\partial r_{13}} g(r_{13}) \times \\ \times \left\{ \int_{r_{23}=|r_{12}-r_{13}|}^{r_{12}+r_{13}} [g(r_{23})-1] \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12}^2} \right) r_{23} dr_{23} \right\} dr_{13}. \end{aligned} \quad (6.46)$$

It should be noted that, conventionally, the pair correlation function $g(r_{23})$ has been replaced by $[g(r_{23}) - 1]$ without any change as $\int \frac{\partial u(r_{13})}{\partial r_{13}} g(r_{13}) d\mathbf{r}_3 \simeq 0$ is obtained by symmetry – see p. 206 of [3]. When $r_{12} < r_{13}$, the integral over r_{23} in brackets must be split into two contributions:

$$\int_{-(r_{12}-r_{13})}^{r_{12}+r_{13}} [\dots] r_{23} dr_{23} = \int_{-(r_{12}-r_{13})}^{r_{12}-r_{13}} [\dots] r_{23} dr_{23} + \int_{r_{12}-r_{13}}^{r_{12}+r_{13}} [\dots] r_{23} dr_{23}. \quad (6.47)$$

However, from the fact that $g(-r_{23}) = g(r_{23})$, the first integral on the right hand side of the previous relation is zero since the integral kernel is an odd function. As a result, the limits for an integration of the integral over r_{23} , in equation (6.46), can simply be replaced by $(r_{12} - r_{13})$ and $(r_{12} + r_{13})$.

To determine $g(r_{12})$, we must yet integrate equation (6.46) over r_{12} , from r_{12} to infinity. Noticing that the integral on the left hand side of this equation tends to zero as $r_{12} \rightarrow \infty$ (by the fact that $g(r_{12}) \rightarrow 1$ and $u(r_{12}) \rightarrow 0$), equation (6.46) becomes:

$$\begin{aligned} - \left[k_B T \ln g(r_{12}) + u(r_{12}) \right] &= -\pi \rho \int_{r_{13}=0}^{\infty} \frac{\partial u(r_{13})}{\partial r_{13}} g(r_{13}) \times \\ &\times \int_{r_{12}}^{\infty} \left\{ \int_{r_{23}=r_{12}-r_{13}}^{r_{12}+r_{13}} [g(r_{23}) - 1] \left(\frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12}^2} \right) r_{23} dr_{23} \right\} dr_{12} dr_{13}. \end{aligned} \quad (6.48)$$

The order of integrations adopted in this multiple integral is r_{23} , r_{12} and r_{13} . We show in what follows that the integral over r_{12} can be expressed in analytical form if the integrals on r_{23} and r_{12} are swapped over. We first consider the integral of general form (Fig. 6.2a):

$$I = \int_a^b \left[\int_{r_{12}-r_{13}}^{r_{12}+r_{13}} F(r_{12}, r_{13}, r_{23}) dr_{23} \right] dr_{12}. \quad (6.49)$$

To reverse the order of integrations over r_{23} and r_{12} , we call on the Fubini theorem to decompose the domain of integration into three distinct regions D_1 , D_2 and D_3 , as shown in figure (6.2b).

The application of this theorem amounts to replacing the integral

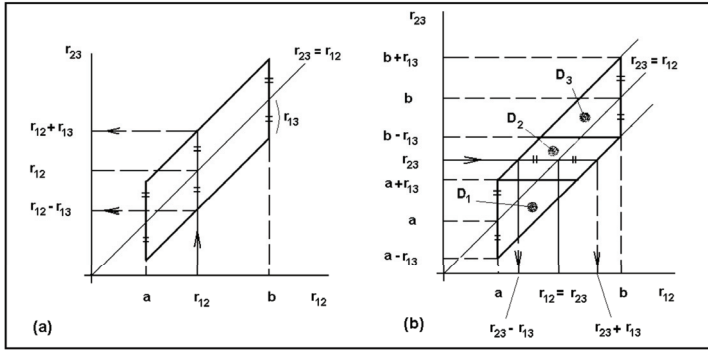


Figure 6.2: Representation of the domains of integration required to reverse the order of integrations over r_{23} and r_{12} .

I by the three following integrals, namely:

$$\begin{aligned}
 I &= \int_{a-r_{13}}^{a+r_{13}} \left[\int_a^{r_{23}+r_{13}} F dr_{12} \right] dr_{23} + \int_{a+r_{13}}^{b-r_{13}} \left[\int_{r_{23}-r_{13}}^{r_{23}+r_{13}} F dr_{12} \right] dr_{23} \\
 &+ \int_{b-r_{13}}^{b+r_{13}} \left[\int_{r_{23}-r_{13}}^b F dr_{12} \right] dr_{23}. \quad (6.50)
 \end{aligned}$$

With the original limits $a = r_{12}$ and $b \rightarrow \infty$, we carry out the calculation of the integral over r_{12} , in the domain D_1 , in the first brackets. The result of this integral is²:

$$\int_a^{r_{23}+r_{13}} F dr_{12} = \int_{r_{12}}^{r_{23}+r_{13}} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12}^2} dr_{12} = \frac{r_{13}^2 - (r_{23} - r_{12})^2}{r_{12}}. \quad (6.51)$$

²After simplifications, the integral in brackets is:

$$\begin{aligned}
 \int_{r_{12}}^{r_{23}+r_{13}} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12}^2} dr_{12} &= \int_{r_{12}}^{r_{23}+r_{13}} dr_{12} + (r_{13}^2 - r_{23}^2) \int_{r_{12}}^{r_{23}+r_{13}} \frac{dr_{12}}{r_{12}^2} \\
 &= (r_{23} + r_{13} - r_{12}) - (r_{13}^2 - r_{23}^2) \left(\frac{1}{r_{23} + r_{13}} - \frac{1}{r_{12}} \right) \\
 &= \frac{r_{13}^2 - (r_{23} - r_{12})^2}{r_{12}}.
 \end{aligned}$$

A similar calculation shows that the integral over r_{12} , in the domain D_2 , in the second brackets is:

$$\int_{r_{23}-r_{13}}^{r_{23}+r_{13}} F dr_{12} = \int_{r_{23}-r_{13}}^{r_{23}+r_{13}} \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{r_{12}^2} dr_{12} = 0. \quad (6.52)$$

With respect to the third term of equation (6.50) defined in the domain D_3 , it is easy to see that it is worth zero, whatever the value of integrand, because the limits of integration over r_{23} are identical when $b \rightarrow \infty$. Consequently, with the foregoing, the integrals over r_{12} in equation (6.50) reduces to the first term, and equation (6.48) simplifies finally to the following expression, which is a unique function of r_{12} , i.e.:

$$k_B T \ln g(r_{12}) + u(r_{12}) = \pi \rho \int_{r_{13}=0}^{\infty} \frac{\partial u(r_{13})}{\partial r_{13}} g(r_{13}) \times \\ \times \left\{ \int_{r_{23}=r_{12}-r_{13}}^{r_{12}+r_{13}} [g(r_{23}) - 1] \left[\frac{r_{13}^2 - (r_{23} - r_{12})^2}{r_{12}} \right] r_{23} dr_{23} \right\} dr_{13}. \quad (6.53)$$

Practically, the *Yvon-Born-Green equation* (Eq. 6.53) is solved numerically by an iterative method. For a given pair potential $u(r)$, an approximate initial form is adopted for the pair correlation functions $g(r_{13})$ and $g(r_{23})$ with the correct limits $g(0) = 0$ and $g(\infty) = 1$. After the first iteration, a new result for the pair correlation function $g(r)$ is obtained and is meant to be used to carry out the second iteration. Then the process is repeated until $g(r)$ converges to a final outcome which does not evolve after a few iterations.

6.2 The fluctuation-dissipation theorem

The poor quality of the YBG equation at high densities is attributed to the Kirkwood approximation. Attempts have been made to modify this approximation [59, 60], but no significant improvement in the results has been obtained. In any case, a new family of integral equations has been developed later. These are based on the Ornstein-Zernike (OZ) relationship, which does not require the Kirkwood approximation, but uses a new correlation function, called *direct correlation function* $c(r)$.

We have, among the integral equations, some more or less effective equations established by very different methods, such as the

field theory [61], the theory of functional derivative [62], the analysis of diagrams [63]. Each one of these equations is to be used as an auxiliary equation supplementing Ornstein–Zernike’s relationship [64] which was introduced heuristically well before the integral equation method. Here, the formalism of functional derivatives has been chosen to establish the integral equations on firm footing. We have taken advantage of this brief overview of the functional derivative technique to outline the fluctuation-dissipation theorem through the determination of the linear density response of a system to an external perturbation.

Functional derivatives

A *functional* is a correspondence law F associating with a function $f(x)$ defined on the given interval $[a, b]$ a specific value I of a real number. The functional differs from the *function* which establishes a correspondence between numbers, and from the *operator* which establishes a correspondence between functions³. The most common example of a functional is the definite integral:

$$I = F[f(x)] = \int_a^b f(x) dx. \quad (6.54)$$

Among the operations on functionals, one of the most important is the *functional derivative*. It is a natural extension of the notion of derivative defined as follows: to the variation $\delta f(x)$ of the function $f(x)$ corresponds a variation of the number I , i.e. the variation $\delta F[f(x)]$

³Given the function $y = f(x)$, we can think of two types of variations of y , one associated with x , the other one with f . For a given function $f(x)$, the ordinary differential calculus measures the rates at which the quantities dx and dy change. Similarly, in a fixed domain of x , the functional variation dy measures how the value y changes as a function of the functional form $f(x)$. This is the variation studied in variational calculus.

The functional is related to the calculus of variations proposed and solved in the late 17th century by Leibniz, L’Hôpital, Newton and Euler. For instance, in classical mechanics, the Lagrangian L is expressed in terms of the generalized coordinates $q(x; t)$ and their temporal derivatives $\dot{q}(x; t)$. The well-known equations of motion $\frac{\delta A[q]}{\delta q(t)} = \frac{\partial L}{\partial q} - \frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{q}} = 0$ are obtained from extremizing the action functional $A[q] = \int L(q, \dot{q}; t) dt$. As another example, the Helmholtz free energy of a system is a functional of the local particle density, as in section (5.8).

of the functional. The functional derivative, denoted as $\frac{\delta F}{\delta f(x)}$, is defined by the general relation

$$\delta F = \int_a^b \frac{\delta F}{\delta f(x)} \delta f(x) dx. \quad (6.55)$$

For the functional of equation (6.54), this relation is written:

$$F + \delta F = \int_a^b [f(x) + \delta f(x)] dx, \quad (6.56)$$

where the variation of the functional is $\delta F = \int_a^b \delta f(x) dx$ and the functional derivative $\frac{\delta F}{\delta f(x)} = 1$.

It is important to note that the calculation of the functional derivative should be performed only with the linear term in $\delta f(x)$. To clarify this question, consider the functional:

$$F[f(x)] = \int_a^b (\sin x)^2 dx, \quad (6.57)$$

where $f(x) = \sin x$. As an example, if the variation of the function is $\delta f(x) = \alpha x^3$ (where α is a parameter whose value is low), the increase ΔF of the functional is calculated with the formula:

$$\begin{aligned} F + \Delta F &= \int_a^b (\sin x + \alpha x^3)^2 dx \\ &= \int_a^b (\sin x)^2 dx + \int_a^b 2(\sin x)(\alpha x^3) dx + \int_a^b (\alpha x^3)^2 dx. \end{aligned} \quad (6.58)$$

Thus, while the increasing ΔF of the functional is:

$$\Delta F = \int_a^b (2 \sin x) (\alpha x^3) dx + \int_a^b (\alpha x^3)^2 dx, \quad (6.59)$$

the variation δF depends only on the linear term in $\delta f(x) = \alpha x^3$, namely:

$$\delta F = \int_a^b (2 \sin x) (\alpha x^3) dx, \quad (6.60)$$

and the functional derivative is expressed as:

$$\frac{\delta F}{\delta f(x)} = 2 \sin x. \quad (6.61)$$

Here the functional derivative is a function of x . However, more generally, it can also be a functional of $f(x)$ and this is the reason why it is better to note it as follows:

$$\frac{\delta F}{\delta f(x)} = A[f(x), x] \quad \text{with} \quad F = \int_a^b A[f(x), x] \delta f(x) dx. \quad (6.62)$$

The concept of functional derivative can be extended to vectorial functions defined in a given volume. If the functional is $F[f(\mathbf{r})]$, its functional derivative is:

$$\frac{\delta F}{\delta f(\mathbf{r})} = A[f(\mathbf{r}), \mathbf{r}] \quad \text{with} \quad \delta F = \int_V A[f(\mathbf{r}), \mathbf{r}] \delta f(\mathbf{r}) d\mathbf{r}. \quad (6.63)$$

The notion of functional derivative may also be extended to vectorial functions of several variables as well as to the derivatives of superior order. A particularly important case appears when the functional is in the form⁴ $F[\prod_{i=1}^N f(\mathbf{r}_i)]$. The variation $\delta f(\mathbf{r})$ generates the variation δF of the functional defined by the relation:

$$F + \delta F = \int \dots \int \prod_{i=1}^N [f(\mathbf{r}_i) + \delta f(\mathbf{r}_i)] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (6.64)$$

where the expansion to first order reduces to⁵:

⁴See, for instance, the integral configuration $Z_N(T, V)$, which is a functional of the potential energy of the system when decomposed into a sum of pair potentials:

$$Z_N(T, V) = \iint \exp\left[-\beta \sum_{i < j} u(r_{ij})\right] d\mathbf{r}^N = \iint \prod_{i < j} \exp[-\beta u(r_{ij})] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N.$$

⁵The integrand is written as:

$$\begin{aligned} \prod_{i=1}^N [f(\mathbf{r}_i) + \delta f(\mathbf{r}_i)] &= f(\mathbf{r}_1)f(\mathbf{r}_2)\dots f(\mathbf{r}_N) + \delta f(\mathbf{r}_1)[f(\mathbf{r}_2)f(\mathbf{r}_3)\dots f(\mathbf{r}_N)] \\ &\quad + \delta f(\mathbf{r}_2)[f(\mathbf{r}_1)f(\mathbf{r}_3)\dots f(\mathbf{r}_N)] + \delta f(\mathbf{r}_3)[f(\mathbf{r}_1)f(\mathbf{r}_2)\dots f(\mathbf{r}_N)] + \dots, \end{aligned}$$

or:

$$\begin{aligned} \prod_{i=1}^N [f(\mathbf{r}_i) + \delta f(\mathbf{r}_i)] &= f(\mathbf{r}_1)f(\mathbf{r}_2)\dots f(\mathbf{r}_N) + \frac{\delta f(\mathbf{r}_1)}{f(\mathbf{r}_1)} [f(\mathbf{r}_1)f(\mathbf{r}_2)f(\mathbf{r}_3)\dots f(\mathbf{r}_N)] \\ &\quad + \frac{\delta f(\mathbf{r}_2)}{f(\mathbf{r}_2)} [f(\mathbf{r}_1)f(\mathbf{r}_2)f(\mathbf{r}_3)\dots f(\mathbf{r}_N)] + \frac{\delta f(\mathbf{r}_3)}{f(\mathbf{r}_3)} [f(\mathbf{r}_1)f(\mathbf{r}_2)f(\mathbf{r}_3)\dots f(\mathbf{r}_N)] + \dots, \end{aligned}$$

$$\begin{aligned}
F + \delta F &= \int \dots \int \prod_{i=1}^N f(\mathbf{r}_i) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \\
&\quad + \int \dots \int \sum_{j=1}^N \frac{\delta f(\mathbf{r}_j)}{f(\mathbf{r}_j)} \prod_{i=1}^N f(\mathbf{r}_i) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (6.65)
\end{aligned}$$

Since the discrete sum over j has N terms and all the terms of the sum are equal, we can write:

$$\sum_{j=1}^N \frac{\delta f(\mathbf{r}_j)}{f(\mathbf{r}_j)} = N \frac{\delta f(\mathbf{r}_1)}{f(\mathbf{r}_1)}, \quad (6.66)$$

where $j = 1$, so that the variation of the functional becomes:

$$\delta F = \int_V \left[\int \dots \int N \prod_{i=2}^N f(\mathbf{r}_i) d\mathbf{r}_2 \dots d\mathbf{r}_N \right] \delta f(\mathbf{r}_1) d\mathbf{r}_1. \quad (6.67)$$

Owing to equation (6.63), the functional derivative with respect to $\delta f(\mathbf{r}_1)$ is extracted from the above relation, namely:

$$\frac{\delta F}{\delta f(\mathbf{r}_1)} = A[f(\mathbf{r}^N), \mathbf{r}_1] = N \int \dots \int \prod_{i=2}^N f(\mathbf{r}_i) d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (6.68)$$

Regarding the second functional derivative of F with respect to $\delta f(\mathbf{r}_2)$, it is defined by:

$$\frac{\delta A}{\delta f(\mathbf{r}_2)} = \frac{\delta^2 F}{\delta f(\mathbf{r}_2) \delta f(\mathbf{r}_1)} = B[f(\mathbf{r}^N), \mathbf{r}_1, \mathbf{r}_2], \quad (6.69)$$

$$\text{with} \quad \delta A = \int_V B[f(\mathbf{r}^N), \mathbf{r}_1, \mathbf{r}_2] \delta f(\mathbf{r}_2) d\mathbf{r}_2. \quad (6.70)$$

As the second derivative $\frac{\delta A}{\delta f(\mathbf{r}_2)}$ depends on the two variables $\mathbf{r}_1$ and $\mathbf{r}_2$, it can be written in a matrix form. And since the inverse of this

$$\text{and finally:} \quad \prod_{i=1}^N [f(\mathbf{r}_i) + \delta f(\mathbf{r}_i)] = \prod_{i=1}^N f(\mathbf{r}_i) + \sum_{j=1}^N \frac{\delta f(\mathbf{r}_j)}{f(\mathbf{r}_j)} \prod_{i=1}^N f(\mathbf{r}_i).$$

derivative, $\frac{\delta f(\mathbf{r}_2)}{\delta A}$ is equal to the inverse matrix, both matrices obey the following important relation [65]:

$$\int \frac{\delta A[f(\mathbf{r}^N), \mathbf{r}_1, \mathbf{r}_3]}{\delta f(\mathbf{r}_3)} \frac{\delta f(\mathbf{r}_3)}{\delta A[f(\mathbf{r}^N), \mathbf{r}_2, \mathbf{r}_3]} d\mathbf{r}_3 = \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (6.71)$$

where the right hand side of the above relation is equal to the Dirac function. It should be mentioned that, if A and B are two independent functionals, the above relation is generalized as:

$$\int \frac{\delta A[f(\mathbf{r}^N), \mathbf{r}_1, \mathbf{r}_3]}{\delta f(\mathbf{r}_3)} \frac{\delta f(\mathbf{r}_3)}{\delta B[f(\mathbf{r}^N), \mathbf{r}_2, \mathbf{r}_3]} d\mathbf{r}_3 = \frac{\delta A[f(\mathbf{r}^N), \mathbf{r}_1]}{\delta B[f(\mathbf{r}^N), \mathbf{r}_2]}. \quad (6.72)$$

Finally, note that the definition of the functional derivatives allows us to write a formula similar to the Maclaurin series, which reads:

$$\begin{aligned} F[f(\mathbf{r}), \mathbf{r}_1] &= F[0, \mathbf{r}_1] + \int \left\{ \frac{\delta F[f(\mathbf{r}), \mathbf{r}_1]}{\delta f(\mathbf{r}_2)} \right\}_{f=0} \delta f(\mathbf{r}_2) d\mathbf{r}_2 \\ &+ \frac{1}{2!} \int \int \left\{ \frac{\delta^2 F[f(\mathbf{r}), \mathbf{r}_1]}{\delta f(\mathbf{r}_2) \delta f(\mathbf{r}_3)} \right\}_{f=0} \delta f(\mathbf{r}_2) \delta f(\mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3 + \dots \end{aligned} \quad (6.73)$$

Application: linear density response to an external perturbation

The formalism of the functional derivatives can be used to justify the OZ direct correlation function. However, it occasionally enables us to determine the very important fluctuation-dissipation theorem, i.e. the linear density response of a liquid to a weak external perturbation. To show this, consider a liquid whose Hamiltonian is:

$$H_N(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\mathbf{r}^N) + \sum_{i=1}^N \phi(\mathbf{r}_i), \quad (6.74)$$

where, as usual, $U(\mathbf{r}^N)$ is the sum of pair potentials and $\phi(\mathbf{r}_i)$ an arbitrary one-body potential applied to each particle of the system and depending only on the positions of particles. According to equation (3.80), the partition function of the system is:

$$Q_N(V, T) = \frac{1}{N!} \frac{1}{\Lambda^{3N}} Z_N(V, T),$$

with

$$Z_N(V, T) = \int \dots \int \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}^N. \quad (6.75)$$

Assuming that the partition function $Q_N(V, T)$ is a functional of $\phi(\mathbf{r}_i)$, the variation of $\ln Q_N[\phi]$ due to a small variation $\delta\phi(\mathbf{r}_j)$ of the applied potential is equal to:

$$\delta \ln Q_N[\phi] = \delta \ln Z_N[\phi] = \frac{\delta Z_N[\phi]}{Z_N[\phi]}, \quad (6.76)$$

and the expansion of the variation of the configuration integral to the first order in $\delta\phi(\mathbf{r}_j)$ is expressed as⁶:

$$\delta Z_N[\phi] = \int \dots \int \left[-\beta \sum_{j=1}^N \delta\phi(\mathbf{r}_j) \right] \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}^N. \quad (6.77)$$

As the N terms of the discrete sum over j give the same contribution, we can still write $\sum_{j=1}^N \delta\phi(\mathbf{r}_j) = N\delta\phi(\mathbf{r}_1)$ and express the variation of the functional $\ln Q_N[\phi]$ as follows:

⁶The expansion of the exponential to first order enables us to write the variation of the functional as follows:

$$\begin{aligned} Z + \delta Z &= \int \dots \int \exp \left\{ -\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N [\phi(\mathbf{r}_i) + \delta\phi(\mathbf{r}_i)] \right\} d\mathbf{r}^N \\ &= \int \dots \int \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] \exp \left[-\beta \sum_{i=1}^N \delta\phi(\mathbf{r}_i) \right] d\mathbf{r}^N \\ &= \int \dots \int \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] \left[1 - \beta \sum_{i=1}^N \delta\phi(\mathbf{r}_i) - \dots \right] d\mathbf{r}^N, \end{aligned}$$

$$\text{hence} \quad \delta Z = \int \dots \int \left[-\beta \sum_{i=1}^N \delta\phi(\mathbf{r}_i) \right] \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}^N.$$

$$\begin{aligned}
\delta \ln Q_N[\phi] &= -\frac{\beta N}{Z_N[\phi]} \int \dots \int \delta\phi(\mathbf{r}_1) \exp\left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i)\right] d\mathbf{r}^N \\
&= -\beta \int_V \left\{ \frac{N!}{(N-1)!} \frac{1}{Z_N[\phi]} \times \right. \\
&\quad \times \left. \int \dots \int \exp\left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i)\right] d\mathbf{r}_2 \dots d\mathbf{r}_N \right\} \delta\phi(\mathbf{r}_1) d\mathbf{r}_1. \quad (6.78)
\end{aligned}$$

However, the expression in brackets coincides with the generic distribution function for one particle (Eq. 3.83) in presence of the applied potential, that is to say:

$$\begin{aligned}
\rho_N^{(1)}[\phi, \mathbf{r}_1] &= \frac{N!}{(N-1)!} \frac{1}{Z_N[\phi]} \times \\
&\quad \times \int \dots \int \exp\left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i)\right] d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (6.79)
\end{aligned}$$

and it also represents the functional derivative (Eq. 6.67) of $\ln Q_N[\phi]$ with respect to $\delta\phi(\mathbf{r}_1)$:

$$\rho_N^{(1)}[\phi, \mathbf{r}_1] = -\frac{1}{\beta} \frac{\delta \ln Q_N[\phi]}{\delta\phi(\mathbf{r}_1)} = \frac{\delta F[\phi]}{\delta\phi(\mathbf{r}_1)}. \quad (6.80)$$

This relation provides a new interpretation of the generic distribution function for one particle $\rho_N^{(1)}[\phi, \mathbf{r}_1]$. Indeed, as $F[\phi] = -k_B T \ln Q_N[\phi]$ is equal to the Helmholtz free energy (Eq. 2.102), $\rho_N^{(1)}[\phi, \mathbf{r}_1]$ is clearly related to the functional derivative of the free energy of the system with respect to the applied potential when it is very small.

Now we calculate the functional derivative of $\rho_N^{(1)}[\phi, \mathbf{r}_1]$. Its variation is written, by means of equation (6.79), as:

$$\delta\rho_N^{(1)}[\phi, \mathbf{r}_1] = N\delta\left\{ \frac{X[\phi]}{Z_N[\phi]} \right\}, \quad (6.81)$$

where $X[\phi]$ is defined, with the help of equation (6.79), by the relation:

$$X[\phi] = \int \dots \int \exp\left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i)\right] d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (6.82)$$

As for the configuration integral (Eq. 6.77), use is made of the expansion of the variation of the functional $X[\phi]$ to the first order (see the previous footnote):

$$\delta X[\phi] = \int \dots \int \left[-\beta \sum_{i=1}^N \delta \phi(\mathbf{r}_i) \right] \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (6.83)$$

In using equation (6.81), we are now in a position to calculate the variation of the generic distribution function for one particle $\delta \rho_N^{(1)}[\phi, \mathbf{r}_1]$ in regards to the variation $\delta \phi$ of the applied potential. It is written:

$$\delta \rho_N^{(1)}[\phi, \mathbf{r}_1] = N \left[\frac{\delta X[\phi] Z_N[\phi] - \delta Z_N[\phi] X[\phi]}{Z_N^2[\phi]} \right]. \quad (6.84)$$

With the functionals $Z_N[\phi]$ and $X[\phi]$ together with their variations $\delta Z_N[\phi]$ and $\delta X[\phi]$ at our disposal, we can make the appropriate simplifications by substituting the terms in brackets of equation (6.84) by their respective expressions. Owing to equations (6.75) and (6.83), the first contribution is transformed as:

$$\begin{aligned} N \frac{\delta X[\phi] Z_N[\phi]}{Z_N^2[\phi]} &= \frac{-N\beta}{Z_N[\phi]} \int \dots \int \left[\delta \phi(\mathbf{r}_1) + \sum_{j=2}^N \delta \phi(\mathbf{r}_j) \right] \times \\ &\times \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N, \end{aligned} \quad (6.85)$$

and written as:

$$\begin{aligned} N \frac{\delta X[\phi] Z_N[\phi]}{Z_N^2[\phi]} &= -\frac{N\beta}{Z_N[\phi]} \int \dots \int \delta \phi(\mathbf{r}_1) \times \\ &\times \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N \\ &- \frac{N\beta}{Z_N[\phi]} \int \dots \int \sum_{j=2}^N \delta \phi(\mathbf{r}_j) \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N. \end{aligned} \quad (6.86)$$

Whereas the $(N-1)$ terms of the sum over j give the same contribution, we can set $\sum_{j=2}^N \delta \phi(\mathbf{r}_j) = (N-1)\delta \phi(\mathbf{r}_2)$ and simplify the above relation as:

$$\begin{aligned}
N \frac{\delta X[\phi] Z_N[\phi]}{Z_N^2[\phi]} &= -\beta \delta\phi(\mathbf{r}_1) \left\{ \frac{N}{Z_N[\phi]} \int \dots \int \times \right. \\
&\quad \times \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N \Big\} \\
&\quad - \beta \int_V \left\{ \frac{N(N-1)}{Z_N[\phi]} \int \dots \int \exp \left[-\beta U(\mathbf{r}^N) \right. \right. \\
&\quad \left. \left. - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_3 \dots d\mathbf{r}_N \right\} \delta\phi(\mathbf{r}_2) d\mathbf{r}_2. \quad (6.87)
\end{aligned}$$

However, the expression in the first brackets of the above equation is the generic distribution function for one particle $\rho_N^{(1)}[\phi, \mathbf{r}_1]$ in presence of the applied potential (Eq. 6.79), and the expression in between the second brackets is the generic distribution function for two particles $\rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2]$. Therefore, the first contribution of equation (6.84) reduces to the expression:

$$N \frac{\delta X[\phi] Z_N[\phi]}{Z_N^2[\phi]} = -\beta \delta\phi(\mathbf{r}_1) \rho_N^{(1)}[\phi, \mathbf{r}_1] - \beta \int_V \rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] \delta\phi(\mathbf{r}_2) d\mathbf{r}_2. \quad (6.88)$$

As regards the second contribution of equation (6.84), it is written with equations (6.77) and (6.82) in the following manner:

$$\begin{aligned}
N \frac{\delta Z_N[\phi] X[\phi]}{Z_N^2[\phi]} &= \frac{N}{Z_N^2[\phi]} \int \dots \int \left[-\beta \sum_{j=1}^N \delta\phi(\mathbf{r}_j) \right] \times \\
&\quad \times \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}^N \times \\
&\quad \times \int \dots \int \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (6.89)
\end{aligned}$$

If the first integral of this equation is ingeniously decomposed in taking $\sum_{j=1}^N \delta\phi(\mathbf{r}_j) = N\delta\phi(\mathbf{r}_2)$, it results in:

$$\begin{aligned}
N \frac{\delta Z_N[\phi] X[\phi]}{Z_N^2[\phi]} &= -\beta \int_V \left\{ \frac{N}{Z_N[\phi]} \times \right. \\
&\times \int \dots \int \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_1 d\mathbf{r}_3 \dots d\mathbf{r}_N \left. \right\} \delta\phi(\mathbf{r}_2) d\mathbf{r}_2 \times \\
&\times \left\{ \frac{N}{Z_N[\phi]} \int \dots \int \exp \left[-\beta U(\mathbf{r}^N) - \beta \sum_{i=1}^N \phi(\mathbf{r}_i) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N \right\}. \quad (6.90)
\end{aligned}$$

Since the expressions in brackets are the generic distribution functions for one particle $\rho_N^{(1)}[\phi, \mathbf{r}_2]$ and $\rho_N^{(1)}[\phi, \mathbf{r}_1]$, respectively, the above relation reduces to:

$$N \frac{\delta Z_N[\phi] X[\phi]}{Z_N^2[\phi]} = -\beta \int_V \rho_N^{(1)}[\phi, \mathbf{r}_2] \rho_N^{(1)}[\phi, \mathbf{r}_1] \delta\phi(\mathbf{r}_2) d\mathbf{r}_2. \quad (6.91)$$

Combining now equations (6.91), (6.88) and (6.84), we obtain the variation of the generic distribution function for one particle, $\delta\rho_N^{(1)}[\phi, \mathbf{r}_1]$:

$$\begin{aligned}
\delta\rho_N^{(1)}[\phi, \mathbf{r}_1] &= -\beta \delta\phi(\mathbf{r}_1) \rho_N^{(1)}[\phi, \mathbf{r}_1] - \beta \int_V \rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] \delta\phi(\mathbf{r}_2) d\mathbf{r}_2 \\
&+ \beta \int_V \rho_N^{(1)}[\phi, \mathbf{r}_2] \rho_N^{(1)}[\phi, \mathbf{r}_1] \delta\phi(\mathbf{r}_2) d\mathbf{r}_2, \quad (6.92)
\end{aligned}$$

or equivalently:

$$\begin{aligned}
\delta\rho_N^{(1)}[\phi, \mathbf{r}_1] &= -\beta \delta\phi(\mathbf{r}_1) \rho_N^{(1)}[\phi, \mathbf{r}_1] - \beta \int_V \left[\rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] \right. \\
&\left. - \rho_N^{(1)}[\phi, \mathbf{r}_2] \rho_N^{(1)}[\phi, \mathbf{r}_1] \right] \delta\phi(\mathbf{r}_2) d\mathbf{r}_2. \quad (6.93)
\end{aligned}$$

This equation is a very important relation of the liquid theory. It not only allows the deduction of the Ornstein–Zernike relation, as will be shown in the following section, but also provides a way to calculate the response of the density of homogeneous and isotropic liquids subject to a weak external perturbation. Indeed, if the generic

distribution functions are expressed in terms of the particle density ρ and the pair correlation function, equation (6.93) is simplified to:

$$\delta\rho_N^{(1)}[\phi, \mathbf{r}_1] = -\beta\rho\delta\phi(\mathbf{r}_1) - \beta\int_V \left[\rho^2 g_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] - \rho^2 \right] \delta\phi(\mathbf{r}_2) d\mathbf{r}_2. \quad (6.94)$$

Taking the Fourier transform of the above relation, with the use of the convolution theorem⁷, it is found that:

$$\begin{aligned} \delta\rho^{(1)}(\mathbf{q}) &= -\beta\rho\delta\phi(\mathbf{q}) - \beta\rho[S(\mathbf{q}) - 1]\delta\phi(\mathbf{q}) \\ &= -\beta\rho S(\mathbf{q})\delta\phi(\mathbf{q}). \end{aligned} \quad (6.95)$$

This relation yields the linear response of density to a weak external perturbation within the reciprocal configuration space, in the simple form:

$$\delta\rho^{(1)}(\mathbf{q}) = \chi^{(1)}(\mathbf{q})\delta\phi(\mathbf{q}) \quad (6.96)$$

$$\text{where} \quad \chi^{(1)}(\mathbf{q}) = -\beta\rho S(\mathbf{q}). \quad (6.97)$$

The function $\chi^{(1)}(\mathbf{q})$, called *linear response function*, is directly proportional to the static structure factor $S(\mathbf{q})$ of the system. This result represents a specific aspect of the *fluctuation-dissipation theorem*. In this context, it gives particular meaning to the structure factor of liquids which thus becomes the linear response of the system with respect to the particle density.

⁷One multiplies both sides of the above equation by $\exp(i\mathbf{q}\cdot\mathbf{r}_1)d\mathbf{r}_1$ and perform the integration over $\mathbf{r}_1$:

$$\begin{aligned} \int \delta\rho_N^{(1)}[\phi, \mathbf{r}_1] \exp(i\mathbf{q}\cdot\mathbf{r}_1) d\mathbf{r}_1 &= -\beta\rho \int \delta\phi(\mathbf{r}_1) \exp(i\mathbf{q}\cdot\mathbf{r}_1) d\mathbf{r}_1 \\ &\quad - \beta\rho^2 \int \left[g_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] - 1 \right] \exp[\mathbf{q}\cdot(\mathbf{r}_1 - \mathbf{r}_2)] \delta\phi(\mathbf{r}_2) \exp(i\mathbf{q}\cdot\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned}$$

Then, in using the changes of variables $\mathbf{r}_2 = \mathbf{r}_2$ and $\mathbf{r}_{21} = \mathbf{r}_1 - \mathbf{r}_2$ in the integral of convolution, for which the Jacobian is equal to unity, the above equation becomes:

$$\begin{aligned} \delta\rho^{(1)}(\mathbf{q}) &= -\beta\rho\delta\phi(\mathbf{q}) - \beta\rho[S(\mathbf{q}) - 1]\delta\phi(\mathbf{q}), \\ \text{where} \quad \delta\rho^{(1)}(\mathbf{q}) &= \int \delta\rho_N^{(1)}[\phi, \mathbf{r}] \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r}, \\ \delta\phi(\mathbf{q}) &= \int \delta\phi(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r}, \quad S(\mathbf{q}) - 1 = \rho \int [g(r) - 1] \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r}. \end{aligned}$$

6.3 The Ornstein-Zernike direct correlation function

Statement of the problem

Before defining the direct correlation functions required to obtain the Ornstein-Zernike relation [66, 67], it seems useful to make some comments on the density functional theory (DFT). Its concept was already contained in the van der Waals square-gradient model although had actually been incorporated into quantum mechanics to study the electron gas by Thomas [10] and Fermi [11]. These authors noted that the energy of the free electrons in the field of ions can be calculated directly with the electron density profile without having recourse to the electronic wave functions. Indeed, the variational method used by Thomas and Fermi to minimize the total energy provides an alternative to the Schrödinger equation to calculate the electronic energy.

Although the method has been used for many years as an application of a simple recipe, its theoretical foundations have been furnished in the early 60's by Kohn, Hohenberg and Sham [68], [69]. These authors rigorously demonstrated that, in an inhomogeneous system at equilibrium, the variation of the particle density $\rho(\mathbf{r})$ is usually set by applying the one-body potential $\phi(\mathbf{r})$ to the system, thus causing the one-body potential $\phi(\mathbf{r})$ to be bijectively associated to the particle density profile $\rho(\mathbf{r})$. This means for an electronic system that the ground state energy E is a unique functional of the electron density, i.e. $E = E[\rho(\mathbf{r})]$. For details on the DFT, the reader should consult the following article [70].

For a classical system, the DFT is formulated in the grand canonical ensemble at temperature T , volume V and chemical potential μ constant. The grand partition function (Eq. 2.38) is written by considering the external potential $\phi(\mathbf{r})$ as in the preceding subsection. Its explicit form is:

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \iint_{6N} \exp \left[-\beta H_N(\mathbf{r}^N, \mathbf{p}^N) - \beta \sum_{i=1}^N [\phi(\mathbf{r}_i) - \mu] \right] d\mathbf{r}^N d\mathbf{p}^N, \quad (6.98)$$

where all the ingredients have been defined previously. The grand partition function is used to define the grand potential Ω , by analogy with equation (2.102) established for the canonical ensemble. It reads:

$$\Omega = -\frac{1}{\beta} \ln \Xi. \quad (6.99)$$

Compared to equation (2.38), the grand partition function Ξ is a function of temperature and volume, and a functional of the one-body potential $\phi(\mathbf{r})$. It is the same for $\Omega[\phi(\mathbf{r})]$ which is also a functional of the one-body potential $\phi(\mathbf{r})$. By analogy with equation (6.80) which was obtained for the canonical ensemble, it is not difficult to accept the expression of the distribution function of a generic particle for the grand canonical ensemble:

$$\rho^{(1)}[\phi, \mathbf{r}_1] = -\frac{1}{\beta} \frac{\delta \ln \Xi[\phi]}{\delta \phi(\mathbf{r}_1)} = \frac{\delta \Omega[\phi]}{\delta \phi(\mathbf{r}_1)}. \quad (6.100)$$

Without going into the details of the theory [48], it is possible to summarize the main result as follows. As $\Omega[\phi(\mathbf{r})]$ is a functional of the one-body potential $\phi(\mathbf{r})$ and there is a correspondence between $\phi(\mathbf{r})$ and $\rho(\mathbf{r})$, it is convenient to introduce a new functional depending only on $\rho(\mathbf{r})$, called the *intrinsic Helmholtz free energy* $F_I[\rho(\mathbf{r})]$, and defined by the relation:

$$F_I[\rho(\mathbf{r})] = \Omega[\phi(\mathbf{r})] - \int [\phi(\mathbf{r}) - \mu] \rho(\mathbf{r}) d\mathbf{r}. \quad (6.101)$$

This relation is a Legendre transformation (section 2.2), in which the thermodynamic variables are functions, and which transforms the functional $\Omega[\phi(\mathbf{r}) - \mu]$ into $F_I[\rho(\mathbf{r})]$ in the same manner as $E = E(S, V)$ is transformed into $F = F(T, V)$ – with the relation $F = E - TS$. Equation (6.101) reflects the fact that $F_I[\rho(\mathbf{r})]$ remains unchanged whatever the form of the one-body potential, that is to say that the intrinsic Helmholtz free energy $F_I[\rho(\mathbf{r})]$ is a quantity specific to the system but still independent of the external action. As far as the functional Ω is concerned, it can be expressed in terms of either $\phi(\mathbf{r})$ or $\rho(\mathbf{r})$.

To determine the particle density profile at equilibrium, it is sufficient to apply the variational principle to the functional $\Omega[\rho(\mathbf{r})]$ stipulating the cancellation of the functional derivative of $\Omega[\rho(\mathbf{r})]$ with

respect to the particle density $\rho(\mathbf{r})$, i.e. $\frac{\delta\Omega[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} = 0$. As in the case of the variational Gibbs–Bogoliubov method (Eq. 5.199), we note that the minimum value $\Omega[\rho(\mathbf{r})]_{(\min)}$ of the functional coincides with the grand potential Ω and the function $\rho(\mathbf{r})$ corresponds to the particle density profile $\rho(\mathbf{r})_{(eq)}$ at equilibrium. This minimum condition modifies immediately equation (6.101) as follows:

$$\frac{\delta F_I[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} = \mu - \phi(\mathbf{r}). \quad (6.102)$$

Knowing the chemical potential μ and the applied potential $\phi(\mathbf{r})$, and using an expression of the intrinsic Helmholtz free energy functional $F_I[\rho(\mathbf{r})]$, it is possible to deduce the equilibrium density profile $\rho(\mathbf{r})_{(eq)}$ by solving the above equation. This equation is formally equivalent to the principle of equilibrium of a inhomogeneous phase established by van der Waals (section 5.8). The difficulty of the DFT lies in the choice of functional $F_I[\rho(\mathbf{r})]$. In practice, the intrinsic Helmholtz free energy functional $F_I[\rho(\mathbf{r})]$ is split into two parts: a first contribution, $F_I^{\text{ex}}[\rho(\mathbf{r})]$, which includes all the correlations between particles and a second contribution, $F_I^{\text{id}}[\rho(\mathbf{r})]$, which does not contain them:

$$F_I[\rho(\mathbf{r})] = F_I^{\text{id}}[\rho(\mathbf{r})] + F_I^{\text{ex}}[\rho(\mathbf{r})]. \quad (6.103)$$

These two contributions, called the *excess* and *ideal* parts, are analogous to the excess thermodynamic functions relative to the ideal gas. Here, the excess intrinsic free energy functional $F_I^{\text{ex}}[\rho(\mathbf{r})]$ provides a measure of the non-ideality in terms of particle correlations. However, being that there is no correlation between particles of an ideal gas, it is legitimate to think that a density change in the system affects the excess intrinsic free energy functional $F_I^{\text{ex}}[\rho(\mathbf{r})]$, whereas it has no effect on the ideal contribution. Even if $F_I^{\text{id}}[\rho(\mathbf{r})]$ is very well known, the excess intrinsic free energy functional $F_I^{\text{ex}}[\rho(\mathbf{r})]$ rests the unknown one, which has to be searched out by developing approximations specific to systems under study, i.e. to the pair potential models used [71, 72, 73]. For instance, a typical expression for the excess intrinsic free energy functional is given by the van der Waals square-gradient model (Eq. 5.226).

After this digression on the density functional theory, we define the direct correlation functions which characterize the response of the intrinsic free energy functional $F_I[\rho(\mathbf{r})]$ to a change in density $\rho(\mathbf{r})$.

In particular, the *direct correlation function for one-particle* $c^{(1)}(\mathbf{r})$ is defined by the equation:

$$c^{(1)}(\mathbf{r}) = -\beta \frac{\delta F_I^{\text{ex}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (6.104)$$

However, the functional derivative of $F_I^{\text{ex}}[\rho(\mathbf{r})]$ with respect to the variation of $\rho(\mathbf{r})$ can also be written with equation (6.102) under the form:

$$\begin{aligned} \frac{\delta F_I^{\text{ex}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} &= \frac{\delta F_I[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} - \frac{\delta F_I^{\text{id}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \mu - \phi(\mathbf{r}) - \mu^{\text{id}} \\ &= \mu^{\text{ex}} - \phi(\mathbf{r}), \end{aligned} \quad (6.105)$$

where, according to equation (5.48), the chemical potential of the ideal gas is $\mu^{\text{id}} = \frac{1}{\beta} \ln [\rho(\mathbf{r})\Lambda^3]$. Therefore, by combining equations (6.104) and (6.105), we obtain the expression of the direct correlation function for the one-particle case:

$$\begin{aligned} c^{(1)}(\mathbf{r}) &= -\beta\mu^{\text{ex}} + \beta\phi(\mathbf{r}), \\ &= -\beta\mu + \ln [\rho(\mathbf{r})\Lambda^3] + \beta\phi(\mathbf{r}), \end{aligned} \quad (6.106)$$

as well as the chemical potential:

$$\beta\mu = \ln [\rho(\mathbf{r})\Lambda^3] + \beta\phi(\mathbf{r}) - c^{(1)}(\mathbf{r}). \quad (6.107)$$

Thus, the chemical potential $\beta\mu$ of an inhomogeneous system consists of two terms: the ideal gas term $\ln [\rho(\mathbf{r})\Lambda^3]$, excluding the particle correlations, and the excess chemical potential $\beta\mu^{\text{ex}} (= \beta\phi(\mathbf{r}) - c^{(1)}(\mathbf{r}))$, which includes the one-body potential $\beta\phi(\mathbf{r})$ and the direct one-particle correlation function $-c^{(1)}(\mathbf{r})$. The latter can be interpreted as the effective one-body potential generated by the direct correlations between particles. It should be noted that, in an inhomogeneous system, the excess chemical potential $\beta\mu^{\text{ex}}(\mathbf{r})$ is a function of position corresponding to the reversible work produced to move a particle of the real system, at position $\mathbf{r}$, into an ideal system at the same position and density. By contrast, in a homogeneous system ($\phi(\mathbf{r}) = 0$), the direct one-particle correlation function coincides with the excess chemical potential ($\beta\mu^{\text{ex}} = -c^{(1)}$) which becomes a quantity independent of the position. In this case, the expression of the chemical potential is:

$$\beta\mu = \ln(\rho\Lambda^3) - c^{(1)}. \quad (6.108)$$

After defining and interpreting the direct correlation function for one particle $c^{(1)}(\mathbf{r})$, we define the *direct correlation function for two particles* $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$. It plays an even more important role than $c^{(1)}(\mathbf{r})$ in the microscopic theory of liquids, as we shall see later. That is why it is commonly called *direct correlation function*, without reference to the number of particles. It corresponds to the functional derivative of the direct correlation function for one particle $c^{(1)}(\mathbf{r})$ with respect to the variation of $\rho(\mathbf{r})$:

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta c^{(1)}(\mathbf{r}_2)}{\delta \rho(\mathbf{r}_1)}. \quad (6.109)$$

With equation (6.106), the above relation is conventionally written as:

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \beta \frac{\delta \phi(\mathbf{r}_2)}{\delta \rho(\mathbf{r}_1)} + \frac{1}{\rho(\mathbf{r}_1)} \delta(\mathbf{r}_1 - \mathbf{r}_2). \quad (6.110)$$

This expression of the direct correlation function for two-particles will be used in the following subsection to establish the Ornstein-Zernike relation.

Obtaining the Ornstein–Zernike relation

To set up the Ornstein–Zernike relation, we transform the first term on the right hand side of equation (6.93) by using the Dirac function $\delta(\mathbf{r}_1 - \mathbf{r}_2)$:

$$\beta \delta \phi(\mathbf{r}_1) \rho_N^{(1)}[\phi, \mathbf{r}_1] = \beta \int_V \rho_N^{(1)}[\phi, \mathbf{r}_1] \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta \phi(\mathbf{r}_2) d\mathbf{r}_2. \quad (6.111)$$

With this expression, equation (6.93) is simplified into:

$$\begin{aligned} \delta \rho_N^{(1)}[\phi, \mathbf{r}_1] &= -\beta \int_V \left\{ \rho_N^{(1)}[\phi, \mathbf{r}_1] \delta(\mathbf{r}_1 - \mathbf{r}_2) + \rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] \right. \\ &\quad \left. - \rho_N^{(1)}[\phi, \mathbf{r}_2] \rho_N^{(1)}[\phi, \mathbf{r}_1] \right\} \delta \phi(\mathbf{r}_2) d\mathbf{r}_2, \end{aligned} \quad (6.112)$$

and the functional derivative of $\rho_N^{(1)}[\phi, \mathbf{r}_1]$ with respect to $\delta \phi(\mathbf{r}_2)$ is written according to equation (6.63) as:

$$\begin{aligned} \frac{\delta \rho_N^{(1)}[\phi, \mathbf{r}_1]}{\delta \phi(\mathbf{r}_2)} &= -\beta \left\{ \rho_N^{(1)}[\phi, \mathbf{r}_1] \delta(\mathbf{r}_1 - \mathbf{r}_2) + \rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] \right. \\ &\quad \left. - \rho_N^{(1)}[\phi, \mathbf{r}_2] \rho_N^{(1)}[\phi, \mathbf{r}_1] \right\}. \end{aligned} \quad (6.113)$$

However, when looking at equation (6.80), we realize that this derivative depends on the partition function considering that:

$$\frac{\delta \rho_N^{(1)}[\phi, \mathbf{r}_1]}{\delta \phi(\mathbf{r}_2)} = -\frac{1}{\beta} \frac{\delta^2 \ln Q_N[\phi]}{\delta \phi(\mathbf{r}_2) \delta \phi(\mathbf{r}_1)} = \frac{\delta^2 F[\phi]}{\delta \phi(\mathbf{r}_2) \delta \phi(\mathbf{r}_1)}, \quad (6.114)$$

where $Q_N[\phi]$ is the partition function and $F[\phi]$ the Helmholtz free energy. Thus, by comparing equations (6.113) and (6.114), we note that the second functional derivative of the Helmholtz free energy $F[\phi]$ with respect to a small external perturbation depends explicitly on the generic distribution functions describing distributions of one particle and two particles.

In addition, as it will be shown in the following, equation (6.113) allows us to derive the Ornstein–Zernike relation, provided that the direct correlation function (Eq. 6.110) is used under the form:

$$c[\phi, \mathbf{r}_1, \mathbf{r}_2] = \beta \frac{\delta \phi(\mathbf{r}_2)}{\delta \rho_N^{(1)}[\phi, \mathbf{r}_1]} + \frac{1}{\rho_N^{(1)}[\phi, \mathbf{r}_1]} \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (6.115)$$

from which it follows:

$$\frac{\delta \phi(\mathbf{r}_2)}{\delta \rho_N^{(1)}[\phi, \mathbf{r}_1]} = \frac{1}{\beta} \left\{ c[\phi, \mathbf{r}_1, \mathbf{r}_2] - \frac{1}{\rho_N^{(1)}[\phi, \mathbf{r}_1]} \delta(\mathbf{r}_1 - \mathbf{r}_2) \right\}. \quad (6.116)$$

Equations (6.113) and (6.116) corresponding to inverse expressions of each other can be substituted in equation (6.71), namely:

$$\int \frac{\delta \rho_N^{(1)}[\phi, \mathbf{r}_1, \mathbf{r}_3]}{\delta \phi(\mathbf{r}_3)} \frac{\delta \phi(\mathbf{r}_3)}{\delta \rho_N^{(1)}[\phi, \mathbf{r}_2, \mathbf{r}_3]} d\mathbf{r}_3 = \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (6.117)$$

thus giving:

$$\begin{aligned} \delta(\mathbf{r}_1 - \mathbf{r}_2) &= \int -\left\{ \rho_N^{(1)}[\phi, \mathbf{r}_1] \delta(\mathbf{r}_1 - \mathbf{r}_3) + \rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_3] \right. \\ &\quad \left. - \rho_N^{(1)}[\phi, \mathbf{r}_3] \rho_N^{(1)}[\phi, \mathbf{r}_1] \right\} \times \left\{ c[\phi, \mathbf{r}_2, \mathbf{r}_3] - \frac{1}{\rho_N^{(1)}[\phi, \mathbf{r}_2]} \delta(\mathbf{r}_2 - \mathbf{r}_3) \right\} d\mathbf{r}_3. \end{aligned} \quad (6.118)$$

However, in taking advantage of the Dirac function, when $\mathbf{r}_1 \neq \mathbf{r}_2$, the above relation reduces to:

$$\begin{aligned}
 0 = & -c[\phi, \mathbf{r}_1, \mathbf{r}_2] \rho_N^{(1)}[\phi, \mathbf{r}_1] - \int c[\phi, \mathbf{r}_2, \mathbf{r}_3] \left\{ \rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_3] \right. \\
 & \left. - \rho_N^{(1)}[\phi, \mathbf{r}_3] \rho_N^{(1)}[\phi, \mathbf{r}_1] \right\} d\mathbf{r}_3 \\
 & + \frac{1}{\rho_N^{(1)}[\phi, \mathbf{r}_2]} \left\{ \rho_N^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_2] - \rho_N^{(1)}[\phi, \mathbf{r}_2] \rho_N^{(1)}[\phi, \mathbf{r}_1] \right\}. \quad (6.119)
 \end{aligned}$$

Now, if the external perturbation is weak and the liquid is homogeneous and isotropic, the generic distribution function for two particles (Eq. 3.89) can be expressed in terms of the pair correlation function $g(r)$, and the above relation simplifies to:

$$0 = -\rho c(r_{12}) - \int c(r_{23}) [\rho^2 g(r_{13}) - \rho^2] d\mathbf{r}_3 + \frac{1}{\rho} [\rho^2 g(r_{12}) - \rho^2], \quad (6.120)$$

or equivalently:

$$g(r_{12}) - 1 = c(r_{12}) + \rho \int c(r_{23}) [g(r_{13}) - 1] d\mathbf{r}_3. \quad (6.121)$$

It is the *Ornstein-Zernike relation* (OZ) that we owe the connection of the pair correlation function $g(r)$ to the direct correlation function $c(r)$. The *total correlation function* $h(r) = g(r) - 1$ is traditionally used to rewrite the OZ relation in the compact form:

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{23}) h(r_{13}) d\mathbf{r}_3. \quad (6.122)$$

The OZ relation is an exact equation, originally established to study the critical fluctuations in fluids [64] by assuming that the total correlation function $h(r_{12})$ splits into two contributions:

$$h(r_{12}) = c(r_{12}) + \gamma(r_{12}) \quad (6.123)$$

with the *direct correlation function* $c(r_{12})$ and the *indirect correlation function* defined by:

$$\gamma(r_{12}) = \rho \int c(r_{23}) h(r_{13}) d\mathbf{r}_3. \quad (6.124)$$

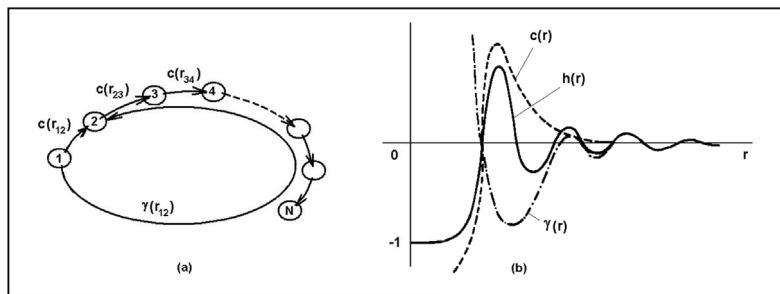


Figure 6.3: (a) Schematic interpretation of the direct correlation function $c(r_{12})$ and the indirect correlation function $\gamma(r_{12})$. (b) Representation of the direct correlation function $c(r_{12})$, indirect correlation function $\gamma(r_{12})$ and total correlation function $h(r_{12}) = c(r_{12}) + \gamma(r_{12})$ in liquids.

Figure (6.3a) illustrates schematically what differentiates the direct correlation function $c(r_{12})$ from the indirect correlation function $\gamma(r_{12})$. While $c(r_{12})$ measures the direct correlation between particle 1 and particle 2, $\gamma(r_{12})$ is a measure of the correlation between particles 1 and 2 through all the other particles.

Considering that the interpretation of the direct correlation function $c(r)$ is somewhat obscure, it is necessary to examine why it is so. There are apparently two reasons for that.

The first one is that it reduces to the Mayer function at low densities. Indeed, considering equation (6.122), it can be seen that $c(r) \rightarrow h(r) = g(r) - 1$ when $\rho \rightarrow 0$. However, at low densities, the considerations of section (5.1) have shown that the pair correlation function $g(r)$ identifies with the Boltzmann factor, $\exp[-\beta u(r)]$, which is itself used to define the Mayer function $f(r)$. In addition, at large distances – when $u(r)$ tends to 0, – it appears that the direct correlation function $c(r)$ behaves approximately⁸ as $c(r) \sim -\beta u(r)$. As it can be noted in figure (6.3b), the variation of $c(r)$ is more regular than that of $h(r)$ and has a shorter range than $\gamma(r)$.

⁸When $u(r)$ tends to 0 at large distances, the direct correlation function $c(r)$ is equivalent to:

$$c(r) \sim g(r) - 1 \sim \exp[-\beta u(r)] - 1 = f(r) \sim -\beta u(r).$$

The second reason for the importance of $c(r)$ is that it is directly accessible from the measurement of the structure factor $S(q)$. Indeed, if the Fourier transform of equation (6.122) is carried out, the use of the convolution theorem⁹ leads to:

$$h(q) = c(q) + \rho c(q) h(q), \quad (6.125)$$

from which it results:

$$[1 + \rho h(q)] [1 - \rho c(q)] = 1. \quad (6.126)$$

However, from equation (3.118), it follows that:

$$S(q) - 1 = \rho \int [g(r) - 1] \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = \rho h(q), \quad (6.127)$$

which, when combined with equation (6.126), provides:

$$S(q) = 1 + \rho h(q) = \frac{1}{1 - \rho c(q)}, \quad (6.128)$$

or:

$$\rho c(q) = 1 - \frac{1}{S(q)} = \rho \int c(r) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}. \quad (6.129)$$

Then, it is easy to extract the direct correlation function $c(r)$ by taking the inverse Fourier transform of equation (6.129):

$$\rho c(r) = \frac{1}{(2\pi)^3} \int \left[1 - \frac{1}{S(q)} \right] \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q}. \quad (6.130)$$

⁹One multiplies both sides of equation (6.122) by $\exp[i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2$ and integrate over $\mathbf{r}_1$ and $\mathbf{r}_2$:

$$\begin{aligned} \int h(r_{12}) \exp[i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2 &= \int c(r_{12}) \exp[i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2 \\ &+ \rho \int c(r_{23}) h(r_{13}) \exp[i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \end{aligned}$$

By using the changes of variables $\mathbf{r}_1 = \mathbf{r}_1$ and $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ in the first two integrals, and $\mathbf{r}_{13} = \mathbf{r}_3 - \mathbf{r}_1$, $\mathbf{r}_{32} = \mathbf{r}_2 - \mathbf{r}_3$ and $\mathbf{r}_3 = \mathbf{r}_3$ in the integral of convolution – for which the Jacobians are equal to unity – the previous equation becomes:

$$h(\mathbf{q}) = c(\mathbf{q}) + \rho c(\mathbf{q}) h(\mathbf{q}),$$

$$\text{with} \quad h(\mathbf{q}) = \int h(r_{12}) \exp(i\mathbf{q} \cdot \mathbf{r}_{12}) d\mathbf{r}_{12}, \quad c(\mathbf{q}) = \int c(r_{12}) \exp(i\mathbf{q} \cdot \mathbf{r}_{12}) d\mathbf{r}_{12}.$$

Incidentally, for $q = 0$, it should be noted that equation (6.129) reduces to the expression:

$$\rho c(0) = 1 - \frac{1}{S(0)} = \rho \int c(r) dr. \quad (6.131)$$

that, on one hand, connects the direct correlation function $c(r)$ to the isothermal compressibility χ_T by means of equation (5.85), namely:

$$S(0) = \rho k_B T \chi_T = \frac{1}{1 - \rho \int c(r) dr} \quad (6.132)$$

and, on the other hand, to the derivative of the chemical potential μ with respect to ρ , thanks to equation (5.88):

$$\rho \beta \frac{\partial \mu}{\partial \rho} = \frac{1}{\rho k_B T \chi_T} = 1 - \rho \int c(r) dr. \quad (6.133)$$

6.4 The Percus–Yevick equation

Obtaining the Percus–Yevick equation

The OZ relation is an exact equation linking the direct correlation function $c(r)$ to the pair correlation function $g(r)$. Since $c(r)$ and $g(r)$ are two unknown functions, it is necessary to use an auxiliary equation likely to determine $c(r)$ and $g(r)$ simultaneously. One of the methods employed to establish this equation is based on the use of the Maclaurin series of functionals. As we shall see, this auxiliary equation, independent of the OZ relation, is an approximate equation depending on the choice of the functional. The approximate equation that gave most satisfaction in liquid theory is the equation of Percus–Yevik [61] (PY) presented below by the functional method [63].

Suppose first that the weak applied potential $\phi(\mathbf{r})$ is generated by a test particle which is identical to all the others and interacts with the N other particles by the same pair potential $u(r)$. When the test particle with index 0 is fixed in position $\mathbf{r}_0$, the expression of the weak applied potential $\phi(\mathbf{r})$ is:

$$\phi(\mathbf{r}^N) = \sum_{i=1}^N u(r_{0i}). \quad (6.134)$$

However, if the potential energy $U(\mathbf{r}^N)$ of the system *without* the test particle is, as usual, decomposed into a sum of pair potentials, the potential energy *with* the test particle can be written as:

$$U(\mathbf{r}^N) + \phi(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j>i}^N u(r_{ij}) + \sum_{i=1}^N u(r_{0i}) = \sum_{i=1}^N \sum_{j>i}^{N+1} u(r_{ij}). \quad (6.135)$$

To implement the method, we choose two functionals of the applied potential $\phi(\mathbf{r})$: one is called *independent functional* $F[\phi(\mathbf{r}), \mathbf{r}_i]$ and the other one the *generating functional* $G[\phi(\mathbf{r}), \mathbf{r}_i]$. A priori, the choice leading to the generating functional, although arbitrary, is proved to be good after the pair correlation function is calculated. Concerning the independent functional $F[\phi(\mathbf{r}), \mathbf{r}_i]$, it is chosen to be the generic distribution function for one particle in the presence of the applied potential, i.e. with the test particle in the system (here $F[\phi(\mathbf{r}), \mathbf{r}_i]$ is not the Helmholtz free energy). As a result, the independent functional reads:

$$F[\phi(\mathbf{r}), \mathbf{r}_i] = \rho_{N+1}^{(1)}[\phi, \mathbf{r}_i], \quad (6.136)$$

and the generating functional¹⁰ $G[\phi(\mathbf{r}), \mathbf{r}_i]$ is taken to be:

$$G[\phi(\mathbf{r}), \mathbf{r}_i] = \rho_{N+1}^{(1)}[\phi, \mathbf{r}_i] \exp[\beta u(r_{0i})]. \quad (6.137)$$

This choice is highly ingenious because both functionals $F[\phi(\mathbf{r}), \mathbf{r}_i]$ and $G[\phi(\mathbf{r}), \mathbf{r}_i]$ become identical with the generic distribution function for one particle when the potential applied is zero [$\phi(\mathbf{r}^N) = \sum_{i=1}^N u(r_{0i}) = 0$], i.e. when the test particle is removed from the system. Indeed:

$$F[0, \mathbf{r}_i] = G[0, \mathbf{r}_i] = \rho_N^{(1)}(\mathbf{r}). \quad (6.138)$$

It should be stressed that the functional $\rho_{N+1}^{(1)}[\phi, \mathbf{r}_i]$ does not represent a genuine generic distribution function for one particle, but rather a generic distribution function for two particles in the system of $(N+1)$

¹⁰Note in passing that the generating functional $G[\phi(\mathbf{r}), \mathbf{r}_i] = \ln\{\rho_{N+1}^{(1)}[\phi(\mathbf{r}), \mathbf{r}_i] \exp[\beta u(r_{0i})]\}$ provides another well known equation: the hypernetted-chain (HNC) equation.

particles. In fact, according to equation (6.79), $\rho_{N+1}^{(1)}[\phi, \mathbf{r}_i]$ is expressed as:

$$\begin{aligned} \rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] &= \\ &= \frac{N!}{(N-1)!} \frac{\int \dots \int \exp \left[-\beta \sum_{i=1}^{N-1} \sum_{j>i}^N u(r_{ij}) - \beta \sum_{i=1}^N u(r_{0i}) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N}{\int \dots \int \exp \left[-\beta \sum_{i=1}^{N-1} \sum_{j>i}^N u(r_{ij}) - \beta \sum_{i=1}^N u(r_{0i}) \right] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N}. \end{aligned} \quad (6.139)$$

After transformations, the foregoing expression can be somewhat simplified to:

$$\begin{aligned} \rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] &= \\ &= \frac{\frac{(N+1)!}{(N-1)!} \frac{1}{Z_{N+1}(V, T)} \int \dots \int \exp \left[-\beta \sum_{i=1}^N \sum_{j>i}^{N+1} u(r_{ij}) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N}{\frac{(N+1)!}{N!} \frac{1}{Z_{N+1}(V, T)} \int \dots \int \exp \left[-\beta \sum_{i=1}^N \sum_{j>i}^{N+1} u(r_{ij}) \right] d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N}. \end{aligned} \quad (6.140)$$

It is remarkable that the numerator of this fraction corresponds to the generic distribution function for two particles (Eq. 3.83), while the denominator corresponds to the generic distribution function for one particle in a system of $(N+1)$ particles, with the first particle fixed at $\mathbf{r}_0$. By denoting these two functions $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_0)$ and $\rho_N^{(1)}(\mathbf{r}_0)$, the expression of the functional $\rho_{N+1}^{(1)}[\phi, \mathbf{r}_1]$ reduces to:

$$\rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] = \frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_0)}{\rho_N^{(1)}(\mathbf{r}_0)}. \quad (6.141)$$

After choosing the generating functional $G[\phi(\mathbf{r}), \mathbf{r}_i]$ specific to the PY approximation, it remains to write its Maclaurin series using equation (6.73):

$$\begin{aligned} G[\phi(\mathbf{r}), \mathbf{r}_1] &= G[0, \mathbf{r}_1] + \int \left\{ \frac{\delta G[\phi(\mathbf{r}), \mathbf{r}_1]}{\delta \phi(\mathbf{r}_2)} \right\}_{\phi=0} \delta \phi(\mathbf{r}_2) d\mathbf{r}_2 \\ &+ \frac{1}{2!} \iint \left\{ \frac{\delta^2 G[\phi(\mathbf{r}), \mathbf{r}_1]}{\delta \phi(\mathbf{r}_2) \delta \phi(\mathbf{r}_3)} \right\}_{\phi=0} \delta \phi(\mathbf{r}_2) \delta \phi(\mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3 + \dots \end{aligned} \quad (6.142)$$

If we realize that the first functional derivative of equation (6.142) depends on the generic distribution functions for one and two particles, whereas the second functional derivative depends on the generic distribution functions for more than two particles, it is justified to determine the pair correlation function by truncating the series after the term to the first order. Moreover, it is legitimate to identify the variation of the applied potential $\delta\phi(\mathbf{r}_2)$ to that of the independent functional $F[\phi(\mathbf{r}), \mathbf{r}_2]$, namely:

$$\delta\phi(\mathbf{r}_2) \simeq \delta F[\phi(\mathbf{r}), \mathbf{r}_2], \quad (6.143)$$

with $\delta F[\phi(\mathbf{r}), \mathbf{r}_2] = F[\phi(\mathbf{r}), \mathbf{r}_2] - F[0, \mathbf{r}_2]$ because, when $\phi(\mathbf{r}) \rightarrow 0$, it follows:

$$F[\phi(\mathbf{r}), \mathbf{r}_2] \rightarrow F[0, \mathbf{r}_2] \quad \text{and} \quad \delta\phi(\mathbf{r}_2) \simeq \delta F[\phi(\mathbf{r}), \mathbf{r}_2] \rightarrow 0. \quad (6.144)$$

The substitution of $\delta\phi(\mathbf{r}_2)$ in equation (6.142) truncated to the first order, enables us to write the generating functional as:

$$G[\phi(\mathbf{r}), \mathbf{r}_1] = G[0, \mathbf{r}_1] + \int \left\{ \frac{\delta G[\phi(\mathbf{r}), \mathbf{r}_1]}{\delta F[\phi(\mathbf{r}), \mathbf{r}_2]} \right\}_{\phi=0} \{F[\phi(\mathbf{r}), \mathbf{r}_2] - F[0, \mathbf{r}_2]\} d\mathbf{r}_2. \quad (6.145)$$

However, the term in large brackets can be changed by using equation (6.72). After transformation, the result is:

$$\begin{aligned} G[\phi(\mathbf{r}), \mathbf{r}_1] &= G[0, \mathbf{r}_1] + \int \left\{ \int \frac{\delta G[\phi(\mathbf{r}), \mathbf{r}_1, \mathbf{r}_3]}{\delta\phi(\mathbf{r}_3)} \times \right. \\ &\times \left. \frac{\delta\phi(\mathbf{r}_3)}{\delta F[\phi(\mathbf{r}), \mathbf{r}_2, \mathbf{r}_3]} d\mathbf{r}_3 \right\} \{F[\phi(\mathbf{r}), \mathbf{r}_2] - F[0, \mathbf{r}_2]\} d\mathbf{r}_2. \end{aligned} \quad (6.146)$$

The functionals G and F in the above equation can still be replaced by their expressions from equations (6.136) and (6.137):

$$\begin{aligned} \rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] \exp[\beta u(r_{01})] &= \rho_N^{(1)}(\mathbf{r}_1) \\ &+ \int \left\{ \int \frac{\delta \left\{ \rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] \exp[\beta u(r_{01})] \right\}}{\delta\phi(\mathbf{r}_3)} \frac{\delta\phi(\mathbf{r}_3)}{\delta\rho_{N+1}^{(1)}[\phi, \mathbf{r}_2]} d\mathbf{r}_3 \right\} \times \\ &\times \left\{ \rho_{N+1}^{(1)}[\phi, \mathbf{r}_2] - \rho_N^{(1)}(\mathbf{r}_2) \right\} d\mathbf{r}_2. \end{aligned} \quad (6.147)$$

The preceding expression will now be transformed in order to deduce the common form of the PY equation. Let us evaluate one of the functional derivatives in large brackets of equation (6.147):

$$\begin{aligned} I_1 &= \frac{\delta \left\{ \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \exp [\beta u(r_{01})] \right\}}{\delta \phi(\mathbf{r}_3)} \\ &= \frac{\delta \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1]}{\delta \phi(\mathbf{r}_3)} \exp [\beta u(r_{01})] + \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \frac{\delta \exp [\beta u(r_{01})]}{\delta \phi(\mathbf{r}_3)}. \quad (6.148) \end{aligned}$$

To determine I_1 , we transform the functional derivatives in the last equation¹¹. The final expression for I_1 becomes:

$$I_1 = -\beta \left\{ \rho_{N+1}^{(2)} [\phi, \mathbf{r}_1, \mathbf{r}_3] - \rho_{N+1}^{(1)} [\phi, \mathbf{r}_3] \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \right\} \exp [\beta u(r_{01})]. \quad (6.149)$$

Then we evaluate the other functional derivative, denoted I_2 , by means of equation (6.116). It results in:

$$I_2 = \frac{\delta \phi(\mathbf{r}_3)}{\delta \rho_{N+1}^{(1)} [\phi, \mathbf{r}_2]} = \frac{1}{\beta} \left\{ c [\phi, \mathbf{r}_2, \mathbf{r}_3] - \frac{\delta(\mathbf{r}_2 - \mathbf{r}_3)}{\rho_{N+1}^{(1)} [\phi, \mathbf{r}_2]} \right\}. \quad (6.150)$$

By using these expressions of the two functional derivatives I_1 and I_2 , the integral between the large brackets of equation (6.147) reduces to:

¹¹Let us write the two functional derivatives on the right hand side of equation (6.148), respectively I_{11} and I_{12} . Given equation (6.113), the term I_{11} is equal to:

$$\begin{aligned} I_{11} &= \frac{\delta \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1]}{\delta \phi(\mathbf{r}_3)} = -\beta \left\{ \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \delta(\mathbf{r}_1 - \mathbf{r}_3) + \rho_{N+1}^{(2)} [\phi, \mathbf{r}_1, \mathbf{r}_3] \right. \\ &\quad \left. - \rho_{N+1}^{(1)} [\phi, \mathbf{r}_3] \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \right\}, \end{aligned}$$

and, since $\phi(\mathbf{r}_3) = u(r_{03})$, the term I_{12} is reduced to:

$$I_{12} = \frac{\delta \exp [\beta u(r_{01})]}{\delta \phi(\mathbf{r}_3)} = \beta \frac{\delta u(r_{01})}{\delta u(r_{03})} \exp [\beta u(r_{01})] = \beta \delta(\mathbf{r}_1 - \mathbf{r}_3) \exp [\beta u(r_{01})].$$

Therefore, the functional derivative $I_1 = I_{11} \exp [\beta u(r_{01})] + \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] I_{12}$ simplifies as:

$$\begin{aligned} I_1 &= -\beta \left\{ \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \delta(\mathbf{r}_1 - \mathbf{r}_3) + \rho_{N+1}^{(2)} [\phi, \mathbf{r}_1, \mathbf{r}_3] \right. \\ &\quad \left. - \rho_{N+1}^{(1)} [\phi, \mathbf{r}_3] \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \right\} \exp [\beta u(r_{01})] + \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \beta \delta(\mathbf{r}_1 - \mathbf{r}_3) \exp [\beta u(r_{01})] \\ &= -\beta \left\{ \rho_{N+1}^{(2)} [\phi, \mathbf{r}_1, \mathbf{r}_3] - \rho_{N+1}^{(1)} [\phi, \mathbf{r}_3] \rho_{N+1}^{(1)} [\phi, \mathbf{r}_1] \right\} \exp [\beta u(r_{01})]. \end{aligned}$$

$$\begin{aligned}
J &= \int (I_1 \times I_2) d\mathbf{r}_3 \\
&= \int -\beta \left\{ \rho_{N+1}^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_3] - \rho_{N+1}^{(1)}[\phi, \mathbf{r}_3] \rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] \right\} \times \\
&\quad \times \exp[\beta u(r_{01})] \frac{1}{\beta} \left\{ c[\phi, \mathbf{r}_2, \mathbf{r}_3] - \frac{\delta(\mathbf{r}_2 - \mathbf{r}_3)}{\rho_{N+1}^{(1)}[\phi, \mathbf{r}_2]} \right\} d\mathbf{r}_3. \quad (6.151)
\end{aligned}$$

Anyway, it is convenient to split the integral J into two terms ($J = J_1 + J_2$) in the following manner:

$$\begin{aligned}
J_1 &= \int -\beta \left\{ \rho_{N+1}^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_3] - \rho_{N+1}^{(1)}[\phi, \mathbf{r}_3] \rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] \right\} \times \\
&\quad \times \exp[\beta u(r_{01})] \frac{1}{\beta} c[\phi, \mathbf{r}_2, \mathbf{r}_3] d\mathbf{r}_3, \quad (6.152)
\end{aligned}$$

and:

$$\begin{aligned}
J_2 &= \int -\beta \left\{ \rho_{N+1}^{(2)}[\phi, \mathbf{r}_1, \mathbf{r}_3] - \rho_{N+1}^{(1)}[\phi, \mathbf{r}_3] \rho_{N+1}^{(1)}[\phi, \mathbf{r}_1] \right\} \times \\
&\quad \times \exp[\beta u(r_{01})] \frac{1}{\beta} \left\{ -\frac{\delta(\mathbf{r}_2 - \mathbf{r}_3)}{\rho_{N+1}^{(1)}[\phi, \mathbf{r}_2]} \right\} d\mathbf{r}_3. \quad (6.153)
\end{aligned}$$

However, if the applied potential is cancelled ($\phi = 0$) by removing the test particle from the system, the integrals J_1 and J_2 are simplified into:

$$J_1 = - \int \left\{ \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - \rho_N^{(1)}(\mathbf{r}_3) \rho_N^{(1)}(\mathbf{r}_1) \right\} c(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3, \quad (6.154)$$

$$J_2 = \frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_N^{(1)}(\mathbf{r}_2)} - \rho_N^{(1)}(\mathbf{r}_1), \quad (6.155)$$

so that J reduces to:

$$\begin{aligned}
J = J_1 + J_2 &= - \int \left\{ \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_3) - \rho_N^{(1)}(\mathbf{r}_3) \rho_N^{(1)}(\mathbf{r}_1) \right\} c(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \\
&\quad + \frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_N^{(1)}(\mathbf{r}_2)} - \rho_N^{(1)}(\mathbf{r}_1). \quad (6.156)
\end{aligned}$$

With equation (6.119), the integral J is finally changed into:

$$J = c(\mathbf{r}_1, \mathbf{r}_2) \rho_N^{(1)}(\mathbf{r}_1) - \frac{1}{\rho_N^{(1)}(\mathbf{r}_2)} \left\{ \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho_N^{(1)}(\mathbf{r}_2) \rho_N^{(1)}(\mathbf{r}_1) \right\} \\ + \frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_N^{(1)}(\mathbf{r}_2)} - \rho_N^{(1)}(\mathbf{r}_1), \quad (6.157)$$

$$\text{or } J = c(\mathbf{r}_1, \mathbf{r}_2) \rho_N^{(1)}(\mathbf{r}_1). \quad (6.158)$$

At this stage, the simplification of equation (6.147) can be achieved by substituting the expression for J and using equation (6.141) to replace the term $\rho_{N+1}^{(1)}[\phi, \mathbf{r}_i]$ by $\frac{\rho_N^{(2)}(\mathbf{r}_i, \mathbf{r}_0)}{\rho_N^{(1)}(\mathbf{r}_0)}$. This gives:

$$\frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_0)}{\rho_N^{(1)}(\mathbf{r}_0)} \exp[\beta u(r_{01})] = \rho_N^{(1)}(\mathbf{r}_1) \\ + \int c(\mathbf{r}_1, \mathbf{r}_2) \rho_N^{(1)}(\mathbf{r}_1) \left\{ \frac{\rho_N^{(2)}(\mathbf{r}_2, \mathbf{r}_0)}{\rho_N^{(1)}(\mathbf{r}_0)} - \rho_N^{(1)}(\mathbf{r}_2) \right\} d\mathbf{r}_2, \quad (6.159)$$

or equivalently:

$$\frac{\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_0)}{\rho_N^{(1)}(\mathbf{r}_0) \rho_N^{(1)}(\mathbf{r}_1)} \exp[\beta u(r_{01})] = \\ = 1 + \int c(\mathbf{r}_1, \mathbf{r}_2) \rho_N^{(1)}(\mathbf{r}_2) \left\{ \frac{\rho_N^{(2)}(\mathbf{r}_2, \mathbf{r}_0)}{\rho_N^{(1)}(\mathbf{r}_0) \rho_N^{(1)}(\mathbf{r}_2)} - 1 \right\} d\mathbf{r}_2. \quad (6.160)$$

This is the *Percus–Yevick equation*. It can also be expressed in terms of the pair correlation function as follows¹²:

$$g(r_{12}) \exp[\beta u(r_{12})] = 1 + \rho \int c(r_{23}) [g(r_{13}) - 1] d\mathbf{r}_3. \quad (6.161)$$

¹²With the definition of the pair correlation function (Eq. 3.89) and the relation $\rho_N^{(1)}(\mathbf{r}_0) = \rho_N^{(1)}(\mathbf{r}_1) = \rho$, the following changes are immediate:

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_0) \exp[\beta u(r_{01})] = 1 + \int c(\mathbf{r}_1, \mathbf{r}_2) \rho_N^{(1)}(\mathbf{r}_2) \{g_N^{(2)}(\mathbf{r}_2, \mathbf{r}_0) - 1\} d\mathbf{r}_2, \\ g(r_{01}) \exp[\beta u(r_{01})] = 1 + \rho \int c(r_{12}) [g(r_{02}) - 1] d\mathbf{r}_2.$$

It should be noted that the PY equation connects the pair correlation function $g(r_{12})$ with the direct correlation function $c(r_{23})$ via the pair potential $u(r_{12})$. It can be written, either by using the exact OZ relation (Eq. 6.121), as follows:

$$g(r_{12}) \exp[\beta u(r_{12})] = 1 + g(r_{12}) - 1 - c(r_{12}), \quad (6.162)$$

that is to say:

$$c(r_{12}) = g(r_{12}) \{1 - \exp[\beta u(r_{12})]\}, \quad (6.163)$$

or with the *cavity function*, $y(r_{12}) = g(r_{12}) \exp[\beta u(r_{12})]$, and the Mayer function, $f(r_{12}) = \exp[-\beta u(r_{12})] - 1$, as follows:

$$c(r_{12}) = y(r_{12}) \{\exp[-\beta u(r_{12})] - 1\} = y(r_{12}) f(r_{12}) \quad (6.164)$$

$$= g(r_{12}) - y(r_{12}). \quad (6.165)$$

The equations (6.163), (6.164) and (6.165) are three equivalent forms of the Percus–Yevick equation.

The Percus–Yevick solution for hard spheres

First of all, it should be noted that the integral equations cannot generally be solved analytically, except for the hard-sphere potential. Indeed, as will be seen, the analytical expressions predicted with the PY equation are those of the direct correlation function $c(r)$ and the structure factor $S(q)$ of the hard-sphere potential [74, 75]. For any other pair potential, the PY equation provides correlation functions under tabulated forms. Consequently, it seems to be beneficial to determine the analytical expression for the HS structure factor because the thermodynamic and structural properties of liquids can be estimated with reasonable accuracy for the HS reference potential.

To solve the PY equation analytically, consider the HS potential (section 5.6):

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma, \\ 0 & \text{if } r > \sigma, \end{cases} \quad (6.166)$$

where σ is the HS diameter. As regards the Boltzmann factor of the HS potential, it can be represented by the Heaviside function, $\exp[-\beta u(r)] = \Theta(r - \sigma)$, since:

$$\exp[-\beta u(r)] = \begin{cases} 0 & \text{if } r \leq \sigma, \\ 1 & \text{if } r > \sigma. \end{cases} \quad (6.167)$$

Considering the PY equation (Eq. 6.163) in the form

$$c(r) \exp [-\beta u(r)] = g(r) \{ \exp [-\beta u(r)] - 1 \} , \quad (6.168)$$

we note that equation (6.167) imposes the following conditions:

$$\begin{aligned} g(r) &= 0 & \text{if } r \leq \sigma , \\ c(r) &= 0 & \text{if } r > \sigma . \end{aligned} \quad (6.169)$$

While the two functions $g(r)$ and $c(r)$ display a discontinuity at $r = \sigma$, it can easily be seen that the cavity function $y(r) = g(r) - c(r)$ (Eq. 6.165) varies continuously throughout the domain of variation:

$$y(r) = \begin{cases} -c(r) & \text{if } r \leq \sigma , \\ g(r) & \text{if } r > \sigma . \end{cases} \quad (6.170)$$

The solution of the PY equation for the HS potential is obtained by straightforward manipulations of the Laplace transforms. The calculations require a prior shaping of equation (6.161) by using the bipolar coordinates to express the integration element $d\mathbf{r}_3$ (Eq. 5.114), and replacing $c(r_{23})$ with equation (6.163). This gives:

$$\begin{aligned} g(r_{12}) \exp [\beta u(r_{12})] &= 1 + \rho \int_{r_{23}=0}^{\infty} \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} g(r_{23}) \{ 1 - \exp [\beta u(r_{23})] \} \times \\ &\times [g(r_{13}) - 1] 2\pi \frac{r_{13} r_{23}}{r_{12}} dr_{13} dr_{23} . \end{aligned} \quad (6.171)$$

The previous equation can yet be transformed in terms of the cavity function $y(r) = g(r) \exp [\beta u(r)]$:

$$\begin{aligned} r_{12} y(r_{12}) &= r_{12} + 2\pi\rho \int_{r_{23}=0}^{\infty} \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} y(r_{23}) \{ \exp [-\beta u(r_{23})] - 1 \} \times \\ &\times \{ y(r_{13}) \exp [-\beta u(r_{13})] - 1 \} r_{13} r_{23} dr_{13} dr_{23} , \end{aligned} \quad (6.172)$$

or:

$$\begin{aligned} r_{12} y(r_{12}) &= r_{12} + 2\pi\rho \int_{r_{23}=0}^{\infty} \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} y(r_{23}) \{ \exp [-\beta u(r_{23})] - 1 \} \times \\ &\times y(r_{13}) \exp [-\beta u(r_{13})] r_{13} r_{23} dr_{13} dr_{23} \\ &- 2\pi\rho \int_{r_{23}=0}^{\infty} \int_{r_{13}=|r_{12}-r_{23}|}^{r_{13}=r_{12}+r_{23}} y(r_{23}) \{ \exp [-\beta u(r_{23})] - 1 \} r_{13} r_{23} dr_{13} dr_{23} . \end{aligned} \quad (6.173)$$

Using the Heaviside function (Eq. 6.167) to write the Boltzmann factor, the integrals in the above equation are even easier:

$$\begin{aligned} r_{12}y(r_{12}) = & r_{12} - 2\pi\rho \int_0^\sigma r_{23}y(r_{23}) \times \\ & \times \left\{ \int_{|r_{12}-r_{23}|}^{r_{12}+r_{23}} y(r_{13}) \Theta(r_{13}-\sigma) r_{13} dr_{13} \right\} dr_{23} \\ & + 2\pi\rho \int_0^\sigma r_{23}y(r_{23}) \left\{ \int_{|r_{12}-r_{23}|}^{r_{12}+r_{23}} r_{13} dr_{13} \right\} dr_{23}. \end{aligned} \quad (6.174)$$

Indeed, using the Heaviside function allows the integration over r_{23} from 0 to σ . As the integral in the second brackets is equal to $2r_{12}r_{23}$, the PY equation reduces finally to:

$$\begin{aligned} r_{12}y(r_{12}) = & r_{12} \left(1 + 4\pi\rho \int_0^\sigma r_{23}^2 y(r_{23}) dr_{23} \right) \\ & - 2\pi\rho \int_0^\sigma r_{23}y(r_{23}) \left\{ \int_{|r_{12}-r_{23}|}^{r_{12}+r_{23}} y(r_{13}) \Theta(r_{13}-\sigma) r_{13} dr_{13} \right\} dr_{23}. \end{aligned} \quad (6.175)$$

This equation is a *Fredholm linear integral equation of the second kind* which is generally solved by a numerical method. However, following a rigorous analysis of the analytic properties of Laplace transforms, Wertheim [74] and Thiele [75] have found the exact analytical expressions for the direct correlation function $c_{HS}(r)$ and the structure factor $S_{HS}(q)$. After calculations, which are not reproduced here, the expression for the direct correlation function $c_{HS}(r)$ in the hard core takes the polynomial form:

$$c_{HS}(r) = -\alpha - \beta \left(\frac{r}{\sigma} \right) - \gamma \left(\frac{r}{\sigma} \right)^3, \quad (6.176)$$

where

$$\alpha = \frac{(1+2\eta)^2}{(1-\eta)^4}, \quad \beta = -\frac{6\eta \left(1+\frac{\eta}{2}\right)^2}{(1-\eta)^4}, \quad \gamma = \frac{\eta(1+2\eta)^2}{2(1-\eta)^4} \quad \text{and} \quad \eta = \frac{\pi}{6} \rho \sigma^3. \quad (6.177)$$

The structure factor $S_{HS}(q)$ can also be determined in analytical form by computing the Fourier transform of the direct correlation function from equation (6.129) as:

$$\rho c_{HS}(q) = 1 - \frac{1}{S_{HS}(q)} = \rho \int c_{HS}(r) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \quad (6.178)$$

and by setting $x = \frac{r}{\sigma}$, it follows:

$$\rho c_{HS}(q) = -4\pi\rho\sigma^3 \int_0^1 [\alpha + \beta x + \gamma x^3] \frac{\sin(q\sigma x)}{q\sigma x} x^2 dx. \quad (6.179)$$

The integral of this relation splits into three contributions allowing to write the Fourier transform of the direct correlation function as¹³:

$$\rho c_{HS}(q) = -24\eta [\alpha J_1(q\sigma) + \beta J_2(q\sigma) + \gamma J_3(q\sigma)]. \quad (6.180)$$

The substitution of $\rho c_{HS}(q)$ by its expression in equation (6.129) gives the possibility of deducing the structure factor of the HS potential in analytical form:

$$S_{HS}(q) = \frac{1}{1 - \rho c_{HS}(q)}. \quad (6.181)$$

It is important to note that there is an analytical expression for the HS structure factor, while there is no equivalent analytical expression for the pair correlation function which must be calculated numerically¹⁴ with equation (6.175). Figure (6.4) displays the representations of correlation functions and their Fourier transforms.

Since the isothermal compressibility χ_T is related to the direct correlation function (Eq. 6.132), we can envisage the possibility of

¹³By performing integrations by parts, we obtain the three partial integrals:

$$\begin{aligned} J_1(q\sigma) &= \frac{1}{(q\sigma)} \int_0^1 x \sin(q\sigma x) dx = \frac{1}{(q\sigma)^3} [\sin(q\sigma) - (q\sigma) \cos(q\sigma)]; \\ J_2(q\sigma) &= \frac{1}{(q\sigma)} \int_0^1 x^2 \sin(q\sigma x) dx \\ &= \frac{1}{(q\sigma)^4} \{2(q\sigma) \sin(q\sigma) - [(q\sigma)^2 - 2] \cos(q\sigma) - 2\}; \\ J_3(q\sigma) &= \frac{1}{(q\sigma)} \int_0^1 x^4 \sin(q\sigma x) dx \\ &= \frac{1}{(q\sigma)^6} \{[4(q\sigma)^3 - 24(q\sigma)] \sin(q\sigma) - [(q\sigma)^4 - 12(q\sigma)^2 + 24] \cos(q\sigma) + 24\}. \end{aligned}$$

¹⁴For a listing of the FORTRAN program to calculate the pair correlation function $g_{HS}(r)$ of the HS potential, consult the book of D. A. McQuarrie, *Statistical Mechanics*, Harper and Row, New-York (1976), p. 600.

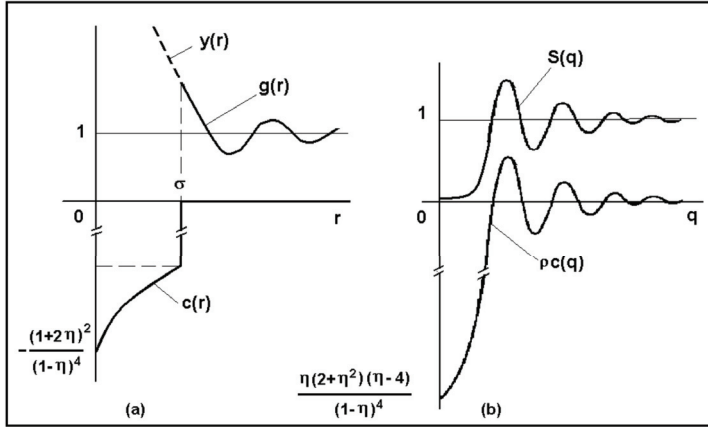


Figure 6.4: (a) Schematic representations of the direct correlation function $c(r)$, pair correlation function $g(r)$ and cavity function $y(r)$ for the HS potential. (b) Schematic representations of the structure factor $S(q)$ and Fourier transform of the direct correlation function $\rho c(q)$ for the HS potential.

linking the thermodynamic properties of the HS potential with the structural properties, and deriving an equation of state for the HS potential different from equation (5.176). Indeed, equation (6.132) reads:

$$\frac{1}{S(0)} = \frac{1}{\rho k_B T \chi_T} = 1 - 4\pi\rho \int_0^\sigma \left[-\alpha - \beta \left(\frac{r}{\sigma} \right) - \gamma \left(\frac{r}{\sigma} \right)^3 \right] r^2 dr \quad (6.182)$$

and reduces to¹⁵ :

$$\frac{1}{\rho k_B T \chi_T} = \frac{1}{k_B T} \left(\frac{\partial p}{\partial \rho} \right)_T = \frac{(1+2\eta)^2}{(1-\eta)^4}. \quad (6.183)$$

¹⁵With the reduced variable $x = \frac{r}{\sigma}$, the integral is written:

$$\begin{aligned} \frac{1}{k_B T} \left(\frac{\partial p}{\partial \rho} \right)_T &= 1 + 4\pi\rho\sigma^3 \int_0^1 [\alpha x^2 + \beta x^3 + \gamma x^5] dx \\ &= 1 + 4\pi\rho\sigma^3 \left[\frac{1}{3} \frac{(1+2\eta)^2}{(1-\eta)^4} - \frac{6\eta \left(1 + \frac{\eta}{2}\right)^2}{4(1-\eta)^4} + \frac{\eta(1+2\eta)^2}{12(1-\eta)^4} \right] = \frac{(1+2\eta)^2}{(1-\eta)^4}. \end{aligned}$$

As regards the HS equation of state resulting from the compressibility, it is obtained by integrating the above relation with respect to ρ (or $\eta = \frac{\pi}{6}\rho\sigma^3$). The expression for this HS equation of state reads:

$$\frac{p^{(c)}}{k_B T} = \int_0^\eta \frac{(1+2\eta)^2}{(1-\eta)^4} \left(\frac{6}{\pi\sigma^3} \right) d\eta, \quad (6.184)$$

that is to say¹⁶:

$$\frac{p^{(c)}}{\rho k_B T} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}. \quad (6.185)$$

This equation of state, called the *compressibility equation*, is also obtained on the basis of purely thermodynamic considerations [76, 77]. It differs substantially from the Carnahan–Starling [42] equation of state (Eq. 5.176).

It should be mentioned that a third HS equation of state can also be derived using the pressure relation (Eq. 5.167). It is written in terms of the cavity function $y(r) = g(r) \exp[\beta u(r)]$ in the form:

$$p = k_B T \frac{N}{V} + \frac{2\pi}{3} k_B T \rho^2 \sigma^3 y(\sigma). \quad (6.186)$$

However, when $r \leq \sigma$, the cavity function is equal to the opposite of the direct correlation function (Eq. 6.170) so that the above equation, called *pressure equation*, is reduced to¹⁷:

$$\frac{p^{(p)}}{\rho k_B T} = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2}. \quad (6.187)$$

¹⁶The calculation of the integral over η is as follows:

$$\begin{aligned} \frac{p^{(c)}}{k_B T} &= \int_0^\eta \frac{(1+2\eta)^2}{(1-\eta)^4} \frac{6}{\pi\sigma^3} d\eta = \frac{6}{\pi\sigma^3} \int_0^\eta \left[\frac{4}{(1-\eta)^2} - \frac{12}{(1-\eta)^3} + \frac{9}{(1-\eta)^4} \right] d\eta \\ &= \frac{6}{\pi\sigma^3} \left[\frac{4}{(1-\eta)} - \frac{6}{(1-\eta)^2} + \frac{3}{(1-\eta)^3} \right]_0^\eta = \rho \frac{1 + \eta + \eta^2}{(1-\eta)^3}. \end{aligned}$$

¹⁷The expression for the pressure equation of state of the HS potential is obtained as follows:

$$\begin{aligned} p &= k_B T \frac{N}{V} - \frac{2\pi}{3} k_B T \rho^2 \sigma^3 c(\sigma) = k_B T \frac{N}{V} - \frac{2\pi}{3} k_B T \rho^2 \sigma^3 [-\alpha - \beta - \gamma]; \\ \frac{p}{\rho k_B T} &= 1 - 4\eta \left[-\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{6\eta \left(1 + \frac{\eta}{2}\right)^2}{(1-\eta)^4} - \frac{\eta(1+2\eta)^2}{2(1-\eta)^4} \right] = \frac{1 + 2\eta + 3\eta^2}{(1-\eta)^2}. \end{aligned}$$

It is easy to check whether the three HS equations of state (Eqs. 6.187, 6.185 and 5.176) provide virtually identical results for values of $\eta < 0.3$. Note that they are linked together by the linear relation:

$$\frac{p^{(CS)}}{\rho k_B T} = \frac{2}{3} \frac{p^{(c)}}{\rho k_B T} + \frac{1}{3} \frac{p^{(p)}}{\rho k_B T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (6.188)$$

6.5 The bridge function

Self-consistent condition of the integral equations

In the previous section, the Percus–Yevick equation has been established with the functional derivative technique by choosing a particular generating functional (Eq. 6.137). The approximate PY equation thus obtained (Eqs. 6.163 to 6.165):

$$c^{PY}(r_{12}) = g(r_{12}) \{1 - \exp[\beta u(r_{12})]\} = h(r_{12}) + 1 - y(r_{12}), \quad (6.189)$$

combined with the exact OZ equation (Eq. 6.122):

$$g(r_{12}) - 1 = c(r_{12}) + \rho \int c(r_{23}) [g(r_{13}) - 1] d\mathbf{r}_3, \quad (6.190)$$

for a given potential $u(r_{12})$, allows the determination of the correlation functions by solving numerically the system of equations formed by equations (6.189) and (6.190).

For the HS potential, the direct correlation function $c_{HS}^{PY}(r)$ (Eq. 6.176) and the structure factor $S_{HS}^{PY}(q)$ (Eq. 6.181) have been derived under analytical forms, and two equations of state (Eqs. 6.185 and 6.187) differing substantially from each other have been obtained. This internal inconsistency of the theory is due to the fact that the PY equation is an approximate relation. Besides, when compared to the simulation results, the pair correlation function $g_{HS}^{PY}(r)$ has some flaws: the height of the main peak is too low, the long-range oscillations are not sufficiently damped and slightly out of phase. Verlet and Weis [78] proposed a correction that improves significantly the amplitude and the position of the oscillations of $g_{HS}^{PY}(r)$.

In addition to the PY equation, other possible choices for the generating functional have also been mentioned (see footnote 11 of this chapter). It turns out that one of them (HNC equation) leads to the

HNC direct correlation function by a calculation similar to that of the PY equation, i.e.:

$$c^{HNC}(r_{12}) = h(r_{12}) - \ln y(r_{12}) . \quad (6.191)$$

According to equation (6.189), the difference between the direct correlation functions $c^{HNC}(r_{12})$ and $c^{PY}(r_{12})$ is:

$$c^{HNC}(r_{12}) - c^{PY}(r_{12}) = y(r_{12}) - 1 - \ln y(r_{12}) . \quad (6.192)$$

For the HS potential, the direct correlation functions are respectively $c_{HS}^{HNC}(r_{12}) = h(r_{12}) - \ln [h(r_{12})+1]$ and $c_{HS}^{PY}(r_{12}) = 0$ (Eq. 6.169), when $r > \sigma$.

Having observed that the direct correlation function of the HNC equation has a contribution at long distances, while that of the PY equation is zero, Rowlinson [79] proposed to combine the two integral equations by mixing the direct correlation functions as follows:

$$\begin{aligned} c^{Ro}(r_{12}) &= c^{PY}(r_{12}) + \alpha(\rho, T) [c^{HNC}(r_{12}) - c^{PY}(r_{12})] \\ &= [h(r_{12})+1-y(r_{12})] + \alpha(\rho, T) [y(r_{12})-1-\ln y(r_{12})] , \end{aligned} \quad (6.193)$$

where $\alpha(\rho, T)$ is an adjustable parameter depending on the density and temperature. This choice allows a recovery of the PY equation when $\alpha(\rho, T)=0$ and the HNC equation when $\alpha(\rho, T)=1$. Concerning the optimal value of $\alpha(\rho, T)$, it is obtained by successive iterations until the thermodynamic consistency is reached by imposing the equality between $\chi_T^{(c)}$ and $\chi_T^{(p)}$ defined respectively by equations (5.85) and (5.87):

$$\chi_T^{(c)} = \frac{1}{\rho k_B T} + \frac{4\pi}{k_B T} \int_0^\infty [g(r) - 1] r^2 dr , \quad (6.194)$$

and

$$\frac{1}{\chi_T^{(p)}} = \rho k_B T - \frac{2\pi\rho^2}{3} \int_0^\infty r^3 \frac{\partial u(r)}{\partial r} \left[2g(r, T, \rho) + \rho \frac{\partial g(r, T, \rho)}{\partial \rho} \right] dr . \quad (6.195)$$

It should be noted that the validity of this trick relies less on physical reliable bases than on the results obtained because the quality of the pair correlation function is significantly improved regardless of the density and the type of potential.

Diagrammatic representation of correlation functions

In the foregoing, the PY and HNC equations have been established by the formalism of functionals. But this is not the only possible way. Historically, the liquid theory has been developed on the basis of knowledge gained through the study of real gases (section 4.3), by replacing the correlation functions by infinite series [80] in ascending powers of the density ρ .

Since the coefficients of these series are cluster integrals difficult to calculate, the series were often truncated to second order in ρ , and a great effort focused on the topological reduction of the cluster integrals by using the diagram approach developed by Mayer [8]. For example, Rushbrooke and Scoins [82] showed that the direct correlation function $c(r)$ is expressed in the form of series in ascending powers of the density ρ :

$$c(r_{12}) = \sum_{n \geq 1} \alpha_{n+1}(r_{12}) \rho^{n-1}, \quad (6.196)$$

where the coefficients $\alpha_{n+1}(r_{12})$ correspond to some types of cluster integrals. To outline the diagram approach, we follow the terminology of Klein and Green [83] and Martynov [84] by writing the expansion of the total correlation function $h(r_{12})$ as:

$$h(r_{12}) = f(r_{12}) + [1 + f(r_{12})] D(r_{12}), \quad (6.197)$$

where $f(r_{12}) (= \exp[-\beta u(r_{12})] - 1)$ is the Mayer function, and $D(r_{12})$ a linear combination of cluster integrals whose formal expression is:

$$D(r_{12}) = \sum_{n=1}^{\infty} \left[\sum \frac{1}{\mu(n, \gamma)} \int \prod_{i,j} f(r_{ij}) d\mathbf{r}_3 \dots d\mathbf{r}_n \right] \rho^n. \quad (6.198)$$

Here the term in brackets is the coefficient associated with a specific power of density and $\mu(n, \gamma)$ a number corresponding to each particular type of cluster. Figure (6.5a) shows the representation of the first few diagrams of $D(r_{12})$.

As in section (3.2), each Mayer function is represented by a segment (an f -bond) joining two points. To differentiate the points 1 and 2 (root points) from the points 3 and 4 (field points) on which the integrations take place, the first are denoted by white dots and the latter ones by black dots. The first term of the expansion in figure

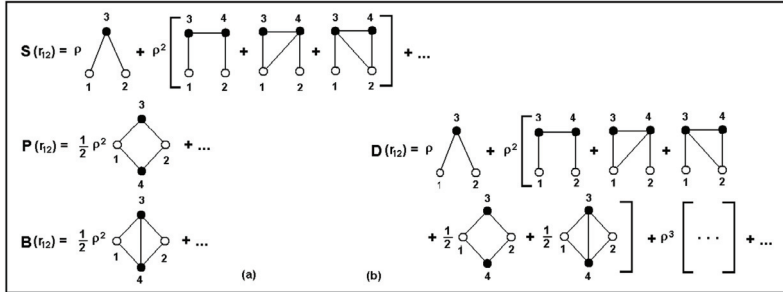


Figure 6.5: (a) Representations of the series diagrams $S(r_{12})$, parallel diagrams $P(r_{12})$ and bridges diagrams $B(r_{12})$. (b) Diagrammatic expansion of the function $D(r_{12})$.

(6.5a) corresponds to a cluster of three particles whose integration is performed on the particle 3, and whose expression is:

$$\int f(r_{13})f(r_{23})dr_3. \quad (6.199)$$

The next terms in between the first brackets contain five clusters of four particles, with integrations carried out on particles 3 and 4. However, these clusters have some common topological characteristics likely to classify them into three categories:

- a) the *series diagrams*, where each cluster contains *at least one black point* through which all the paths pass connecting the base points 1 and 2,
- b) the *parallel diagrams*, where each cluster contains *at least two independent paths* connecting the base points 1 and 2,
- c) the *bridges diagrams* which are neither parallel nor series.

Thus, the graph $D(r_{12})$ represented in figure (6.5a) is composed of four series clusters, one parallel cluster and one bridge cluster. As a result, if the sum of all the cluster series, when assigned to their respective coefficients, is labelled as $S(r)$, the cluster parallel as $P(r)$ and the cluster bridge as $B(r)$ (Fig. 6.5b), the diagram $D(r_{12})$ can be written:

$$D(r_{12}) = S(r_{12}) + P(r_{12}) + B(r_{12}). \quad (6.200)$$

The substitution of this expression of $D(r_{12})$ in equation (6.197) gives the total correlation function $h(r_{12})$:

$$\begin{aligned} h(r_{12}) &= f(r_{12}) + [1 + f(r_{12})] [S(r_{12}) + P(r_{12}) + B(r_{12})] \\ &= S(r_{12}) + P(r_{12}) + B(r_{12}) + f(r_{12}) [1 + S(r_{12}) + P(r_{12}) + B(r_{12})]. \end{aligned} \quad (6.201)$$

However, the total correlation function $h(r_{12})$ is traditionally decomposed into two contributions: the *direct correlation function* $c(r_{12})$ and the *indirect correlation function* $\gamma(r_{12})$:

$$h(r_{12}) = c(r_{12}) + \gamma(r_{12}), \quad (6.202)$$

where $\gamma(r_{12})$ is assumed to be the sum of the series clusters and $c(r_{12})$ the sum of the remaining clusters, namely:

$$\gamma(r_{12}) = S(r_{12}), \quad (6.203)$$

$$\begin{aligned} c(r_{12}) &= P(r_{12}) + B(r_{12}) \\ &\quad + f(r_{12}) [1 + S(r_{12}) + P(r_{12}) + B(r_{12})]. \end{aligned} \quad (6.204)$$

A thorough examination (Fig. 6.5a) of the diagram $S(r_{12})$ shows that all the clusters contain a single segment between a base point (for instance: point 1) and a point at which the integration takes place (for instance: point 3), whereas a bundle of segments between the other base point (point 2) and the point 3 can exist. This suggests that the diagram $S(r_{12})$ is equivalent to the following convolution product of correlation functions:

$$S(r_{12}) = \gamma(r_{12}) = \rho \int c(r_{23}) h(r_{13}) d\mathbf{r}_3. \quad (6.205)$$

The validity of this assumption is immediately recognized in substituting the foregoing expression of $\gamma(r_{12})$ in equation (6.202), as it allows us to find directly the Ornstein–Zernike relation:

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{23}) h(r_{13}) d\mathbf{r}_3, \quad (6.206)$$

and its Fourier transform (Eq. 6.126):

$$[1 + \rho h(q)] [1 - \rho c(q)] = 1, \quad (6.207)$$

as well as the expressions of $h(q)$ and $\gamma(q)$:

$$h(q) = \frac{1}{\rho} \left[\frac{1}{1 - \rho c(q)} - 1 \right] = \frac{c(q)}{1 - \rho c(q)}, \quad (6.208)$$

$$\gamma(q) = h(q) - c(q) = \frac{\rho c^2(q)}{1 - \rho c(q)}. \quad (6.209)$$

Some expressions for the bridge function

With equation (6.201), it is easy to express the cavity function in terms of diagrams as¹⁸:

$$\begin{aligned} y(r_{12}) &= g(r_{12}) \exp [\beta u(r_{12})] \\ &= [1 + S(r_{12}) + P(r_{12}) + B(r_{12})], \end{aligned} \quad (6.210)$$

and to simplify the direct correlation function (Eq. 6.204) as:

$$c(r_{12}) = P(r_{12}) + B(r_{12}) + f(r_{12}) y(r_{12}). \quad (6.211)$$

Incidentally, it can be noted that equation (6.211) coincides with the PY equation (Eq. 6.164) when $P(r_{12}) = B(r_{12}) = 0$. By contrast, if only $B(r_{12}) = 0$ (condition for the HNC equation), the expression for the parallel cluster $P(r_{12})$ is obtained by comparing equations (6.191) and (6.211):

$$\begin{aligned} c^{HNC}(r_{12}) &= g(r_{12}) - 1 - \ln y(r_{12}) \\ &= P(r_{12}) + f(r_{12}) y(r_{12}), \end{aligned} \quad (6.212)$$

$$\text{or} \quad P(r_{12}) = g(r_{12}) - 1 - \ln y(r_{12}) - f(r_{12}) y(r_{12}). \quad (6.213)$$

¹⁸Using the Mayer function $f(r_{12})$, equation (6.201) is simplified as follows:

$$\begin{aligned} h(r_{12}) &= f(r_{12}) + [1 + f(r_{12}) [S(r_{12}) + P(r_{12}) + B(r_{12})]], \\ g(r_{12}) - 1 &= \{ \exp [-\beta u(r_{12})] - 1 \} \\ &\quad + \{ \exp [-\beta u(r_{12})] \} [S(r_{12}) + P(r_{12}) + B(r_{12})], \\ g(r_{12}) &= \{ \exp [-\beta u(r_{12})] \} [1 + S(r_{12}) + P(r_{12}) + B(r_{12})], \\ g(r_{12}) \exp [\beta u(r_{12})] &= [1 + S(r_{12}) + P(r_{12}) + B(r_{12})]. \end{aligned}$$

Replacing $P(r_{12})$ in equation (6.210) yields the pair correlation function¹⁹:

$$g(r_{12}) = \exp[-\beta u(r_{12}) + S(r_{12}) + B(r_{12})] . \quad (6.214)$$

Similarly, replacing $P(r_{12})$ in equation (6.211) provides the following exact expression which can be seen as the key relation of the contemporary integral equation theory:

$$c(r_{12}) = g(r_{12}) - 1 - \ln y(r_{12}) + B(r_{12}) . \quad (6.215)$$

Note in passing that the direct correlation function can also be written²⁰ :

$$c(r) = \exp[-\beta u(r) + \gamma(r) + B(r)] - \gamma(r) - 1 . \quad (6.216)$$

The integral equation theory reduces essentially to the search for the bridge function $B(r_{12})$ because, once $B(r_{12})$ is known, it is sufficient to solve the system of equations constituted by the OZ relation (Eq. 6.206) and the auxiliary relation (Eq. 6.215) to derive $g(r)$ and $c(r)$. Many studies have been conducted in this direction over the last twenty years. Some were referred to the direct calculation of integrals of dominant clusters [85, 86]. However, most of them [87] were devoted to search for an approximate expression for the bridge function $B(r_{12})$.

¹⁹After inserting the foregoing expression of $P(r_{12})$ in equation (6.210), we proceed to subsequent simplifications with the cavity function $y(r_{12})$ and the Mayer function $f(r_{12})$:

$$\begin{aligned} g(r_{12}) \exp[\beta u(r_{12})] &= S(r_{12}) + g(r_{12}) - \ln y(r_{12}) \\ &\quad - \{\exp[-\beta u(r_{12})] - 1\} g(r_{12}) \exp[\beta u(r_{12})] + B(r_{12}), \\ 0 &= S(r_{12}) - \ln y(r_{12}) + B(r_{12}), \\ 0 &= S(r_{12}) - \ln \{g(r_{12}) \exp[\beta u(r_{12})]\} + B(r_{12}), \\ g(r_{12}) &= \exp[-\beta u(r_{12}) + S(r_{12}) + B(r_{12})] . \end{aligned}$$

²⁰With the expressions for the cavity function $y(r) = g(r) \exp[\beta u(r)]$ and the total correlation function $h(r) = g(r) - 1 = c(r) + \gamma(r)$, the direct correlation function is transformed as follows:

$$\begin{aligned} c(r) &= h(r) - \ln\{g(r) \exp[\beta u(r)]\} + B(r) , \\ \ln g(r) &= \ln[h(r) + 1] = \gamma(r) - \beta u(r) + B(r) , \\ \text{hence } c(r) &= g(r) - \gamma(r) - 1 = \exp[-\beta u(r) + \gamma(r) + B(r)] - \gamma(r) - 1 . \end{aligned}$$

The simplest expression is obviously that of the HNC equation as $B^{HNC}(r) = 0$. The bridge function of the PY equation is found by replacing the cavity function taken from equation (6.165) in equation (6.215). The result is²¹:

$$B^{PY}(r) = -\gamma(r) + \ln[1 + \gamma(r)] . \quad (6.217)$$

Other more accurate relations have been proposed [92], as for instance:

$$\begin{aligned} B^V(r) &= -\frac{\zeta}{2} \gamma^2(r) \frac{1}{1 + \alpha \gamma(r)} && \text{(Verlet 1980);} \\ B^{RY}(r) &= \ln \left[1 + \frac{\exp \{ \alpha \gamma(r) \} - 1}{\alpha} \right] - \gamma(r) && \text{(Rogers and Young 1984);} \\ B^{MS}(r) &= [1 - 2\gamma(r)]^{1/2} - 1 - \gamma(r) && \text{(Martynov and Sarkisov 1999).} \end{aligned}$$

where the parameters ζ and α are determined by means advocated by the authors. We see that $B(r)$ is not directly related to r by a simple function, but rather depends on it via the indirect correlation function $\gamma(r)$. In fact, the bridge function $B(r)$ becomes a functional [90, 93] of the indirect correlation function $\gamma(r)$. This has implications on the calculation of thermodynamic properties of liquids [94].

6.6 Thermodynamics and structure from the bridge function

It has been shown in section (5.4) that the thermodynamic properties of liquids are calculated by using the pair correlation function $g(r)$. Among the thermodynamic properties, the chemical potential is one of the quantities which are most sensitive to details of the bridge function $B(r)$. For proof, consider equation (5.48):

$$\beta\mu = \ln(\rho\Lambda^3) + \beta\mu^{\text{ex}}, \quad (6.218)$$

²¹Use is made of the total correlation function $h(r) = g(r) - 1$ and the indirect correlation function $\gamma(r) = h(r) - c(r)$. It follows that:

$$\begin{aligned} B(r) &= c(r) - g(r) + 1 + \ln y(r), \\ B^{PY}(r) &= c(r) - g(r) + 1 + \ln [g(r) - c(r)], \\ B^{PY}(r) &= -\gamma(r) + \ln [1 + \gamma(r)] . \end{aligned}$$

$$\text{with} \quad \beta\mu^{\text{ex}} = \rho \int_0^1 d\lambda \int \frac{\partial \beta u(r, \lambda)}{\partial \lambda} g(r, \lambda) d\mathbf{r}, \quad (6.219)$$

where $u(r, \lambda) = \lambda u(r)$ and the integrand in the above relation can also be written as²² :

$$\begin{aligned} \frac{\partial \beta u(r, \lambda)}{\partial \lambda} g(r, \lambda) &= h(r, \lambda) \frac{\partial}{\partial \lambda} [B(r, \lambda) - c(r, \lambda)] \\ &+ \frac{\partial}{\partial \lambda} \left[\frac{1}{2} h^2(r, \lambda) - c(r, \lambda) + B(r, \lambda) \right]. \end{aligned} \quad (6.220)$$

Having inverted the sequence of the integrations in equation (6.219) and taken that the functions $h(r, \lambda)$, $c(r, \lambda)$ and $B(r, \lambda)$ are zero when $\lambda = 0$, the expression for the excess chemical potential becomes:

$$\begin{aligned} \beta\mu^{\text{ex}} &= \rho \int \left\{ \frac{1}{2} h^2(r) - c(r) + B(r) \right. \\ &\quad \left. + \int_0^1 h(r, \lambda) \frac{\partial}{\partial \lambda} [B(r, \lambda) - c(r, \lambda)] d\lambda \right\} d\mathbf{r}. \end{aligned} \quad (6.221)$$

This relation is the *first exact expression for the excess chemical potential* in terms of the bridge function. The first three contributions to the integral over $\mathbf{r}$ can easily be calculated. As far as the integral over λ is concerned, it is a topological homotopy problem because the λ dependence for the functions $B(r, \lambda)$ and $c(r, \lambda)$ is unknown, whereas their values at $\lambda = 0$ and $\lambda = 1$ are. Therefore, the result

²²In explaining the cavity function $y(r) = g(r) \exp[\beta u(r)]$, equation (6.215) is

$$c(r, \lambda) = h(r, \lambda) - \ln g(r, \lambda) - \beta u(r, \lambda) + B(r, \lambda),$$

and its derivative with respect to λ is transformed as follows:

$$\begin{aligned} \frac{\partial \beta u(r, \lambda)}{\partial \lambda} &= \frac{\partial}{\partial \lambda} [h(r, \lambda) - c(r, \lambda) + B(r, \lambda)] - \frac{1}{g(r, \lambda)} \frac{\partial g(r, \lambda)}{\partial \lambda}, \\ \frac{\partial \beta u(r, \lambda)}{\partial \lambda} g(r, \lambda) &= [h(r, \lambda) + 1] \frac{\partial}{\partial \lambda} [h(r, \lambda) - c(r, \lambda) + B(r, \lambda)] - \frac{\partial h(r, \lambda)}{\partial \lambda} \\ &= h(r, \lambda) \frac{\partial h(r, \lambda)}{\partial \lambda} + h(r, \lambda) \frac{\partial}{\partial \lambda} [-c(r, \lambda) + B(r, \lambda)] \\ &\quad + \frac{\partial}{\partial \lambda} [-c(r, \lambda) + B(r, \lambda)] \\ &= h(r, \lambda) \frac{\partial}{\partial \lambda} [-c(r, \lambda) + B(r, \lambda)] \\ &\quad + \frac{\partial}{\partial \lambda} \left[\frac{h^2(r, \lambda)}{2} - c(r, \lambda) + B(r, \lambda) \right]. \end{aligned}$$

of the integral should depend on the selected path. For simplicity, most of the authors [94, 95, 96, 90] assume a linear dependence for the correlation functions, $c(r, \lambda) = \lambda c(r)$ and $h(r, \lambda) = \lambda h(r)$, but not for the bridge function. As can be seen by consulting the original articles, it allows replacing the integration on λ by the integration on γ . This raises some difficulties that will not be discussed here.

There is however another way to calculate the excess chemical potential based on the renormalization of the diagrammatic expansion of the bridge function. This *second expression for the excess chemical potential* obtained by Kiselyov and Martynov [97] is an exact relation not containing the coupling parameter λ . According to these authors, the excess chemical potential is expressed as:

$$\begin{aligned} \beta\mu^{\text{ex}} = & \rho \int \left[\frac{1}{2} h^2(r) - c(r) + B(r) \right] d\mathbf{r} \\ & + \rho \frac{1}{2} \int \left\{ -h(r)c(r) + h(r)[B(r) + M(r)] \right\} d\mathbf{r}, \quad (6.222) \end{aligned}$$

where $B(r)$ and $M(r)$ are the bridge functions represented by the diagrams in figure (6.6) to third order in density.

Since equations (6.221) and (6.222) are equivalent, their identification leads to the relation:

$$\begin{aligned} -\frac{1}{2} h(r)c(r) + \frac{1}{2} h(r)[B(r) + M(r)] = & \int_0^1 h(r, \lambda) \frac{\partial B(r, \lambda)}{\partial \lambda} d\lambda \\ & - \int_0^1 h(r, \lambda) \frac{\partial c(r, \lambda)}{\partial \lambda} d\lambda. \quad (6.223) \end{aligned}$$

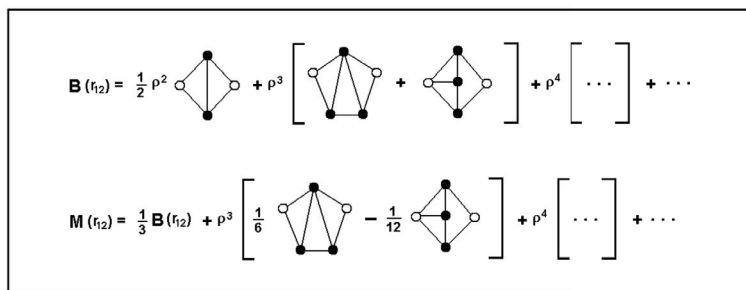


Figure 6.6: Representations of the bridge diagrams $B(r_{12})$ and $M(r_{12})$.

It is tempting to try to impose the thermodynamic consistency of the chemical potential by choosing the path of integration [98] on λ as element of adjustment. In this context, let us evaluate the last integral of the above relation by assuming that the λ dependence on the correlation functions is under the form $h(r, \lambda) = \lambda^n h(r)$ and $c(r, \lambda) = \lambda^n c(r)$ with $n > 0$. Thus, the right hand side of equation (6.223) is written²³:

$$h(r) \int_0^1 \lambda^n \frac{\partial B(r, \lambda)}{\partial \lambda} d\lambda - \frac{1}{2} h(r) c(r), \quad (6.224)$$

and equation (6.223) simplifies to:

$$B(r) + M(r) = 2 \int_0^1 \lambda^n \frac{\partial B(r, \lambda)}{\partial \lambda} d\lambda. \quad (6.225)$$

Then, we evaluate the integral of the foregoing relation by assuming a λ dependence on the bridge function under the form $B(r, \lambda) = \lambda^m B(r)$, where $m \neq n$ with $m > 0$. It gives:

$$B(r) + M(r) = 2mB(r) \int_0^1 \lambda^{n+m-1} d\lambda = 2 \frac{m}{m+n} B(r), \quad (6.226)$$

$$\text{hence} \quad M(r) = \left(\frac{m-n}{m+n} \right) B(r). \quad (6.227)$$

When $m = n$, it results that $M(r) = 0$ which is forbidden by the analysis of diagrams by Kiselyov and Martynov since, according to these authors, $0 < |M(r)| < \frac{1}{3} |B(r)|$. By inserting this expression of $M(r)$ in equation (6.222), the excess chemical potential reads:

$$\begin{aligned} \beta\mu^{\text{ex}} &= \rho \int \left[\frac{1}{2} h^2(r) - c(r) + B(r) \right] d\mathbf{r} \\ &\quad + \rho \frac{1}{2} \int \left[-h(r)c(r) + h(r)B(r) \left(\frac{2m}{m+n} \right) \right] d\mathbf{r} \\ &= \rho \int \left[\frac{1}{2} h^2(r) - c(r) + B(r) - \frac{1}{2} h(r)c(r) \right] d\mathbf{r} \\ &\quad + \left(\frac{2m}{m+n} \right) \rho \int \frac{1}{2} h(r)B(r) d\mathbf{r}, \end{aligned} \quad (6.228)$$

²³The second integral is solved analytically as follows:

$$\int_0^1 h(r, \lambda) \frac{\partial c(r, \lambda)}{\partial \lambda} d\lambda = h(r) c(r) n \int_0^1 \lambda^{2n-1} d\lambda = h(r) c(r) n \left[\frac{\lambda^{2n}}{2n} \right]_0^1 = \frac{1}{2} h(r) c(r).$$

or:

$$\beta\mu^{\text{ex}} = P(\rho) + \alpha Q(\rho), \quad (6.229)$$

with

$$P(\rho) = \rho \int \left[\frac{1}{2} h^2(r) - c(r) - \frac{1}{2} h(r) c(r) + B(r) \right] d\mathbf{r}, \quad (6.230)$$

$$Q(\rho) = \rho \int \frac{1}{2} h(r) B(r) d\mathbf{r}, \quad (6.231)$$

$$\text{and} \quad \alpha = \frac{2m}{m+n}. \quad (6.232)$$

To determine the value of α , we use equations (6.133) and (6.218) in conjunction with equation (6.229), namely:

$$\beta \frac{\partial \mu^{\text{ex}}}{\partial \rho} = - \int c(r) d\mathbf{r} = \frac{\partial P(\rho)}{\partial \rho} + \alpha \frac{\partial Q(\rho)}{\partial \rho}, \quad (6.233)$$

from which one derives:

$$\alpha = - \frac{\partial \rho}{\partial Q(\rho)} \left[\int c(r) d\mathbf{r} + \frac{\partial P(\rho)}{\partial \rho} \right]. \quad (6.234)$$

This relation permits a self-consistent calculation of the chemical potential for any bridge function. Furthermore, equation (6.232) provides the link between the path of integration taken to determine the correlation functions $h(r, \lambda)$ and $c(r, \lambda)$ affected to n , and the path of integration taken to obtain the bridge function $B(r, \lambda)$ affected to m :

$$m = \frac{\alpha}{2 - \alpha} n. \quad (6.235)$$

The random phase approximation

The problem mentioned here refers to the influence of the long-range pair potential contribution on the pair correlation function $g(r)$. This issue has already been discussed in connection with the Zwanzig perturbation theory (section 5.5). In this theory, the free energy F of the system was expanded in increasing powers of the coupling parameter λ , and the influence of perturbation on the thermodynamic properties was investigated. The method used here consists in expanding the pair correlation function $g(r)$ in ascending powers of a parameter ξ which characterizes the extent of the perturbation, and in doing a

diagrammatic representation of $g(r)$ likely to distinguish between the effects of repulsive and attractive parts of the potential. The need to cut the pair potential $u(r)$ into a repulsive part $u_0(r)$, at short distance, and an attractive part $u_1(r)$ at large distance, is due to the fact that the PY and HNC equations provide the same results for purely short-range potentials, whereas they give different results when the potentials contain a long-range attractive part [99, 100, 101].

For a brief account of the problem, we consider the pair potential:

$$u(r) = u_0(r) + u_1(r), \quad (6.236)$$

where $u_0(r)$ is the short-range repulsive part and $u_1(r)$ the long-range attractive part. However, if the perturbation $u_1(r)$ is small, the additivity of correlation functions can be assumed according to [102]:

$$h(r) = h_0(r) + h_1(r), \quad (6.237)$$

$$c(r) = c_0(r) + c_1(r), \quad (6.238)$$

$$\gamma(r) = \gamma_0(r) + \gamma_1(r), \quad (6.239)$$

as a consequence of the additivity of series and parallel diagrams. By contrast, it seems reasonable to suppose that the bridge diagrams are virtually unaffected by the presence of the perturbation, i.e. $B(r) \sim B_0(r)$.

With these assumptions, the pair correlation function $g_0(r)$ associated with the short-range repulsive part is written according to equation (6.214) as:

$$g_0(r_{12}) = \exp[-\beta u_0(r_{12}) + S_0(r_{12}) + B_0(r_{12})], \quad (6.240)$$

and the pair correlation function of the full potential $u(r)$ is:

$$g(r_{12}) = g_0(r_{12}) \exp[-\beta u_1(r_{12}) + S_1(r_{12})]. \quad (6.241)$$

If $g_0(r_{12})$ is known, the pair correlation function $g(r_{12})$ reduces to the knowledge of the series diagram $S_1(r_{12})$, i.e. the indirect correlation function $\gamma_1(r_{12}) = S_1(r_{12})$ (Eq. 6.203). For the purposes of calculation, it is more advantageous to work in reciprocal space by taking the Fourier transform of $\gamma_1(r_{12})$ in equation (6.239). With equation

(6.209), $\gamma_1(q)$ can be transformed as:

$$\gamma_1(q) = \gamma(q) - \gamma_0(q) = \frac{\rho c^2(q)}{1 - \rho c(q)} - \frac{\rho c_0^2(q)}{1 - \rho c_0(q)}, \quad (6.242)$$

$$= \frac{c_1(q) [1 + \rho h_0(q)]^2}{1 - \rho c_1(q) \frac{1}{1 - \rho c_0(q)}} - c_1(q), \quad (6.243)$$

where equation (6.243) has been obtained²⁴ with the help of equation (6.208). Then, by using equation (6.207), it follows:

$$\gamma_1(q) = \frac{c_1(q) [1 + \rho h_0(q)]^2}{1 - \rho c_1(q) [1 + \rho h_0(q)]} - c_1(q), \quad (6.244)$$

or:

$$h_1(q) = c_1(q) + \gamma_1(q) = \frac{c_1(q) [1 + \rho h_0(q)]^2}{1 - \rho c_1(q) [1 + \rho h_0(q)]}. \quad (6.245)$$

To determine $h_1(q)$, it remains to evaluate $c_1(q)$. Since the direct correlation function, at large distances, can be considered equivalent to the tail of the pair potential (Eq. 6.254), it is justified to take $c_1(q) \sim -\beta u_1(q)$ (see footnote 9 of this chapter). With this approximation, equation (6.245) reduces to:

$$h_1(q) = -\beta u_1(q) + \gamma_1(q) = -\frac{[1 + \rho h_0(q)]^2 \beta u_1(q)}{1 + \rho [1 + \rho h_0(q)] \beta u_1(q)}, \quad (6.246)$$

²⁴We use equation (6.208) to transform the denominators $1 - \rho c_0(q)$ ($= \frac{c_0(q)}{h_0(q)}$) of fractions in equation (6.242) and make the following simplifications:

$$\begin{aligned} \gamma_1(q) &= \frac{h_0(q) [\rho c_0^2(q) + 2\rho c_0(q)c_1(q) + \rho c_1^2(q)]}{c_0(q) - \rho c_1(q)h_0(q)} - \rho c_0(q)h_0(q) \\ &= \frac{2\rho c_0(q)c_1(q)h_0(q) + \rho c_1^2(q)h_0(q) + \rho^2 c_0(q)c_1(q)h_0^2(q)}{c_0(q) - \rho c_1(q)h_0(q)} \\ &= \frac{c_0(q)c_1(q) [2\rho h_0(q) + \rho^2 h_0^2(q) + 1] - c_0(q)c_1(q) + \rho c_1^2(q)h_0(q)}{c_0(q) - \rho c_1(q)h_0(q)} \\ &= \frac{c_1(q) [1 + \rho h_0(q)]^2}{1 - \rho c_1(q) \frac{h_0(q)}{c_0(q)}} - c_1(q) = \frac{c_1(q) [1 + \rho h_0(q)]^2}{1 - \rho c_1(q) \frac{1}{1 - \rho c_0(q)}} - c_1(q). \end{aligned}$$

and its inverse Fourier transform is written:

$$\begin{aligned} h_1(r_{12}) &= FT[-\beta u_1(q) + \gamma_1(q)] \\ &= -\beta u_1(r_{12}) + \gamma_1(r_{12}) \end{aligned} \quad (6.247)$$

$$= -\frac{1}{(2\pi)^3} \int \frac{[1 + \rho h_0(q)]^2 \beta u_1(q)}{1 + \rho[1 + \rho h_0(q)] \beta u_1(q)} \exp(-i \mathbf{q} \cdot \mathbf{r}_{12}) d\mathbf{q}. \quad (6.248)$$

If $S_1(r_{12}) = \gamma_1(r_{12})$ is taken for granted, a short look at equation (6.247) is sufficient to identify the argument of the exponential function in equation (6.241) as $h_1(r_{12})$:

$$-\beta u_1(r_{12}) + S_1(r_{12}) = -\beta u_1(r_{12}) + \gamma_1(r_{12}) = h_1(r_{12}). \quad (6.249)$$

Therefore, the pair correlation function $g(r_{12})$ is obtained by replacing $h_1(r_{12})$ (Eq. 6.248) in equation (6.241):

$$\begin{aligned} g(r_{12}) &= g_0(r_{12}) \exp \left[-\frac{1}{(2\pi)^3} \times \right. \\ &\quad \left. \times \int \frac{[1 + \rho h_0(q)]^2 \beta u_1(q)}{1 + \rho[1 + \rho h_0(q)] \beta u_1(q)} \exp(-i \mathbf{q} \cdot \mathbf{r}_{12}) d\mathbf{q} \right]. \end{aligned} \quad (6.250)$$

Before closing this subsection, let us use the result of equation (6.245) to deduce the structure factor $S(q)$. Indeed, with equation (6.128), the structure factor reads:

$$S(q) = 1 + \rho h(q) = 1 + \rho h_0(q) + \rho h_1(q), \quad (6.251)$$

where $1 + \rho h_0(q) = S_0(q)$ is the structure factor corresponding to the potential $u_0(r_{12})$ and $\rho h_1(q)$ is given by equation (6.245). Then, after replacing $\rho h_1(q)$ by its expression in the above equation, we obtain the structure factor:

$$S(q) = S_0(q) + \frac{\rho c_1(q) S_0(q)^2}{1 - \rho c_1(q) S_0(q)} = \frac{S_0(q)}{1 - \rho c_1(q) S_0(q)}, \quad (6.252)$$

or equivalently:

$$S(q) = \frac{S_0(q)}{1 + \rho \beta u_1(q) S_0(q)}. \quad (6.253)$$

Equation (6.250) has been demonstrated in various ways and used in many applications [33], especially with the potentials of Coulomb, Kac, Gauss, Lennard-Jones, and even with the oscillating potentials

for metals. As far as equation (6.253) is concerned, it allows calculating the structure factor $S(q)$ in the *random phase approximation* (RPA) as a function of the structure factor $S_0(q)$ of the unperturbed system and the Fourier transform of the perturbation $u_1(r)$. Note that it is possible to improve significantly the result of $S(q)$ with the *optimized random phase approximation* (ORPA) as it was developed by Weeks et al. [39, 101].

It appeared in all the works involved in the microscopic liquid theory that the long-range contribution to the direct correlation function plays a secondary – though not negligible – role on the structural and thermodynamic properties of liquids. Therefore, it has been proposed to make no distinction between the direct correlation function $c(r)$ and the pair potential, at large distances, via the formula (see footnote 9 of this chapter):

$$c(r) \sim -\beta u(r). \quad (6.254)$$

A model frequently used in the liquid theory is known as the *mean sphere approximation* [103] (MSA). In this approximation, the PY equation is used in conjunction with the OZ relation for studying the attractive contribution of potential. The MSA requiring that the direct correlation function is $c(r) = -\beta u(r)$ outside the core and the pair correlation function $g(r) = 0$ in the core differs from the RPA by the second condition. As an example, for the hard-core Yukawa (HCY) potential, the MSA reads:

$$g(r) = 0 \quad \text{if } r \leq \sigma, \quad (6.255)$$

$$c_{HCY}(r) = \beta \left(\frac{\varepsilon \sigma}{r} \right) \exp \left[-\lambda \left(\frac{r}{\sigma} - 1 \right) \right] \quad \text{if } r > \sigma, \quad (6.256)$$

where σ is the HS diameter. In using the same type of calculation as that of Wertheim [74] and Thiele [75] for hard spheres, Waisman [104] found an analytical solution for the direct correlation function for HCY potential, whose expression outside the core is the same as the previous one, whereas it contains inside the core the contributions of the HS potential (Eq. 6.176) and the HCY potential, namely:

$$\begin{aligned}
c_{HCY}(r) = & \left[-\alpha' - \beta' \left(\frac{r}{\sigma} \right) - \gamma' \left(\frac{r}{\sigma} \right)^3 \right] \\
& - \left(\frac{\beta \varepsilon \sigma w}{r} \right) \left\{ \frac{1 - \exp \left(-\lambda \frac{r}{\sigma} \right)}{\lambda} \right. \\
& \left. + \frac{w}{2\lambda^2 \exp(\lambda)} \left[\cosh \left(\lambda \frac{r}{\sigma} \right) - 1 \right] \right\}, \text{ if } r \leq \sigma, \quad (6.257)
\end{aligned}$$

in addition to the condition $g(r) = 0$. The determination of the parameters α' , β' , γ' and w should be made with other relations not provided here but found, for example, in the article by Hoyer and Stell [105]. Observing the HS structure factor, the structure factor $S_{HCY}(q)$ can likewise be determined in analytical form by taking the Fourier transform of $c_{HCY}(r)$, whereas the calculation of the pair correlation function $g_{HCY}(r)$ must be performed numerically.

7 Numerical solutions and simulation

7.1 Solution of the integral equations

Once the foundations of the integral equation theory have been posed, it seems appropriate to give some guidance on how to solve the system of equations formed by the Ornstein–Zernike relation (Eq. 6.206) and the auxiliary relation (Eq. 6.216). Usually these equations are presented using the indirect correlation function $\gamma(r)$ in the following forms:

$$h(r) = c(r) + \gamma(r), \quad (7.1)$$

$$c(r) = \exp[-\beta u(r) + \gamma(r) + B(r)] - \gamma(r) - 1. \quad (7.2)$$

The traditional numerical solution of these equations is obtained by the direct iteration method developed by Picard according to the following principle: $u(r)$ and $B(r)$ being known, an arbitrary function $h_0(r)$ is chosen as close as possible to the actual function, and then the functions $\gamma_1(r)$ and $c_1(r)$ are obtained after the first iteration with equations (7.1) and (7.2). The function $h_1(r)$ thus deduced generally differs from $h_0(r)$. This is why it is reinjected into the system of equations in order to determine $\gamma_2(r)$ and $c_2(r)$ at the end of the second iteration. The iterative procedure is repeated until the functions $\gamma(r)$ and $c(r)$ stop varying. Unfortunately, for liquids, the method converges slowly, even when the function $h_0(r)$ is correctly chosen. Another method is to transform the system of equations in reciprocal space by discretizing the correlation functions and solving the system of nonlinear equations by the Newton–Raphson method.

Even if the convergence is better than the Picard iterative method, the resolution is time consuming because it requires a large number of matrix inversions.

A third more efficient method, proposed by Gillan [106], consists in separating the correlation functions into two parts, then integrate successively the first part with the Newton–Raphson method and the second part with the Picard method. A compromise in the separation of the two parts to be treated must be done to have maximum rapidity and efficiency. It should be noted that the part of the correlation functions to be handled by the Newton–Raphson method is decomposed in reciprocal space on carefully selected basis functions. In the next paragraphs, we present the method of Labik et al. [107] who advocated to use the sine function as basis function.

Let us write the Fourier transforms of the functions $c(r)$ and $\gamma(r)$ with the standard formulas, namely:

$$\gamma(q) = \int \gamma(r) \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r} = 4\pi \int_0^\infty r\gamma(r) \frac{\sin(qr)}{q} dr \quad (7.3)$$

$$\text{and } c(q) = \int c(r) \exp(i\mathbf{q}\cdot\mathbf{r}) d\mathbf{r} = 4\pi \int_0^\infty rc(r) \frac{\sin(qr)}{q} dr, \quad (7.4)$$

with

$$\gamma(r) = \frac{1}{(2\pi)^3} \int \gamma(q) \exp(-i\mathbf{q}\cdot\mathbf{r}) d\mathbf{q} = \frac{4\pi}{(2\pi)^3} \int q\gamma(q) \frac{\sin(qr)}{r} dq, \quad (7.5)$$

$$c(r) = \frac{1}{(2\pi)^3} \int c(q) \exp(-i\mathbf{q}\cdot\mathbf{r}) d\mathbf{q} = \frac{4\pi}{(2\pi)^3} \int qc(q) \frac{\sin(qr)}{r} dq. \quad (7.6)$$

Then, we take advantage of the symmetry of these relations to define the new functions:

$$\Gamma(r) = r\gamma(r) = \frac{1}{2\pi^2} \int \Gamma(q) \sin(qr) dq \quad (7.7)$$

$$\text{and } C(r) = rc(r) = \frac{1}{2\pi^2} \int C(q) \sin(qr) dq, \quad (7.8)$$

with $\Gamma(q) = q\gamma(q)$ and $C(q) = qc(q)$, which will allow us to write the auxiliary relation (Eq. 7.2) and the Fourier transform of the OZ relation (Eq. 6.209) in the following forms:

$$C(r) = r \exp \left[-\beta u(r) + \frac{\Gamma(r)}{r} + B(r) \right] - \Gamma(r) - r, \quad (7.9)$$

$$\Gamma(q) = \frac{\rho C^2(q)}{q - \rho C(q)}. \quad (7.10)$$

Since the method is meant to juggle with the functions $\Gamma(r)$ and $C(r)$ and their Fourier transforms, we discretize the functions $\Gamma(r)$ and $C(q)$ by using the sampling theorem. Assuming that the number of sampled values is N , and Δr and Δq are the respective mesh size in real and reciprocal spaces, these three quantities are related by:

$$\Delta q = \frac{\pi}{N\Delta r}. \quad (7.11)$$

If, moreover, it is admitted to identify the variables in the direct space with index i and in the reciprocal space with the index j , the discrete variables r_i and q_j can be written $r_i = i\Delta r$ and $q_j = j\Delta q = j\frac{\pi}{N\Delta r}$. Thus, by replacing the integrals with discrete sums, equations (7.7) and (7.4) are transformed as follows¹:

$$\Gamma(r_i) = r_i \gamma(r_i) = \frac{1}{2\pi^2} \sum_{j=1}^{N-1} \Gamma(q_j) \sin(q_j r_i) \Delta q, \quad (7.12)$$

$$\text{hence } \Gamma_i = \frac{\Delta q}{2\pi^2} \sum_{j=1}^{N-1} \tilde{\Gamma}_j \sin\left(\frac{\pi}{N} i j\right), \quad i = 1, 2, \dots, N-1, \quad (7.13)$$

and

$$C(q_j) = q_j c(q_j) = 4\pi \sum_{i=1}^{N-1} C(r_i) \sin(q_i r_i) \Delta r, \quad (7.14)$$

$$\text{hence } \tilde{C}_j = 4\pi \Delta r \sum_{i=1}^{N-1} C_i \sin\left(\frac{\pi}{N} i j\right), \quad j = 1, 2, \dots, N-1. \quad (7.15)$$

The method also consists in developing separately the function C_i around the original function Γ_i^0 and the function $\tilde{\Gamma}_j$ around the original function $\tilde{C}_j^0$ in a first-order Taylor series as:

¹From here, the variables r and q will be omitted and the functions in reciprocal space will be marked with a tilde.

$$C_i = C_i^0 + \left(\frac{dC}{d\Gamma_i} \right)_{\Gamma_i^0} (\Gamma_i - \Gamma_i^0), \quad (7.16)$$

$$\tilde{\Gamma}_j = \tilde{\Gamma}_j^0 + \left(\frac{d\tilde{\Gamma}}{d\tilde{C}_j} \right)_{\tilde{C}_j^0} (\tilde{C}_j - \tilde{C}_j^0), \quad (7.17)$$

in order to combine the equations from (Eq. 7.9) to (Eq. 7.17).

As a first step, we write $\tilde{C}_j$ (Eq. 7.15) replacing C_i thanks to equation (7.16). It results:

$$\tilde{C}_j = 4\pi\Delta r \sum_{i=1}^{N-1} C_i^0 \sin\left(\frac{\pi}{N}ij\right) + 4\pi\Delta r \sum_{i=1}^{N-1} \left(\frac{dC}{d\Gamma_i} \right)_{\Gamma_i^0} (\Gamma_i - \Gamma_i^0) \sin\left(\frac{\pi}{N}ij\right), \quad (7.18)$$

where the quantity $(\Gamma_i - \Gamma_i^0)$ is evaluated in using equation (7.13) as:

$$(\Gamma_i - \Gamma_i^0) = \frac{\Delta q}{2\pi^2} \sum_{k=1}^{N-1} (\tilde{\Gamma}_k - \tilde{\Gamma}_k^0) \sin\left(\frac{\pi}{N}ik\right). \quad (7.19)$$

After simplifications, $\tilde{C}_j$ can be written in the following form:

$$\tilde{C}_j = \tilde{C}_j^0 + 4\pi\Delta r \sum_{i=1}^{N-1} \left(\frac{dC}{d\Gamma_i} \right)_{\Gamma_i^0} \left[\frac{\Delta q}{2\pi^2} \sum_{k=1}^{N-1} (\tilde{\Gamma}_k - \tilde{\Gamma}_k^0) \sin\left(\frac{\pi}{N}ik\right) \right] \sin\left(\frac{\pi}{N}ij\right), \quad (7.20)$$

hence

$$\tilde{C}_j - \tilde{C}_j^0 = \sum_{k=1}^{N-1} (\tilde{\Gamma}_k - \tilde{\Gamma}_k^0) \left[\frac{2}{N} \sum_{i=1}^{N-1} \left(\frac{dC}{d\Gamma_i} \right)_{\Gamma_i^0} \sin\left(\frac{\pi}{N}ik\right) \sin\left(\frac{\pi}{N}ij\right) \right]. \quad (7.21)$$

Then, if the term in brackets is denoted by $\tilde{C}_{j,k}$, we obtain:

$$\tilde{C}_j - \tilde{C}_j^0 = \sum_{k=1}^{N-1} \tilde{C}_{j,k} (\tilde{\Gamma}_k - \tilde{\Gamma}_k^0). \quad (7.22)$$

In a second step, we determine $\tilde{\Gamma}_j$ with equation (7.17) after calculating the derivative $\frac{d\tilde{\Gamma}}{d\tilde{C}_j}$ with the equation (7.10), i.e.:

$$\frac{d\tilde{\Gamma}}{d\tilde{C}_j} = \frac{2\rho\tilde{C}_j(q)}{q - \rho\tilde{C}_j(q)} + \frac{\rho^2\tilde{C}_j^2(q)}{[q - \rho\tilde{C}_j(q)]^2}, \quad (7.23)$$

so that equation (7.17) can be written:

$$\tilde{\Gamma}_j - \tilde{\Gamma}_j^0 = \frac{\rho\tilde{C}_j}{q_j - \rho\tilde{C}_j} \left(2 + \frac{\rho\tilde{C}_j}{q_j - \rho\tilde{C}_j} \right) (\tilde{C}_j - \tilde{C}_j^0). \quad (7.24)$$

Equations (7.22) and (7.24) are the basis for the Newton–Raphson integration method. Substituting equation (7.22) in equation (7.24) and posing $\Delta\tilde{\Gamma} = \tilde{\Gamma} - \tilde{\Gamma}^0$, it comes:

$$\Delta\tilde{\Gamma}_j = \frac{\rho\tilde{C}_j}{q_j - \rho\tilde{C}_j} \left(2 + \frac{\rho\tilde{C}_j}{q_j - \rho\tilde{C}_j} \right) \sum_{k=1}^{N-1} \tilde{C}_{j,k} \Delta\tilde{\Gamma}_k. \quad (7.25)$$

Finally, being combined with the Fourier transform of the OZ relation (Eq. 7.10),

$$\tilde{\Gamma}_j = \frac{\rho\tilde{C}_j^2}{q_j - \rho\tilde{C}_j}, \quad (7.26)$$

equation (7.25) allows us to solve the integral equations numerically.

Algorithmic procedure

The algorithm described here corresponds to the FORTRAN program of Labik et al. [107], and the solution of the integral equation involves both Newton–Raphson and Picard methods.

(1) After the total number N of Fourier components is chosen, the first M Fourier components are treated by the Newton–Raphson method. Then, the step length Δr and the initial estimates of the indirect correlation function Γ_i^0 for $i = 1, 2, \dots, N-1$ are chosen, and the Fourier transforms $\tilde{\Gamma}_j^0$ are calculated.

Note that the final solution is independent of the choice of M , whereas the efficiency of the method is not. If M is too small, the convergence is slow because the majority of iterations are performed by the direct method of Picard. If M is too large, the calculation is long because the majority of iterations is performed with the Newton–Raphson method, which requires many matrix inversions. A good

compromise is to choose M between 15 and 30, and values of $N = 2^{10} = 1024$ and $\Delta r = 0,025$ (reduced variable by the HS diameter σ). As for the initial values of Γ , we can take $\Gamma_i^0 = 0$.

(2) The function C_i^0 is calculated with equation (7.9), then its Fourier transform $\tilde{C}_j^0$ is carried out.

(3) Then we determine:

$$\tilde{C}_{j,k} = \frac{2}{N} \sum_{i=1}^{N-1} \left(\frac{dC}{d\Gamma_i} \right)_{\Gamma_i^0} \sin\left(\frac{\pi}{N} ik\right) \sin\left(\frac{\pi}{N} ij\right), \quad (7.27)$$

where $\left(\frac{dC}{d\Gamma_i}\right)_{\Gamma_i^0}$ is calculated by means of equation (7.9), in order to deduce $\tilde{C}_j$ from equation (7.22), for j and $k = 1, 2, \dots, M$, where $\tilde{\Gamma}_k$ is drawn from equation (7.26).

(4) The first M Fourier components are solved with the Newton-Raphson method for the unknowns $\Delta\tilde{\Gamma}_j$ in combining both equations (7.25) and (7.26) in the following form:

$$\Delta\tilde{\Gamma}_j - \frac{\rho\tilde{C}_j}{q_j - \rho\tilde{C}_j} \left(2 + \frac{\rho\tilde{C}_j}{q_j - \rho\tilde{C}_j} \right) \sum_{k=1}^M q\tilde{C}_{j,k} \Delta\tilde{\Gamma}_k = -\tilde{\Gamma}_j + \frac{\rho\tilde{C}_j^2}{q_j - \rho\tilde{C}_j}. \quad (7.28)$$

(5) The convergence test is performed on the first M Fourier components. As long as the condition

$$\left[\sum_{j=1}^M \left(\Delta\tilde{\Gamma}_j \right)^2 \right]^{1/2} > \delta \quad (7.29)$$

is not fulfilled (with $\delta \sim 10^{-5}$), a new estimate of the M Fourier components is carried out with the relation $\tilde{\Gamma}_j^{0(\text{new})} = \tilde{\Gamma}_j^{0(\text{old})} + \Delta\tilde{\Gamma}_j$, and step 4 is repeated, otherwise the Picard method is continued.

(6) The inverse Fourier transforms of the last $\tilde{\Gamma}_j$ are carried out. With Γ_i thus obtained, C_i are calculated through equation (7.9). Then, the Fourier transforms $\tilde{C}_j$ are calculated and injected into equation (7.10) to obtain $\tilde{\Gamma}_j$.

(7) A second test of convergence is performed. If:

$$\left[\sum_{j=1}^{N-1} (\Gamma_j - \Gamma_j^0)^2 \right]^{1/2} < \delta, \quad (7.30)$$

with $\delta \sim 10^{-5}$, the solution converges and the total correlation function is determined from $\tilde{\Gamma}_j$ and $\tilde{C}_j$, otherwise step 4 is repeated with the new estimates $\tilde{\Gamma}_j^0 = \tilde{\Gamma}_j$.

7.2 Statements on the computer simulations

The growing power of microprocessors and the manufacturing of computers becoming more efficient and inexpensive have contributed in recent years to spectacular progress based on simulation methods in all branches of science. When applied to liquids, numerical simulation makes it possible to produce the microscopic states of a system for a given potential as a model of interaction to extract its macroscopic properties. A major success of the simulation methods is the absence of physical approximations, unlike most analytical theories. For example, to calculate the pair correlation function $g(r)$ by the analytical methods as numerous as what we could see while, with the simulation methods, $g(r)$ is extracted directly from the configurations produced with the interaction model employed.

Before the extensive use of simulation, the approximations of the analytical theory of liquids and the interaction models were tested by comparing the results with experimental results. The differences could be assigned, either to the choice of the approximations, or to the potential used. Moreover, real experiments are often not specific enough and it is sometimes even impossible to carry out a proper check of the theory. By contrast, the simulation methods can be considered as *numerical experiments* on which the analytical approximations can be tested for a given potential. As a result, a simulation is a powerful tool to *justify the approximations of the theory* (by comparing the results with the results of the theory) and *test the interaction potentials* (by comparing the results with experimental results).

The simulation has definitely emerged in 1955 with the famous experiment of Fermi–Pasta–Ulam (FPU) [108, 109] performed on the most powerful computer manufactured at that time (10^4 operations per second against 10^8 for any current computer) in the Los Alamos

National Laboratory. This experiment was designed to check through simulation whether a system composed of a few tens of oscillators behaves like a system of statistical mechanics. In other words, it was used to test the hypothesis of ergodicity and make sure that all points in phase space are visited with equal probability.

The ergodicity principle states that the average value of a macroscopic property, when evaluated at equilibrium and using a statistical ensemble of identical systems, coincides with the average value calculated on the fluctuations in time for a unique system (section 1.4). This statement has already been justified for a harmonic oscillator in the microcanonical ensemble (section 2.1) by showing that the ensemble average and time average are tantamount, and all the elements of phase extension corresponding to the energy between $E - \Delta E$ and $E + \Delta E$ are visited with equal probability. If a system composed of N *independent* harmonic oscillators with the total energy E (each of them with its own frequency and its own energy), the dynamic state of each oscillator explores its own region of phase space, so that the system is not ergodic. Fermi, Pasta and Ulam thought that the system could become ergodic if the movements of the oscillators were made *dependent* on each other by introducing a weak degree of anharmonicity.

The FPU model is a chain of 32 anharmonic oscillators whose ends are fixed. The equations of motion are:

$$\frac{d^2 x_n}{dt^2} = (x_{n+1} - 2x_n + x_{n-1}) + \alpha [(x_{n+1} - x_n)^2 - (x_n - x_{n-1})^2], \quad (7.31)$$

where $\alpha \ll 1$ is a parameter that introduces the anharmonicity into the model. If the system is harmonic ($\alpha = 0$), the movements are divided into independent modes and the system is not ergodic. Otherwise, if the system has a small anharmonicity, any initial movement concentrated on a specific mode is shared out between all the modes until complete energy equipartition which excludes the possibility of splitting into independent modes. The beginning of the simulation goes as planned. Yet, against all odds and after a sufficiently long time, almost all the energy distributed over the normal modes returns gradually to the initial mode set at the beginning of the simulation. When the experiment is repeated with more powerful computers, it appears that the phenomenon is reproducible. This result, known as the FPU paradox, has led to the theorem of Kolmogorov–Arnold–Moser (KAM) [110]; this theorem indicates that the anharmonicity

is not the only factor leading to ergodicity. Interested readers can by themselves carry out the FPU experiment with the Matlab code provided in the article by Dauxois et al. [108].

Simulation methods fall into two categories: the Monte Carlo and molecular dynamics simulations. In the first method, particles being subjected to an interaction potential are placed in a succession of randomly generated configurations. The physical property $f(\mathbf{r}_i^N)$ is determined as a function of the coordinates of the particles. Then, the ensemble average $\langle f(\mathbf{r}^N) \rangle$ of this property is calculated with the configuration integral $Z = \sum_i \exp[-\beta U_N(i)]$:

$$\langle f(\mathbf{r}^N) \rangle = \frac{\sum_i f(i) \exp[-\beta U_N(i)]}{\sum_i \exp[-\beta U_N(i)]}, \quad (7.32)$$

where i is an index running through all the possible configurations. In molecular dynamics, the particles are also subjected to an interaction potential although an initial position and initial velocity are assigned to them in phase space. Then, the successive dynamic states describing the phase trajectory are calculated by a finite difference method. Note that the molecular dynamics simulation (MD), which requires the integration of the motion equations of particles, is a purely deterministic method, while the Monte Carlo simulation (MC), which requires the random generation of a large number of configurations, is a stochastic method. Moreover, the MC allows calculating the static properties of systems, such as energy or structure factor, while MD provides, in addition, the atomic transport properties belonging to time dependent phenomena.

Some difficulties are encountered when the simulations are implemented; this is related to the representation of the real systems in the simulation box due to the problems of *size effects*, *boundary conditions*, etc. Moreover, we have to make a choice concerning the *optimal duration* of the simulation (neither too short for the thermal equilibrium to be reached, nor too long to be prohibitive). This issue being related to the ergodicity, is crucial when it comes to studying the supercooled liquids. Here again, we have to face the *calculation errors* because, even if the simulation does not need any approximations of physical nature, it is impossible to exclude the statistical errors arising from the exploitation of results and the systematic errors due, in particular, to the nature of interaction potential. For instance, a HS

system involving collisions cannot be dealt with as a system of particles subjected to a long-range potential which has therefore to be truncated for practical purpose.

In the rest of this chapter, we state the principles of the MC and MD simulations, and outline synthetically some difficulties in the implementation and the sequence of a simulation.

7.3 The Monte Carlo methods

The Monte Carlo method requires using a generator of random numbers, not only for generating the succession of configurations, but also to decide whether a new configuration should be accepted or rejected. If it is assumed, to have clear ideas, that the sample contains $N=100$ particles moving in the three-dimensional configuration space and each component of the positions could take, say, one of the $Q=10$ values available, the number of accessible configurations is $M \sim (Q^d)^N = 10^{300}$. As the number of configurations in a typical MC experiment does not generally exceed 10^7 , it is necessary to reject a very large number of them. Before describing the process of acceptance or rejection of one configuration, let us define the principle of the MC method in the simplest case. To evaluate the integral

$$I = \int_a^b f(x) dx, \quad (7.33)$$

in the range $[a, b]$, the average value of $f(x)$ can be computed either in continuous form or in discrete form, namely:

$$\langle f(x) \rangle = \frac{1}{(b-a)} \int_a^b f(x) dx = \frac{1}{M} \sum_{i=1}^M f(x_i), \quad (7.34)$$

where $f(x_i)$ are the discrete values of the function $f(x)$ at points chosen *randomly and uniformly* in the range $[a, b]$. Therefore, an estimate of I is:

$$I \approx \frac{(b-a)}{M} \sum_{i=1}^M f(x_i). \quad (7.35)$$

In the MC simulation, the primary purpose is to calculate the average value of a function $f(\mathbf{r}^N)$ in discrete form by using the formula:

$$\langle f(\mathbf{r}^N) \rangle = \frac{\sum_{i=1}^M f(i) \exp[-\beta U_N(i)]}{\sum_{i=1}^M \exp[-\beta U_N(i)]}, \quad (7.36)$$

where the index i runs over the set of M configurations. Yet, given the extremely high value of M ($\sim 10^{300}$), the evaluation of the sum is not an option. A much lower number of configurations m ($\sim 10^7$) has to be used. If should equation (7.36) be a simple average, the calculation concerned will surely not cause more difficulty than equation (7.34), but equation (7.36) is a weighted average written as:

$$\langle f(\mathbf{r}^N) \rangle = \frac{\sum_{i=1}^M f(i) \exp[-\beta U_N(i)]}{\sum_{i=1}^M \exp[-\beta U_N(i)]} = \sum_{i=1}^M f(i) p(i), \quad (7.37)$$

where the weight

$$p(i) = \frac{\exp[-\beta U_N(i)]}{\sum_{i=1}^M \exp[-\beta U_N(i)]} \quad (7.38)$$

is a *non-uniform random* distribution. As a matter of fact, if the distribution had been uniform, i.e. $p(i) = \frac{1}{M}$, then equation (7.36) should have been reduced to:

$$\langle f(\mathbf{r}^N) \rangle = \frac{1}{M} \sum_{i=1}^M f(i) \simeq \frac{1}{m} \sum_{i=1}^m f(i), \quad (7.39)$$

– but this did not apply! Actually, the difficulty lies in the fact that the distribution $p(i)$ is not uniform. Insofar as the function $f(\mathbf{r}^N)$ takes significant values only in a given domain of the configuration space, it is understandable that the configurations are not equally likely and it is useless to compute $f(\mathbf{r}^N)$ at points where the value is very low. The currently used method, known as accepting the configurations which are most contributive to the result, and rejecting the other ones, is actually the *preferential sampling method* proposed by Metropolis et al. [111]. We will present it briefly in the next paragraph.

Considering the set of M configurations available, it is assumed that $w(i \rightarrow j)$ is the *conditional probability* that the system will be in

the configuration j at time $t+1$, knowing that it was in the configuration i at time t . Then, the *joint probability* for having the system in state i at time t and in state j at time $t+1$, is (Eq. 2.141):

$$w(i \rightarrow j)p(i, t), \quad (7.40)$$

where $p(i, t)$ is the probability that the system was in the state i at time t , and where the conditional probability $w(i \rightarrow j)$ denotes, in fact, the probability of transition from configuration i toward configuration j . Thus, the evolution of states in the system out-of-equilibrium is governed by the *master equation*² that reads:

$$p(i, t+1) = p(i, t) + \sum_j [w(j \rightarrow i)p(j, t) - w(i \rightarrow j)p(i, t)] . \quad (7.41)$$

Moreover, it is assumed that the succession of states is described by a *Markovian process* (see section 9.1) converging to an equilibrium distribution. It should be noted that the time used in equation (7.41) takes discrete values and has no physical meaning. Its purpose is only to identify chronologically the configurations in the Markov chain. The relation $p(i, t+1) = p(i, t)$ is observed when the equilibrium is reached, at the asymptotic limit ($t \rightarrow \infty$). This condition corresponding to the *microscopic reversibility* leads to cancelling the term in square brackets of equation (7.41):

$$w(j \rightarrow i)p(j) = w(i \rightarrow j)p(i), \quad (7.42)$$

where $p(j)$ and $p(i)$ denote the probabilities when $t \rightarrow \infty$. Being combined with equation (7.38), this relation allows determining the ratio of transition probabilities, as a function of the energies, in the form:

$$\frac{w(i \rightarrow j)}{w(j \rightarrow i)} = \frac{p(j)}{p(i)} = \exp \{-\beta [U_N(j) - U_N(i)]\} . \quad (7.43)$$

This expression just sets the ratio of transition probabilities, and hence some freedom when choosing. Without going into details [112],

²The master equation is a special case of the Smoluchowski equation, as the basis of the theory of the temporal evolution of random processes. Under this form, the master equation is understood as follows: the probability that the system will be in the state i at time $t+1$ is equal to the probability that it was in the same state (state i) at the preceding time (time t), plus the algebraic sum of probabilities that it goes from any state j toward state i and the probability that it goes from state i toward any state j .

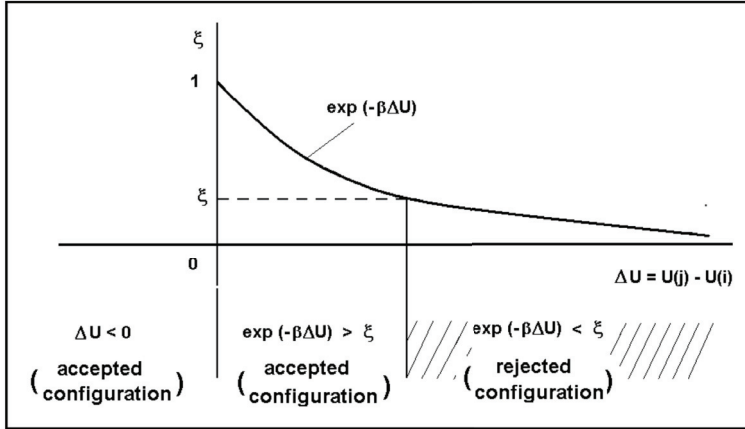


Figure 7.1: Representative scheme of the acceptance criterium of configurations in a MC experiment as a function of $\Delta U = U(j) - U(i)$.

we provide a standard method to accept or reject a new configuration:

1) If the energy of the new configuration is less than or equal to the energy of the former $U_N(j) \leq U_N(i)$, the new configuration is accepted.

2) If the energy of the new configuration is greater than the energy of the former $U_N(j) > U_N(i)$, the Boltzmann factor

$$\exp \{-\beta [U_N(j) - U_N(i)]\}$$

is compared with a random number ξ between 0 and 1. When

$$\exp \{-\beta [U_N(j) - U_N(i)]\} > \xi ,$$

the new configuration is accepted, otherwise it is denied. This is illustrated in figure (7.1).

It should be recalled that the MC method is used to simulate the equilibrium properties of systems. It means that the averaging process can only start when the system is in equilibrium. There is no particular test to determine precisely the beginning of the period of equilibrium. The safest way is to follow the evolution of the system energy. The equilibrium is considered as being achieved when the energy stabilizes around a given value.

7.4 Molecular dynamics simulations

Main algorithms of the molecular dynamics

Under analytical form, the solution of Newton's equation is obtained by integrating the second-order differential equation with respect to time. The resulting positions and velocities, given the initial values, permit tracking the evolution of the system along a path at constant energy in phase space. Under numerical form, the equation of motion must first be discretized and then solved by a finite difference method. To simplify the presentation of algorithms, consider the motion of a particle in one dimension, as described by the Newton equation:

$$\frac{dv}{dt} = \gamma, \quad (7.44)$$

with $v = \frac{dx}{dt}$ and $\gamma = \frac{F(x)}{m}$, where m is the mass of the particle and $F(x)$ the force applied to it. The purpose of the finite difference methods is to determine the values x_{n+1} and v_{n+1} , at time $t_{n+1} = t_n + \Delta t$, when the law of force $F(x)$ as well as x_n and v_n are known. All the integration algorithms are based on the Taylor series expansions of the positions and velocities.

The Euler algorithm

The simplest method is to stop the series expansion of x_{n+1} at the term Δt^2 and that of v_{n+1} at the term Δt , i.e. to consider the system of equations:

$$v_{n+1} = v_n + \gamma_n \Delta t, \quad (7.45)$$

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} \gamma_n \Delta t^2. \quad (7.46)$$

The algorithm of this method, called *Euler 1*, amounts to:

- (1) initializing the velocity v_0 , the position x_0 and the acceleration $\gamma_0 (= \frac{F(x_0)}{m})$ by using the force $F(x_0)$;
- (2) determining the velocity v_1 with equation (7.45) and the position x_1 with equation (7.46);
- (3) repeating the steps (1) and (2) with the values of v_1 , x_1 and $\gamma_1 = \frac{F(x_1)}{m}$, and so on.

The success of an algorithm lies in several factors, including selecting the time interval Δt , which should be long enough so that the numerical integration can generate a stable solution without being excessive for the time of calculation. If the simulation is performed in the microcanonical ensemble, with N , V and E being fixed, the stability of the solution is checked by ensuring that the total energy is conserved during the course of calculation. Incidentally, note that the simulation can also be carried out in the canonical ensemble, with N , V and T being fixed. In this case, the temperature is controlled by putting the system in contact with a thermostat thus making the exchange of heat possible with the surroundings. To generate this ensemble, the most common method [113] is to call an additional dynamical variable, denoted s , which is associated with the temperature and whose conjugate momentum is p_s . Nevertheless, a simulation can also be performed in a ensemble with fixed N , P and H . It is an extension of the microcanonical ensemble in which the pressure is fixed, contrary to the volume. The system thus evolves along a path to constant enthalpy in phase space. To set this ensemble, the volume is used as a dynamical variable and the pressure as a conjugate momentum [114].

Quite remarkably, the Euler algorithm provides asymmetrical results in x and v since the position x_{n+1} is calculated with the velocity v_n stemming from the previous step. But this defect can be easily eliminated by replacing v_n by v_{n+1} , in equation (7.46), which is calculated in the same loop. The position x_{n+1} can thus be determined by eliminating $\gamma_n \Delta t^2$ between equations (7.45) and (7.46). Apart from this difference, the algorithm is the same as in Euler's 1 method. This provides a new algorithm, called *Euler 2*, whose equations are:

$$v_{n+1} = v_n + \gamma_n \Delta t, \quad (7.47)$$

$$x_{n+1} = x_n + \frac{1}{2} (v_n + v_{n+1}) \Delta t. \quad (7.48)$$

This algorithm does not provide better results than the Euler 1 algorithm, except in the case where acceleration is constant.

The Verlet algorithm

Better results are obtained by combining differently the expressions of the position (Eq. 7.46):

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} \gamma_n \Delta t^2, \quad (7.49)$$

$$x_{n-1} = x_n - v_n \Delta t + \frac{1}{2} \gamma_n \Delta t^2, \quad (7.50)$$

where the second relation follows from the first one by replacing Δt by $-\Delta t$. Indeed, after the addition of the two above relations is done, a new expression for the position x_{n+1} is deduced:

$$x_{n+1} + x_{n-1} = x_n + \frac{1}{2} \gamma_n \Delta t^2 + x_n + \frac{1}{2} \gamma_n \Delta t^2, \quad (7.51)$$

$$x_{n+1} = 2x_n - x_{n-1} + \gamma_n \Delta t^2, \quad (7.52)$$

whereas their subtraction yields a new expression for the velocity v_n :

$$x_{n+1} - x_{n-1} = 2v_n \Delta t, \quad (7.53)$$

$$v_n = \frac{x_{n+1} - x_{n-1}}{2\Delta t}. \quad (7.54)$$

This is the explicit central difference method [115], called *Verlet 1*. Its algorithm is different from those of Euler's ones because the recursive relation of the positions does not require knowledge of the velocities. When only the pair correlation function $g(r)$ has to be calculated, the velocity can be ignored and equation (7.52) used. In practice, however suitable it might be to calculate the velocities in view of determining the kinetic energy, the temperature, as well as the velocity autocorrelation function and the atomic transport properties.

Being more accurate than the Euler 2 algorithm, the Verlet 1 algorithm is often used in MD. However, it has the major drawback of involving a second algorithm to initialize the calculations. Indeed, as velocity is not used to find the position (Eq. 7.52), it is necessary to supply the first two values x_0 and x_1 in order to determine x_2 . Thus, x_1 must be calculated by one of the self-sufficient Euler algorithms. Note that the Verlet 1 algorithm can be reformulated to make it self-sufficient and numerically more stable. This is done by adding and

subtracting simultaneously the quantity $\frac{1}{2}x_{n+1}$ onto the right hand side of equation (7.52):

$$\begin{aligned} x_{n+1} &= 2x_n - x_{n-1} + \gamma_n \Delta t^2 + \frac{1}{2}x_{n+1} - \frac{1}{2}x_{n+1} \\ &= x_n + \frac{1}{2}(x_{n+1} - x_{n-1}) + \gamma_n \Delta t^2 - \frac{1}{2}(x_{n+1} - 2x_n + x_{n-1}). \end{aligned} \quad (7.55)$$

Then equations (7.54) and (7.52) are used to simplify the terms in brackets. We obtain:

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} \gamma_n \Delta t^2. \quad (7.56)$$

Considering equation (7.54) to express v_{n+1} :

$$v_{n+1} = \frac{x_{n+2} - x_n}{2\Delta t}, \quad (7.57)$$

and equation (7.52) to replace x_{n+2} in the foregoing relation, it results:

$$v_{n+1} = \frac{(2x_{n+1} - x_n + \gamma_{n+1} \Delta t^2) - x_n}{2\Delta t}. \quad (7.58)$$

Finally, the substitution of x_{n+1} stemming from equation (7.56) in the above relation leads to:

$$v_{n+1} = \frac{[2(x_n + v_n \Delta t + \frac{1}{2} \gamma_n \Delta t^2) - x_n + \gamma_{n+1} \Delta t^2] - x_n}{2\Delta t}, \quad (7.59)$$

or equivalently:

$$v_{n+1} = v_n + \frac{1}{2}(\gamma_n + \gamma_{n+1}) \Delta t. \quad (7.60)$$

The two equations (7.56) and (7.60) set up Verlet's velocity algorithm called *Verlet 2*, which is self-sufficient and more accurate than previous algorithms.

The prediction-correction algorithm

There are yet other algorithms for the finite difference methods. Among them, the *prediction-correction algorithm* [57] is frequently used in MD. To present it in its simplest form, we proceed in three stages.

First of all, a predicted value of the position is supplied with the approximate relation:

$$x_{n+1}^p = x_n^c + v_n^c \Delta t, \quad (7.61)$$

where the index p specifies the predictive nature of the position, and the index c the corrective nature (calculated at the previous step) of the quantity in question.

In the second step, the force is assessed at the position x_{n+1}^p with the force law under study, from which the acceleration $\gamma_{n+1}^p = \frac{F(x_{n+1}^p)}{m}$ is obtained, and the corrected velocity v_{n+1}^c is calculated with equation (7.60):

$$v_{n+1}^c = v_n^c + \frac{1}{2} (\gamma_n^c + \gamma_{n+1}^p) \Delta t. \quad (7.62)$$

In the third step, the corrected position x_{n+1}^c is determined with equation (7.48):

$$x_{n+1}^c = x_n^c + \frac{1}{2} (v_n^c + v_{n+1}^c) \Delta t. \quad (7.63)$$

The corrected force $F(x_{n+1}^c)$ and the corrected acceleration $\gamma_{n+1}^c = \frac{F(x_{n+1}^c)}{m}$ can then be evaluated. However, the method does not stop there: the calculations are repeated by a newly corrected velocity v_{n+1}^c and a newly corrected position x_{n+1}^c until stable values are created. It is only after reaching the intended accuracy that a new cycle can be undertaken to provide the next target position x_{n+2}^p , and so on.

Process of conducting an experiment of molecular dynamics

When a system has few degrees of freedom, a MD simulation looks like a problem of classical physics. On the contrary, when the system contains a large number of degrees of freedom, the MD simulation is closer to the experimental approach, and the arising problems are highly similar to those of a real experiment. An incorrect preparation of the sample - the excessively short or long duration of simulation - and a change made for an undesirable thermodynamic state, etc. are factors that may alter the results of the simulation.

As an illustration, consider a particle submitted to translation along the x -axis under the action of a spring. The force applied to the particle is $F(x) = -kx$ and the Hamiltonian is:

$$H(x, p) = \frac{p^2}{2m} + \frac{kx^2}{2}, \quad (7.64)$$

where m is the mass of the particle and k the stiffness coefficient of the spring. For given values of m , k and the initial conditions x_0 and v_0 , the problem is completely determined and solved analytically. The equations of motion are (Eqs. 1.38 and 1.39):

$$\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}, \quad (7.65)$$

$$\dot{p} = -\frac{\partial H}{\partial x} = -kx, \quad (7.66)$$

and the solution is:

$$x = x_0 \cos(\omega t + \varphi), \quad (7.67)$$

$$p = -m\omega x_0 \sin(\omega t + \varphi), \quad (7.68)$$

where $\omega = \sqrt{\frac{k}{m}}$ and $E = \frac{1}{2}m\omega^2 x_0^2$. The trajectory of the representative point of the dynamic state in phase space describes an ellipse of constant energy E according to the equation:

$$\frac{p^2}{2mE} + \frac{kx^2}{2E} = 1. \quad (7.69)$$

Although the simulation of this problem is incidental, it is instructive to understand how the MD calculation should be carried out. In this case, the algorithm of Verlet 2 is chosen:

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} \gamma_n \Delta t^2, \quad (7.70)$$

$$v_{n+1} = v_n + \frac{1}{2} (\gamma_n + \gamma_{n+1}) \Delta t, \quad (7.71)$$

where $\gamma_n = -\frac{kx_n}{m}$. First of all, the initial acceleration $\gamma_0 = -\frac{kx_0}{m}$ is evaluated in accordance with the initial conditions x_0 and v_0 , and the energy of the particle is:

$$E_0 = \frac{1}{2}mv_0^2 + \frac{1}{2}kx_0^2. \quad (7.72)$$

As the Verlet 2 algorithm is self-sufficient, we start directly calculating:

(1) the next position:

$$x_1 = x_0 + v_0 \Delta t + \frac{1}{2} \gamma_0 \Delta t^2, \quad (7.73)$$

(2) the acceleration at position x_1 :

$$\gamma_1 = -\frac{kx_1}{m}, \quad (7.74)$$

(3) the velocity at x_1 :

$$v_1 = v_0 + \frac{1}{2} (\gamma_0 + \gamma_1) \Delta t, \quad (7.75)$$

(4) the energy E_1 , allowing us to check that the solution is stable:

$$E_1 = \frac{1}{2} m v_1^2 + \frac{1}{2} k x_1^2, \quad (7.76)$$

(5) and the next position x_2 by repeating the calculations of step (1).

An interested reader may refer to the FORTRAN code for the Verlet 2 and Euler 1 algorithms in single precision and by using the following values of parameters: $m = 4$ kg, $k = 5$ N·m⁻¹, $x_0 = 2$ m and $v_0 = 0$ m·s⁻¹. By changing the time step from $\Delta t = 0.005$ s to 0.05 s, and the number of iterations from 1000 to 100, it will thus be seen how the rounding errors accumulated over the simulation generate harmful effects and make the solution unstable.

When facing a system containing a large number of degrees of freedom, we see that there are as many Newton's equations as particles. The equations are the vector equations:

$$\frac{d\mathbf{v}_i}{dt} = \gamma_i, \quad (7.77)$$

with $\gamma_i = \frac{\mathbf{F}_i}{m_i}$, where the force applied to the particle i is:

$$\mathbf{F}_i = -\mathbf{grad}_{\mathbf{r}_i} U(\mathbf{r}^N), \quad (7.78)$$

where $\mathbf{r}_i$ is the position of particle i and $U(\mathbf{r}^N)$ the potential energy of the system. As regards the resultant of forces applied to the particle i , the general expression is:

$$\mathbf{F}_i = \sum_{i \neq j}^N \mathbf{F}_{ij} + \sum_{i \neq j \neq k}^N \mathbf{F}_{i,jk} + \dots, \quad (7.79)$$

where the pair interaction force $\mathbf{F}_{ij}$ and the three-body interaction force $\mathbf{F}_{i,jk}$ are submitted to the action-reaction principle:

$$\mathbf{F}_{ij} = -\mathbf{F}_{ji}, \quad (7.80)$$

$$\mathbf{F}_{i,jk} = -\mathbf{F}_{j,ik} - \mathbf{F}_{k,ij}. \quad (7.81)$$

It turns out that the calculation of forces is highly time consuming ($\sim 90\%$ of the time) because, at each calculation step, $N(N-1)$ two-body interactions, $N(N-1)(N-2)$ three-body interactions, and so on have to be calculated. For the pair potentials, the computation time varies in $O(N^2)$ and, even if it is reduced by half through the action-reaction principle, it remains prohibitive. Choosing among the *algorithms*, *time interval*, etc. are very important elements in MD to eliminate unnecessary calculations and reduce the duration of simulations.

7.5 Guidelines for designing simulation experiments

Time interval and duration of simulation

For systems containing only few degrees of freedom, it is possible to follow the trajectory of the point representing the dynamic state of the system in phase space. In practice, the MD calculations, although limited by the size of the memory of the computers and the speed of execution of programs, are performed on systems containing several hundreds or even thousands of particles. Because of a very large number of initial conditions, it becomes impossible to follow the trajectory of the moving phase point whereas the physical properties can nevertheless be calculated. If N is the number of particles and $H(\mathbf{r}^N, \mathbf{p}^N)$ the Hamiltonian, any macroscopic property A can theoretically be predicted by calculating the ensemble average (Eq. 1.127):

$$\langle A \rangle = \iint_{6N} A [\mathbf{r}^N(t), \mathbf{p}^N(t)] P_N(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N. \quad (7.82)$$

Unfortunately, in a simulation experiment, the probability density function $P_N(\mathbf{r}^N, \mathbf{p}^N)$ is inaccessible and the time average (Eq. 1.123) must be used:

$$\bar{A} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(t) dt. \quad (7.83)$$

Remember that, in any system endowed with the property of ergodicity, the time average $\bar{A}$ of a quantity A is equal to the ensemble average $\langle A \rangle$. This also applies to the central moments such as the variance V_A and the autocorrelation function c_A (see Eq. 9.24):

$$V_A = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T [A(t) - \bar{A}]^2 dt, \quad (7.84)$$

$$c_A(\tau) = \lim_{T \rightarrow \infty} \frac{1}{T - \tau} \int_0^{T - \tau} [A(t) - \bar{A}] [A(t + \tau) - \bar{A}] dt. \quad (7.85)$$

It is easy to see in figure (7.2) that the upper bound of the integral of the autocorrelation function $c_A(\tau)$ cannot exceed $(T - \tau)$ for a given value τ .

The numerical calculations of $\bar{A}$, V_A and $c_A(\tau)$ require the transformation of integrals into discrete sums. For this, the observation time T is divided into n equal parts $\Delta t = \frac{T}{n}$, and $t_1, t_2, \dots$ denote

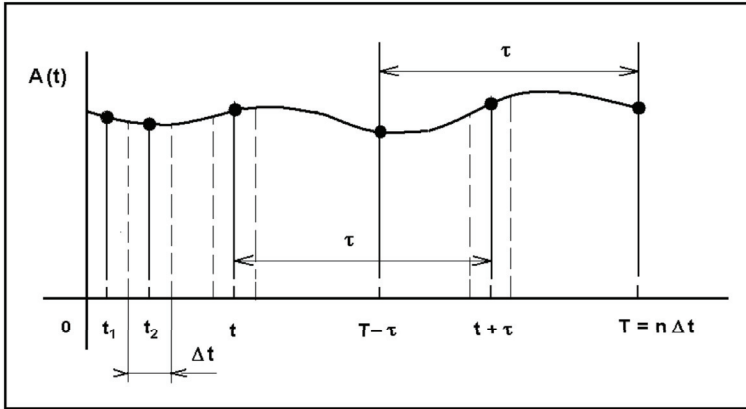


Figure 7.2: Discretization of the function $A(t)$ required to perform the calculation of the autocorrelation function $c_A(\tau)$.

the midpoints of the successive time intervals Δt . The discretization of the integrals is then achieved as follows:

$$\bar{A} \simeq \frac{1}{T} \sum_{i=1}^n A(t_i) \frac{T}{n} = \frac{1}{n} \sum_{i=1}^n A(t_i), \quad (7.86)$$

$$V_A \simeq \frac{1}{T} \sum_{i=1}^n \left[A(t_i) - \bar{A} \right]^2 \frac{T}{n} = \frac{1}{n} \sum_{i=1}^n \left[A(t_i) - \bar{A} \right]^2, \quad (7.87)$$

$$c_A(\tau) \simeq \frac{1}{T-\tau} \sum_{i=1}^{n-m} \left[A(t_i) - \bar{A} \right] \left[A(t_i+\tau) - \bar{A} \right] \frac{T}{n}. \quad (7.88)$$

As shown in figure (7.2), $\tau = m\Delta t = \frac{m}{n}T$ has been taken to rewrite the autocorrelation function in the appropriate form:

$$c_A(\tau) \simeq \frac{1}{n-m} \sum_{i=1}^{n-m} \left[A(t_i) - \bar{A} \right] \left[A(t_i+\tau) - \bar{A} \right]. \quad (7.89)$$

In practice, the simulation cannot be performed on an infinite time. It is therefore important to choose an optimal duration of observation which would be long enough for the thermal equilibrium to be reached without consuming too much time. It turns out that the time interval Δt and the observation time $T = n\Delta t$ are determined by the intrinsic behaviour of the system and the interaction potential used. Thus, in a MD calculation, the first thing to do is to specify the interaction potential best adapted to the system. To illustrate our purpose, let us suppose that the system is composed of spherical particles with mass m , monatomic and chemically inert, and interacting with the Lennard-Jones pair potential defined as:

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (7.90)$$

where the Hamiltonian is:

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} u(r_{ij}). \quad (7.91)$$

The LJ potential is a short-range potential because the energy is only 1.6% of the potential well at $r = 2.5\sigma$. When considering the dimensional analysis, we define the *characteristic time* of the system by the

quantity $\left(\frac{m\sigma^2}{\varepsilon}\right)^{1/2}$ which depends on the parameters σ and ε of the LJ potential, and the mass m of particles³. Practically, the characteristic time should always be shorter than the observation time T and longer than the time interval Δt :

$$\Delta t < \left(\frac{m\sigma^2}{\varepsilon}\right)^{1/2} < T. \quad (7.92)$$

Argon, for instance, has a characteristic time $\left(\frac{m\sigma^2}{\varepsilon}\right)^{1/2} = 2.16 \cdot 10^{-12}$ s (with values of $\sigma = 3.405 \cdot 10^{-10}$ m, $\varepsilon = 165.32 \cdot 10^{-23}$ J and $m = 6.69 \cdot 10^{-26}$ kg). Consequently, the simulation may be achieved with an observation time $T \simeq 10^{-11}$ s, divided into $n = 1000$ equal time intervals $\Delta t = \frac{T}{n} \simeq 10^{-14}$ s. However, in MD, the calculations are usually performed in reduced units. By considering one fraction of the characteristic time (for example 10^{-12} s) as an unit of simulation time, the reduced observation time is $T^* = \frac{T}{10^{-12}} = 10$ and the reduced time interval is $\Delta t^* = \frac{\Delta t}{10^{-12}} = 10^{-2}$, namely $T^* = 1000 \Delta t^*$. Finally, note that, if the characteristic time of the system is unknown, the value of it may be chosen at random and tested, in retrospect, by checking whether the velocity autocorrelation function⁴ $c_v(\tau)$ tends to zero for high values of τ .

The periodic boundary conditions

It has been reported that the MD calculations are very sensitive to the choice of the time factor. Yet, we will have to examine the sensitivity of calculations to the surface effects which gain importance when the sample size is insufficient. In fact, the fraction of particles in contact with the walls of a box is proportional to the surface area to volume ratio: for a cubic box of side L , this ratio is $\frac{S}{V} = \frac{6L^2}{L^3} \propto N^{-1/3}$, with $N = \rho L^3$. Therefore, in real systems, where N is of the order of 10^{23} , the ratio $\frac{S}{V}$ is 10^{-8} , whereas in a sample containing $N = 1000$ particles the ratio $\frac{S}{V}$ is 10^{-1} . The surface effects are thus much more important in a sample than in the real system. Consequently, it is advantageous

³Note in passing that the *characteristic velocity* is defined by the quantity $\left(\frac{\varepsilon}{m}\right)^{1/2}$.

⁴The velocity autocorrelation function $c_v(\tau)$ will be defined in section (9.4).

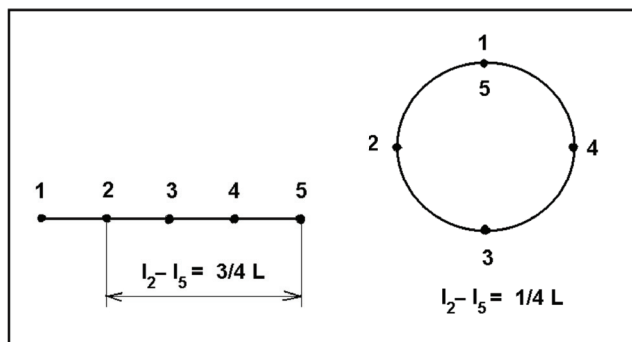


Figure 7.3: (a) Linear chain of length L with four intervals. (b) Closed chain of same length, containing the same number of intervals.

to use the highest possible number of particles to reduce the surface effects in the simulation box.

Another way to reduce the surface effects in the sample is to use the *periodic boundary conditions*. Using such boundary conditions for a linear chain of length L amounts to closing the chain on itself. By this method, the maximum distance of separation between two particles placed on the closed chain of length L is $\frac{L}{2}$, i.e. not L .

As explicitly shown in figure (7.3), on a straight line of length L , the points 2 and 5 are separated by the distance $l_2 - l_5 = \frac{3}{4}L$ whereas, if the curve is closed on itself, the distance between the points 2 and 5 is $l_2 - l_5 = (L - \frac{3}{4}L) = \frac{L}{4}$. More generally, if the distance d between two particles on a straight line is longer than $\frac{L}{2}$, the minimum distance on the closed curve is $l = (L - d)$.

For a sample in a cubic cell of side L , establishing the periodic boundary conditions is done by surrounding the cell by replicas identical to the original cell considered as basic unit. The principle is depicted in figure (7.4a) for a two-dimensional representation. It is assumed that the walls between the cells are fictitious, so that the particles move continuously from place to place without bouncing on the walls. When a particle leaves the original cell, it enters immediately into the adjacent cell under the same angle. Choosing the periodic boundary conditions (stack of cells and absence of wall) permits eliminating the surface effects. In contrast, it gives no way to count the

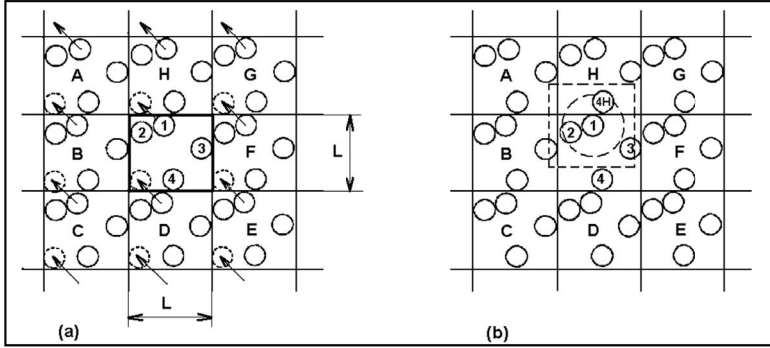


Figure 7.4: (a) Original cell surrounded by eight replicas in a two-dimensional representation (the number of replicas in a three-dimensional representation is 26). (b) Schematic representation of the minimum image convention: the dotted square represents the minimum image and the dotted circle the area beyond which interactions are neglected.

interaction number between particles required to determine the potential energy $U(\mathbf{r}^N) = \sum_{i < j} u(r_{ij})$. For instance, if the original cell contains 4 particles (Fig. 7.4b), the absence of wall implies that the particle 1 interacts a priori with the particles 2, 3 and 4 located in the original cell, as well as with their images within the adjacent cells. As it is illegal to repeat the interaction between two particles, the choice is made to take account of the interactions between the particles which are closest to 1. In the case of figure (7.4b), among the 3 interactions involving the particle 1, the interactions to be considered are 1 – 2, 1 – 3, and 1 – 4H, where the particle 4H belongs to the cell labelled H. The latter interaction is obtained from the minimum distance between particles 1 and 4. This artefact is known as the *minimum image convention*.

If the original cell contains N particles, it is well known that the interaction number is $\frac{1}{2}(N^2 - N)$. However, it has been reported that the calculation of the interaction potentials is the most time-consuming operation in MD simulation. Therefore, to save time, it is customary to make an additional approximation resulting from the following observation. Given that the major contribution to the potential energy between one particle and the $(N - 1)$ other ones is provided by the particles which are closest from each other, the interactions between

the particles which are furthest apart can be put aside. The shorter range of the pair potential, the better the degree of correction. The implementation of this approximation is carried out by using a cutoff distance r_c beyond which the pair potential is considered to be equal to zero, $u(r \geq r_c) = 0$.

Practically, the minimum image convention and the cutoff potential are two approximations made by (i) centering the original cell on particle 1, (ii) drawing a sphere of radius r_c centered on particle 1 and (iii) neglecting the interactions between particle 1 and those outside this sphere. Figure (7.4b) gives a two-dimensional representation of it: the dotted square is the new original cell of side L centered on particle 1 and the dotted circle of radius $r_c < \frac{L}{2}$ corresponds to the domain of action of particle 1. As a result, it is sufficient to calculate the interactions 1 – 2 and 1 – 4*H* while the interaction 1 – 3 is neglected. Note that the calculation time is significantly reduced as the number of interactions is also reduced within the volume ratio $\frac{4\pi r_c^3}{3L^3}$. Referring to the Lennard–Jones potential, whose energy at $r = 2.5\sigma$ is only 1.6% of the well depth, it is common to choose as side of the cell $L = 6\sigma$ and as cutoff radius $r_c = \frac{L}{2} = 3\sigma$. Other methods have been put forward to further reduce the computing time of the interaction forces [115, 116], but they will not be discussed here. Simply note that they reflect the fact that the environment of a particle does not change drastically from one step of calculation to the next and one particle interacts with the same neighbouring particles during several consecutive calculation steps, so that calculating all interactions is not necessary for each calculation step.

Initial conditions imposed on the system

Although the MD simulations do not use physical approximations, it is confirmed that the results are very sensitive to a number of factors such as algorithm, interaction potential, observation time, sample size, etc.

In addition, the implementation of a MD simulation also requires selection of initial conditions. For a system containing only few degrees of freedom, the MD simulations are conducted like those of a classical mechanical problem with the use of specific initial conditions. However, when the system contains several hundred particles, it must be prepared by placing it in an initial state generally not known in

advance. Fortunately, the selection of initial conditions is not important because, after a more or less long observation time, the system loses memory of its initial state. Therefore, arbitrary values for the initial conditions may be assigned. The particles can thus be placed in any position with zero velocity. Anyway, it is generally recommended to set the particles on a regular network and assign them velocities extracted from the Maxwell distribution. The evolution of the positions and velocities must be controlled carefully because the calculation does not provide directly the required macroscopic properties. For instance, in the microcanonical ensemble, N and V are imposed whereas the energy E should be continuously adjusted until the required value is reached. In the canonical ensemble, N and V are also imposed, and the temperature T is adjusted continuously by changing the velocities of particles.

By changing the velocity in successive steps, it is possible that the time taken by the system to reach the equilibrium is very long. If the initial state is unsuitably chosen, it may happen that the system is trapped in a metastable state, so that the simulation must be performed with new initial conditions and various time intervals. It is only after this phase of *thermalization*, when the system has reached the thermodynamic equilibrium, that the phase for the *production* of results can be undertaken. Consequently, the raw results are stored in computer files for a subsequent statistical analysis. When necessary, the phase trajectory can also be safeguarded every x time steps. It is generally accepted that the phase of thermalization does not exceed 10 to 20% of the total duration of simulation.

Statistics of raw results

Among the collected raw data, there are the configurations of particles allowing us to determine the pair correlation function $g(r)$. For a *given configuration*, recall that the number of particles $\Delta N_i(r, \Delta r)$ located in a spherical crown of radius r and thickness Δr – centered on the particle i taken as the origin – is related to the pair correlation function $g(r)$ by the formula (Eq. 3.93):

$$g(r) = \frac{\Delta N_i(r, \Delta r)}{4\pi\rho r^2 \Delta r}. \quad (7.93)$$

It is clear that replacing $\Delta N_i(r, \Delta r)$ by the *average over the particles* $\langle \Delta N(r, \Delta r) \rangle = \frac{1}{N} \sum_{i=1}^N \Delta N_i(r, \Delta r)$, where each particle is considered in turn as a central particle, enables reducing the dispersion of results by smoothing $g(r)$.

Moreover, if one configuration is stored every 10 steps of calculation, we have $n' = \frac{n}{10} = \frac{T}{10\Delta t}$ configurations (Fig. 7.2) from which the *average over the configurations* can be calculated to go on raising the accuracy of the pair correlation function. In this case, $g(r)$ is determined by the relation:

$$g(r) = \frac{1}{4\pi\rho r^2\Delta r} \frac{1}{Nn'} \sum_{\alpha=1}^{n'} \sum_{i=1}^N \Delta N_{i,\alpha}(r, \Delta r). \quad (7.94)$$

The kinetic and potential energies can be calculated with the values of velocity and the pair potential stored during the production phase. As before, if N is the number of particles and n' the number of the configurations collected, the kinetic energy E_c and the potential energy U are deduced from the relations:

$$\langle E_c \rangle = \frac{1}{n'} \sum_{\alpha=1}^{n'} \left(\sum_{i=1}^N \frac{1}{2} m_i v_i^2 \right)_{\alpha}, \quad (7.95)$$

$$\langle U \rangle = \frac{1}{n'} \sum_{\alpha=1}^{n'} \left(\sum_{i<j}^N u(r_{ij}) \right)_{\alpha}. \quad (7.96)$$

Having good knowledge of the velocities can be used to calculate the temperature T . Indeed, in the thermodynamic limit, where all the statistical ensembles are equivalent, the theorem of equipartition of energy can be applied:

$$\langle T \rangle = \frac{2}{3(N-1)k_B} \langle E_c \rangle. \quad (7.97)$$

However, all the collected velocities permit the deduction of the velocity autocorrelation function $c_v(\tau)$ with equation (7.89):

$$c_v(\tau) = \frac{1}{N} \sum_{i=1}^N \left(\frac{1}{n-m} \sum_{\alpha=1}^{n-m} \mathbf{v}_i(t_{\alpha}) \mathbf{v}_i(t_{\alpha} + \tau) \right), \quad (7.98)$$

where the average in brackets is performed on the different origins of time t_α and the second average on the particles. The velocity autocorrelation function permits checking whether the thermalization phase is achieved when $c_v(\tau)$ goes toward zero at large values of τ , and also permits determining the diffusion coefficient (see Eq. 9.71).

Whereas kinetic energy, temperature and velocity autocorrelation function are obtained without physical approximations, this does not apply to the potential energy whose absolute value is underestimated as the pair potential $u(r)$ is cut off at a certain distance. According to equation (5.14), the potential energy is indeed expressed as:

$$U = 2\pi\rho N \int_0^\infty u(r)g(r)r^2 dr. \quad (7.99)$$

However, in MD simulations, the upper limit of integration does not extend beyond the cutoff radius r_c , so that the following corrective term has to be added:

$$U_{corr} = 2\pi\rho N \int_{r_c}^\infty u(r)g(r)r^2 dr. \quad (7.100)$$

Since the pair potential is known for all the values of r , it is easy to calculate U_{corr} when $g(r)$ can be evaluated over distances exceeding r_c . In such cases where $g(r)$ is unknown beyond r_c , it is yet possible to model its long-range contribution (it can possibly be equalized to unity) which brings a significant improvement in the result of potential energy.

The cutoff of the pair potential has an influence on the result of the pressure too. According to equation (5.27), it is written:

$$p = \rho k_B T - \frac{2\pi}{3} \rho^2 \int_0^\infty \frac{du(r)}{dr} g(r) r^3 dr. \quad (7.101)$$

Here again, the MD simulations are performed with the truncated potential, thereby neglecting the quantity:

$$p_{corr} = -\frac{2\pi}{3} \rho^2 \int_{r_c}^\infty \frac{du(r)}{dr} g(r) r^3 dr, \quad (7.102)$$

which can be evaluated in the same manner as the potential energy.

It should be stressed that calculating the free energy F by MD simulations is rather difficult, and this also applies to the thermodynamic properties obtained in differentiating F . The next question

then is; how should the specific heat at constant volume be calculated without using equation (2.106):

$$c_V = -\frac{\partial}{\partial T} \left[T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right]_V. \quad (7.103)$$

The answer is simple. It can be easily done with the average value of energy $\langle E \rangle$ by evaluating the square of the energy fluctuation (Eq. 2.151) from which the specific heat at constant volume is extracted:

$$c_V = \frac{1}{k_B T^2} \langle (E - \langle E \rangle)^2 \rangle_V = \frac{1}{k_B T^2} [\langle E^2 \rangle - \langle E \rangle^2]. \quad (7.104)$$

The general principles of numerical simulation described in the above subsections show that the success of simulation computations is mainly due to (i) choosing an algorithm and time step which makes it possible to reach the thermodynamic equilibrium as rapidly as possible, and (ii) using periodic conditions which reduce the surface effects. When these conditions are fulfilled, it becomes possible to calculate the macroscopic properties of systems with the raw data stored in computer files. Specifically, information has been delivered concerning the method of calculation of the pair correlation function characterizing the system structure, which may deduce a set of thermodynamic properties, and the velocity autocorrelation function likely deducing the diffusion coefficient. Notwithstanding the MD simulation offers many other possibilities. Specialists wishing enlarge and improve their knowledge about simulation will find additional reading in the literature [117, 118, 119].

8 Kinetic theory of gases

The preceding chapters were devoted to the principles of statistical mechanics necessary for a good understanding of the *systems in equilibrium* by means of the probability density functions and the distribution functions. The study began with the determination of the thermodynamic properties of imperfect and real gases according to the partition function (Chapter 4). Then, the spatial correlation functions were used extensively to calculate the thermodynamic and structural properties of simple liquids in equilibrium (Chapter 5 and 6). It should be emphasized that the study of gases calls only the partition function, whereas that of liquids requires the spatial correlation functions and the proper knowledge of interaction potential.

In practice, we are often faced with the *out-of-equilibrium systems*. In this case, a question arises concerning what happens with the probability density and the distribution functions and which kind of new concepts should be defined to describe the non-equilibrium systems. Investigating such systems is a complex problem which is usually a matter meant to be examined while studying diluted gases, i.e. investigating a system of particles whose interactions are so weak that they can be overlooked.

In the next section, we establish the Boltzmann kinetic equation sustaining the kinetic theory of gases. It is based on the one-particle distribution function out-of-equilibrium. This function involved in the kinetic theory differs from the Maxwell–Boltzmann distribution function which applies to systems in equilibrium. In the remainder of this chapter, we outline the fundamental equations of continuum mechanics leading to the conservation laws of matter. Finally, it is shown that the one-particle distribution function out-of-equilibrium allows, under certain conditions, to deduce the atomic transport properties of diluted gases that constitutes the Chapman and Enskog theory.

8.1 The Boltzmann kinetic equation

Recall that a system of N particles is specified by the position vector $\mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and momentum vector $\mathbf{p}^N = (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$, and its dynamic state is described by the distribution function $f(\mathbf{r}^N, \mathbf{p}^N, t)$ in the γ -space (section 1.3). Moreover, the variation of the distribution function over the time is given by the Liouville equation (Eq. 1.108):

$$\frac{\partial}{\partial t} f(\mathbf{r}^N, \mathbf{p}^N, t) = - \sum_{i=1}^{3N} \left[\dot{r}_i \frac{\partial f}{\partial r_i} + \dot{p}_i \frac{\partial f}{\partial p_i} \right]. \quad (8.1)$$

In the general case, this equation with $6N$ unknowns is very difficult to solve. By contrast, the problem is simplified for diluted gases because the interactions between particles – apart from *binary collisions* – are neglected. It is indeed unlikely that a particle would simultaneously strike several other particles in a dilute gas. Moreover, when two particles collide, the other particles are so distant from one another that none has any influence. The binary nature of collisions is related to the *molecular chaos* with the consequence that the positions and velocities of particles are not correlated [2]. Note in particular the crucial role played by the collisions allowing a non-equilibrium system to get back to equilibrium when the disturbance has ceased. The binary nature of collisions does not really exclude the independence of individual motions of particles as each particle moves freely between two collisions. Obviously, in dense fluids, this assumption is no longer justified because of the permanent long-range interactions.

Taking the molecular chaos (independent particles) into account makes it possible to deduce the characteristics of the system of N particles, not with the distribution function $f(\mathbf{r}^N, \mathbf{p}^N, t)$ in the γ -space, but with the generic distribution function for *one particle* $\rho^{(1)}(\mathbf{r}, \mathbf{p}, t)$ in the μ -space (section 1.4). Note that this method has been used in section (4.4) to find the Maxwell–Boltzmann distribution. According to the notation commonly in use, the generic distribution function for one particle $\rho^{(1)}(\mathbf{r}, \mathbf{p}, t)$ is denoted $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$. In this case, the elementary probability that the particle will be found in the volume $d\mathbf{r} d\mathbf{p}$ is (Eq. 1.95):

$$\frac{dn}{N} = \frac{1}{N} f^{(1)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p}, \quad (8.2)$$

and the corresponding Liouville equation reads (Eq. 1.108):

$$\frac{\partial}{\partial t} f^{(1)}(\mathbf{r}, \mathbf{p}, t) = - \sum_{i=1}^3 \left[\dot{r}_i \frac{\partial f^{(1)}}{\partial r_i} + \dot{p}_i \frac{\partial f^{(1)}}{\partial p_i} \right]. \quad (8.3)$$

Thereafter, the superior index (1) in the function $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$ will be omitted for simplification. Given the momentum ($\mathbf{p} = m\dot{\mathbf{r}}$) and Newton's law ($\mathbf{F} = m\ddot{\mathbf{r}} = \dot{\mathbf{p}}$), the above relation can also be written in the vector form:

$$\frac{\partial}{\partial t} f(\mathbf{r}, \mathbf{p}, t) = - \frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f - \mathbf{F} \cdot \mathbf{grad}_{\mathbf{p}} f, \quad (8.4)$$

with:

$$\frac{\mathbf{p}}{m} = \dot{r}_x \mathbf{i} + \dot{r}_y \mathbf{j} + \dot{r}_z \mathbf{k}, \quad (8.5)$$

$$\mathbf{F} = \dot{p}_x \mathbf{i} + \dot{p}_y \mathbf{j} + \dot{p}_z \mathbf{k}, \quad (8.6)$$

$$\mathbf{grad}_{\mathbf{r}} f = \frac{\partial f}{\partial r_x} \mathbf{i} + \frac{\partial f}{\partial r_y} \mathbf{j} + \frac{\partial f}{\partial r_z} \mathbf{k}, \quad (8.7)$$

$$\mathbf{grad}_{\mathbf{p}} f = \frac{\partial f}{\partial p_x} \mathbf{i} + \frac{\partial f}{\partial p_y} \mathbf{j} + \frac{\partial f}{\partial p_z} \mathbf{k}. \quad (8.8)$$

It is found that equation (8.4), called the *Boltzmann kinetic equation*, is a simplified form of the Liouville equation designed to calculate the one-particle distribution function $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$. However, the Boltzmann equation, is still very complicated and there is virtually no analytical solution in the general case. As a consequence, such simplifications should be made. According to Boltzmann, the real nature of the force $\mathbf{F}$ should be thoroughly examined.

Boltzmann suggests separating the actions of external forces from those of internal forces (binary collisions), and analyzing the binary collisions mechanism from the point of view of statistics. Note that the external and internal forces have antagonistic actions: while the external forces impose a directional movement on the particles, the internal forces give rise to an opposite movement which tends to bring the system back into equilibrium. Therefore, thanks to collisions, the out-of-equilibrium system returns to equilibrium. To better highlight the differences between these two types of forces, they are separated as follows:

$$\mathbf{F} \cdot \mathbf{grad}_{\mathbf{p}} f = \mathbf{F}_{ext} \cdot \mathbf{grad}_{\mathbf{p}} f - \left(\frac{\partial f}{\partial t} \right)_{col}, \quad (8.9)$$

where the partial derivative $\left(\frac{\partial f}{\partial t}\right)_{\text{col}}$ is called the *collision integral*, as it usually has the form of an integral depending on the type of collisions.

By combining equations (8.9) and (8.4), the Boltzmann equation is written as:

$$\frac{\partial}{\partial t}f(\mathbf{r}, \mathbf{p}, t) = -\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}}f - \mathbf{F}_{ext} \cdot \mathbf{grad}_{\mathbf{p}}f + \left(\frac{\partial f}{\partial t}\right)_{\text{col}}. \quad (8.10)$$

This relation shows that the distribution function varies as a function of the velocity $\mathbf{v}(= \frac{\mathbf{p}}{m})$ of particles, as well as external and internal strains. The first two terms on the right hand side of equation (8.10) represent the variations of the distribution function caused by the motion of particles and the external forces, whereas the last term represents the variation of f coming exclusively from the collisions.

8.2 Molecular collisions

The purpose of this section and the following one is to find an analytical form for the collision integral $\left(\frac{\partial f}{\partial t}\right)_{\text{col}}$. Before carrying out the statistical analysis that should permit the finding of this expression, it is necessary to supply the mechanical description of a binary collision. The movement of a system consisting of two particles of masses m_1 and m_2 , acting upon each other, is a well known two-body problem. Problem solving is traditionally achieved by replacing vicariously the real system by a fictitious system, i.e. using the method described in the next paragraph.

Trajectories of two particles

Consider two point particles A and B interacting¹ with the potential $u(|\mathbf{r}_2 - \mathbf{r}_1|)$. When denoting the radius vector of the first particle by $\mathbf{r}_1 = \mathbf{OA}$ and that of the second particle by $\mathbf{r}_2 = \mathbf{OB}$, the respective velocities of the particles are $\mathbf{v}_1 = \dot{\mathbf{r}}_1$ and $\mathbf{v}_2 = \dot{\mathbf{r}}_2$, and the Newton law applied to each particle yields (Fig. 8.1):

¹It is assumed here that the interaction between two particles can occur at very short range (collision) or long distance.

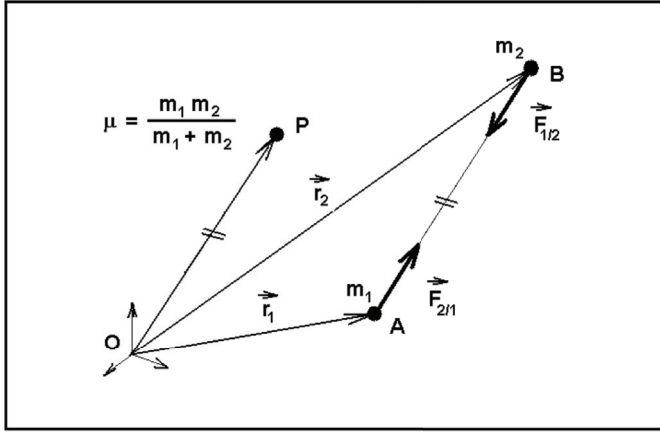


Figure 8.1: Fictitious particle P of reduced mass μ as the equivalent system of two interacting point particles A and B .

$$\mathbf{F}_{2/1} = m_1 \ddot{\mathbf{r}}_1 \quad \text{and} \quad \mathbf{F}_{1/2} = m_2 \ddot{\mathbf{r}}_2, \quad (8.11)$$

where $\mathbf{F}_{1/2}$ and $\mathbf{F}_{2/1} = -\mathbf{F}_{1/2}$ are the forces deriving from the potential $u(|\mathbf{r}_2 - \mathbf{r}_1|)$. With the following linear combination provided by equation (8.11):

$$\begin{aligned} m_2 \mathbf{F}_{2/1} - m_1 \mathbf{F}_{1/2} &= m_1 m_2 (\ddot{\mathbf{r}}_1 - \ddot{\mathbf{r}}_2), \\ (m_2 + m_1) \mathbf{F}_{1/2} &= m_1 m_2 \ddot{\mathbf{r}}_2 - \ddot{\mathbf{r}}_1, \end{aligned} \quad (8.12)$$

it follows:

$$\mathbf{F}_{1/2} = \mu \ddot{\mathbf{r}}, \quad (8.13)$$

$$\text{with} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad (8.14)$$

$$\text{and} \quad \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 = \mathbf{AB} = \mathbf{OP}. \quad (8.15)$$

Equation (8.13) is the equation of motion for a *fictitious particle* P of *reduced mass* μ submitted to the force $\mathbf{F}_{1/2}$. As $\mathbf{F}_{1/2}$ and $\mathbf{r}$ are collinear vectors, their vector product is zero, namely:

$$\mathbf{r} \wedge \mathbf{F}_{1/2} = \mathbf{r} \wedge \mu \ddot{\mathbf{r}} = \mathbf{0}, \quad (8.16)$$

$$\text{or} \quad \frac{d}{dt} (\mathbf{r} \wedge \mu \dot{\mathbf{r}}) = \mathbf{0}. \quad (8.17)$$

This relation implies that the angular momentum vector $\sigma = \mathbf{r} \wedge \mu \dot{\mathbf{r}}$ of the system is constant, thus meaning that the particles A and B move in a fixed plane containing the centre of mass G defined by the formula:

$$\mathbf{OG} = \frac{m_1 \mathbf{OA} + m_2 \mathbf{OB}}{m_1 + m_2}. \quad (8.18)$$

To find the trajectories of particles in the centre of mass reference frame, we place the origin in G according to the relation:

$$m_1 \mathbf{GA} + m_2 \mathbf{GB} = \mathbf{0}. \quad (8.19)$$

It follows that the trajectories of the two particles are homothetic with respect to the centre of mass (Fig. 8.2a) in the ratio $\frac{GA}{GB} = \frac{m_2}{m_1}$. In using equation (8.19) together with the Chasles relation $\mathbf{AB} = \mathbf{AG} + \mathbf{GB}$, we deduce the expressions of the radius vectors of the two particles from the centre of mass:

$$\mathbf{GA} = -\frac{m_2}{m_1 + m_2} \mathbf{AB} \quad \text{and} \quad \mathbf{GB} = \frac{m_1}{m_1 + m_2} \mathbf{AB}, \quad (8.20)$$

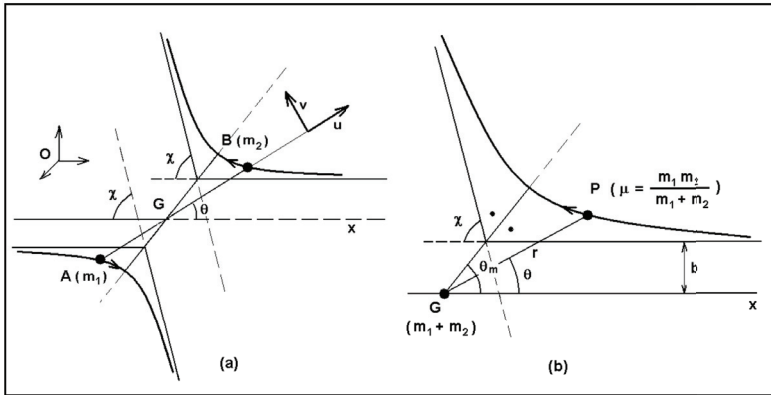


Figure 8.2: (a) Trajectories of the real particles A and B of respective masses m_1 et m_2 . (b) Trajectory of the fictitious particle P of the reduced mass μ interacting with a particle of mass $(m_1 + m_2)$ attached to the centre of mass G . The deflection angles of the trajectories of particles A , B and P are equal to χ .

as well as their radius vectors with respect to the fixed reference frame:

$$\mathbf{OA} = \mathbf{OG} + \mathbf{GA} = \frac{m_1 \mathbf{OA} + m_2 \mathbf{OB}}{m_1 + m_2} - \frac{m_2 \mathbf{AB}}{m_1 + m_2}, \quad (8.21)$$

$$\mathbf{OB} = \mathbf{OG} + \mathbf{GB} = \frac{m_1 \mathbf{OA} + m_2 \mathbf{OB}}{m_1 + m_2} + \frac{m_1 \mathbf{AB}}{m_1 + m_2}. \quad (8.22)$$

When putting $\mathbf{OG} = \mathbf{R}$ and using equation (8.15), these relations take the form:

$$\mathbf{OA} = \mathbf{r}_1 = \mathbf{R} - \frac{m_2 \mathbf{r}}{m_1 + m_2}, \quad (8.23)$$

$$\mathbf{OB} = \mathbf{r}_2 = \mathbf{R} + \frac{m_1 \mathbf{r}}{m_1 + m_2}. \quad (8.24)$$

The position vectors $\mathbf{r}_1(t)$ and $\mathbf{r}_2(t)$ of the particles relative to the fixed reference frame are deduced from the position vectors $\mathbf{R}(t)$ and $\mathbf{r}(t)$, where $\mathbf{R}(t)$ describes the trajectory of the centre of mass G and $\mathbf{r}(t)$ that of the fictitious particle P . Consequently, the motion of two particles A and B , interacting with each other, reduces to that of the motion of a fictitious particle P of reduced mass $\mu (= \frac{m_1 m_2}{m_1 + m_2})$. The method amounts to replacing the real system by a fictitious system consisting of one particle of mass equal to the total mass $m_1 + m_2$ fixed at the centre of mass, and one particle P of reduced mass μ , placed at the position $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. The advantage of this stratagem - at first glance artificial - is based on the fact that the angles are preserved in a homothety. It should indeed be noted that the trajectories of the two particles A and B as well as that of the fictitious particle P are homothetic (Figs. 8.2a and 8.2b). Therefore, the angle between the respective asymptotes is the same for the three trajectories. This angle, called the *deflection angle* χ , is the main characteristic of a binary collision.

Angular momentum and energy of two particles

The easiest way to determine the deflection angle χ is to take as starting point the laws of conservation of angular momentum and energy. If the radius vectors of particles are designated (in this paragraph) by

$\mathbf{GA} = \mathbf{r}_1$ and $\mathbf{GB} = \mathbf{r}_2$ (Fig. 8.2a), with $\mathbf{r} = \mathbf{AB}$, the velocities in polar coordinates on the reference frame $(\mathbf{G}, \mathbf{u}, \mathbf{v})$ are:

$$\mathbf{v}_1 = \dot{r}_1 \mathbf{u} + r_1 \dot{\theta} \mathbf{v}, \quad (8.25)$$

$$\text{and} \quad \mathbf{v}_2 = \dot{r}_2 \mathbf{u} + r_2 \dot{\theta} \mathbf{v}, \quad (8.26)$$

and the angular momenta of the two particles, with respect to G , are:

$$\mathbf{r}_1 \wedge m_1 \mathbf{v}_1 = m_1 r_1^2 \dot{\theta} \mathbf{k}, \quad (8.27)$$

$$\text{and} \quad \mathbf{r}_2 \wedge m_2 \mathbf{v}_2 = m_2 r_2^2 \dot{\theta} \mathbf{k}. \quad (8.28)$$

Now, by using equations (8.20), the total angular momentum σ is written as:

$$\sigma = (m_1 r_1^2 + m_2 r_2^2) \dot{\theta} \mathbf{k} = \left[m_1 \left(\frac{m_2}{m_1 + m_2} \right)^2 r^2 + m_2 \left(\frac{m_1}{m_1 + m_2} \right)^2 r^2 \right] \dot{\theta} \mathbf{k}, \quad (8.29)$$

or

$$\sigma = (m_1 r_1^2 + m_2 r_2^2) \dot{\theta} \mathbf{k} = \mu r^2 \dot{\theta} \mathbf{k}. \quad (8.30)$$

Regarding the kinetic energies of individual particles, they read:

$$\frac{1}{2} m_1 \mathbf{v}_1^2 = \frac{1}{2} m_1 \left[\dot{r}_1^2 + r_1^2 \dot{\theta}^2 \right], \quad (8.31)$$

$$\text{and} \quad \frac{1}{2} m_2 \mathbf{v}_2^2 = \frac{1}{2} m_2 \left[\dot{r}_2^2 + r_2^2 \dot{\theta}^2 \right], \quad (8.32)$$

so that the total kinetic energy E_c is:

$$\frac{1}{2} m_1 \mathbf{v}_1^2 + \frac{1}{2} m_2 \mathbf{v}_2^2 = \frac{1}{2} \left[m_1 \dot{r}_1^2 + m_2 \dot{r}_2^2 + \dot{\theta}^2 (m_1 r_1^2 + m_2 r_2^2) \right]. \quad (8.33)$$

According to equation (8.30), it can be seen that the contribution of the energy coming from the circumferential component of velocity is:

$$\frac{1}{2} \dot{\theta}^2 (m_1 r_1^2 + m_2 r_2^2) = \frac{1}{2} r^2 \dot{\theta}^2, \quad (8.34)$$

and the radial component of velocity reduces to²:

$$\frac{1}{2} (m_1 \dot{r}_1^2 + m_2 \dot{r}_2^2) = \frac{1}{2} \mu \dot{r}^2. \quad (8.35)$$

²Since the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are collinear, equation (8.19) transforms into:

$$\begin{aligned} (m_1 \dot{\mathbf{r}}_1 + m_2 \dot{\mathbf{r}}_2)^2 &= 0, \\ \text{or} \quad m_1^2 \dot{r}_1^2 + m_2^2 \dot{r}_2^2 - 2m_1 m_2 \dot{r}_1 \dot{r}_2 &= 0, \end{aligned}$$

Therefore, by summing the kinetic energy E_c and the potential energy $u(r)$ we obtain the mechanical energy E of the system:

$$E = \frac{1}{2}\mu\dot{r}^2 + \frac{1}{2}\mu r^2\dot{\theta}^2 + u(r), \quad (8.36)$$

which can still be written as a function of the angular momentum σ (Eq. 8.30) under the following form³ :

$$E = \frac{1}{2}\mu\dot{r}^2 + \frac{1}{2}\frac{\sigma^2}{\mu r^2} + u(r). \quad (8.37)$$

The term $\frac{1}{2}\frac{\sigma^2}{\mu r^2}$ in this equation is traditionally known as the *centrifugal energy* and constitutes with the potential energy $u(r)$ the *effective potential energy*.

Deflection angle of particles in a binary collision

In the previous paragraph, the formal equivalence has been shown between the actual collision of two real particles A and B and the collision of a fictitious particle P (reduced mass μ) with a fixed particle (mass $m_1 + m_2$) located at the centre of mass. To calculate the *deflection angle* χ , we consider the motion of the fictitious particle P interacting with the motionless particle G . After some time, the particle P is deflected from its initial direction by the angle χ (Fig. 8.2b).

and equation (8.14) in:

$$\begin{aligned} \dot{\mathbf{r}}^2 &= (\dot{\mathbf{r}}_2 - \dot{\mathbf{r}}_1)^2, \\ \text{or } \dot{r}^2 &= \dot{r}_2^2 + \dot{r}_1^2 + 2\dot{r}_1\dot{r}_2. \end{aligned}$$

Then, the elimination of $2\dot{r}_1\dot{r}_2$ between these two relations yields:

$$\begin{aligned} m_1^2\dot{r}_1^2 + m_2^2\dot{r}_2^2 - m_1m_2(\dot{r}^2 - \dot{r}_2^2 - \dot{r}_1^2) &= 0, \\ \text{or } m_1\dot{r}_1^2 + m_2\dot{r}_2^2 &= \frac{m_1m_2}{m_1+m_2}\dot{r}^2. \end{aligned}$$

³Indeed, with $\sigma = \mu r^2\dot{\theta}$ it is deduced immediately:

$$\mu r^2\dot{\theta}^2 = \frac{\sigma^2}{\mu r^2}.$$

In equation (8.37), the quantity $\left[u(r) + \frac{1}{2}\frac{\sigma^2}{\mu r^2}\right]$ is the effective potential energy and the quantity $\frac{1}{2}\frac{\sigma^2}{\mu r^2}$ is traditionally known as the *centrifugal energy*.

Note that the deflection angle χ is related to the angle θ_m corresponding to the position of the fictitious particle which is the closest from the centre of mass, i.e.:

$$\chi = \pi - 2\theta_m. \quad (8.38)$$

It is well known for an elastic collision that the total energy E and angular momentum σ are kept constant. However, in the collision process studied here, rather than calling on the energy and angular momentum, it is more convenient to use the velocity v_∞ of the particle at infinity and the *impact parameter* b , i.e. the length of the perpendicular drawn from the centre of mass to the linear asymptote coinciding with the initial direction of the fictitious particle. At the initial moment, when the particle is still at infinity, the total energy is $E \approx \frac{\mu v_\infty^2}{2}$ (since $u(r) \approx 0$) and the angular momentum is $\sigma = \mu r^2 \dot{\theta} = \mu b v_\infty$. Substituting these expressions of E and σ in equation (8.37), we obtain⁴ :

$$\frac{d\theta}{dr} = -\frac{b}{r^2} \left[1 - \frac{b^2}{r^2} - \frac{2u(r)}{\mu v_\infty^2} \right]^{-1/2}, \quad (8.39)$$

where the sign $-$ comes from the fact that, before the collision, θ increases when r is decreasing. Finally, the convenient expression for θ_m needed to calculate the deflection angle χ is reduced to:

$$\int_0^{\theta_m} d\theta = \theta_m = \int_{r_m}^{\infty} \frac{b}{r^2} \left[1 - \frac{b^2}{r^2} - \frac{2u(r)}{\mu v_\infty^2} \right]^{-1/2} dr, \quad (8.40)$$

where the minimum distance r_m is determined with the condition $\frac{dr}{d\theta} = 0$.

⁴From the expression of angular momentum, it follows:

$$\dot{r} = \frac{dr}{d\theta} \frac{d\theta}{dt} = \frac{dr}{d\theta} \frac{b v_\infty}{r^2},$$

so that equation (8.37) reads:

$$\begin{aligned} \frac{\mu v_\infty^2}{2} &= \frac{1}{2} \mu \left(\frac{dr}{d\theta} \right)^2 \frac{b^2 v_\infty^2}{r^4} + \frac{1}{2} \frac{b^2 \mu v_\infty^2}{r^2} + u(r), \\ \left(\frac{dr}{d\theta} \right)^2 \frac{b^2 v_\infty^2}{r^4} &= v_\infty^2 - \frac{b^2 v_\infty^2}{r^2} - \frac{2u(r)}{\mu}. \end{aligned}$$

8.3 The collision integral

Scattering cross section

The kinetic theory of gases is not concerned with the deflection of an individual particle by a diffuser, but rather with the deflection of *beam-like particles*. It is a matter of fact that the incident beam particles have different velocities and different impact parameters. However, when only the particles with the same initial velocity v_∞ are involved, some of them travel without deviation from the initial direction while the other ones undergo a deflection angle $\chi(b)$. Besides, if ϕ is the particle flux of the incident beam, the particle number with an impact parameter between b and $b + db$, carried along during the time dt , is (Fig. 8.3):

$$dn = \phi dt dS = \phi dt (2\pi b db). \quad (8.41)$$

Having shown the one-to-one correspondence between the impact parameter and deflection angle (Eq. 8.40), it follows that these dn particles are scattered (Fig. 8.3) in the solid angle between Ω and $\Omega + d\Omega$, where Ω is the solid angle associated with the deflection angle χ by the formula $\Omega = 2\pi(1 - \cos \chi)$. Its differential element is also:

$$d\Omega = 2\pi \sin \chi \cdot d\chi. \quad (8.42)$$

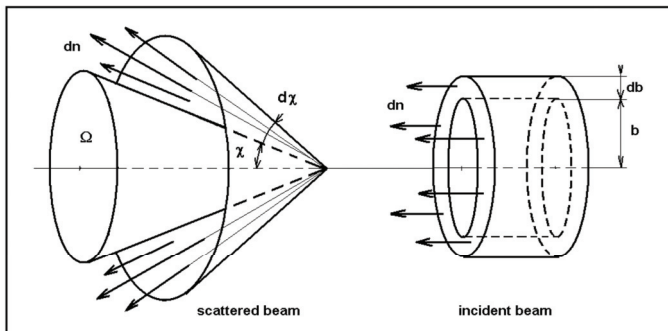
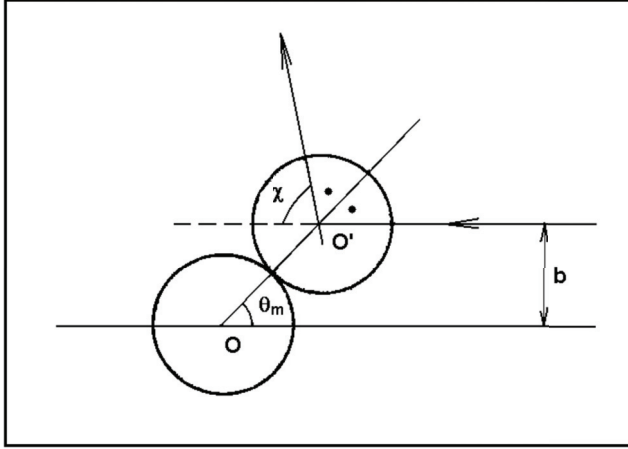


Figure 8.3: Diffusion of a particle beam during the time dt , with the impact parameter between b and $b + db$.

Figure 8.4: Collision between two hard spheres of diameter d .

Therefore the number dn of scattered particles is equal to:

$$dn = \phi dt \sigma d\Omega = \phi dt \sigma (2\pi \sin \chi d\chi) . \quad (8.43)$$

The coefficient σ should not be confused with the angular momentum introduced above⁵. In atomic physics, the coefficient σ is called the *differential scattering cross section* and is expressed in barn (1 barn = 10^{-24} cm²).

By identifying equations (8.41) and (8.43), we come to the relation between the differential cross section σ and the impact parameter b through the deflection angle χ :

$$\sigma = \frac{b}{\sin \chi} \left| \frac{db}{d\chi} \right| . \quad (8.44)$$

The absolute value of the derivative ($\frac{db}{d\chi}$) is retained here because the latter is usually negative.

For example, in the scattering by hard spheres (Fig. 8.4) of diameter d , the impact parameter is $b = d \sin \theta_m$, with $\theta_m = \frac{\pi - \chi}{2}$ and

⁵The coefficient σ used here has the dimensions of a surface ($\sigma \sim L^2$) which is consistent with the definition of the solid angle ($d\Omega = \frac{dS}{L^2}$).

$\sin \chi = \sin 2\theta_m = 2 \sin \theta_m \cos \theta_m$, so that:

$$\left| \frac{db}{d\chi} \right| = \left| \frac{db}{d\theta_m} \frac{d\theta_m}{d\chi} \right| = \frac{d}{2} \cos \theta_m, \quad (8.45)$$

and the differential scattering cross section is:

$$\sigma = \frac{d \sin \theta_m}{2 \sin \theta_m \cos \theta_m} \frac{d}{2} \cos \theta_m = \frac{d^2}{4}. \quad (8.46)$$

In fact, the total scattering cross section⁶ $\sigma_t = \int \sigma d\Omega$ is rather used. In the case of scattering by hard spheres, σ_t becomes simply:

$$\sigma_t = \int_0^\pi \frac{d^2}{4} 2\pi \sin \chi d\chi = \pi d^2. \quad (8.47)$$

This result has an obvious geometric interpretation by the fact that σ_t coincides with the area of the cross section of radius $b = d$.

Collision integral

To obtain the expression for the collision integral, we consider a volume element $d\mathbf{r}$ in the particle beam. This volume must be large enough to contain several pairs of particles A and B , but is small enough for the distribution function $f(\mathbf{r}, \mathbf{p}, t)$ to avoid being dependent on the position.

Among the couples of particles likely to collide, we still limit ourselves to consider only the particles A having the momentum p_1 , to $d\mathbf{p}_1$, and the particles B with the momentum p_2 , to $d\mathbf{p}_2$. As the distribution function is constant in the volume $d\mathbf{r}$, the numbers of particles A and B are respectively (Eq. 8.2):

$$\delta n_1 = f(\mathbf{r}, \mathbf{p}_1, t) d\mathbf{r} d\mathbf{p}_1, \quad (8.48)$$

$$\delta n_2 = f(\mathbf{r}, \mathbf{p}_2, t) d\mathbf{r} d\mathbf{p}_2. \quad (8.49)$$

Then, we choose a time interval dt significantly higher than the duration of a collision, but small enough so that the variation in the

⁶The total scattering cross section is better defined by the relation:

$$\sigma_t = \int \sigma (1 - \cos \chi) d\Omega = \int_0^\pi \sigma (1 - \cos \chi) 2\pi \sin \chi d\chi,$$

which does not affect the result because $\int_0^\pi \cos \chi \sin \chi d\chi = 0$.

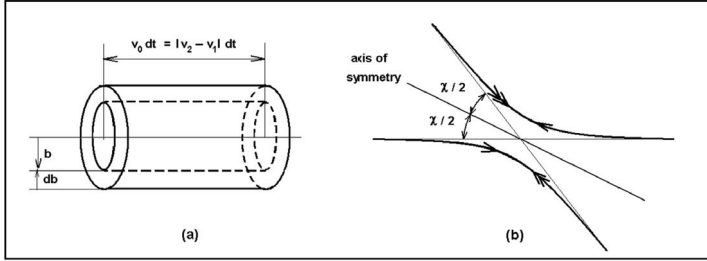


Figure 8.5: (a) Domain of action of a collision. (b) Reverse path principle in a collision process.

number of particles in the volume $d\mathbf{r}$ can be left aside. The aim is to define the infinitesimal domain of action ($2\pi b db$) ($v_0 dt$) of the collision (Fig. 8.5a), where b is the impact parameter and $v_0 = |\mathbf{v}_2 - \mathbf{v}_1|$ the relative velocity of particles A and B during the collision.

With these considerations in mind, the probability of collision can be determined by the ratio of the action domain of the collision to the volume element $d\mathbf{r}$:

$$\frac{2\pi b db |\mathbf{v}_2 - \mathbf{v}_1| dt}{d\mathbf{r}}. \quad (8.50)$$

The average number of particles undergoing a scattering with the impact parameter b in the volume $d\mathbf{r}$, should be calculated by multiplying the probability obtained above by the number of particles A and B contained in the volume $d\mathbf{r}$. We denote the average number of particles by:

$$dn^- = \left[\frac{2\pi b db |\mathbf{v}_2 - \mathbf{v}_1| dt}{d\mathbf{r}} \right] \delta n_1 \delta n_2, \quad (8.51)$$

or:

$$dn^- = 2\pi b |\mathbf{v}_2 - \mathbf{v}_1| f(\mathbf{r}, \mathbf{p}_1, t) f(\mathbf{r}, \mathbf{p}_2, t) d\mathbf{p}_1 d\mathbf{p}_2 db dt d\mathbf{r}. \quad (8.52)$$

During the collision between two particles A and B , with a given impact parameter, the momentum of particle A passes from $\mathbf{p}_1$ to $\mathbf{p}'_1$, and that of particle B goes from $\mathbf{p}_2$ to $\mathbf{p}'_2$. It should be emphasized that equation (8.52) gives the number of particles A whose momentum passes from $\mathbf{p}_1$ to $\mathbf{p}'_1$ (which is the same as the number of particles B whose momentum passes from $\mathbf{p}_2$ to $\mathbf{p}'_2$). However, to assess the

actual number of particles having undergone the changes of momenta $|\mathbf{p}'_1 - \mathbf{p}_1|$ and $|\mathbf{p}'_2 - \mathbf{p}_2|$, it is necessary to take account the inverse collisions for which the particles A have their momenta going from $\mathbf{p}'_1$ to $\mathbf{p}_1$ and the particles B have their momenta going from $\mathbf{p}'_2$ to $\mathbf{p}_2$. These inverse transitions play an opposite role against the direct transitions because the latter transitions involve dn^- particles with $\mathbf{p}_1$ and $\mathbf{p}_2$ as initial momenta (Eq. 8.52), whereas the inverse transitions entail dn^+ particles with $\mathbf{p}'_1$ and $\mathbf{p}'_2$ as initial momenta. Therefore, the overall outcome must be calculated by subtracting the number dn^+ (resulting from the inverse collisions) from the number dn^- (resulting from the direct collisions).

From the symmetry properties of the collision process (Fig. 8.5b), it follows that the number of particles dn^+ scattered in the inverse collisions is deduced from equation (8.52) by swapping the momenta. This allows deducing directly:

$$dn^+ = 2\pi b |\mathbf{v}_2 - \mathbf{v}_1| f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) d\mathbf{p}'_1 d\mathbf{p}'_2 db dt d\mathbf{r}. \quad (8.53)$$

Taking account of the relative velocity:

$$\mathbf{v}_2 - \mathbf{v}_1 = \frac{\mathbf{p}_2^2}{m_2} - \frac{\mathbf{p}_1^2}{m_1}, \quad (8.54)$$

and from the relation⁷ $d\mathbf{p}_1 d\mathbf{p}_2 = d\mathbf{p}'_1 d\mathbf{p}'_2$, the total number of particles A (or B) having undergone changes of momentum, with the same impact parameter during the time dt in the volume $d\mathbf{r}$, is:

$$\begin{aligned} dn^+ - dn^- &= 2\pi b |\mathbf{v}_2 - \mathbf{v}_1| \left[f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t) \right. \\ &\quad \left. - f(\mathbf{r}, \mathbf{p}_1, t) f(\mathbf{r}, \mathbf{p}_2, t) \right] d\mathbf{p}_1 d\mathbf{p}_2 db dt d\mathbf{r}. \end{aligned} \quad (8.55)$$

If we are interested in the particles A with the given momentum $\mathbf{p}_1$, while the particles B have any values of momentum, equation (8.55)

⁷From equations (8.23) and (8.24) it follows the transformations of $\mathbf{p}_1$ and $\mathbf{p}_2$ into $\mathbf{p}_R$ and $\mathbf{p}_r$:

$$\begin{aligned} \mathbf{p}_1 &= \mathbf{p}_R - \frac{m_2 \mathbf{p}_r}{m_1 + m_2}, \\ \mathbf{p}_2 &= \mathbf{p}_R + \frac{m_1 \mathbf{p}_r}{m_1 + m_2}. \end{aligned}$$

The identity $d\mathbf{p}_1 d\mathbf{p}_2 = d\mathbf{p}_R d\mathbf{p}_r = d\mathbf{p}'_1 d\mathbf{p}'_2$ arises from the fact that the Jacobian of this transformation is equal to unity.

must be integrated over all the possible values of $\mathbf{p}_2$ and impact parameter b . As regards the collision integral, it is defined as the total variation of the number of particles per elements of time dt and volume $d\mathbf{r}d\mathbf{p}_1$ of the phase subspace, namely:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = \iint 2\pi b |\mathbf{v}_2 - \mathbf{v}_1| (f'_1 f'_2 - f_1 f_2) d\mathbf{p}_2 db, \quad (8.56)$$

where the notation of the distribution functions has been significantly simplified. By substituting equation (8.56) in equation (8.10), we obtain the *Boltzmann equation* in the approximation of binary collisions:

$$\begin{aligned} \frac{\partial f_1}{\partial t} = & -\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_r f_1 - \mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_p f_1 \\ & + 2\pi \iint b |\mathbf{v}_2 - \mathbf{v}_1| (f'_1 f'_2 - f_1 f_2) d\mathbf{p}_2 db. \end{aligned} \quad (8.57)$$

When the distribution function f_2 is known, we obtain the law of variation applying to the distribution function f_1 . A priori, f'_1 and f'_2 depend respectively on momenta $\mathbf{p}'_1$ and $\mathbf{p}'_2$, which are themselves functions of $\mathbf{p}_1$ and $\mathbf{p}_2$.

8.4 The one-particle non-equilibrium distribution function

Definition of relaxation time

The Boltzmann equation (Eq. 8.57) is an integro-differential equation whose solution is complicated, even when the collisions are elastic (with kinetic energy conservation) and the masses of particles A and B are very different from each other⁸. However, in this case, it can be assumed that the large particles are motionless ($\mathbf{v}_2 \simeq \mathbf{0}$). Since the momenta $\mathbf{p}_1$ of light particles are not related to the momenta $\mathbf{p}_2$ of heavy particles, the integrations of distribution functions over $\mathbf{p}_2$ can be achieved independently. Therefore, the integration of equation (8.56) over $\mathbf{p}_2$ is expressed through the integrals:

$$\int f_2 d\mathbf{p}_2 = \int f'_2 d\mathbf{p}_2 = n_2, \quad (8.58)$$

⁸The *Lorentz gas* is a system containing two types of particles: (i) some are very heavy and the others very light, and (ii) the mutual collisions between light particles are neglected compared to their collisions with heavy particles.

that represents the number of heavy particles n_2 in the volume element $d\mathbf{r}$ according to equation (8.2). Taking account of these considerations, the collision integral (Eq. 8.56) reads:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = 2\pi n_2 |\mathbf{v}_1| \int (f'_1 - f_1) b db. \quad (8.59)$$

Then, we suppose that the distribution function f out-of-equilibrium may be decomposed as:

$$f = f_0 + \Delta f, \quad (8.60)$$

where f_0 is the distribution function at equilibrium and Δf the non-equilibrium contribution. We also assume that the difference is $(f'_1 - f_1) \simeq -\Delta f = f_0 - f$, this being easily justified as the collision integral $\left(\frac{\partial f}{\partial t}\right)_{\text{col}}$ is equal to zero at equilibrium ($f = f_0$) and proportional to $(f - f_0)$ when the deviation from equilibrium is small.

Concerning the type of collisions described above, the collision integral can be simplified to:

$$\left(\frac{\partial f}{\partial t}\right)_{\text{col}} = 2\pi n_2 |\mathbf{v}_1| (f_0 - f) \int b db = -\frac{f - f_0}{\tau}, \quad (8.61)$$

where the parameter τ having the dimension of time is called *relaxation time*. It is expressed as follows:

$$\tau = \frac{1}{\pi b^2 n_2 |\mathbf{v}_1|}. \quad (8.62)$$

As a consequence, the Boltzmann equation (Eq. 8.57) is written explicitly as a function of the relaxation time τ and is reduced to the following expression:

$$\frac{\partial f}{\partial t} = -\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f - \mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_{\mathbf{p}} f - \frac{f - f_0}{\tau}. \quad (8.63)$$

The physical interpretation of the relaxation time τ is easy understood in the following circumstances: when the external force is suddenly phased out ($\mathbf{F}_{\text{ext}} = \mathbf{0}$) and the distribution function is assumed to be homogeneous throughout the system ($\mathbf{grad}_{\mathbf{r}} f = \mathbf{0}$), the Boltzmann equation (Eq. 8.63) is simplified to:

$$\frac{df}{dt} = -\frac{f - f_0}{\tau}, \quad (8.64)$$

and its solution is:

$$f(t) = f_0 + [f(0) - f_0] \exp\left(-\frac{t}{\tau}\right), \quad (8.65)$$

where $f(0)$ is the non-equilibrium distribution function at the initial moment. In this way, the system initially out-of-equilibrium goes back to equilibrium by means of the collision process that follows an exponential decrease with a time constant corresponding to the relaxation time τ .

Approximate expression of the distribution function

As the Boltzmann equation (Eq. 8.57) cannot possibly be solved analytically, extensive use of equation (8.63) has been made for many collision mechanisms and various types of external force field. From equation (8.63) it results the following expression for the non-equilibrium distribution function:

$$f = f_0 - \tau \frac{\partial f}{\partial t} - \tau \frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f - \tau \mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_{\mathbf{p}} f, \quad (8.66)$$

where the relaxation time τ can be calculated or used as an adjustable parameter obtained from experiment. As expected, the relaxation time in Boltzmann's equation is characteristic of the collision process in the system and determines its return to the equilibrium. The shorter the relaxation time, the faster the return to equilibrium. Generally the calculation of the relaxation time τ is very difficult.

As a rough approximation, it can be assumed that the non-equilibrium distribution function is slightly different from the equilibrium distribution function. In this case, the replacement of f by f_0 in the right hand side of equation (8.66) allows us to write the distribution function f in the form:

$$f \simeq f_0 - \tau \frac{\partial f_0}{\partial t} - \tau \frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f_0 - \tau \mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_{\mathbf{p}} f_0. \quad (8.67)$$

As the equilibrium distribution function f_0 does not depend on the time ($\frac{\partial f_0}{\partial t} = 0$), the non-equilibrium distribution function (Eq. 8.67) can be written simply as:

$$f \simeq f_0 - \tau \frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f_0 - \tau \mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_{\mathbf{p}} f_0, \quad (8.68)$$

where f_0 is the equilibrium distribution function given by the Maxwell distribution (Eq. 4.95), namely:

$$f_0 = n \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\frac{p^2}{2m k_B T} \right). \quad (8.69)$$

Because the equilibrium distribution function f_0 remains unchanged throughout the system ($\mathbf{grad}_{\mathbf{r}} f_0 = 0$), the solution of the Boltzmann equation (Eq. 8.68) is very imprecise. A way to improve accuracy is to admit that the particle density n is not constant throughout the system. In order to take account of this hypothesis, the system is assumed to consist of a set of small subsystems of volume $d\mathbf{r}$ with each of them being in *local equilibrium* of its own, i.e. different from the *global equilibrium*⁹. The argument to support this hypothesis is based on the fact that a sudden change of the particle density in a subsystem leaves the particle density unchanged in the neighbouring subsystems. In other words, the local density of particles in a given volume $d\mathbf{r}$ rapidly reaches an equilibrium value which is different from the overall density of particles whose equilibrium is recovered much more slowly. The local density of particles correspond to the number dn of particles per unit volume. Remember that the volume $d\mathbf{r}$ should be large enough to contain a great number of particles, but small enough so that the ratio $\frac{dn}{d\mathbf{r}} = n(\mathbf{r}, t)$ is a continuous function of $\mathbf{r}$ over the system. Consequently, the solution of Boltzmann's equation is more accurate if the distribution function f_0 is supposed to vary from one subsystem to another. Its expression is:

$$f_0 = n(\mathbf{r}, t) \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\frac{p^2}{2m k_B T} \right), \quad (8.70)$$

where the particle density $n(\mathbf{r}, t)$ depends on the time and the position.

Assuming that an expression for the local density of particles $n(\mathbf{r}, t)$ is known, the non-equilibrium distribution function can be deduced easily from the following observations. Consider first the last term of equation (8.68) written explicitly as:

$$\mathbf{grad}_{\mathbf{p}} f_0 = \frac{\partial f_0}{\partial p_x} \mathbf{i} + \frac{\partial f_0}{\partial p_y} \mathbf{j} + \frac{\partial f_0}{\partial p_z} \mathbf{k}. \quad (8.71)$$

⁹To better understand the concept of local equilibrium, see, for example, the article by J. M. G. Vilar and J. M. Rubi, *Thermodynamics beyond local equilibrium*, in [arXiv:cond-mat/0110614v1](https://arxiv.org/abs/cond-mat/0110614v1)

Given equation (8.70), the component $\frac{\partial f_0}{\partial p_x}$ is:

$$\frac{\partial f_0}{\partial p_x} = n(\mathbf{r}, t) \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \left(-\frac{p_x}{m k_B T} \right) \exp \left(-\frac{p^2}{2m k_B T} \right) = -\frac{p_x f_0}{m k_B T}. \quad (8.72)$$

The calculation of the other components being performed similarly, we obtain the expression of $\mathbf{grad}_{\mathbf{p}} f_0$ as well as:

$$\tau \mathbf{F}_{ext} \cdot \mathbf{grad}_{\mathbf{p}} f_0 = -\tau \left(\mathbf{F}_{ext} \cdot \frac{\mathbf{p}}{m} \right) \frac{f_0}{k_B T}. \quad (8.73)$$

As regards the second term of the right hand side of equation (8.68), it transforms as follows:

$$\begin{aligned} \mathbf{grad}_{\mathbf{r}} f_0 &= \frac{\partial f_0}{\partial r_x} \mathbf{i} + \frac{\partial f_0}{\partial r_y} \mathbf{j} + \frac{\partial f_0}{\partial r_z} \mathbf{k} = \frac{\partial f_0}{\partial n} \mathbf{grad}_{\mathbf{r}} n \\ &= \frac{f_0}{n} \mathbf{grad}_{\mathbf{r}} n, \end{aligned} \quad (8.74)$$

as the particle density $n(\mathbf{r}, t)$ depends on the position. This allows writing the penultimate term of the equation (8.68) as:

$$\tau \frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f_0 = \tau \frac{f_0}{n} \left(\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} n \right). \quad (8.75)$$

Therefore, in using equations (8.73) and (8.75), the non-equilibrium distribution function is expressed in a substantially more tractable form than equation (8.68), i.e.:

$$f \simeq f_0 - \tau \frac{f_0}{n} \left(\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} n \right) + \tau \frac{f_0}{k_B T} \left(\mathbf{F}_{ext} \cdot \frac{\mathbf{p}}{m} \right). \quad (8.76)$$

This expression is based on adequate knowledge of the local density of particles $n(\mathbf{r}, t)$ and the relaxation time τ .

8.5 Kinematic considerations in continuum mechanics

The twentieth century began with the confrontation between two schools of thought in physics: the *atomistic approach* led by Boltzmann, Gibbs, etc. and the *energetic approach* represented by Duhem,

Mach, etc. For the first authors, the systems are described according to a microscopic point of view with the probability density function in the phase space. When the systems are out-of-equilibrium, use is made of the one-particle distribution function whose variation is provided by Boltzmann's equation (Eq. 8.4) as seen in the previous section. With regard to the other authors, the description of systems is carried out macroscopically by using the particle density, momentum density and energy density whose changes are governed by the laws of conservation and the equations of transfer. These include the transfer of particles characterized by the Fick equation, the transfer of momentum characterized by the Navier–Stokes equation and the transfer of energy characterized by the Fourier equation.

To perform the macroscopic description, the fluid must be considered as a continuum where each volume element $d\mathbf{r}$ is in local equilibrium. Accordingly, if dn is the particle number in the volume element $d\mathbf{r}$, with the momentum $p + d\mathbf{p}$ and energy $E + dE$, the local densities of particles, momenta and energies are defined regardless of the size of the volume element. These local densities are intensive functions depending on the continuous variables $\mathbf{r}$ and t , and defined by:

$$n(\mathbf{r}, t) = \frac{dn}{d\mathbf{r}}, \quad (8.77)$$

$$\mathbf{p}(\mathbf{r}, t) = \frac{d\mathbf{p}}{d\mathbf{r}}, \quad (8.78)$$

$$E(\mathbf{r}, t) = \frac{dE}{d\mathbf{r}}. \quad (8.79)$$

The next subsections are devoted to an introduction to the continuous medium and the conservation laws of mass (particles), momentum and energy. These conservation laws are required to study the motion of a volume element $d\mathbf{r}$ taken in the continuum.

First of all, we determine the distribution laws of velocities and accelerations by means of the Euler variables. For this purpose, consider a volume element $d\mathbf{r}$ at the point M with coordinates $\mathbf{r}(x, y, z)$. Assuming that the velocity of this volume element at the point O taken as the origin, was $\mathbf{v}_O$, the velocity of the volume element $d\mathbf{r}$ at the point M is a continuous and differentiable function of the coordinates $\mathbf{r}(x, y, z)$. Thus, the velocity of $d\mathbf{r}$ at the point M denoted $\mathbf{v}$ has components v_x, v_y and v_z which are the Euler variables relying on the coordinates (x, y, z) . If the distance OM is short, we can keep only

the first derivatives of the Maclaurin series expansion of the velocity components in the vicinity of $x_O = 0$, $y_O = 0$ and $z_O = 0$, namely:

$$\mathbf{v} = \begin{vmatrix} v_x = v_{O,x} + x \frac{\partial v_x}{\partial x} + y \frac{\partial v_x}{\partial y} + z \frac{\partial v_x}{\partial z} \\ v_y = v_{O,y} + x \frac{\partial v_y}{\partial x} + y \frac{\partial v_y}{\partial y} + z \frac{\partial v_y}{\partial z} \\ v_z = v_{O,z} + x \frac{\partial v_z}{\partial x} + y \frac{\partial v_z}{\partial y} + z \frac{\partial v_z}{\partial z} \end{vmatrix}. \quad (8.80)$$

The velocity vector $\mathbf{v}$ can also be written as:

$$\mathbf{v} = \mathbf{v}_O + \bar{b} \cdot \mathbf{OM}, \quad (8.81)$$

where $\bar{b}$ is the tensor:

$$\bar{b} = \begin{vmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{vmatrix}. \quad (8.82)$$

It will be seen later that the tensor $\bar{b}$ can be usefully split into the antisymmetric tensor $\bar{b}_a$ and the symmetric tensor $\bar{b}_s$ ($\bar{b} = \bar{b}_a + \bar{b}_s$), having respectively the components:

$$\bar{b}_a = \begin{vmatrix} 0 & \frac{1}{2} \left(\frac{\partial v_x}{\partial y} - \frac{\partial v_y}{\partial x} \right) & -\frac{1}{2} \left(\frac{\partial v_z}{\partial x} - \frac{\partial v_x}{\partial z} \right) \\ -\frac{1}{2} \left(\frac{\partial v_x}{\partial y} - \frac{\partial v_y}{\partial x} \right) & 0 & \frac{1}{2} \left(\frac{\partial v_y}{\partial z} - \frac{\partial v_z}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial v_z}{\partial x} - \frac{\partial v_x}{\partial z} \right) & -\frac{1}{2} \left(\frac{\partial v_y}{\partial z} - \frac{\partial v_z}{\partial y} \right) & 0 \end{vmatrix} \quad (8.83)$$

and:

$$\bar{b}_s = \begin{vmatrix} \frac{\partial v_x}{\partial x} & \frac{1}{2} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) \\ \frac{1}{2} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) & \frac{\partial v_y}{\partial y} & \frac{1}{2} \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) & \frac{\partial v_z}{\partial z} \end{vmatrix}. \quad (8.84)$$

This decomposition allows us to write the velocity vector in terms of the tensors $\overline{\overline{b}}_a$ and $\overline{\overline{b}}_s$ as:

$$\mathbf{v} = \mathbf{v}_O + \overline{\overline{b}}_a \cdot \mathbf{OM} + \overline{\overline{b}}_s \cdot \mathbf{OM}. \quad (8.85)$$

It is quite easy to examine and confirm that the tensor product $\overline{\overline{b}}_a \cdot \mathbf{OM}$ is equivalent to the vector product of the vorticity vector $\boldsymbol{\Omega}$ (which is half of the curl operator¹⁰ of the vector $\mathbf{v}$, i.e. $\boldsymbol{\Omega} = \frac{1}{2} \nabla \wedge \mathbf{v}$) by the position vector $\mathbf{OM}$, so that the velocity is reduced to the expression:

$$\mathbf{v} = \mathbf{v}_O + \boldsymbol{\Omega} \wedge \mathbf{OM} + \overline{\overline{b}}_s \cdot \mathbf{OM}. \quad (8.86)$$

This formula shows that the velocity of a volume element results from the superposition of a translation, a rotation and a deformation.

In looking at a volume element along its trajectory, we notice that each component of the velocity (Eq. 8.80) is a function of the coordinates and time, i.e. $v_x = v_x(x, y, z, t), \dots$, and each component of the acceleration has the following form:

$$\gamma_x = \frac{\partial v_x}{\partial x} \frac{\partial x}{\partial t} + \frac{\partial v_x}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial v_x}{\partial z} \frac{\partial z}{\partial t} + \frac{\partial v_x}{\partial t}. \quad (8.87)$$

¹⁰Remember that:

(1) the gradient operator transforms a scalar field A into a vector field $\mathbf{V}$ by the relation:

$$\mathbf{V} = \mathbf{grad} A = \nabla A = \frac{\partial A}{\partial x} \mathbf{i} + \frac{\partial A}{\partial y} \mathbf{j} + \frac{\partial A}{\partial z} \mathbf{k},$$

where ∇ is the symbolic nabla vector $\nabla = \frac{\partial}{\partial x} \mathbf{i} + \frac{\partial}{\partial y} \mathbf{j} + \frac{\partial}{\partial z} \mathbf{k}$,

(2) the divergence operator transforms a vector field $\mathbf{V}$ into a scalar field A by the relation:

$$A = \text{div} \mathbf{V} = \nabla \cdot \mathbf{V} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z},$$

(3) the curl operator transforms a vector field $\mathbf{V}$ into another vector field $\boldsymbol{\Omega}$ by the relation:

$$\boldsymbol{\Omega} = \text{rot} \mathbf{V} = \nabla \wedge \mathbf{V},$$

(4) the Laplace operator is defined by the formula:

$$\nabla^2 = \text{div}(\mathbf{grad}) = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

Therefore, the vector acceleration of a volume element is given by:

$$\gamma = \begin{cases} \gamma_x = \frac{\partial v_x}{\partial t} + \frac{\partial v_x}{\partial x} \frac{\partial x}{\partial t} + \frac{\partial v_x}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial v_x}{\partial z} \frac{\partial z}{\partial t} \\ \gamma_y = \frac{\partial v_y}{\partial t} + \frac{\partial v_y}{\partial x} \frac{\partial x}{\partial t} + \frac{\partial v_y}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial v_y}{\partial z} \frac{\partial z}{\partial t} \\ \gamma_z = \frac{\partial v_z}{\partial t} + \frac{\partial v_z}{\partial x} \frac{\partial x}{\partial t} + \frac{\partial v_z}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial v_z}{\partial z} \frac{\partial z}{\partial t} \end{cases} . \quad (8.88)$$

By noting that $\frac{\partial x}{\partial t} = v_x$, $\frac{\partial y}{\partial t} = v_y$ and $\frac{\partial z}{\partial t} = v_z$ are the components of velocity $\mathbf{v}$, the acceleration can also be written as:

$$\gamma = \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v}, \quad (8.89)$$

where the operator¹¹

$$(\mathbf{v} \cdot \nabla) = v_x \frac{\partial}{\partial x} + v_y \frac{\partial}{\partial y} + v_z \frac{\partial}{\partial z} \quad (8.90)$$

is applied to the velocity $\mathbf{v}(v_x, v_y, v_z)$. The acceleration γ is the *particle derivative* of the velocity $\mathbf{v}$ with respect to the time; it is denoted by:

$$\gamma = \frac{D\mathbf{v}}{Dt} = \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v}, \quad (8.91)$$

where the term $\frac{\partial \mathbf{v}}{\partial t}$ represents the *local acceleration*, i.e. the local rate of change of velocity at a given point in the flow field, which is zero in a steady flow. In turn, the term $(\mathbf{v} \cdot \nabla) \mathbf{v}$ called *convective acceleration* refer to the rate of change of velocity produced by the displacement of the volume element $d\mathbf{r}$ in the flow field. Note in passing that the term $(\mathbf{v} \cdot \nabla) \mathbf{v}$ can also be written as¹²:

$$(\mathbf{v} \cdot \nabla) \mathbf{v} = \frac{1}{2} \nabla \mathbf{v}^2 + (\nabla \wedge \mathbf{v}) \wedge \mathbf{v}. \quad (8.92)$$

¹¹The operator $(\mathbf{v} \cdot \nabla)$ applies equally to a vector, as here, or a scalar. This operator should not be confused with the scalar $(\nabla \cdot \mathbf{v})$ which represents the divergence of the vector $\mathbf{v}$.

¹²This relation is obtained by arranging all the components of the acceleration (Eq. 8.88) in a form similar to what is written below for the x -component:

$$\gamma_x = \frac{\partial v_x}{\partial t} + \left[v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_y}{\partial x} + v_z \frac{\partial v_z}{\partial x} \right] + \left[v_z \left(\frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x} \right) - v_y \left(\frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y} \right) \right].$$

The first term on the RHS is the component of the local acceleration $\frac{\partial \mathbf{v}}{\partial t}$ on the x -axis, the terms in the first brackets represent the component of $\frac{1}{2} \nabla \mathbf{v}^2$ on the x -axis, and the terms in the second brackets represent the component of the vector triple product $(\nabla \wedge \mathbf{v}) \wedge \mathbf{v}$ on the x -axis.

8.6 The strain rate tensor and stress tensor

Rate-of-strain tensor

By observing equation (8.86), it is easily seen that, if the symmetric tensor $\bar{\bar{b}}_s$ is zero at any point of the medium, the velocity $\mathbf{v}$ is reduced to the velocity distribution formula of an undeformable solid body. By contrast, if $\bar{\bar{b}}_s$ is not zero, the medium undergoes a deformation which is fully characterized by the *strain rate tensor* $\bar{\bar{b}}_s$.

The trace of the symmetric tensor $\bar{\bar{b}}_s$ (Eq. 8.84) is equal to the divergence of the velocity $\mathbf{v}$. It is also called the *cubic expansion rate* and denoted:

$$\theta = \nabla \cdot \mathbf{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}. \quad (8.93)$$

In view of subsequent calculations, it is convenient to split $\bar{\bar{b}}_s$ into a spherical tensor $\bar{\bar{d}}_s$ defined in terms of the cubic expansion rate θ , and a deviator tensor $\bar{\bar{d}}_{dev}$ such as:

$$\bar{\bar{b}}_s = \bar{\bar{d}}_s + \bar{\bar{d}}_{dev}, \quad (8.94)$$

whose respective expressions are:

$$\bar{\bar{d}}_s = \begin{vmatrix} \frac{\theta}{3} & 0 & 0 \\ 0 & \frac{\theta}{3} & 0 \\ 0 & 0 & \frac{\theta}{3} \end{vmatrix} = \frac{\theta}{3} \bar{\bar{\delta}}, \quad (8.95)$$

where $\bar{\bar{\delta}}$ is the unit tensor, and

$$\bar{\bar{d}}_{dev} = \begin{vmatrix} \frac{\partial v_x}{\partial x} - \frac{\theta}{3} & \frac{1}{2} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) \\ \frac{1}{2} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) & \frac{\partial v_y}{\partial y} - \frac{\theta}{3} & \frac{1}{2} \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) & \frac{\partial v_z}{\partial z} - \frac{\theta}{3} \end{vmatrix}. \quad (8.96)$$

In fact, it is customary to write the strain rate tensor $\overline{\overline{b}}_s$ ($= \frac{\theta}{3}\overline{\overline{\delta}} + \overline{\overline{d}}_{dev}$) with the new components ε_{ij} under the following matrix form:

$$\begin{aligned} \overline{\overline{b}}_s &= \frac{\theta}{3} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \\ &+ \begin{vmatrix} \frac{\partial v_x}{\partial x} - \frac{\theta}{3} & \frac{1}{2}\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & \frac{1}{2}\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) \\ \frac{1}{2}\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & \frac{\partial v_y}{\partial y} - \frac{\theta}{3} & \frac{1}{2}\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) \\ \frac{1}{2}\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) & \frac{1}{2}\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) & \frac{\partial v_z}{\partial z} - \frac{\theta}{3} \end{vmatrix} \\ &= \begin{vmatrix} \varepsilon_{xx} & \varepsilon_{yx} & \varepsilon_{zx} \\ \varepsilon_{xy} & \varepsilon_{yy} & \varepsilon_{zy} \\ \varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_{zz} \end{vmatrix}. \end{aligned} \quad (8.97)$$

Cauchy stress tensor

Studying equilibrium applying to an elementary parallelepiped in a continuous medium leads to defining the *stress tensor* $\overline{\overline{t}}$ as follows [121]:

$$\overline{\overline{t}} = \begin{vmatrix} \sigma_{xx} & \sigma_{yx} & \sigma_{zx} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{zy} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{vmatrix}, \quad (8.98)$$

where σ_{ii} are the normal stresses and σ_{ij} the tangential stresses. Like the strain rate tensor $\overline{\overline{b}}_s$, the stress tensor $\overline{\overline{t}}$ is a second-order symmetric tensor. Moreover, in *non viscous fluids*, the tangential stresses σ_{ij} are zero ($\sigma_{xy} = \sigma_{yz} = \sigma_{zx} = 0$) and the normal stresses σ_{ii} are equal to the pressure p at the point considered ($\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = -p$), so that the stress tensor is a spherical tensor equal to $-p\overline{\overline{\delta}}$ where p is the hydrostatic pressure and $\overline{\overline{\delta}}$ the unit tensor.

In contrast, it makes sense for *viscous fluids* to decompose the stress symmetric tensor $\overline{\overline{t}}$ as the strain rate tensor, into a stress spherical tensor $\overline{\overline{t}}_s$ coming from the pressure forces, and a stress deviator

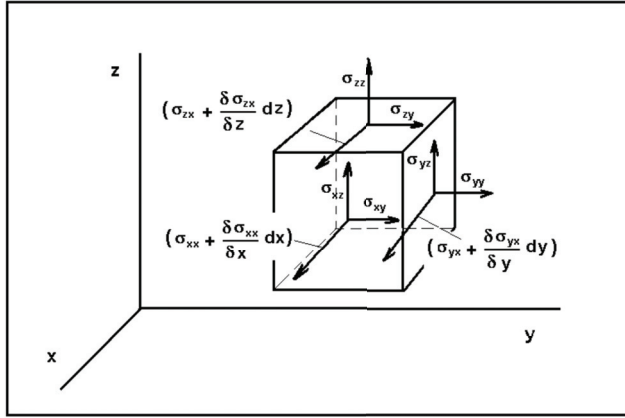


Figure 8.6: Components of stress in three imensions on the faces of a volume element. To avoid overloading the figure, the variations of stresses in the directions y and z are not indicated.

tensor $\bar{\bar{t}}_\eta$ called the *viscous stress tensor*. These tensors are linked by the relation $\bar{\bar{t}} = \bar{\bar{t}}_s + \bar{\bar{t}}_\eta$ and their expressions are respectively:

$$\bar{\bar{t}}_s = \begin{vmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{vmatrix} = -p \bar{\bar{\delta}}, \quad (8.99)$$

and:

$$\bar{\bar{t}}_\eta = \begin{vmatrix} \sigma_{xx} + p & \sigma_{yx} & \sigma_{zx} \\ \sigma_{xy} & \sigma_{yy} + p & \sigma_{zy} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} + p \end{vmatrix}. \quad (8.100)$$

Therefore, the stress tensor in viscous fluids is:

$$\bar{\bar{t}} = -p \bar{\bar{\delta}} + \bar{\bar{t}}_\eta. \quad (8.101)$$

It should be recalled that the stress tensor follows from the analysis of an equilibrium elementary parallelepiped submitted to internal forces (pressure forces and viscous forces) exerted by the adjacent volume elements (Fig. 8.6). The resulting force along the x -axis is:

$$df_x = \left(\frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{yx}}{\partial y} + \frac{\partial \sigma_{zx}}{\partial z} \right) dx dy dz, \quad (8.102)$$

and the components of the internal force $\mathbf{f}$ per unit volume in the three orthogonal directions x , y and z are:

$$f_x = \frac{df_x}{dx dy dz} = \frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{yx}}{\partial y} + \frac{\partial \sigma_{zx}}{\partial z}, \quad (8.103)$$

$$f_y = \frac{df_y}{dx dy dz} = \frac{\partial \sigma_{xy}}{\partial x} + \frac{\partial \sigma_{yy}}{\partial y} + \frac{\partial \sigma_{zy}}{\partial z}, \quad (8.104)$$

$$f_z = \frac{df_z}{dx dy dz} = \frac{\partial \sigma_{xz}}{\partial x} + \frac{\partial \sigma_{yz}}{\partial y} + \frac{\partial \sigma_{zz}}{\partial z}, \quad (8.105)$$

symbolically denoted¹³:

$$\mathbf{f} = \nabla \cdot \bar{\bar{t}} a = -\nabla p + \nabla \cdot \bar{\bar{t}} \eta. \quad (8.106)$$

Relations between stress and strain rate tensors

We know that the stress distribution in a volume element $d\mathbf{r}$ is defined by the 6 coefficients σ_{xx} , σ_{yy} , σ_{zz} , σ_{xy} , σ_{yz} , σ_{zx} and the strain rate distribution by the 6 coefficients ε_{xx} , ε_{yy} , ε_{zz} , ε_{xy} , ε_{yz} , ε_{zx} . In this subsection, we propose to find the relation connecting the viscous stress tensor $\bar{\bar{t}}_\eta$ (Eq. 8.100) with the strain rate tensor $\bar{\bar{b}}_s$ (Eq. 8.97) in *incompressible fluids* named Newtonian fluids. It is assumed, in such fluids, that the components of stress tensor are linear functions of the components of the strain rate tensor. For reasons of symmetry – not discussed here – it is found that:

$$\begin{aligned} \sigma_{xx} + p &= \mu \varepsilon_{xx} + \lambda (\varepsilon_{yy} + \varepsilon_{zz}) = \lambda (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) + 2\eta \varepsilon_{xx}, \\ \sigma_{yy} + p &= \mu \varepsilon_{yy} + \lambda (\varepsilon_{xx} + \varepsilon_{zz}) = \lambda (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) + 2\eta \varepsilon_{yy}, \\ \sigma_{zz} + p &= \mu \varepsilon_{zz} + \lambda (\varepsilon_{xx} + \varepsilon_{yy}) = \lambda (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) + 2\eta \varepsilon_{zz}, \end{aligned} \quad (8.107)$$

¹³The *divergence of a tensor* is the vector obtained by performing the contracted product of the symbolic vector ∇ by the tensor in question. The practical layout of the operation $\nabla \cdot \bar{\bar{t}}$ can be achieved by multiplying the matrices as follows:

$$\begin{vmatrix} \sigma_{xx} & \sigma_{yx} & \sigma_{zx} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{zy} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{vmatrix} \begin{vmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{vmatrix} = \begin{vmatrix} \frac{\partial \sigma_{xx}}{\partial x} + \frac{\partial \sigma_{yx}}{\partial y} + \frac{\partial \sigma_{zx}}{\partial z} \\ \frac{\partial \sigma_{xy}}{\partial x} + \frac{\partial \sigma_{yy}}{\partial y} + \frac{\partial \sigma_{zy}}{\partial z} \\ \frac{\partial \sigma_{xz}}{\partial x} + \frac{\partial \sigma_{yz}}{\partial y} + \frac{\partial \sigma_{zz}}{\partial z} \end{vmatrix}.$$

The splitting of equation (8.106) owing to equation (8.101) gives the term $\nabla p = \mathbf{grad} p$ which corresponds to the pressure force per unit of volume, and the term $\nabla \cdot \bar{\bar{t}}_\eta = \mathbf{div} \bar{\bar{t}}_\eta$ which represents the force per unit of volume resulting in the viscosity of the medium.

$$\begin{aligned}
\sigma_{xy} = \sigma_{yx} &= 2\eta\varepsilon_{xy}, \\
\sigma_{yz} = \sigma_{zy} &= 2\eta\varepsilon_{yz}, \\
\sigma_{zx} = \sigma_{xz} &= 2\eta\varepsilon_{zx},
\end{aligned} \tag{8.108}$$

where λ and $\eta(=\frac{\mu-\lambda}{2})$ are two parameters characterizing the viscous incompressible fluids. They are generally supposed to be constant and they have a great similarity with the Lamé coefficients defined in elasticity, though they do not have the same dimensions. By replacing the new components of the strain rate tensor by the old ones (Eq. 8.97), the six previous relations will be written¹⁴:

$$\begin{aligned}
\sigma_{xx} + p &= \lambda\theta + 2\eta\frac{\partial v_x}{\partial x}, \\
\sigma_{yy} + p &= \lambda\theta + 2\eta\frac{\partial v_y}{\partial y}, \\
\sigma_{zz} + p &= \lambda\theta + 2\eta\frac{\partial v_z}{\partial z},
\end{aligned} \tag{8.109}$$

$$\begin{aligned}
\sigma_{xy} = \sigma_{yx} &= \eta\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right), \\
\sigma_{yz} = \sigma_{zy} &= \eta\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right), \\
\sigma_{zx} = \sigma_{xz} &= \eta\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right).
\end{aligned} \tag{8.110}$$

Consequently, the viscous stress tensor (Eq. 8.100) can be expressed in terms of the coefficients λ and η , with the above relations, namely:

$$\overset{=}{t}_\eta = \begin{vmatrix} \lambda\theta + 2\eta\frac{\partial v_x}{\partial x} & \eta\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & \eta\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) \\ \eta\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & \lambda\theta + 2\eta\frac{\partial v_y}{\partial y} & \eta\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) \\ \eta\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) & \eta\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) & \lambda\theta + 2\eta\frac{\partial v_z}{\partial z} \end{vmatrix}. \tag{8.111}$$

¹⁴The cubic expansion rate can also be used as:

$$\theta = \nabla \cdot \mathbf{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz},$$

which is the trace of the tensor $\overset{=}{b}_s$ (Eq. 8.97).

However, it is convenient to split the viscous stress tensor $\overline{\overline{t}}_\eta$ into the form:

$$\begin{aligned} \overline{\overline{t}}_\eta = & 3\lambda \begin{vmatrix} \frac{\theta}{3} & 0 & 0 \\ 0 & \frac{\theta}{3} & 0 \\ 0 & 0 & \frac{\theta}{3} \end{vmatrix} \\ & + 2\eta \begin{vmatrix} \frac{\partial v_x}{\partial x} & \frac{1}{2}\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & \frac{1}{2}\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) \\ \frac{1}{2}\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & \frac{\partial v_y}{\partial y} & \frac{1}{2}\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) \\ \frac{1}{2}\left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) & \frac{1}{2}\left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) & \frac{\partial v_z}{\partial z} \end{vmatrix}. \end{aligned} \quad (8.112)$$

Hence, it appears that the viscous stress tensor $\overline{\overline{t}}_\eta$ is a linear combination of the spherical tensor $\overline{\overline{d}}_s$ (Eq. 8.95) and the strain rate tensor $\overline{\overline{b}}_s$ (Eq. 8.97) written as:

$$\overline{\overline{t}}_\eta = 3\lambda \overline{\overline{d}}_s + 2\eta \overline{\overline{b}}_s. \quad (8.113)$$

Furthermore, by clarifying the tensor $\overline{\overline{b}}_s$ with equation (8.94), the foregoing relation may still be transformed into:

$$\overline{\overline{t}}_\eta = 3\left(\lambda + \frac{2}{3}\eta\right)\overline{\overline{d}}_s + 2\eta\overline{\overline{d}}_{dev}. \quad (8.114)$$

Finally, the expression of the viscous stress tensor $\overline{\overline{t}}_\eta$ depends (i) on the cubic expansion rate θ through the tensor $\overline{\overline{d}}_s$, and (ii) on the rate of strain without volume change through the tensor $\overline{\overline{d}}_{dev}$. Note also that the coefficient η , called the *shear viscosity*, is the dynamic viscosity coefficient whose values are known for most liquids, and $(\lambda + \frac{2}{3}\eta) = \eta_v$ is the *bulk viscosity* (always lower than the shear viscosity since $\lambda < \frac{\eta}{3}$), whose data are approximative. The viscosity is defined as the ratio between the shearing stress ($\text{N}\cdot\text{m}^{-2}$) and the strain rate (s^{-1}); it follows that its unity is expressed in $\text{N}\cdot\text{m}^{-2}\cdot\text{s}$, unlike the Lamé coefficients whose dimensions are those of the shearing stress.

8.7 Conservation laws

Law of conservation of mass: Fick equation

As it does not depend on the properties of the medium, the law of conservation of mass has a general character. To find its expression, we consider the *local density of mass* $\rho_m(\mathbf{r}, t) = mn(\mathbf{r}, t)$ defined by the product of the local density of particles $n(\mathbf{r}, t)$ times the mass m of one particle. The mass M of a given volume V of fluid is:

$$M = \int_V \rho_m(\mathbf{r}, t) d\mathbf{r}. \quad (8.115)$$

The rate of change of this mass is given by the equation:

$$\frac{dM}{dt} = \int_V \frac{\partial \rho_m}{\partial t} d\mathbf{r}. \quad (8.116)$$

However, the rate of change of mass is also equal to the flux of the *rate of flow of mass* $\mathbf{v}\rho_m(\mathbf{r}, t)$ through the surface A surrounding the volume V , i.e.¹⁵:

$$\frac{dM}{dt} = - \oint_A \rho_m \mathbf{v} \cdot d\mathbf{A}. \quad (8.117)$$

In using the Ostrogradski formula¹⁶, the above relation transforms as:

$$\frac{dM}{dt} = - \oint_A \rho_m \mathbf{v} \cdot d\mathbf{A} = - \int_V \nabla \cdot (\rho_m \mathbf{v}) d\mathbf{r}. \quad (8.118)$$

¹⁵The proof is analogous to what has been given to find equation (1.102). It follows from the mass balance in the volume $d^2V = (\mathbf{v}dt) \cdot (\mathbf{n}dA)$, where $\mathbf{n}$ is the unit vector normal to the surface element dA directed outward. The mass dM of the volume dV is:

$$dM = - \oint_A \rho_m (\mathbf{v}dt) \cdot (\mathbf{n}dA),$$

and the rate of change of mass is:

$$\frac{dM}{dt} = - \oint_A \rho_m \mathbf{v} \cdot \mathbf{n}dA.$$

Note the difference between the *local density of mass* $\rho_m(\mathbf{r}, t) = mn(\mathbf{r}, t)$ and the *rate of flow of mass* $\mathbf{v}\rho_m(\mathbf{r}, t)$.

¹⁶According to Ostrogradski's formula, the flux of a vector across a closed surface A is equal to the integral of the divergence of this vector in the encapsulated volume V .

The *law of conservation of mass* is obtained by equating equations (8.116) and (8.118) for any arbitrary volume, i.e.:

$$\frac{\partial \rho_m}{\partial t} + \nabla \cdot (\rho_m \mathbf{v}) = 0. \quad (8.119)$$

After transformations, the law of conservation of mass can also be written in using the particle derivative of ρ_m as¹⁷:

$$\frac{D\rho_m}{Dt} + \rho_m \nabla \cdot \mathbf{v} = 0. \quad (8.120)$$

It is worth recalling that the *empirical Fick's law* is based on the assumption that the rate of flow of mass $\rho_m \mathbf{v}$ is proportional to the gradient of local density of mass ρ_m , that is to say:

$$\rho_m \mathbf{v} = -D \nabla \rho_m, \quad (8.121)$$

where the minus sign means that the gradient of density is opposite to the flow of particles, and the parameter D is the diffusion coefficient expressed in $\text{m}^2 \cdot \text{s}^{-1}$ (not to be confused with the symbol used to define the particle derivative). By using Fick's law (Eq. 8.121) in the law of conservation of mass (Eq. 8.119), we obtain the *diffusion equation*:

$$\frac{\partial \rho_m}{\partial t} = -\nabla \cdot (-D \nabla \rho_m) = D \nabla^2 \rho_m = D \operatorname{div}(\mathbf{grad} \rho_m). \quad (8.122)$$

Law of conservation of momentum: Navier–Stokes equation

When the volume element $d\mathbf{r}$ in the continuum is moving through space with the velocity $\mathbf{v}$, its momentum is $d\mathbf{p} = \mathbf{v} \rho_m(\mathbf{r}, t) d\mathbf{r}$, where

¹⁷The quantity $\nabla \cdot (\rho_m \mathbf{v})$ is developed under analytical form as:

$$\begin{aligned} \nabla \cdot (\rho_m \mathbf{v}) &= \frac{\partial (\rho_m v_x)}{\partial x} + \frac{\partial (\rho_m v_y)}{\partial y} + \frac{\partial (\rho_m v_z)}{\partial z} \\ &= v_x \frac{\partial \rho_m}{\partial x} + v_y \frac{\partial \rho_m}{\partial y} + v_z \frac{\partial \rho_m}{\partial z} + \rho_m \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \\ &= (\mathbf{v} \cdot \nabla) \rho_m + \rho_m \nabla \cdot \mathbf{v}, \end{aligned}$$

which makes it possible to write equation (8.120) according to the particle derivative operator $\frac{D}{Dt} = \frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla)$ applying to any scalar or vector function (see Eq. 8.91).

$\rho_m(\mathbf{r}, t)$ is the local density of mass. Regarding the arbitrary volume V , the momentum is:

$$\mathbf{p} = \int_V \mathbf{v} \rho_m(\mathbf{r}, t) d\mathbf{r}, \quad (8.123)$$

and its rate of change is:

$$\frac{d\mathbf{p}}{dt} = \int_V \frac{\partial(\mathbf{v} \rho_m)}{\partial t} d\mathbf{r}. \quad (8.124)$$

Contrary to what happens to the mass (Eq. 8.117), the variation of the momentum comes, not only from the flux of the *rate of flow of momentum* $\mathbf{v} \rho_m(\mathbf{r}, t)$ across the surface A bounding the volume V , but also from the action of forces: the internal force $\mathbf{f}$ given by equation (8.106) and possibly an external force $\mathbf{F}$ applied to the element volume $d\mathbf{r}$.

Firstly, the rate of change of momentum produced from the flux of the rate of momentum flow is calculated in the same manner as the rate of change of mass¹⁸:

$$\frac{d\mathbf{p}}{dt} = - \oint_A \rho_m \mathbf{v} \mathbf{v} \cdot d\mathbf{A}. \quad (8.125)$$

Making use of the Ostrogradski formula, this relation is transformed into:

$$- \oint_A \rho_m \mathbf{v} \mathbf{v} \cdot d\mathbf{A} = - \int_V \nabla \cdot (\rho_m \mathbf{v} \mathbf{v}) d\mathbf{r}. \quad (8.126)$$

¹⁸The evidence is identical to what is provided by equation (8.117):

$$\begin{aligned} d\mathbf{p} &= - \oint_A \mathbf{v} \rho_m (\mathbf{v} dt) \cdot (\mathbf{n} dA), \\ \frac{d\mathbf{p}}{dt} &= - \oint_A \rho_m \mathbf{v} \mathbf{v} \cdot \mathbf{n} dA, \end{aligned}$$

where $\mathbf{n}$ is the unit vector normal to the surface element dA directed outward. Note that $\mathbf{v} \mathbf{v}$ is not the scalar square of the vector $\mathbf{v}$, but a dyadic tensor written in the following matrix form:

$$\mathbf{v} \mathbf{v} = \begin{vmatrix} v_x v_x & v_x v_y & v_x v_z \\ v_y v_x & v_y v_y & v_y v_z \\ v_z v_x & v_z v_y & v_z v_z \end{vmatrix}.$$

While the rate of mass flow $\rho_m \mathbf{v}$ is a tensor of rank 1 (ordinary vector), the rate of momentum flow $\rho_m \mathbf{v} \mathbf{v}$ should obviously be a tensor of rank 2 making a vector from its flux through any surface.

Secondly, if $\mathbf{f}$ is the internal force per unit volume and $\mathbf{F}$ the external force per unit mass, the overall rate of change of momentum in the volume V is composed of three contributions which are:

$$\frac{d\mathbf{p}}{dt} = - \int_V \nabla \cdot (\rho_m \mathbf{v}\mathbf{v}) d\mathbf{r} + \int_V \mathbf{f} d\mathbf{r} + \int_V \mathbf{F} \rho_m d\mathbf{r}. \quad (8.127)$$

The *law of conservation of momentum*, which is meant to be for any arbitrary volume V , is obtained by identifying equation (8.124) with equation (8.127). After expressing the internal force $\mathbf{f}$ per unit volume as a function of the stress tensor $\bar{t}$ (Eq. 8.106), the law of conservation of momentum is obtained under the local form:

$$\frac{\partial (\mathbf{v} \rho_m)}{\partial t} = - \nabla \cdot (\rho_m \mathbf{v}\mathbf{v}) + \nabla \cdot \bar{t} + \mathbf{F} \rho_m. \quad (8.128)$$

When the fluid is motionless ($\mathbf{v} \rho_m = \mathbf{0}$ and $\nabla \cdot \bar{t} = -\nabla p$), we find the standard hydrostatic equation: $\mathbf{F} \rho_m = \mathbf{grad} p$, where $\mathbf{F}$ is the force applied per unit mass, and ρ_m the local density of mass.

Other expressions of the law of conservation of momentum can be derived by transforming the various terms of equation (8.128). Let us start by developing the first term $\nabla \cdot (\rho_m \mathbf{v}\mathbf{v})$ on the right hand side of equation (8.128). This is achieved by changing the divergence of the tensor $\rho_m \mathbf{v}\mathbf{v}$ from the obvious form:

$$\nabla \cdot (\rho_m \mathbf{v}\mathbf{v}) = \mathbf{v}\mathbf{v} \cdot \nabla \rho_m + \rho_m \nabla \cdot (\mathbf{v}\mathbf{v}), \quad (8.129)$$

into the more suitable form¹⁹:

$$\nabla \cdot (\rho_m \mathbf{v}\mathbf{v}) = \mathbf{v} \nabla \cdot (\rho_m \mathbf{v}) + \rho_m (\mathbf{v} \cdot \nabla) \mathbf{v}. \quad (8.130)$$

¹⁹To obtain this expression, we first decompose the matrix form of $\nabla \cdot (\mathbf{v}\mathbf{v})$ as follows (see note 13 about the divergence of a tensor):

$$\begin{aligned} \nabla \cdot (\mathbf{v}\mathbf{v}) &= \begin{vmatrix} \frac{\partial v_x v_x}{\partial x} + \frac{\partial v_x v_y}{\partial y} + \frac{\partial v_x v_z}{\partial z} \\ \frac{\partial v_y v_x}{\partial x} + \frac{\partial v_y v_y}{\partial y} + \frac{\partial v_y v_z}{\partial z} \\ \frac{\partial v_z v_x}{\partial x} + \frac{\partial v_z v_y}{\partial y} + \frac{\partial v_z v_z}{\partial z} \end{vmatrix} \\ &= \begin{vmatrix} v_x \frac{\partial v_x}{\partial x} + v_x \frac{\partial v_y}{\partial y} + v_x \frac{\partial v_z}{\partial z} \\ v_y \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_y \frac{\partial v_z}{\partial z} \\ v_z \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_z}{\partial z} \end{vmatrix} + \begin{vmatrix} v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \\ v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \\ v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \end{vmatrix}, \end{aligned}$$

where the two contributions on the right hand side represent the quantities $\mathbf{v} (\nabla \cdot \mathbf{v})$ and $(\mathbf{v} \cdot \nabla) \mathbf{v}$, respectively, according to equation (8.90), so that:

$$\nabla \cdot (\mathbf{v}\mathbf{v}) = \mathbf{v} (\nabla \cdot \mathbf{v}) + (\mathbf{v} \cdot \nabla) \mathbf{v}.$$

However, in using this relation, equation (8.128) reads:

$$\rho_m \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \frac{\partial \rho_m}{\partial t} = -\mathbf{v} \nabla \cdot (\rho_m \mathbf{v}) - \rho_m (\mathbf{v} \cdot \nabla) \mathbf{v} + \nabla \cdot \bar{\bar{t}} + \mathbf{F} \rho_m. \quad (8.131)$$

Then, by transforming the second term on the left hand side of the above relation with equation (8.119), it gives:

$$\begin{aligned} \rho_m \frac{\partial \mathbf{v}}{\partial t} - \mathbf{v} \nabla \cdot (\rho_m \mathbf{v}) &= -\mathbf{v} \nabla \cdot (\rho_m \mathbf{v}) - \rho_m (\mathbf{v} \cdot \nabla) \mathbf{v} + \nabla \cdot \bar{\bar{t}} + \mathbf{F} \rho_m, \\ \text{or} \quad \rho_m \frac{\partial \mathbf{v}}{\partial t} &= -\rho_m (\mathbf{v} \cdot \nabla) \mathbf{v} + \nabla \cdot \bar{\bar{t}} + \mathbf{F} \rho_m. \end{aligned} \quad (8.132)$$

In fact, after the above simplifications have been performed, this equation can be expressed in terms of the particle derivative of the velocity (Eq. 8.91) and the viscous stress tensor (Eq. 8.106) as

$$\begin{aligned} \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} &= \mathbf{F} + \frac{1}{\rho_m} \nabla \cdot \bar{\bar{t}}, \\ \text{or} \quad \frac{D\mathbf{v}}{Dt} &= \mathbf{F} - \frac{1}{\rho_m} \nabla p + \frac{1}{\rho_m} \nabla \cdot \bar{\bar{t}}_\eta. \end{aligned} \quad (8.133)$$

This is the simplest form of the Navier–Stokes equation. Note in passing that equation (8.133) reduces to the *Euler equation* in the case of non viscous fluids ($\bar{\bar{t}}_\eta = 0$), namely:

$$\begin{aligned} \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} &= \mathbf{F} - \frac{1}{\rho_m} \nabla p, \\ \text{or} \quad \frac{D\mathbf{v}}{Dt} &= \mathbf{F} - \frac{1}{\rho_m} \nabla p. \end{aligned} \quad (8.134)$$

In the rest of this subsection, we would like to show other forms for the Navier–Stokes equations when applied to viscous fluids – when the viscous stress tensor $\bar{\bar{t}}_\eta$ is used. If the viscosity is supposed to be

Then we replace $\nabla \cdot (\mathbf{v} \mathbf{v})$ in equation (8.129) and perform the following developments:

$$\begin{aligned} \nabla \cdot (\rho_m \mathbf{v} \mathbf{v}) &= \mathbf{v} \mathbf{v} \cdot \nabla \rho_m + \rho_m \mathbf{v} (\nabla \cdot \mathbf{v}) + \rho_m (\mathbf{v} \cdot \nabla) \mathbf{v} \\ &= \mathbf{v} [\mathbf{v} \cdot \nabla \rho_m + \rho_m (\nabla \cdot \mathbf{v})] + \rho_m (\mathbf{v} \cdot \nabla) \mathbf{v} \\ &= \mathbf{v} \nabla \cdot (\rho_m \mathbf{v}) + \rho_m (\mathbf{v} \cdot \nabla) \mathbf{v}. \end{aligned}$$

constant, the gradient of the viscous stress tensor $\nabla \cdot \bar{\bar{t}}_\eta$ has to be written as²⁰:

$$\nabla \cdot \bar{\bar{t}}_\eta = \left[(\eta_v - \frac{2}{3}\eta) \nabla \theta + 2\eta \nabla \cdot \bar{\bar{b}}_s \right]. \quad (8.135)$$

In this case, equation (8.133) reduces to:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{F} - \frac{1}{\rho_m} \nabla p + \frac{1}{\rho_m} \left[(\eta_v - \frac{2}{3}\eta) \nabla \theta + 2\eta \nabla \cdot \bar{\bar{b}}_s \right]. \quad (8.136)$$

Equation (8.136) is a form of the *Navier–Stokes equation*, which can also be written alternatively. For example, a possible simplification is made by expressing the cubic expansion rate θ as a function of the velocity (Eq. 8.93), i.e. $\nabla \theta = \nabla(\nabla \cdot \mathbf{v})$, and using the equation²¹ $\nabla \cdot \bar{\bar{b}}_s = \frac{1}{2} \nabla^2 \mathbf{v} + \frac{1}{2} \nabla(\nabla \cdot \mathbf{v})$. With these identities, the viscous stress tensor (Eq. 8.135) becomes an explicit function of the viscosity coefficients η and η_v as well as the velocity $\mathbf{v}$. Indeed:

$$\begin{aligned} \nabla \cdot \bar{\bar{t}}_\eta &= (\eta_v - \frac{2}{3}\eta) \nabla(\nabla \cdot \mathbf{v}) + \eta \nabla^2 \mathbf{v} + \eta \nabla(\nabla \cdot \mathbf{v}), \\ &= (\eta_v + \frac{\eta}{3}) \nabla(\nabla \cdot \mathbf{v}) + \eta \nabla^2 \mathbf{v}. \end{aligned} \quad (8.137)$$

This allows us to rewrite the Navier–Stokes equation (Eq. 8.136) as follows:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{F} - \frac{1}{\rho_m} \nabla p + \frac{1}{\rho_m} (\eta_v + \frac{\eta}{3}) \nabla(\nabla \cdot \mathbf{v}) + \frac{1}{\rho_m} \eta \nabla^2 \mathbf{v}. \quad (8.138)$$

²⁰With the relation $\lambda + \frac{2}{3}\eta = \eta_v$ and equation (8.94), the calculation of $\nabla \cdot \bar{\bar{t}}_\eta$ is conducted from equation (8.114) as follows:

$$\begin{aligned} \nabla \cdot \bar{\bar{t}}_\eta &= \nabla \cdot (3\eta_v \bar{\bar{d}}_s + 2\eta \bar{\bar{d}}_{dev}) = 3\eta_v \nabla \cdot \bar{\bar{d}}_s + 2\eta \nabla \cdot (\bar{\bar{b}}_s - \bar{\bar{d}}_s) \\ &= (3\eta_v - 2\eta) \nabla \cdot \bar{\bar{d}}_s + 2\eta \nabla \cdot \bar{\bar{b}}_s = (\eta_v - \frac{2}{3}\eta) \nabla \theta + 2\eta \nabla \cdot \bar{\bar{b}}_s, \end{aligned}$$

where the last line of the calculation is obtained by using the identity $\nabla \cdot \bar{\bar{d}}_s = \frac{1}{3} \nabla \theta$ (Eq. 8.95).

²¹This relation is obtained by using the following decomposition of the strain rate tensor $\bar{\bar{b}}_s$:

$$\bar{\bar{b}}_s = \frac{1}{2} \begin{vmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_x}{\partial y} & \frac{\partial v_x}{\partial z} \\ \frac{\partial v_y}{\partial x} & \frac{\partial v_y}{\partial y} & \frac{\partial v_y}{\partial z} \\ \frac{\partial v_z}{\partial x} & \frac{\partial v_z}{\partial y} & \frac{\partial v_z}{\partial z} \end{vmatrix} + \frac{1}{2} \begin{vmatrix} \frac{\partial v_x}{\partial x} & \frac{\partial v_y}{\partial x} & \frac{\partial v_z}{\partial x} \\ \frac{\partial v_x}{\partial y} & \frac{\partial v_y}{\partial y} & \frac{\partial v_z}{\partial y} \\ \frac{\partial v_x}{\partial z} & \frac{\partial v_y}{\partial z} & \frac{\partial v_z}{\partial z} \end{vmatrix}.$$

Then, after the divergence of the tensor $\bar{\bar{b}}_s$ has been calculated with the rule set out in footnote 13 in this chapter, it is easy to verify the identity $\nabla \cdot \bar{\bar{b}}_s = \frac{1}{2} \nabla^2 \mathbf{v} + \frac{1}{2} \nabla(\nabla \cdot \mathbf{v})$.

However, with the formula of the vector triple product $\nabla \wedge (\nabla \wedge \mathbf{v}) = \nabla(\nabla \cdot \mathbf{v}) - \nabla^2 \mathbf{v}$, the Navier–Stokes equation is changed into the form:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = \mathbf{F} - \frac{1}{\rho_m} \nabla p + \frac{1}{\rho_m} \left(\eta_v + \frac{4\eta}{3} \right) \nabla(\nabla \cdot \mathbf{v}) - \frac{1}{\rho_m} \eta \nabla \wedge (\nabla \wedge \mathbf{v}). \quad (8.139)$$

Another possible expression can be found in using equation (8.92), i.e., $(\mathbf{v} \cdot \nabla) \mathbf{v} = \frac{1}{2} \nabla \mathbf{v} \mathbf{v}^2 + (\nabla \wedge \mathbf{v}) \wedge \mathbf{v}$, to transform the convective acceleration on the left hand side of equation (8.139). The Navier–Stokes equation becomes:

$$\begin{aligned} \frac{\partial \mathbf{v}}{\partial t} + \frac{1}{2} \nabla \mathbf{v}^2 + (\nabla \wedge \mathbf{v}) \wedge \mathbf{v} &= \mathbf{F} - \frac{1}{\rho_m} \nabla p + \frac{1}{\rho_m} \left(\eta_v + \frac{4\eta}{3} \right) \nabla(\nabla \cdot \mathbf{v}) \\ &\quad - \frac{1}{\rho_m} \eta \nabla \wedge (\nabla \wedge \mathbf{v}). \end{aligned} \quad (8.140)$$

It should be stressed that the Navier–Stokes equation, whatever its form, can be integrated only in particular cases. As an example, the Navier–Stokes equation can be linearized – when within slow flows – by neglecting the contributions of second order in the terms $v_x \frac{\partial v_y}{\partial x}$ contained in the expressions $\nabla \mathbf{v}^2$ and $(\nabla \wedge \mathbf{v}) \wedge \mathbf{v}$, as well as in the terms $\frac{\partial^2 v_y}{\partial y \partial x}$ contained in the vector triple product $\nabla \wedge (\nabla \wedge \mathbf{v})$. In this specific case, the *linearized Navier–Stokes equation* reduces to:

$$\frac{\partial \mathbf{v}}{\partial t} = \mathbf{F} - \frac{1}{\rho_m} \nabla p + \frac{1}{\rho_m} \left(\eta_v + \frac{4\eta}{3} \right) \nabla(\nabla \cdot \mathbf{v}). \quad (8.141)$$

Law of conservation of energy

The third law of conservation needed to study the behaviour of continuous media is the law of conservation of energy. We define it in the same way as the laws of conservation of mass and momentum. If the volume element $d\mathbf{r}$ in a continuum is moving at velocity $\mathbf{v}$, its energy is $dE = \left(e + \frac{1}{2} \mathbf{v}^2 \right) \rho_m(\mathbf{r}, t) d\mathbf{r}$, where $\rho_m(\mathbf{r}, t)$ is the local density of mass, $\frac{1}{2} \mathbf{v}^2$ the kinetic energy per unit mass and e the internal energy per unit mass – including the potential energy of interaction due to the applied forces, but excluding the kinetic energy. As far as an arbitrary volume V is concerned, the energy is:

$$E = \int_V \left(e + \frac{1}{2} \mathbf{v}^2 \right) \rho_m(\mathbf{r}, t) d\mathbf{r}, \quad (8.142)$$

and its rate of change is:

$$\frac{dE}{dt} = \int_V \frac{\partial}{\partial t} \left[\left(e + \frac{1}{2} \mathbf{v}^2 \right) \rho_m \right] d\mathbf{r}. \quad (8.143)$$

However, the rate of change of energy comes from three effects [122]:

(a) the flux of the *rate of flow of energy* $(e + \frac{1}{2} \mathbf{v}^2) \mathbf{v} \rho_m$, which is calculated as the rate of change of mass (Eq. 8.118) thanks to the Ostrogradski relation, and whose contribution is:

$$- \oint_A \rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \mathbf{v} \cdot d\mathbf{A} = - \int_V \nabla \cdot \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \mathbf{v} \right] d\mathbf{r}. \quad (8.144)$$

(b) the pressure forces exerted on the fluid in motion, and whose contribution depends on the stress tensor (Eq. 8.101). It is written:

$$\oint_A (\mathbf{v} \cdot \bar{\bar{t}}) \cdot d\mathbf{A} = \int_V \nabla \cdot (\mathbf{v} \cdot \bar{\bar{t}}) d\mathbf{r}. \quad (8.145)$$

For non-viscous fluids, the stress tensor $\bar{\bar{t}} = -p\delta + \bar{\bar{t}}_\eta$ reduces to the pressure $-p$, and the above expression is equal to the rate of change of work due to the pressure forces, i.e. $\oint_A \mathbf{v} \cdot (-p\delta) \cdot d\mathbf{A} \simeq - \int \frac{dx}{dt} p dA \simeq - \frac{d}{dt} \int p dV$.

(c) the loss of energy through heat conduction, whose contribution is:

$$- \oint_A \mathbf{Q} \cdot d\mathbf{A} = - \int_V \nabla \cdot \mathbf{Q} d\mathbf{r}, \quad (8.146)$$

where $\mathbf{Q}$ is the density of heat flow.

In summing up these three contributions, the expression of the overall rate of change of energy in the volume V becomes:

$$\frac{dE}{dt} = - \int_V \nabla \cdot \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \mathbf{v} \right] d\mathbf{r} + \int_V \nabla \cdot (\mathbf{v} \cdot \bar{\bar{t}}) d\mathbf{r} - \int_V \nabla \cdot \mathbf{Q} d\mathbf{r}, \quad (8.147)$$

and the general form of the *law of conservation of energy* is deduced by identifying equations (8.143) and (8.147):

$$\frac{\partial}{\partial t} \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \right] = - \nabla \cdot \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \mathbf{v} \right] + \nabla \cdot (\mathbf{v} \cdot \bar{\bar{t}}) - \nabla \cdot \mathbf{Q}. \quad (8.148)$$

This expression takes different forms depending on the choice made for the formulas derived from the vector analysis. For instance, there is a possibility of transforming the first and second terms on the right hand side of equation (8.148), respectively, as²²:

$$\nabla \cdot \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \mathbf{v} \right] = \rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \nabla \cdot \mathbf{v} + (\mathbf{v} \cdot \nabla) \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \right], \quad (8.149)$$

and

$$\nabla \cdot (\mathbf{v} \cdot \bar{\bar{t}}) = \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}) + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v}, \quad (8.150)$$

in order to write equation (8.148) as follows²³ :

$$\begin{aligned} \rho_m \frac{D}{Dt} \left(e + \frac{1}{2} \mathbf{v}^2 \right) + \left(e + \frac{1}{2} \mathbf{v}^2 \right) \frac{D\rho_m}{Dt} &= -\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \nabla \cdot \mathbf{v} \\ &+ \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}) + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q}. \end{aligned} \quad (8.151)$$

By referring to the law of conservation of mass (Eq. 8.120), we can replace $\frac{D\rho_m}{Dt}$ ($= -\rho_m \nabla \cdot \mathbf{v}$) in the above relation, hence:

$$\begin{aligned} \rho_m \frac{D}{Dt} \left(e + \frac{1}{2} \mathbf{v}^2 \right) - \rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \nabla \cdot \mathbf{v} &= -\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \nabla \cdot \mathbf{v} \\ &+ \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}) + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q}, \end{aligned} \quad (8.152)$$

$$\text{or} \quad \rho_m \frac{D}{Dt} \left(e + \frac{1}{2} \mathbf{v}^2 \right) = \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}) + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q}. \quad (8.153)$$

²²The first term corresponds to the relationship mentioned in footnote 13 in this chapter.

²³Indeed, the substitution of the two foregoing relations in equation (8.148) gives:

$$\begin{aligned} \frac{\partial}{\partial t} \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \right] &= -\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \nabla \cdot \mathbf{v} - (\mathbf{v} \cdot \nabla) \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \right] \\ &+ \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}) + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q}, \\ \frac{\partial}{\partial t} \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \right] + (\mathbf{v} \cdot \nabla) \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \right] &= -\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \nabla \cdot \mathbf{v} \\ &+ \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}) + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q}, \\ \frac{D}{Dt} \left[\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \right] &= -\rho_m \left(e + \frac{1}{2} \mathbf{v}^2 \right) \nabla \cdot \mathbf{v} + \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}) + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q}. \end{aligned}$$

By using the law of conservation of momentum (Eq. 8.133) to perform the following scalar product:

$$\rho_m \mathbf{v} \cdot \frac{D\mathbf{v}}{Dt} - \rho_m \mathbf{v} \cdot \mathbf{F} = \mathbf{v} \cdot (\nabla \cdot \bar{\bar{t}}), \quad (8.154)$$

equation (8.153) is transformed into:

$$\begin{aligned} \rho_m \frac{D}{Dt} \left(e + \frac{1}{2} \mathbf{v}^2 \right) &= \rho_m \mathbf{v} \cdot \frac{D\mathbf{v}}{Dt} - \rho_m \mathbf{v} \cdot \mathbf{F} + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q} \\ &= \frac{1}{2} \rho_m \frac{D\mathbf{v}^2}{Dt} - \rho_m \mathbf{v} \cdot \mathbf{F} + \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q}, \end{aligned} \quad (8.155)$$

$$\text{or} \quad \frac{De}{Dt} = -\mathbf{v} \cdot \mathbf{F} + \frac{1}{\rho_m} \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \frac{1}{\rho_m} \nabla \cdot \mathbf{Q}. \quad (8.156)$$

This expression is one of the simplest forms of the *law of conservation of energy*. It can be written again as a function of temperature by noting that, according to *Fourier's law*, the density of heat flow $\mathbf{Q}$ is proportional to the temperature gradient:

$$\mathbf{Q} = -\lambda \nabla T, \quad (8.157)$$

where λ is the thermal conductivity²⁴, T is the temperature, and the minus sign comes from the fact that the density of heat flow is opposite to the thermal gradient. In this case, the last term of equation (8.156) is:

$$-\frac{1}{\rho_m} \nabla \cdot \mathbf{Q} = \frac{\lambda}{\rho_m} \nabla^2 T. \quad (8.158)$$

In summary, the laws of conservation of mass (Eq. 8.120), momentum (Eq. 8.133) and energy (Eq. 8.156) yield five scalar differential equations:

$$\frac{D\rho_m}{Dt} = -\rho_m \nabla \cdot \mathbf{v}, \quad (8.159)$$

$$\frac{D\mathbf{v}}{Dt} = \mathbf{F} + \frac{1}{\rho_m} \nabla \cdot \bar{\bar{t}}, \quad (8.160)$$

$$\frac{De}{Dt} = -\mathbf{v} \cdot \mathbf{F} + \frac{1}{\rho_m} \bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \frac{1}{\rho_m} \nabla \cdot \mathbf{Q}, \quad (8.161)$$

²⁴The coefficient of thermal conductivity λ is expressed in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. Indeed, since e is an energy per unit of mass, $\frac{De}{Dt}$ is given in $\text{J} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$, $\nabla \cdot \mathbf{Q}$ in $\text{J} \cdot \text{s}^{-1} \cdot \text{m}^{-3}$ and $\mathbf{Q}$ in $\text{J} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$. So, according to Fourier's law, the coefficient of thermal conductivity λ is expressed in $\text{J} \cdot \text{s}^{-1} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, i.e. in Watt per meter and per Kelvin ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$).

describing the behaviour of continuous media when they are coupled with empirical equations defining the diffusion coefficient D , the viscosity coefficient η and the thermal conductivity λ . Naturally, in each specific case, initial conditions and boundary conditions should be clearly defined.

8.8 Generalized diffusion equation

After this brief presentation of elements necessary to provide a framework for the macroscopic description of continuum, we aim at determining the transport coefficients by a microscopic route. It is made by using the one-particle distribution function under the form of equation (8.70):

$$f_0 = n(\mathbf{r}, t) \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\frac{p^2}{2m k_B T} \right), \quad (8.162)$$

where $n(\mathbf{r}, t)$ is the local density of particles depending on time and position.

Smoluchowski equation

In this subsection, Boltzmann's equation (Eq. 8.63) is integrated over the momentum space²⁵ for a given volume element $d\mathbf{r}$:

$$\int \frac{\partial f}{\partial t} d\mathbf{p} = - \int \left(\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f \right) d\mathbf{p} - \int (\mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_{\mathbf{p}} f) d\mathbf{p} - \int \frac{f - f_0}{\tau} d\mathbf{p}. \quad (8.163)$$

(a) With the help of equation (8.2), and after permutation of the operators for differentiation and integration, the left-hand side of the above relation reads:

$$\int \frac{\partial f}{\partial t} d\mathbf{p} = \frac{\partial}{\partial t} \int f d\mathbf{p} = \frac{\partial n}{\partial t}, \quad (8.164)$$

where n is the number of particles in the volume element $d\mathbf{r}$.

²⁵In the following, we write the element of momentum space indifferently as:

$$d\mathbf{p} = d^3p = dp_x dp_y dp_z.$$

(b) If we suppose that the relaxation time τ does not depend on velocity, the collision integral is zero. Indeed:

$$\int \frac{f - f_0}{\tau} d\mathbf{p} = \frac{1}{\tau} \left[\int f d\mathbf{p} - \int f_0 d\mathbf{p} \right] = 0, \quad (8.165)$$

as the two integrals in brackets represent the local density of particles which is invariable in the volume element $d\mathbf{r}$ concerned. It should be noted that, more generally, the integral $\int (\frac{\partial f}{\partial t})_{\text{col}} d\mathbf{p}$ is always equal to zero [122].

(c) Assuming that the external force does not depend on the velocity, the component on x -axis of the second integral on the right hand side of equation (8.163) is written in the explicit form:

$$\begin{aligned} F_{\text{ext}.x} \int \frac{\partial f}{\partial p_x} d\mathbf{p} &= F_{\text{ext}.x} \int_{-\infty}^{+\infty} \frac{\partial f}{\partial p_x} dp_x \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z \\ &= F_{\text{ext}.x} (f_{p_x=+\infty} - f_{p_x=-\infty}) \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z = 0, \end{aligned} \quad (8.166)$$

as the distribution function $f \sim f_0$ (Maxwell distribution) is equal to zero when the momentum is infinitely large. The calculation of the other components being carried out similarly, we obtain:

$$\int (\mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_{\mathbf{p}} f) d\mathbf{p} = 0. \quad (8.167)$$

(d) As regards the first integral on the right-hand side of equation (8.163), it is transformed as follows, after permuting the operators for differentiation and integration:

$$\begin{aligned} \int \left(\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_{\mathbf{r}} f \right) d\mathbf{p} &= \int \frac{\mathbf{p}}{m} \cdot \left[\frac{\partial f}{\partial r_x} \mathbf{i} + \frac{\partial f}{\partial r_y} \mathbf{j} + \frac{\partial f}{\partial r_z} \mathbf{k} \right] d\mathbf{p} \\ &= \frac{\partial}{\partial r_x} \int \frac{\mathbf{p} \cdot \mathbf{i}}{m} f d\mathbf{p} + \frac{\partial}{\partial r_y} \int \frac{\mathbf{p} \cdot \mathbf{j}}{m} f d\mathbf{p} + \frac{\partial}{\partial r_z} \int \frac{\mathbf{p} \cdot \mathbf{k}}{m} f d\mathbf{p}. \end{aligned} \quad (8.168)$$

Since the integrals are related to the volume element $d\mathbf{r}$ in which the local particle density is constant, it is legitimate to use the approximate expression of the out-of-equilibrium distribution function given by equation (8.68). After the transformation of f in equation (8.168)

thanks to equation (8.68), the component of the integral along the $\mathbf{i}$ direction is:

$$\begin{aligned} \int \frac{\mathbf{p} \cdot \mathbf{i}}{m} f d\mathbf{p} &= \int \frac{\mathbf{p} \cdot \mathbf{i}}{m} \left[f_0 - \tau \frac{\mathbf{p}}{m} \cdot \mathbf{grad}_r f_0 - \tau \mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_p f_0 \right] d\mathbf{p} \\ &= \int \frac{p_x}{m} f_0 d\mathbf{p} - \int \frac{p_x}{m} \tau \left(\frac{\mathbf{p}}{m} \cdot \mathbf{grad}_r f_0 \right) d\mathbf{p} - \int \frac{p_x}{m} \tau (\mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_p f_0) d\mathbf{p}. \end{aligned} \quad (8.169)$$

(d1) Firstly, we start by evaluating the first integral on the right hand side of equation (8.169). As we are focused on the component p_x of the momentum, the integrand is an odd function of p_x and the integral is zero:

$$\int \frac{p_x}{m} f_0 d\mathbf{p} = 0. \quad (8.170)$$

(d2) Then, we calculate the second integral that can be written in the form:

$$\begin{aligned} \int \frac{p_x}{m} \tau \frac{\mathbf{p}}{m} \cdot \left[\frac{\partial f_0}{\partial r_x} \mathbf{i} + \frac{\partial f_0}{\partial r_y} \mathbf{j} + \frac{\partial f_0}{\partial r_z} \mathbf{k} \right] d\mathbf{p} &= \\ = \int \frac{p_x}{m} \tau \frac{p_x}{m} \frac{\partial f_0}{\partial r_x} d\mathbf{p} + \int \frac{p_x}{m} \tau \frac{p_y}{m} \frac{\partial f_0}{\partial r_y} d\mathbf{p} + \int \frac{p_x}{m} \tau \frac{p_z}{m} \frac{\partial f_0}{\partial r_z} d\mathbf{p}. \end{aligned} \quad (8.171)$$

The last two integrals of the above relation are zero because their integrands are odd functions of p_x while the first integral reads:

$$\int \frac{p_x}{m} \tau \frac{p_x}{m} \frac{\partial f_0}{\partial r_x} d\mathbf{p} = \frac{\partial n}{\partial r_x} \int \frac{p_x^2}{m^2} \tau \frac{\partial f_0}{\partial n} d\mathbf{p} = D_x \frac{\partial n}{\partial r_x}, \quad (8.172)$$

where the coefficient D_x is defined by:

$$D_x = \int \frac{p_x^2}{m^2} \tau \frac{\partial f_0}{\partial n} d\mathbf{p} = \frac{\partial}{\partial n} \int \frac{p_x^2}{m^2} \tau f_0 d\mathbf{p}. \quad (8.173)$$

(d3) Finally, we determine the last integral of equation (8.169):

$$\begin{aligned} \int \frac{p_x}{m} \tau (\mathbf{F}_{\text{ext}} \cdot \mathbf{grad}_p f_0) d\mathbf{p} &= \int \frac{p_x}{m} \tau \mathbf{F}_{\text{ext}} \cdot \left[\frac{\partial f_0}{\partial p_x} \mathbf{i} + \frac{\partial f_0}{\partial p_y} \mathbf{j} + \frac{\partial f_0}{\partial p_z} \mathbf{k} \right] d\mathbf{p} \\ &= \int \frac{p_x}{m} \tau F_{\text{ext}.x} \frac{\partial f_0}{\partial p_x} d\mathbf{p} + \int \frac{p_x}{m} \tau F_{\text{ext}.y} \frac{\partial f_0}{\partial p_y} d\mathbf{p} + \int \frac{p_x}{m} \tau F_{\text{ext}.z} \frac{\partial f_0}{\partial p_z} d\mathbf{p}. \end{aligned}$$

As their integrands are odd functions of p_x , the last two integrals are zero, unlike the first integral whose integrand is a more complicated function of p_x . However, since the external force does not depend on velocity, this integral can be written:

$$\int \frac{p_x}{m} \tau F_{\text{ext}.x} \frac{\partial f_0}{\partial p_x} d\mathbf{p} = F_{\text{ext}.x} \int \frac{p_x}{m} \tau \frac{\partial f_0}{\partial p_x} d\mathbf{p} = -\frac{1}{\mu_x} n F_{\text{ext}.x}, \quad (8.174)$$

where the coefficient μ_x is defined by:

$$\frac{1}{\mu_x} = -\frac{1}{n} \int \frac{p_x}{m} \tau \frac{\partial f_0}{\partial p_x} d\mathbf{p}. \quad (8.175)$$

Thus, with the use of equations (8.172) and (8.174), the equation (8.169) appears in the form:

$$\int \frac{\mathbf{p} \cdot \mathbf{i}}{m} f d\mathbf{p} = -D_x \frac{\partial n}{\partial r_x} + \frac{1}{\mu_x} n F_{\text{ext}.x}. \quad (8.176)$$

It is clear that the components of the other two integrals of equation (8.168) in the directions of projection of $\mathbf{j}$ and $\mathbf{k}$ have expressions similar to equation (8.176) which are obtained by circular permutation, namely:

$$\int \frac{\mathbf{p} \cdot \mathbf{j}}{m} f d\mathbf{p} = -D_y \frac{\partial n}{\partial r_y} + \frac{1}{\mu_y} n F_{\text{ext}.y}, \quad (8.177)$$

$$\int \frac{\mathbf{p} \cdot \mathbf{k}}{m} f d\mathbf{p} = -D_z \frac{\partial n}{\partial r_z} + \frac{1}{\mu_z} n F_{\text{ext}.z}. \quad (8.178)$$

Looking carefully at equations (8.173) and (8.175), we note that the two coefficients D_x and $\frac{1}{\mu_x}$ are proportional to the integral $\int p_x^2 e^{-\frac{\beta p_x^2}{2m}} dp_x$ – use equation (8.162) with the help of equation (3.6). As p_x is a dummy variable, it follows that the coefficients D_x , D_y and D_z are equal one to another and this also apply to coefficients μ_x , μ_y and μ_z . The parameter D is known as the *diffusion coefficient*:

$$D = D_x = D_y = D_z = \frac{\partial}{\partial n} \int \frac{p_x^2}{m^2} \tau f_0 d\mathbf{p}, \quad (8.179)$$

and the parameter μ as the *friction coefficient* (not to be confused with the chemical potential):

$$\frac{1}{\mu} = \frac{1}{\mu_x} = \frac{1}{\mu_y} = \frac{1}{\mu_z} = -\frac{1}{n} \int \frac{p_x}{m} \tau \frac{\partial f_0}{\partial p_x} d\mathbf{p}. \quad (8.180)$$

Finally, the determination of equation (8.163) is achieved by the substitution of equations (8.176), (8.177) and (8.178) into equation (8.168) and the identification of equations (8.164) and (8.168). After these simplifications, equation (8.163) is expressed as a function of the coefficients D and μ in the following explicit form:

$$\begin{aligned} \frac{\partial n}{\partial t} = & -\frac{\partial}{\partial r_x} \left[-D \frac{\partial n}{\partial r_x} + \frac{1}{\mu} n F_{\text{ext}.x} \right] - \frac{\partial}{\partial r_y} \left[-D \frac{\partial n}{\partial r_y} + \frac{1}{\mu} n F_{\text{ext}.y} \right] \\ & - \frac{\partial}{\partial r_z} \left[-D \frac{\partial n}{\partial r_z} + \frac{1}{\mu} n F_{\text{ext}.z} \right]. \end{aligned} \quad (8.181)$$

Under operational form, it is still being written as²⁶:

$$\begin{aligned} \frac{\partial n(\mathbf{r}, t)}{\partial t} &= D \nabla^2 n(\mathbf{r}, t) - \frac{1}{\mu} \nabla \cdot [n(\mathbf{r}, t) \mathbf{F}_{\text{ext}}] \\ &= \text{div} \left\{ D \mathbf{grad} n(\mathbf{r}, t) - \left[\frac{1}{\mu} n(\mathbf{r}, t) \mathbf{F}_{\text{ext}} \right] \right\}. \end{aligned} \quad (8.182)$$

This relation is the *generalized diffusion equation* in the presence of external forces. If the external forces are absent, equation (8.182) reduces to the Fick diffusion equation (Eq. 8.122). It should be stressed that the generalized diffusion equation has been demonstrated by Smoluchowski [123] by following a completely different route which is based on an analysis of stochastic processes occurring in Brownian motion. The equation can be written either with the local density of particles $n(\mathbf{r}, t)$ or with the one-particle distribution function $f(\mathbf{r}, \mathbf{p}, t)$. Note also that, in the one-dimensional case, the Smoluchowski equation reduces to the *Fokker-Planck equation*:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D \frac{\partial^2}{\partial x^2} n(\mathbf{r}, t) + \frac{1}{\mu} \frac{\partial}{\partial x} \left[n(\mathbf{r}, t) \frac{\partial u(x)}{\partial x} \right], \quad (8.183)$$

where $u(x)$ is the potential providing the external force $\mathbf{F}_{\text{ext}} (= -\mathbf{grad} u)$.

²⁶According to the definitions given in footnote 12 in this chapter, equation (8.181) is transformed as:

$$\begin{aligned} \frac{\partial n}{\partial t} &= D \left(\frac{\partial^2 n}{\partial r_x^2} + \frac{\partial^2 n}{\partial r_y^2} + \frac{\partial^2 n}{\partial r_z^2} \right) - \frac{1}{\mu} \left[\frac{\partial}{\partial r_x} (n F_{\text{ext}.x}) + \frac{\partial}{\partial r_y} (n F_{\text{ext}.y}) + \frac{\partial}{\partial r_z} (n F_{\text{ext}.z}) \right] \\ &= D \nabla^2 n - \frac{1}{\mu} \nabla \cdot (n \mathbf{F}_{\text{ext}}). \end{aligned}$$

Sutherland–Einstein equation

To close this subsection, we deduce expressions for the diffusion coefficient (Eq. 8.179) and the friction coefficient (Eq. 8.180) by using the one-particle distribution function f_0 defined by equation (8.162).

The diffusion coefficient (Eq. 8.179) is expressed as:

$$\begin{aligned} D &= D_x = \int \frac{p_x^2}{m^2} \tau \frac{\partial}{\partial n} \left[n(\mathbf{r}, t) \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\frac{p^2}{2m k_B T} \right) \right] d\mathbf{p} \\ &= \int \frac{p_x^2}{m^2} \tau \left[\left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\frac{p^2}{2m k_B T} \right) \right] d\mathbf{p} = \left\langle \frac{p_x^2}{m^2} \tau \right\rangle. \end{aligned} \quad (8.184)$$

Indeed, D is the ensemble average of the quantity $\frac{p_x^2}{m^2} \tau$ calculated with the probability density function of Maxwell's distribution (Eq. 4.95). Under the conditions of calculation (where τ is small), the diffusion coefficient is a function of the component of velocity $v_x (= \frac{p_x}{m})$ and the relaxation time τ . However as:

$$\langle v^2 \tau \rangle = \langle (v_x^2 + v_y^2 + v_z^2) \tau \rangle = \langle v_x^2 \tau \rangle + \langle v_y^2 \tau \rangle + \langle v_z^2 \tau \rangle \quad (8.185)$$

$$\text{with} \quad \langle v_x^2 \tau \rangle = \langle v_y^2 \tau \rangle = \langle v_z^2 \tau \rangle, \quad (8.186)$$

the diffusion coefficient is:

$$D = \frac{1}{3} \langle v^2 \tau \rangle. \quad (8.187)$$

As far as the friction coefficient is concerned, it can be calculated by using the same method as for the diffusion coefficient²⁷:

$$\frac{1}{\mu} = \left\langle \frac{p_x^2}{m^2 k_B T} \tau \right\rangle = \left\langle \frac{v_x^2}{k_B T} \tau \right\rangle = \frac{1}{3 k_B T} \langle v^2 \tau \rangle. \quad (8.188)$$

²⁷With equation (8.175), the friction coefficient is transformed as :

$$\begin{aligned} \frac{1}{\mu_x} &= -\frac{1}{n(\mathbf{r}, t)} \int \frac{p_x}{m} \tau \frac{\partial}{\partial p_x} \left[n(\mathbf{r}, t) \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\frac{p^2}{2m k_B T} \right) \right] d\mathbf{p} \\ &= -\frac{1}{n(\mathbf{r}, t)} \int \frac{p_x}{m} \tau n(\mathbf{r}, t) \left(\frac{1}{2\pi m k_B T} \right)^{3/2} \frac{\partial}{\partial p_x} \left[\exp \left(-\frac{p^2}{2m k_B T} \right) \right] d\mathbf{p} \\ &= \int \frac{p_x^2}{m^2 k_B T} \tau \left[\left(\frac{1}{2\pi m k_B T} \right)^{3/2} \exp \left(-\frac{p^2}{2m k_B T} \right) \right] d\mathbf{p} = \left\langle \frac{p_x^2}{m^2 k_B T} \tau \right\rangle. \end{aligned}$$

However, by comparing equations (8.187) and (8.188) we deduce:

$$D = \frac{k_B T}{\mu}. \quad (8.189)$$

This expression was established independently by Einstein [124] and Sutherland [125] by applying methods that were different than those here. It is a very important relation connecting the diffusion coefficient D and the friction coefficient μ . It is worth noting that the expressions of the two coefficients D and μ rely on the mean value $\langle v^2 \tau \rangle$.

8.9 Method of Chapman and Enskog

The determination of the one-particle distribution function $f(\mathbf{r}, \mathbf{p}, t)$, as the solution to the Boltzmann equation, is a major problem with statistics of the non-equilibrium systems. For violent collisions and short relaxation times, there is an approximate expression of $f(\mathbf{r}, \mathbf{p}, t)$ with equation (8.76) which differs slightly from the local distribution function f_0 (Eq. 8.162). However, a more accurate solution to the Boltzmann equation (Eq. 8.57) has been found independently by Chapman and Enskog [126] with a perturbation method. The purpose of this method is to develop a solution by successive approximations, in which the spatiotemporal dependence of $f(\mathbf{r}, \mathbf{p}, t)$ is introduced implicitly via the hydrodynamic variables (density, velocity and temperature) associated with the laws of conservation of mass, momentum and energy, respectively. It is important to note that the theory of Chapman and Enskog, as outlined in the following²⁸, is rigorously suitable for dilute gases in which only the binary collisions are considered. For liquids, the formalism is not appropriate because of other types of interactions (including multiple collisions) which are superimposed on the binary collisions.

For the implementation of the theory of Chapman and Enskog, the Boltzmann equation (Eq. 8.57) is written with the velocity $\mathbf{v} (= \frac{\mathbf{p}}{m})$

²⁸Given the complexity of the calculations, we will present only an outline of the method. The reader interested in the details of the calculations will refer to reference books, including the book by S. Chapman and T. G. Cowling [126].

and the ordering parameter ξ as:

$$\begin{aligned} \frac{\partial f}{\partial t} + \mathbf{v} \cdot \mathbf{grad}_{\mathbf{r}} f + \frac{\mathbf{F}_{\text{ext}}}{m} \cdot \mathbf{grad}_{\mathbf{v}} f = \\ = \frac{2\pi m}{\xi} \iint |\mathbf{v}_2 - \mathbf{v}_1| (f'_1 f'_2 - f_1 f_2) b \, d\mathbf{v}_2 \, db. \end{aligned} \quad (8.190)$$

The solution for this equation is sought under the form of the perturbation series as:

$$f = f^{[0]} + \xi f^{[1]} + \xi^2 f^{[2]} + \dots, \quad (8.191)$$

where the superscripts in square brackets correspond to the degree of approximation of the distribution function. Then, this solution is substituted into the modified Boltzmann equation (Eq. 8.190) via the expansion:

$$\begin{aligned} f'_1 f'_2 - f_1 f_2 = & \left(f'^{[0]}_1 f'^{[0]}_2 - f^{[0]}_1 f^{[0]}_2 \right) \\ & + \xi \left[\left(f'^{[1]}_1 f'^{[0]}_2 + f'^{[0]}_1 f'^{[1]}_2 \right) - \left(f^{[1]}_1 f^{[0]}_2 + f^{[0]}_1 f^{[1]}_2 \right) \right] \\ & + \xi^2 [\dots] + \dots \end{aligned} \quad (8.192)$$

When the terms having the same degree of ξ are identified in equation (8.190), the following equations are obtained:

$$\begin{aligned} 0 = & \frac{2\pi m}{\xi} \iint |\mathbf{v}_2 - \mathbf{v}_1| (f'^{[0]}_1 f'^{[0]}_2 - f^{[0]}_1 f^{[0]}_2) b \, d\mathbf{v}_2 \, db, \\ \frac{\partial f^{[0]}}{\partial t} + \mathbf{v} \cdot \mathbf{grad}_{\mathbf{r}} f^{[0]} + \frac{\mathbf{F}_{\text{ext}}}{m} \cdot \mathbf{grad}_{\mathbf{v}} f^{[0]} = \\ = & 2\pi m \iint |\mathbf{v}_2 - \mathbf{v}_1| \xi \left[(f'^{[1]}_1 f'^{[0]}_2 + f'^{[0]}_1 f'^{[1]}_2) \right. \\ & \left. - (f^{[1]}_1 f^{[0]}_2 + f^{[0]}_1 f^{[1]}_2) \right] b \, d\mathbf{v}_2 \, db, \end{aligned} \quad (8.193)$$

$$\begin{aligned} \xi \left[\frac{\partial f^{[1]}}{\partial t} + \mathbf{v} \cdot \mathbf{grad}_{\mathbf{r}} f^{[1]} + \frac{\mathbf{F}_{\text{ext}}}{m} \cdot \mathbf{grad}_{\mathbf{v}} f^{[1]} \right] = \\ = 2\pi m \xi \iint |\mathbf{v}_2 - \mathbf{v}_1| \xi^2 [\dots] b \, d\mathbf{v}_2 \, db, \end{aligned} \quad (8.194)$$

... = ...

Furthermore, by using the one-particle distribution function of velocity $f(\mathbf{r}, \mathbf{v}, t) = m^3 f(\mathbf{r}, \mathbf{p}, t)$ (see Eqs. 4.95 and 4.96), it can be seen

that the hydrodynamic variables (density, velocity, temperature) are nothing else than the first moments of the velocity:

$$n(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}, \quad (8.195)$$

$$\mathbf{v}_0(\mathbf{r}, t) = \frac{1}{n(\mathbf{r}, t)} \int \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}, \quad (8.196)$$

$$3 \frac{k_B T(\mathbf{r}, t)}{m} = \frac{1}{n(\mathbf{r}, t)} \int (\mathbf{v} - \mathbf{v}_0)^2 f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}. \quad (8.197)$$

Equation (8.195) reflects the normalization condition for the distribution function. According to equation (8.2), it provides the local density of particles $n(\mathbf{r}, t)$. Equation (8.196) represents the mathematical expectation of velocity, i.e. the velocity $\mathbf{v}_0(\mathbf{r}, t)$ of the centre of mass of the volume element $d\mathbf{r}$ located at $\mathbf{r}$. Equation (8.197) gives the variance of the velocity: it yields the temperature $T(\mathbf{r}, t)$ of the volume element because $\langle (\mathbf{v} - \mathbf{v}_0)^2 \rangle = \langle (v_x - v_{x0})^2 + (v_y - v_{y0})^2 + (v_z - v_{z0})^2 \rangle = 3 \frac{k_B T}{m}$. Then, in multiplying equation (8.190) successively by 1, by $m\mathbf{v}$ and by $\frac{1}{2}m(\mathbf{v} - \mathbf{v}_0)^2$, and integrating the equations over the velocity, we obtain the three following conservation laws:

$$\frac{Dn}{Dt} + n \nabla \cdot \mathbf{v} = 0, \quad (8.198)$$

$$\frac{D\mathbf{v}_0}{Dt} - \frac{1}{mn} \nabla \cdot \bar{\bar{t}} = 0, \quad (8.199)$$

$$\frac{DT}{Dt} - \frac{2}{3nk_B} \left(\bar{\bar{t}} \cdot \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{Q} \right) = 0, \quad (8.200)$$

which coincide with those obtained by a macroscopic route (Eqs. 8.159, 8.160 and 8.161), when the external force $\mathbf{F}_{\text{ext}}$ is omitted.

In its usual form, the method of Chapman and Enskog consists in solving the Boltzmann equation (Eq. 8.57) and the three conservation laws (Eqs. 8.198, 8.199 and 8.200) in a self-consistent manner for each degree of approximation of the distribution function. After complicated calculations, it results that

(i) the general solution of the distribution function to a zero-order approximation is:

$$f^{[0]}(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t) \left[\frac{1}{2\pi m k_B T(\mathbf{r}, t)} \right]^{3/2} \exp \left\{ -\frac{m [\mathbf{v} - \mathbf{v}_0(\mathbf{r}, t)]^2}{2k_B T(\mathbf{r}, t)} \right\}, \quad (8.201)$$

(ii) the stress tensor is $\overset{=}{t}^{[0]} = nk_{\text{B}}T\overset{=}{\delta}$ and

(iii) the density of heat flow $Q^{[0]}$ is zero.

Regarding the solution of the perturbation to order one $f^{[1]}(\mathbf{r}, \mathbf{v}, t)$, the authors recommended searching for it under the following form:

$$f^{[1]}(\mathbf{r}, \mathbf{v}, t) = \phi(\mathbf{r}, \mathbf{v}, t)f^{[0]}(\mathbf{r}, \mathbf{v}, t), \quad (8.202)$$

where the function to be determined $\phi(\mathbf{r}, \mathbf{v}, t)$ is calculated with the integro-differential equation corresponding to the second line of equation (8.195), i.e.:

$$\begin{aligned} \frac{\partial f^{[0]}}{\partial t} + \mathbf{v} \cdot \mathbf{grad}_{\mathbf{r}} f^{[0]} + \frac{\mathbf{F}_{\text{ext}}}{m} \cdot \mathbf{grad}_{\mathbf{v}} f^{[0]} = \\ = 2\pi m \iint |\mathbf{v}_2 - \mathbf{v}_1| \left[(f_1'^{[1]} f_2'^{[0]} + f_1'^{[0]} f_2'^{[1]}) \right. \\ \left. - (f_1^{[1]} f_2^{[0]} + f_1^{[0]} f_2^{[1]}) \right] b d\mathbf{v}_2 db. \end{aligned} \quad (8.203)$$

With equation (8.202), the right-hand side of equation (8.203) is written as a function of $\phi(\mathbf{r}, \mathbf{v}, t)$ as:

$$2\pi m \iint |\mathbf{v}_2 - \mathbf{v}_1| f_1^{[0]} f_2^{[0]} [\phi_1' + \phi_2' - \phi_1 - \phi_2] b d\mathbf{v}_2 db, \quad (8.204)$$

so that, if the external force $\mathbf{F}_{\text{ext}}$ is omitted, equation (8.203) reduces to:

$$\frac{\partial f^{[0]}}{\partial t} + (\mathbf{v} \cdot \nabla_{\mathbf{r}}) f^{[0]} = 2\pi m \iint |\mathbf{v}_2 - \mathbf{v}_1| f_1^{[0]} f_2^{[0]} [\phi_1' + \phi_2' - \phi_1 - \phi_2] b d\mathbf{v}_2 db. \quad (8.205)$$

It remains to express the time dependence of $f^{[0]}$ on the left-hand side of the above relation. For this purpose, it makes sense to use the relation:

$$\frac{\partial f^{[0]}}{\partial t} = \frac{\partial f^{[0]}}{\partial n} \frac{\partial n}{\partial t} + \nabla_{\mathbf{v}_0} f^{[0]} \frac{\partial \mathbf{v}_0}{\partial t} + \frac{\partial f^{[0]}}{\partial T} \frac{\partial T}{\partial t}, \quad (8.206)$$

together with equations (8.198), (8.199) and (8.200), in order to replace the time dependence of hydrodynamic variables n , $\mathbf{v}_0$ and T by

spatial dependence. After in-depth calculations not reproduced here, equation (8.203) becomes:

$$\begin{aligned} & \left[\left(\frac{m\mathbf{v}\mathbf{v}}{k_B T} - \frac{m\mathbf{v}^2}{3k_B T} \bar{\delta} \right) \nabla \cdot \mathbf{v}_0 + \frac{1}{T} \left(\frac{m\mathbf{v}^2}{2k_B T} - \frac{5}{2} \right) \mathbf{v} \cdot \nabla T \right] f^{[0]} = \\ & = 2\pi m \iint |\mathbf{v}_2 - \mathbf{v}_1| f_1^{[0]} f_2^{[0]} [\phi'_1 + \phi'_2 - \phi_1 - \phi_2] b d\mathbf{v}_2 db. \quad (8.207) \end{aligned}$$

As the function ϕ depends on the hydrodynamic variables n , $\mathbf{v}_0$, T as well as on their spatial derivatives, it is chosen under the following form:

$$\phi = \bar{B} \cdot \nabla \cdot \mathbf{v}_0 + \mathbf{A} \cdot \nabla T, \quad (8.208)$$

where the tensor $\bar{B}$ and the vector $\mathbf{A}$ are unknown functions determined by substituting this expression of ϕ into equation (8.207) and identifying separately the coefficients of the term $\nabla \cdot \mathbf{v}_0$ and those of the term ∇T . The tensor $\bar{B}$, the vector $\mathbf{A}$ and the atomic transport coefficients are obtained after expanded calculations [126, 127].

Without further comment, we give the expressions of the diffusion coefficient D , the viscosity coefficient η and the thermal conductivity λ thus obtained:

$$D = \frac{3}{8} \frac{k_B T}{mn} \frac{1}{\Omega^{(1,1)}}, \quad (8.209)$$

$$\eta = \frac{5}{8} k_B T \frac{1}{\Omega^{(2,2)}}, \quad (8.210)$$

$$\lambda = \frac{75}{32} \frac{k_B^2 T}{m} \frac{1}{\Omega^{(2,2)}}, \quad (8.211)$$

as a function of the collision integrals $\Omega^{(l,s)}$:

$$\Omega^{(l,s)} = \left(\frac{k_B T}{2\pi\mu} \right)^{1/2} \int_0^\infty \exp(-\gamma^2) \gamma^{2s+3} Q^{(l)}(\gamma) d\gamma, \quad (8.212)$$

$$\text{with} \quad Q^{(l)}(\gamma) = 2\pi \int_0^\infty (1 - \cos^l \chi) b db \quad (8.213)$$

$$\text{and} \quad \chi(b, \gamma) = \pi - 2b \int_{r_m}^\infty \frac{dr}{r^2 \left[1 - \frac{b^2}{r^2} - \frac{u(r)}{\gamma^2 k_B T} \right]^{1/2}}, \quad (8.214)$$

where $\mu = \frac{m}{2}$ is the reduced mass, and $Q^{(l)}(\gamma)$ and $\chi(b, \gamma)$ represent, respectively, the total scattering cross section and the deflection angle, both being defined in section (8.2). For the hard-sphere potential of diameter d and mass m , these quantities take very simple forms because they do not depend on the parameter $\gamma^2 = \frac{\mu v_\infty^2}{2k_B T}$. In particular, the values of the first two total scattering cross sections are equal to $Q^{(1)} = \pi d^2$ and $Q^{(2)} = \frac{2}{3}\pi d^2$, and the collision integrals are $\Omega^{(1,1)} = \left(\frac{k_B T}{2\pi\mu}\right)^{1/2} \pi d^2$ and $\Omega^{(2,2)} = \left(\frac{k_B T}{2\pi\mu}\right)^{1/2} 2\pi d^2$. In substituting these quantities into equations (8.209), (8.210) and (8.211), the atomic transport coefficients of the hard-sphere fluid are expressed in that manner:

$$D = \frac{3 k_B T}{8 m n} \frac{1}{\Omega^{(1,1)}} = \frac{3}{8} \left(\frac{\pi k_B T}{m}\right)^{1/2} \frac{1}{n \pi d^2}, \quad (8.215)$$

$$\eta = \frac{5}{8} k_B T \frac{1}{\Omega^{(2,2)}} = \frac{5}{16} \left(\frac{\pi k_B T}{m}\right)^{1/2} \frac{m}{\pi d^2}, \quad (8.216)$$

$$\lambda = \frac{75}{32} \frac{k_B^2 T}{m} \frac{1}{\Omega^{(2,2)}} = \frac{75}{64} \left(\frac{\pi k_B T}{m}\right)^{1/2} \frac{k_B}{\pi d^2}. \quad (8.217)$$

It should be noted that there are many kinds of expressions for these atomic transport coefficients depending on the potentials $u(r)$, due to the fact that calculating the deflection angle, the total scattering cross section and the collision integrals [126] are more difficult. Note also that the atomic transport coefficients have been calculated up to the second order of the distribution function, but it appears that these calculations are much more complicated and do not provide any significant improvement.

Lastly, it should be stressed that the Chapman–Enskog theory applies exclusively to diluted gases, in which only binary collisions exerting forces for a very short interval of time are taken into account. Concerning the liquids, additional forces become apparent when particles are submitted to constraints imposed collectively by the neighbouring particles, and the Chapman–Enskog theory is no longer valid. This new process will be investigated in the next chapter.

9 The Brownian motion

9.1 Specificities of the Brownian motion

The Brownian motion characterizes the incessant random motion of colloidal particles suspended within a liquid. Although the first observations of Brownian motion go back to the manufacturing of the microscope, quantitative data on the movement of pollen grains suspended in water were obtained much later by the botanists Brongniart [128] and Brown [129]. Similar experiments have been conducted with tobacco smoke particles in gases, and the same results were observed.

In short, the history of the Brownian motion covers three periods corresponding to the observation, the theoretical prediction and the confirmation.

During the *observation period*, which extends up to the end of the 19th century, crucial questions are asked and conflicting explanations are provided. At the very beginning, they noticed that the Brownian motion is not caused by a “vital force”, as it was thought initially, because the mineral particles behave the same way as organic particles. However, it was suspected that the Brownian motion could be due to various influences of external origin (convection currents, vibrations, electric fields, capillary actions, etc.). This long period of hesitation ended with a series of extremely accurate experiments specifically carried out by Gouy [130]. Through them, it became clear that the Brownian motion increases gradually as the size of suspended particles decreases and increases with the temperature of the liquid, i.e. when the viscosity is decreasing.

The *prediction period* of the Brownian motion began with the works of Einstein [124], Sutherland [125], Smoluchowski [131] and Langevin [132]. At that time, two schools of thought were at odds: one

defending the *continuous description* of systems with Newton's mechanics and Maxwell's electromagnetism and the other one complying with the *discrete description* of systems with the Boltzmann kinetic theory. It was in seeking to establish the existence of molecules and determine the value of Avogadro's number that Einstein managed, more or less intentionally, to tackle the problem of the Brownian motion. His approach was based on (1) the Stokes hydrodynamic theory according to which the liquid is a continuous medium without molecular agitation, and (2) the kinetic theory according to which the particles in suspension are subject to the laws of molecular agitation. Einstein deduced the famous eponymous relation (Eq. 8.189) connecting the diffusion coefficient with the coefficient of friction, as well as the expression of the mean square displacement of a particle as a function of time. The next year, he presented a more general theoretical approach taking real account of the Brownian motion [133]. The same year, Smoluchowski [131] developed the theory of the Brownian motion by a probabilistic approach, establishing the link between the random walk on network and the Brownian diffusion. In 1908, Langevin [132] gave a formulation of the Brownian motion taking into account the effects of inertia on the suspended particle, whereas such effects were neglected in the theories of Einstein and Smoluchowski. In this context, Langevin introduced, for the first time, a stochastic differential equation containing a random force with specific properties, and urged experimenters to perform more precise suspensions with better known sizes.

The *confirmation period* opened when Perrin [134] confirmed the theoretical predictions and the existence of molecules without any qualification. Subsequently, several analogous phenomena to the Brownian motion have been discovered, including the fluctuations in the frame of a galvanometer suspended by a torsion wire in a gas, the fluctuations within the electrical current in conductors, the fluctuations in biological systems... The rest of this chapter is devoted to the modern formulation of the Brownian motion proposed by Langevin.

The main feature of the Brownian motion is being *random*, hence the processes involved must be treated by statistical methods (section 2.4).

As a first hypothesis for the study of the Brownian motion, it is assumed that the displacement of a suspended particle over *two intervals of time successive and distinct* are statistically independent.

The consequence is the following. Let us first see how a suspended particle moves during a period which is long enough for a continuous change of direction. And, for the sake of argument, consider the projection of the displacement along the x -axis. We are thus faced with the problem of the symmetric random walk in a given direction.

If x_1 is the path traveled by the suspended particle during the time interval $(0, \tau)$ and x_2 the path covered during the time interval (τ, t) , with $t > \tau$, then $x = x_1 + x_2$ is the path traveled during the time $(0, t)$. Since the displacements in one direction and in the opposite direction are equally probable, and the displacements x_1 and x_2 are statistically independent, the mean value and covariance of the displacements x_1 and x_2 are equal to zero:

$$\langle x_1(\tau) \rangle = \langle x_2(t-\tau) \rangle = 0, \quad (9.1)$$

and

$$\langle x_1(\tau)x_2(t-\tau) \rangle = \langle x_1(\tau) \rangle \langle x_2(t-\tau) \rangle = 0. \quad (9.2)$$

By contrast, the variance of the total displacement x is:

$$\begin{aligned} \langle x^2(t) \rangle &= \langle [x_1(\tau) + x_2(t-\tau)]^2 \rangle \\ &= \langle x_1^2(\tau) \rangle + 2 \langle x_1(\tau) \rangle \langle x_2(t-\tau) \rangle + \langle x_2^2(t-\tau) \rangle. \end{aligned} \quad (9.3)$$

It is not equal to zero and, according to equation (9.2), it simplifies to:

$$\langle x^2(t) \rangle = \langle x_1^2(\tau) \rangle + \langle x_2^2(t-\tau) \rangle. \quad (9.4)$$

If one writes $\langle x^2(t) \rangle = \varphi(t)$, $\langle x_1^2(\tau) \rangle = \varphi(\tau)$ and $\langle x_2^2(t-\tau) \rangle = \varphi(t-\tau)$, the above relation takes the functional form:

$$\varphi(t) = \varphi(\tau) + \varphi(t-\tau), \quad (9.5)$$

which is verified when the variance of the displacement is a linear function of time¹:

$$\langle x^2(t) \rangle = \varphi(t) = \alpha t. \quad (9.6)$$

As a second hypothesis of the Brownian motion, it is assumed that the average kinetic energy per degree of freedom of a suspended

¹The derivative of equation (9.5) with respect to t is $\varphi'(t) = \varphi'(t-\tau)$ for a given value of τ constant and arbitrary. Consequently, φ' is a stationary function (see section 9.2) that does not depend on t . Hence, as to whether $\varphi'(t) = \alpha$ where α is a constant, we find equation (9.6) and see that the constant α has the dimensions of the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$).

particle is equal to $\frac{1}{2}m\langle v^2 \rangle = \frac{1}{2}k_B T$, as it would be for the molecules of liquids in thermal equilibrium.

Lastly, since a suspended particle is submitted to the actions caused by molecules surrounding it, it is assumed that the global action can be separated into two contributions: the first one is the *random force* $F(t)$, which is the *driving force* giving rise to the motion and the second one is the *systematic force* $X(t)$ that is opposed to the motion of the suspended particle. Both forces having the same origin, they have to be related in some specific way.

The systematic force $X(t)$ running counter to the movement is a *force of friction*. It is an ordinary function assumed to be proportional to the velocity of the particle. It is expected that the Brownian motion corresponds to a laminar flow in the fluid with a low Reynolds number:

$$\text{Re} = \frac{\rho r v}{\eta}, \quad (9.7)$$

where ρ and η are the density of mass and the dynamic viscosity of the fluid, respectively, and r and v the radius and the velocity of the suspended particle. By using the expression of the average kinetic energy of the suspended particle to evaluate the velocity $v \sim \left(\frac{k_B T}{m}\right)^{1/2}$, where $m \sim r^3 \rho_p$, the Reynolds number reads:

$$\text{Re} \simeq \frac{\rho}{\eta} \left(\frac{k_B T}{r \rho_p} \right)^{1/2}. \quad (9.8)$$

For suspended particles (with characteristics $\rho_p \sim 10^3 \text{ kg}\cdot\text{m}^{-3}$ and $r \sim 10^{-8} \text{ m}$) in water at room temperature ($\rho \sim 10^3 \text{ kg}\cdot\text{m}^{-3}$, $\eta \sim 10^{-3} \text{ N}\cdot\text{m}^{-2}\cdot\text{s}$, $k_B T \sim 4 \cdot 10^{-21} \text{ J}$), the Reynolds number is very low ($\text{Re} \sim 2 \cdot 10^{-2}$), indicating that inertial forces are much weaker than the viscous friction forces². Therefore, it can be assumed that the systematic force has the following form:

$$X(t) = -\mu \frac{dx}{dt}, \quad (9.9)$$

where μ is the coefficient of friction provided by the Stokes formula $\mu = 6\pi\eta r$.

As regards the random force $F(t)$, it is the fluctuating part of the action of the molecules of liquid on the suspended particle. As

²This is why Einstein neglected the inertial forces in his research studies.

it results from a large number of collisions, it is reasonable to admit that it has a Gaussian character which is justified by the central limit theorem whose mean value is zero:

$$\langle F(t) \rangle = 0. \quad (9.10)$$

In addition, given that the duration of a collision is extremely short compared to the observation time, it is also reasonable to admit that the driving force $F(t)$ is a random function over statistically independent intervals of time such as the displacement $x(t)$, and its autocorrelation function (see section 9.2) can be modeled by a Dirac function of weight A :

$$\langle F(t)F(t') \rangle = A\delta(t - t'), \quad (9.11)$$

where A is defined by the relation:

$$\int_{-\infty}^{+\infty} \langle F(t)F(t') \rangle dt' = A. \quad (9.12)$$

9.2 Random functions

The concept of random functions

When an experiment is performed in time-independent conditions, the random phenomenon concerned is treated in terms of random variables. However, often we are dealing with random phenomena varying continuously during the experiment. In this case, the phenomena can no longer be assimilated to random variables; they must be treated as random functions.

A *random function* $X(t)$ is a function that takes a form $x(t)$ unknown in advance. The function $x(t)$ taken by the random function during the experiment which is an ordinary function is the *achievement* of the random function. As a matter of fact, we can see that a series of r experiments of the random function $X(t)$ provides a family of r achievements $[x_1(t), x_2(t), \dots, x_r(t)]$. Like the random variables, the random functions will be designated by upper-case letters and the ordinary functions by lower-case letters.

Figure (9.1a) represents a series of recordings of the mains voltage with different voltmeters acting over a given duration τ . In practice,

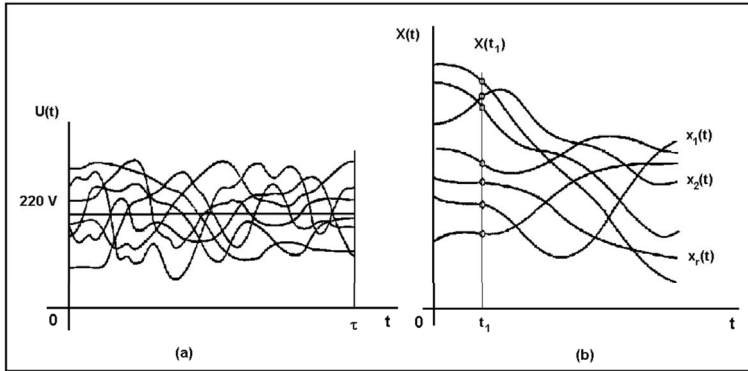


Figure 9.1: (a) Recordings of the mains voltage $U(t)$ over a time interval τ . (b) Definition of the random function $X(t)$ by a set of random variables $X(t_i)$.

there are also random functions depending, not on time, but on distance, as well as random functions depending on several arguments. As an example, the component in a given direction of the velocity of a particle in the Brownian motion is a random function.

Studying random functions often reduces to a set of random variables of known numerical characteristics, among which are the *expected value* and the *variance* (section 2.4). Indeed, the physical quantities evolving over time, such as the position and speed of an atom, can be regarded as a sequence of random variables defined at successive times (Fig. 9.1b). However, to fully describe a random function, an additional characteristic called the *correlation function* must be introduced in addition to the expected value and the variance which characterizes the degree of dependence of the random variables measured at various instants.

Consider r achievements $[x_1(t), x_2(t), \dots, x_r(t)]$ of the random function $X(t)$. If the argument is fixed at the value t_1 , the random variable $X(t_1)$ can be defined with the set of r values $[x_1(t_1), x_2(t_1), \dots, x_r(t_1)]$ at the instant t_1 (Fig. 9.1b). Now, taking a sample of the random function at sufficiently close instants $t_1, t_2, \dots, t_n$, we get a fairly accurate picture of the random function $X(t)$ and, most importantly,

the random function $X(t)$ is defined by a set of random variables corresponding to the different instants. Therefore, a random function can be regarded as a set of random variables.

Probability densities

It is well known that one random variable is characterized by a distribution in one dimension, two random variables by a distribution in two dimensions and a set of n random variables by a distribution in n dimensions. So, it seems evident that a random function $X(t)$, as described by the set of n random variables $[X(t_1), X(t_2), \dots, X(t_n)]$, should be characterized by a distribution in n dimensions.

The one-dimensional probability density function $f_1(x_1, t_1)$ of the random variable $X(t_1)$ is a non exhaustive feature of the random function $X(t)$ because it gives the distribution of $X(t)$ at the instant t_1 . It only allows the calculation of the elementary probability $f_1(x_1, t_1)dx_1$ of finding the event $\{x_1 < X(t_1) < x_1 + dx_1\}$. The two-dimensional probability density function $f_2(x_1, t_1; x_2, t_2)$ of the couple of random variables $X(t_1)$ and $X(t_2)$ is another non exhaustive feature of the random function $X(t)$, although more complex than the previous one, that gives the distribution of $X(t)$ at times t_1 and t_2 . It allows the calculation of the elementary probability $f_2(x_1, t_1; x_2, t_2)dx_1dx_2$ of finding the event $\{x_1 < X(t_1) < x_1 + dx_1 \text{ and } x_2 < X(t_2) < x_2 + dx_2\}$. Formally, we can thus increase the number of random variables for giving a more detailed description of the random function. However, the use of a multi-dimensional probability density function is difficult if not impossible.

The full description of the random function $X(t)$ depends on the probability density function in n dimensions, $f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n)$, which is very difficult to determine. Fortunately, there are a number of random processes that do not require knowledge of the multi-dimensional probability density function $f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n)$ to describe the random function $X(t)$. The simplest case is that of a *purely random* process. A function is purely random when the random variables $[X(t_1), X(t_2), \dots, X(t_n)]$ defining the random function $X(t)$ are *independent*. In such a process, all probability densities are

expressed in terms of the one-dimensional probability density function according to equation (2.140), i.e.:

$$f_2(x_1, t_1; x_2, t_2) = f_1(x_1, t_1) \cdot f_1(x_2, t_2), \quad (9.13)$$

$$\dots\dots = \dots\dots,$$

$$f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n) = f_1(x_1, t_1) \cdot f_1(x_2, t_2) \cdot \dots \cdot f_1(x_n, t_n). \quad (9.14)$$

There is another interesting case corresponding to the *Markov* process, for which the probability density function $f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n)$ is expressed in terms of the two-dimensional function $f_2(x_1, t_1; x_2, t_2)$ alone. Before defining the Markov process, consider the conditional probability density function $f_n(x_n, t_n | x_1, t_1; x_2, t_2; \dots; x_{n-1}, t_{n-1})$ of the random variable $X(t_n)$, given that the random variables $X(t_1), X(t_2), \dots, X(t_{n-1})$ have numerical characteristics known. According to equation (2.141), the conditional probability density function is related to the probability density function in n dimensions by:

$$\begin{aligned} f_n(x_n, t_n | x_1, t_1; x_2, t_2; \dots; x_{n-1}, t_{n-1}) &= \\ &= \frac{f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n)}{f_{n-1}(x_1, t_1; x_2, t_2; \dots; x_{n-1}, t_{n-1})}. \end{aligned} \quad (9.15)$$

In the Markov process, it is admitted that the features of the random function evaluated at the given instant t_i does not depend on the history of the process, but only on the features evaluated at the previous instant, t_{i-1} . In this case, the conditional probability density function $f_n(x_n, t_n | x_1, t_1; x_2, t_2; \dots; x_{n-1}, t_{n-1})$ of the random variable $X(t_n)$ is written:

$$f_n(x_n, t_n | x_1, t_1; x_2, t_2; \dots; x_{n-1}, t_{n-1}) = f_2(x_n, t_n | x_{n-1}, t_{n-1}). \quad (9.16)$$

Indeed, this equation stems from the fact that the history of the process can be ignored, with the exception of what happened at the preceding instant. In addition, by virtue of equation (2.141), the second member of equation (9.16) reads:

$$f_2(x_n, t_n | x_{n-1}, t_{n-1}) = \frac{f_2(x_n, t_n; x_{n-1}, t_{n-1})}{f_1(x_{n-1}, t_{n-1})}. \quad (9.17)$$

Therefore, by combining equations (9.15), (9.16) and (9.17), the probability density function at n dimensions can be written as follows:

$$\begin{aligned} f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n) &= \\ &= f_{n-1}(x_1, t_1; x_2, t_2; \dots; x_{n-1}, t_{n-1}) \frac{f_2(x_n, t_n; x_{n-1}, t_{n-1})}{f_1(x_{n-1}, t_{n-1})}. \end{aligned} \quad (9.18)$$

When the probability density functions $f_1(x_{n-1}, t_{n-1})$ and $f_2(x_n, t_n; x_{n-1}, t_{n-1})$ are known, it results from the above relation that the knowledge of $f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n)$ is deduced from that of $f_{n-1}(x_1, t_1; x_2, t_2; \dots; x_{n-1}, t_{n-1})$, which in turn comes from the function $f_{n-2}(x_1, t_1; x_2, t_2; \dots; x_{n-2}, t_{n-2})$ and so on until $f_2(x_n, t_n; x_{n-1}, t_{n-1})$, by a set of hierarchical equations similar to equation (9.18). Hence the unidimensional and bidimensional probability density functions are sufficient to describe a Markov process.

There is also a random process, called *stationary*, which deserves special attention. A random function is stationary if a time shift in all times $t_1, t_2, \dots, t_n$, of the same value τ , does not affect the probability density functions. This type of random function corresponds, for example, to the voltage fluctuation of the mains voltage portrayed in figure (9.1a). The statistical nature of a stationary random process remains unchanged over time, and its probability density function verifies the following property:

$$f_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n) = f_n(x_1, t_1 + \tau; x_2, t_2 + \tau; \dots; x_n, t_n + \tau). \quad (9.19)$$

Specifically, the one-dimensional probability density function $f_1(x_1, t_1) = f_1(x_1, t_1 + \tau) = f_1(x_1)$ does not depend on time, and the two-dimensional probability density function $f_2(x_1, t_1; x_2, t_2) = f_2(x_1, t_1 + \tau; x_2, t_2 + \tau) = f_2(x_1, x_2, \tau)$ depends only on the time difference $t_2 - t_1 = \tau$. In saying, in figurative manner, that a stationary random process has neither beginning nor end, it is easy to accept the *hypothesis of ergodicity* according to which r achievements of the random function $X(t)$ over a time interval t_n are equivalent to a single achievement on the time interval of r times t_n .

Characteristics of random functions

We had the opportunity to see in the previous paragraphs the important role played by the numerical characteristics of random variables. Considering that a random function can be regarded as a set of random variables, it is logical to introduce characteristics for random functions analogous to the numerical characteristics of random variables. When several outcomes of the random function $X(t)$ are available from an experiment, it is then possible to calculate the numerical characteristics of n random variables $[X(t_1), X(t_2), \dots, X(t_n)]$. It is also possible to calculate the mean value and the variance of each random variable from the unidimensional probability density function. Indeed, the mean value of the random function $X(t)$, at the instant t_1 , corresponds to the mean value of the random variable $X(t_1)$ in accordance with equation (2.121):

$$\mu_1 [X(t_1)] = \int_{-\infty}^{\infty} x_1 f_1(x_1, t_1) dx_1. \quad (9.20)$$

In the same way, the variance of the random function $X(t)$, at the instant t_1 , corresponds to the variance of the random variable $X(t_1)$ according to equation (2.122):

$$\alpha_2 [X(t_1)] = \int_{-\infty}^{\infty} \{x_1 - \mu_1 [X(t_1)]\}^2 f_1(x_1, t_1) dx_1. \quad (9.21)$$

Therefore, the mean value of the random function $X(t)$ is an ordinary function $\mu_1 [X(t)]$ which, for any value of the argument t , is equal to the mean value of the random variable corresponding to the argument t . Similarly, the variance of the random function $X(t)$ is an ordinary function $\alpha_2 [X(t)]$ which, for any value of the argument t , is equal to the variance of the random variable corresponding to the argument t . Thus, the mean value $\mu_1 [X(t)]$ and the variance $\alpha_2 [X(t)]$ are the most remarkable features of the random function $X(t)$. For instance, we show in figure (9.2) the achievements of two different random functions having same mean value and same variance.

However, in order to distinguish these two random functions, it is necessary to introduce the covariance (Eq. 2.143) between all pairs of random variables $[X(t_1), X(t_2), \dots, X(t_n)]$ as a measure of the degree of dependence of the random function at different values of t . This new

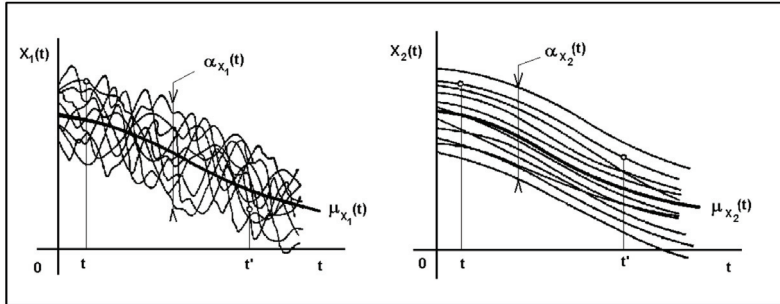


Figure 9.2: The two random processes have the same mean value $\mu_{X_1}(t) = \mu_{X_2}(t)$ and the same variance $\alpha_{X_1}(t) = \alpha_{X_2}(t)$, although they possess different internal structures.

characteristic, called the *correlation (or autocorrelation) function*, is defined by the ordinary function:

$$\begin{aligned}
 C[X(t_1)X(t_2)] &= \\
 &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \{x_1 - \mu_1[X(t_1)]\} \{x_2 - \mu_1[X(t_2)]\} f_2(x_1, t_1; x_2, t_2) dx_1 dx_2.
 \end{aligned}
 \tag{9.22}$$

The correlation function is a major characteristic of random functions. It should be stressed that it depends on the bidimensional probability density function while the mean value and variance depend on the unidimensional probability density function.

Correlation and convolution of two functions

Let us start by defining the *correlation* and the *convolution* of two random functions as these two notions will be frequently used. By using two functions $f_1(t)$ and $f_2(t)$, a new function called *correlation* can be provided and defined as:

$$F(\tau) = \int_{-\infty}^{\infty} f_1(t) f_2(t + \tau) dt. \tag{9.23}$$

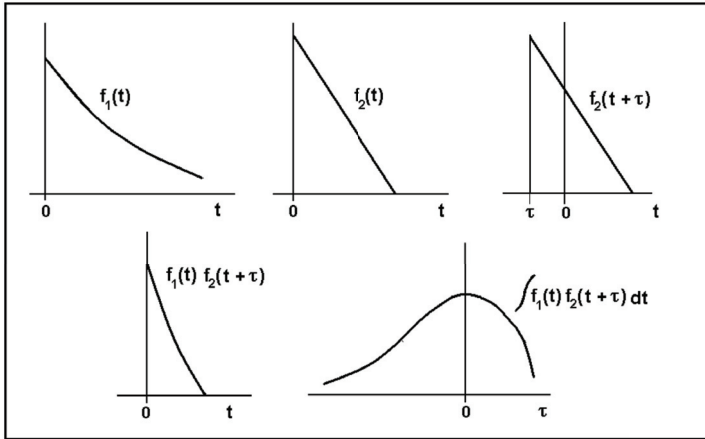


Figure 9.3: Schematic representation of the correlation of two functions.

The calculation of this function depends on the variable τ as follows. Firstly, the function f_2 is subjected to a moving of the time length τ to the left, then the product of f_1 is performed by the shift of the function f_2 and, finally, this product is integrated over time (Fig. 9.3).

When the integral in equation (9.23) does not converge, we see that the correlation function of the two functions $f_1(t)$ and $f_2(t)$ is the limit:

$$F(\tau) = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T f_1(t) f_2(t + \tau) dt. \quad (9.24)$$

With the two functions $f_1(t)$ and $f_2(t)$, another function called *convolution* can also be provided and defined by the following integral:

$$G(\tau) = \int_{-\infty}^{\infty} f_1(t) f_2(\tau - t) dt. \quad (9.25)$$

The calculation of this function depending on τ requires an intermediate operation. After the shifting of the function f_2 by the time length τ to the left, its reflection about the vertical axis must be performed about the vertical axis to obtain the function $f_2(\tau - t)$. Then, one just needs to make the product of function f_1 by the transformed function, and to integrate the product over time (Fig. 9.4).

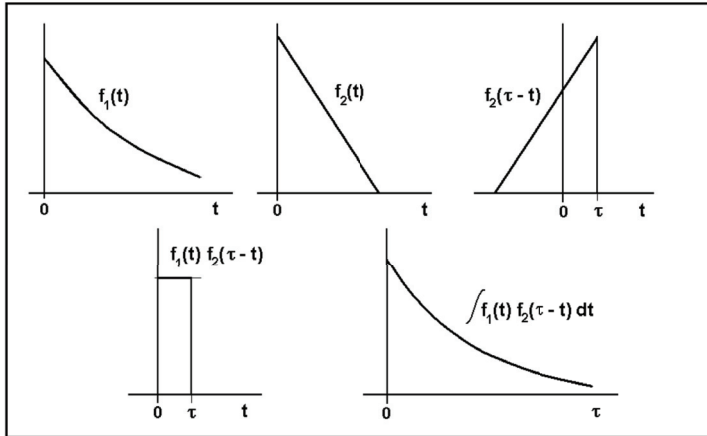


Figure 9.4: Schematic representation of the convolution of two functions over time.

Obviously the correlation and convolution of two functions exist only for certain values of τ , when functions overlap.

Most random processes are stationary in statistical physics. This results in their numerical characteristics having particularly important properties. Indeed, as the properties of a stationary random function are invariant under any change of time origin, the mean value (Eq. 9.20) does not depend on time:

$$\mu_1[X(0)] = \int_{-\infty}^{\infty} x_1 f_1(x_1) dx_1, \quad (9.26)$$

and the correlation function (Eq. 9.22) depends only on the variable $\tau = t_2 - t_1$:

$$\begin{aligned} C[X(0)X(\tau)] &= \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \{x_1 - \mu_1[X(0)]\} \{x_2 - \mu_1[X(\tau)]\} f_2(x_1, x_2, \tau) dx_1 dx_2. \end{aligned} \quad (9.27)$$

Since a stationary random process has neither beginning nor end, it can be assumed that average of r graphic representations of the

random function $X(t)$ on r successive time interval t_n is equivalent to a single outcome for $X(t)$ on the time interval $T = rt_n$ (assuming the ergodicity). This property is reflected by the fact that the *mean value* (Eq. 9.26) – usually denoted by $\langle x \rangle = \mu_1[X(0)]$ – is equal to the *time average* $\bar{x}$ defined by the expression:

$$\bar{x} = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T x(t) dt. \quad (9.28)$$

Therefore, for a stationary random function, the equality $\bar{x} = \langle x \rangle$ between the two averages is verified:

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T x(t) dt = \int_{-\infty}^{\infty} x_1 f_1(x_1) dx_1. \quad (9.29)$$

The assumption of ergodicity is also reflected by the fact that the *correlation function* (Eq. 9.27) is equal to the *time correlation function* (Eq. 9.24) defined by the relation:

$$C_x(\tau) = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T x(t) x(t + \tau) dt, \quad (9.30)$$

which leads to the equality $C_x(\tau) = C[X(0)X(\tau)]$, that is to say:

$$\begin{aligned} \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T x(t) x(t + \tau) dt &= \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \{x_1 - \mu_1[X(0)]\} \{x_2 - \mu_1[X(\tau)]\} f_2(x_1, x_2, \tau) dx_1 dx_2. \end{aligned} \quad (9.31)$$

It should be noted that the time correlation function $C_x(\tau)$ is an even function, $C_x(-\tau) = C_x(\tau)$. Consequently, we are confined to studying the positive values of τ . Besides, if $\tau = 0$, equation (9.27) is reduced to the variance:

$$C[X(0)X(0)] = \int_{-\infty}^{\infty} f_2(x_2, 0) dx_2 \int_{-\infty}^{\infty} \{x_1 - \mu_1[X(0)]\}^2 f_1(x_1, 0) dx_1, \quad (9.32)$$

which coincides with the variance resulting from equation (9.30), namely:

$$C_x(0) = \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T x^2(t) dt. \quad (9.33)$$

The just mentioned property of ergodicity is usually established on the basis of physical considerations related to the nature of the processes involved (section 1.4). In practice, it can be checked that a random function is ergodic by considering its correlation function $C_x(\tau)$. If the correlation function of a stationary random function tends to zero for large values of τ , this generally reflects the ergodicity of the process. On the contrary, if the correlation function tends to a constant value different from zero when τ goes to infinity, the process is nonergodic.

9.3 The Wiener-Khinchin theorem

The time correlation function $C_x(\tau)$ is of great importance when studying stationary random functions due to the relationship existing between the representative curve of $C_x(\tau)$ and the internal structure of the random process wherefrom it originates. It turns out that the graph of $C_x(\tau)$ has often damped oscillations for large values of τ . Specifically, these oscillations give information about the dominant frequencies in the random process leading naturally to the concept of *spectral composition* of a random function.

Achieving the spectral decomposition of the stationary random function $X(t)$ implies using the appropriate Fourier transform:

$$F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} x(t) \exp(-i\omega t) dt, \quad (9.34)$$

$$\text{with} \quad x(t) = \int_{-\infty}^{\infty} F(\omega) \exp(i\omega t) d\omega. \quad (9.35)$$

If the function $x(t)$ taken by the random function $X(t)$ is defined on a limited time interval, the relevant Fourier transform is calculated in writing down $x(t) = 0$ outside this interval. Before performing the spectral decomposition of the random function, the following integral is first evaluated in using equations (9.34) and (9.35), i.e.:

$$\begin{aligned}
\int_{-\infty}^{\infty} |F(\omega)|^2 d\omega &= \int_{-\infty}^{\infty} F^*(\omega) F(\omega) d\omega \\
&= \int_{-\infty}^{\infty} F^*(\omega) \left[\frac{1}{2\pi} \int_{-\infty}^{\infty} x(t) \exp(-i\omega t) dt \right] d\omega. \quad (9.36)
\end{aligned}$$

After inverting the integrals and reintroducing the expression of $x(t)$ in the previous equation, we obtain:

$$\begin{aligned}
\int_{-\infty}^{\infty} |F(\omega)|^2 d\omega &= \frac{1}{2\pi} \int_{-\infty}^{\infty} x(t) \left[\int_{-\infty}^{\infty} F^*(\omega) \exp(-i\omega t) d\omega \right] dt \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} x^2(t) dt, \quad (9.37)
\end{aligned}$$

which is the mathematical form of the *Parseval theorem*.

This theorem allows us to express the variance $C_x(0)$ of the random function $X(t)$ in terms of its Fourier transform $F(\omega)$. Indeed, by combining equations (9.37) and (9.33), it results that:

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-\infty}^{\infty} |F(\omega)|^2 d\omega = \frac{1}{2\pi} \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T x^2(t) dt = \frac{1}{2\pi} C_x(0). \quad (9.38)$$

Moreover, if the *spectral density* of the stationary random function $X(t)$ is defined by the quantity $S_x(\omega)$, whose expression is:

$$S_x(\omega) = 2\pi \lim_{T \rightarrow \infty} \frac{1}{2T} |F(\omega)|^2, \quad (9.39)$$

then, the variance $C_x(0)$ is related to the spectral density $S_x(\omega)$ by means of equations (9.38) and (9.39):

$$C_x(0) = \lim_{T \rightarrow \infty} \frac{2\pi}{2T} \int_{-\infty}^{\infty} |F(\omega)|^2 d\omega = \int_{-\infty}^{\infty} S_x(\omega) d\omega. \quad (9.40)$$

This formula is very important because it shows, on the one hand, that the variance of the stationary random function $X(t)$ equals the area under the curve of the spectral density $S_x(\omega)$ and, on the other

hand, it is linked up to the Fourier transform $F(\omega)$ of the stationary random function $X(t)$.

More generally, the spectral density $S_x(\omega)$ is connected to the correlation function $C_x(\tau)$ by the *Wiener-Khinchin theorem*. This is shown by calculating the Fourier transform of the correlation function thanks to equation (9.30), namely:

$$\begin{aligned} \frac{1}{2\pi} \int_{-\infty}^{\infty} C_x(\tau) \exp(-i\omega\tau) d\tau &= \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T x(t) x(t+\tau) dt \right] \exp(-i\omega\tau) d\tau. \end{aligned} \quad (9.41)$$

Now if $x(t) = 0$ is written down outside the interval of definition, the following transformation is obvious:

$$\begin{aligned} \int_{-\infty}^{\infty} C_x(\tau) \exp(-i\omega\tau) d\tau &= \\ &= \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-\infty}^{\infty} \left[\int_{-\infty}^{\infty} x(t) x(t+\tau) dt \right] \exp(-i\omega\tau - i\omega t) \exp(i\omega t) d\tau \\ &= \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-\infty}^{\infty} x(t) \exp(i\omega t) \left[\int_{-\infty}^{\infty} x(t+\tau) \exp[-i\omega(t+\tau)] d\tau \right] dt. \end{aligned} \quad (9.42)$$

Given the change of variables $u = t + \tau$, with $du = d\tau$, and equation (9.34), it is easy to see the integral over τ in square brackets in the above equation is equal to $2\pi F(\omega)$, and the integral over t is equal to $2\pi F(-\omega)$. Consequently, the Fourier transform of the correlation function $C_x(\tau)$ is equal to the spectral density $S_x(\omega)$. Indeed, with the help of equation (9.39), we get:

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} C_x(\tau) \exp(-i\omega\tau) d\tau = \frac{4\pi^2}{2\pi} \lim_{T \rightarrow \infty} \frac{1}{2T} F(\omega) F(-\omega) = S_x(\omega). \quad (9.43)$$

As regards the time correlation function $C_x(\tau)$, it is equal to the inverse Fourier transform of the spectral density, i.e.:

$$C_x(\tau) = \int_{-\infty}^{\infty} S_x(\omega) \exp(i\omega\tau) d\omega. \quad (9.44)$$

By putting $\tau = 0$ in equation (9.44), we obtain the spectral decomposition of the variance (Eq. 9.40) as a sum of elementary variances $S_x(\omega)d\omega$ spread over the continuous frequency spectrum.

9.4 Langevin equation

In the absence of an external field, the equation of motion in one dimension of a suspended particle is:

$$m \frac{d^2x}{dt^2} = -\mu \frac{dx}{dt} + F(t), \quad (9.45)$$

where the force is decomposed into two parts: the frictional force $-\mu \frac{dx}{dt}$ and the driving force $F(t)$. Equation (9.45) is the *Langevin stochastic differential equation* yielding the velocity after integration³:

$$v(t) = v_0 \exp\left(-\frac{\mu}{m}t\right) + \frac{1}{m} \exp\left(-\frac{\mu}{m}t\right) \int_0^t F(t') \exp\left(\frac{\mu}{m}t'\right) dt', \quad (9.46)$$

³We can verify that the expression of $v(t)$ is correct by differentiating it with respect to t . Indeed, it comes:

$$\begin{aligned} \frac{dv(t)}{dt} &= -\frac{\mu}{m} v_0 \exp\left(-\frac{\mu}{m}t\right) - \frac{\mu}{m^2} \exp\left(-\frac{\mu}{m}t\right) \int_0^t F(t') \exp\left(\frac{\mu}{m}t'\right) dt' \\ &\quad + \frac{1}{m} \exp\left(-\frac{\mu}{m}t\right) \left[F(t) \exp\left(\frac{\mu}{m}t\right) \right], \\ &= -\frac{\mu}{m} v(t) + \frac{1}{m} F(t). \end{aligned}$$

Note that the third term on the right hand side of $\frac{dv(t)}{dt}$ comes from the derivation of the upper limit of the integral which depends on t . The derivation of an integral whose integration limits depend on t is carried out with the general formula:

$$\frac{d}{dt} \int_{a(t)}^{b(t)} f(\tau, t) d\tau = \int_{a(t)}^{b(t)} \frac{\partial}{\partial t} f(\tau, t) d\tau + b'(t) f[b(t), t] - a'(t) f[a(t), t].$$

where v_0 is the velocity at time $t = 0$. The velocity $v(t)$ is a random function from which the average value can be easily calculated. Because the average value of the driving force is zero (Eq. 9.10), the average velocity is:

$$\langle v(t) \rangle = v_0 \exp\left(-\frac{\mu}{m}t\right). \quad (9.47)$$

This shows that the average velocity relaxes exponentially towards zero with the relaxation time $\frac{m}{\mu}$. For times much larger than the relaxation time, the average velocity vanishes and the velocity becomes a stationary random function. Indeed, since the suspended particle is at equilibrium with the liquid, its motion has neither beginning nor end, and the velocity is a stationary random function (section 9.2). Regarding the variance of the velocity, its expression is⁴:

$$\langle [v(t) - \langle v(t) \rangle]^2 \rangle = \frac{A}{2\mu m} \left[1 - \exp\left(-\frac{2\mu}{m}t\right) \right]. \quad (9.48)$$

Thus, as long as t remains small compared to the relaxation time ($t \ll \frac{m}{\mu}$), the variance of the velocity increases linearly with time, reaching an asymptotic value when t is large, according to the formulas:

$$\langle [v(t) - \langle v(t) \rangle]^2 \rangle \simeq \frac{A}{m^2} t \quad \left(t \ll \frac{m}{\mu}\right), \quad (9.49)$$

$$\simeq \frac{A}{2\mu m} \quad \left(t \gg \frac{m}{\mu}\right). \quad (9.50)$$

Moreover, it is evident that the variance of the velocity is zero as long as the driving force has not acted ($t = 0$) yet. It means that the velocity becomes a random function, and the fluctuations in the velocity are present for as long as the driving force is acting.

⁴With equations (9.46) and (9.47), and taking account of equation (9.11), the calculation of the variance is done as follows:

$$\begin{aligned} \langle [v(t) - \langle v(t) \rangle]^2 \rangle &= \frac{1}{m^2} \exp\left(-\frac{2\mu}{m}t\right) \int_0^t \int_0^t \langle F(t') F(t'') \rangle \exp\left[\frac{\mu}{m}(t' + t'')\right] dt' dt'' \\ &= \frac{1}{m^2} \exp\left(-\frac{2\mu}{m}t\right) \int_0^t \int_0^t A \delta(t' - t'') \exp\left[\frac{\mu}{m}(t' + t'')\right] dt' dt'' \\ &= \frac{A}{m^2} \exp\left(-\frac{2\mu}{m}t\right) \int_0^t \exp\left(\frac{2\mu}{m}t'\right) dt' = \frac{A}{2\mu m} \left[1 - \exp\left(-\frac{2\mu}{m}t\right) \right]. \end{aligned}$$

Note that it is possible to determine the value of the constant A by calculating the average kinetic energy of the suspended particle in thermal equilibrium with the liquid, that is to say, after a sufficiently long time. In fact, according to the assumptions of the preceding subsection, the kinetic energy of the suspended particle is $\frac{1}{2}m\langle v^2(t)\rangle = \frac{1}{2}k_B T$ when $t \gg \frac{m}{\mu}$. To determine A , it is sufficient to evaluate $\langle v^2(t)\rangle$ in using the variance formula (Eq. 2.124):

$$\langle [v(t) - \langle v(t) \rangle]^2 \rangle = \langle v^2(t) \rangle - \langle v(t) \rangle^2, \quad (9.51)$$

hence:

$$\langle v^2(t) \rangle = \langle [v(t) - \langle v(t) \rangle]^2 \rangle + \langle v(t) \rangle^2. \quad (9.52)$$

Then, by multiplying this equation by $\frac{m}{2}$ and expressing the terms on the right hand side with equations (9.47) and (9.48), it results:

$$\frac{1}{2}m\langle v^2(t) \rangle = \frac{A}{4\mu} \left[1 - \exp\left(-\frac{2\mu}{m}t\right) \right] + \frac{1}{2}mv_0^2 \exp\left(-\frac{2\mu}{m}t\right). \quad (9.53)$$

What we need them is to identify this expression with $\frac{1}{2}k_B T$ for large values of t . We deduce that:

$$A = 2\mu k_B T. \quad (9.54)$$

The second stage for solving the Langevin equation is to seek the expression of the displacement $x(t)$ as well as its mean value and variance. Assuming the position of the particle at time $t = 0$ to be $x(0) = x_0$, the integration of equation (9.46) leads to the relation⁵:

$$\begin{aligned} x(t) &= \int_0^t v(t)dt = x_0 + \frac{m}{\mu}v_0 \left[1 - \exp\left(-\frac{\mu}{m}t\right) \right] \\ &\quad + \frac{1}{\mu} \int_0^t F(t') \left\{ 1 - \exp\left[-\frac{\mu}{m}(t-t')\right] \right\} dt'. \end{aligned} \quad (9.55)$$

As the mean value of the driving force is zero, the mean value of the displacement reads:

$$\langle x(t) \rangle = x_0 + \frac{m}{\mu}v_0 \left[1 - \exp\left(-\frac{\mu}{m}t\right) \right], \quad (9.56)$$

⁵The result of this integration can be easily verified by differentiating $x(t)$ with respect to t , bearing in mind to differentiate the upper limit of integration which also depends on t .

and the variance of the displacement is reduced to⁶:

$$\begin{aligned} \langle [x(t) - \langle x(t) \rangle]^2 \rangle &= \\ &= \frac{A}{\mu^2} \left\{ t + \frac{2m}{\mu} \left[\exp\left(-\frac{\mu}{m}t\right) - 1 \right] - \frac{m}{2\mu} \left[\exp\left(-\frac{2\mu}{m}t\right) - 1 \right] \right\}. \end{aligned} \quad (9.57)$$

The examination of this expression shows that, at short times ($t \ll \frac{m}{\mu}$), the variance of the displacement varies as t^3 , whereas, at long times ($t \gg \frac{m}{\mu}$), it varies linearly according to the behaviour laws:

$$\langle [x(t) - \langle x(t) \rangle]^2 \rangle \simeq \frac{1}{3} \frac{A}{m^2} t^3 \quad \left(t \ll \frac{m}{\mu} \right), \quad (9.58)$$

$$\simeq \frac{A}{\mu^2} t \quad \left(t \gg \frac{m}{\mu} \right). \quad (9.59)$$

For a better understanding of the physical meaning of the Brownian motion, it is recommended to define the *mean square displacement* $\langle [x(t) - x_0]^2 \rangle$ as⁷:

$$\langle [x(t) - x_0]^2 \rangle = \langle [x(t) - \langle x(t) \rangle]^2 \rangle + \langle [\langle x(t) \rangle - x_0]^2 \rangle. \quad (9.60)$$

⁶The variance of the displacement is calculated in the same way as the variance of the velocity:

$$\begin{aligned} \langle [x(t) - \langle x(t) \rangle]^2 \rangle &= \\ &= \frac{1}{\mu^2} \int_0^t \int_0^t \langle F(t') F(t'') \rangle \left\{ 1 - \exp\left[-\frac{\mu}{m}(t-t')\right] \right\} \left\{ 1 - \exp\left[-\frac{\mu}{m}(t-t'')\right] \right\} dt' dt'' \\ &= \frac{1}{\mu^2} \int_0^t \int_0^t A \delta(t' - t'') \left\{ 1 - \exp\left[-\frac{\mu}{m}(t-t')\right] \right\} \left\{ 1 - \exp\left[-\frac{\mu}{m}(t-t'')\right] \right\} dt' dt'' \\ &= \frac{A}{\mu^2} \int_0^t \left\{ 1 - \exp\left(-\frac{\mu}{m}t'\right) \right\}^2 dt' = \frac{A}{\mu^2} \int_0^t \left\{ 1 - 2 \exp\left(-\frac{\mu}{m}t'\right) + \exp\left(-\frac{2\mu}{m}t'\right) \right\} dt' \\ &= \frac{A}{\mu^2} \left\{ t + \frac{2m}{\mu} \left[\exp\left(-\frac{\mu}{m}t\right) - 1 \right] - \frac{m}{2\mu} \left[\exp\left(-\frac{2\mu}{m}t\right) - 1 \right] \right\}. \end{aligned}$$

⁷The mean square displacement – not to be confused with the variance – is obtained as follows:

$$\begin{aligned} x(t) - x_0 &= [x(t) - \langle x(t) \rangle] + [\langle x(t) \rangle - x_0], \\ \text{or } [x(t) - x_0]^2 &= [x(t) - \langle x(t) \rangle]^2 + 2[x(t) - \langle x(t) \rangle][\langle x(t) \rangle - x_0] + [\langle x(t) \rangle - x_0]^2, \end{aligned}$$

and since $\langle x(t) - \langle x(t) \rangle \rangle = 0$, one gets:

$$\langle [x(t) - x_0]^2 \rangle = \langle [x(t) - \langle x(t) \rangle]^2 \rangle + \langle [\langle x(t) \rangle - x_0]^2 \rangle.$$

Now, by using equations (9.56) and (9.57), we obtain:

$$\begin{aligned} \langle [x(t) - x_0]^2 \rangle &= \frac{A}{\mu^2} \left\{ t + \frac{2m}{\mu} \left[\exp\left(-\frac{\mu}{m}t\right) - 1 \right] \right. \\ &\quad \left. - \frac{m}{2\mu} \left[\exp\left(-\frac{2\mu}{m}t\right) - 1 \right] \right\} + \frac{m^2}{\mu^2} v_0^2 \left[1 - \exp\left(-\frac{\mu}{m}t\right) \right]^2. \end{aligned} \quad (9.61)$$

At short times ($t \ll m/\mu$), it can be seen that the term in brackets in the above equation vanishes, so that the mean square displacement behaves as:

$$\langle [x(t) - x_0]^2 \rangle \simeq v_0^2 t^2. \quad (9.62)$$

It depends on the value of the initial velocity v_0 . In particular, if the suspended particle is in thermal equilibrium with the liquid, its initial velocity is such that $v_0^2 = \frac{k_B T}{m}$ and the mean square displacement is $\langle [x(t) - x_0]^2 \rangle \simeq \frac{k_B T}{m} t^2$. If the particle is not in equilibrium with the liquid, the relaxation is slightly more complicated, though continuing to vary as t^2 .

At long times ($t \gg m/\mu$), the mean square displacement is governed by the term t in brackets of equation (9.61). And if equation (9.54) is taken into account to explain the constant $A (= 2\mu k_B T)$, the mean square displacement is reduced to:

$$\langle [x(t) - x_0]^2 \rangle \simeq 2 \frac{k_B T}{\mu} t = 2Dt, \quad (9.63)$$

where D is the diffusion coefficient related to the coefficient of friction μ by equation (8.189).

Temporal correlation functions in the Langevin model

First consider the force autocorrelation function $\langle F(t)F(t') \rangle$ defined by equation (9.12). After replacing the constant A by its expression (Eq. 9.54) one obtains directly:

$$\mu = \frac{1}{2k_B T} \int_{-\infty}^{+\infty} \langle F(t)F(t') \rangle dt'. \quad (9.64)$$

This very important equation links the coefficient of friction μ to the force autocorrelation function $\langle F(t)F(t') \rangle$, and shows that the frictional force $X(t) (= -\mu v(t))$ (dissipation) and the driving force $F(t)$

(fluctuation) are two complementary aspects of the same phenomenon. It should be noted that it is the simplest form of the fluctuation-dissipation theorem mentioned in section (6.2).

Now look at the velocity autocorrelation function $\langle v(t)v(t') \rangle$. This question can be best answered by writing the expression of the displacement $x(t)$ in terms of the velocity, assuming that the position of the particle at time $t = 0$ is $x(0) = x_0$, that is to say:

$$x(t) = x_0 + \int_0^t v(t) dt. \quad (9.65)$$

Then calculate the mean square displacement $\langle [x(t) - x_0]^2 \rangle$ from the above relation. This is expressed as:

$$\langle [x(t) - x_0]^2 \rangle = \int_0^t \int_0^t \langle v(t')v(t'') \rangle dt' dt''. \quad (9.66)$$

To perform this integration, the change of variables $t'' = t' + \tau$ is made by reminding that $v(t)$ is a stationary random function. It follows that $dt'' = d\tau$, that the limits of integration are $-t' \leq \tau \leq t - t'$ and the integral is transformed as:

$$\langle [x(t) - x_0]^2 \rangle = \int_0^t \left[\int_{-t'}^{t-t'} \langle v(0)v(\tau) \rangle d\tau \right] dt'. \quad (9.67)$$

This expression is simplified by reversing the order of integration and splitting the integration domain in two. Using the Fubini theorem, with the help of figure (9.5), we find:

$$\begin{aligned} \int_0^t \left[\int_{-t'}^{t-t'} \dots d\tau \right] dt' &= \int_0^t \left[\int_0^{t-\tau} \dots dt' \right] d\tau + \int_{-t}^0 \left[\int_{-\tau}^t \dots dt' \right] d\tau, \\ &= 2 \int_0^t \left[\int_0^{t-\tau} \dots dt' \right] d\tau, \end{aligned} \quad (9.68)$$

or:

$$\begin{aligned} \int_0^t \left[\int_{-t'}^{t-t'} \langle v(0)v(\tau) \rangle d\tau \right] dt' &= 2 \int_0^t \langle v(0)v(\tau) \rangle \left[\int_0^{t-\tau} dt' \right] d\tau \\ &= 2 \int_0^t \langle v(0)v(\tau) \rangle (t-\tau) d\tau. \end{aligned} \quad (9.69)$$

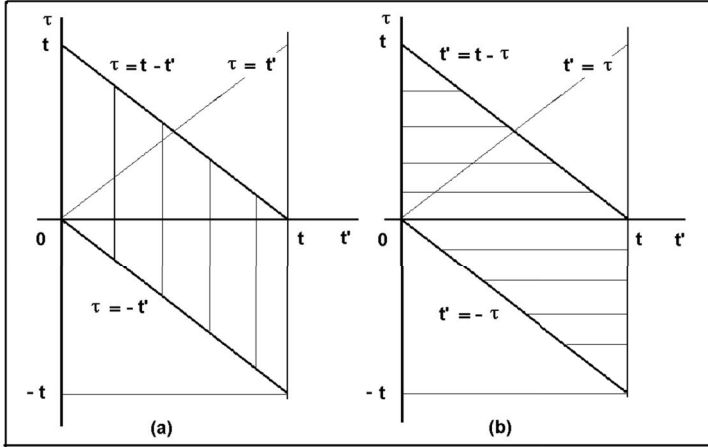


Figure 9.5: Domains of integration to invert integrations over τ and t' . (a) The first integration is on τ , from $-t'$ to $t - t'$. (b) The first integration is on t' from 0 to $t - \tau$ when $\tau > 0$, and from $-\tau$ to t when $\tau < 0$.

Hence, the mean square displacement is finally written:

$$\langle [x(t) - x_0]^2 \rangle = 2t \int_0^t \langle v(0)v(\tau) \rangle \left(1 - \frac{\tau}{t}\right) d\tau. \quad (9.70)$$

However, concerning the long times, it has been shown that the mean square displacement is proportional to time (Eq. 9.63). Thus, by identifying equations (9.63) and (9.70), it follows the expression of the diffusion coefficient D in terms of the velocity autocorrelation function:

$$D = \lim_{t \rightarrow \infty} \int_0^t \langle v(0)v(\tau) \rangle \left(1 - \frac{\tau}{t}\right) d\tau = \int_0^\infty \langle v(0)v(\tau) \rangle d\tau. \quad (9.71)$$

Unlike equation (9.64), valid only for the Langevin model, equation (9.71) is true in all circumstances⁸.

⁸Equation (9.71) connects the diffusion coefficient D to the unidirectional velocity autocorrelation function $\langle v(0)v(\tau) \rangle$. Consequently, with the autocorrelation function of the velocity vector $\langle \mathbf{v}(0)\mathbf{v}(\tau) \rangle$, the following equation must be used:

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(0)\mathbf{v}(\tau) \rangle d\tau.$$

After showing how the coefficient of friction μ and the diffusion coefficient D are connected to the integrals of the force autocorrelation function and the velocity autocorrelation function, respectively, we compute the velocity-force correlation function in the Langevin model. For this, consider the expression of the velocity of the suspended particle (Eq. 9.46) in thermal equilibrium with the liquid at the initial instant t_0 :

$$v(t) = v_0 \exp\left[-\frac{\mu}{m}(t - t_0)\right] + \frac{1}{m} \int_{t_0}^t F(t') \exp\left[-\frac{\mu}{m}(t - t')\right] dt'. \quad (9.72)$$

Then, we stretch the initial time t_0 to $-\infty$ so that the suspended particle is steadily in thermal equilibrium with the liquid and the velocity becomes a stationary random function. Its expression is therefore:

$$v(t) = \frac{1}{m} \int_{-\infty}^t F(t') \exp\left[-\frac{\mu}{m}(t - t')\right] dt'. \quad (9.73)$$

Now the velocity-force correlation function can be found by multiplying the above equation by $F(t'')$ and calculating the mean value:

$$\langle v(t)F(t'') \rangle = \frac{1}{m} \int_{-\infty}^t \langle F(t')F(t'') \rangle \exp\left[-\frac{\mu}{m}(t - t')\right] dt', \quad (9.74)$$

and, finally, we use equation (9.11) to perform the integration. From equation (9.74):

$$\langle v(t)F(t'') \rangle = \frac{A}{m} \int_{-\infty}^t \delta(t'' - t') \exp\left[-\frac{\mu}{m}(t - t')\right] dt', \quad (9.75)$$

we obtain the expression of the velocity-force correlation function for $t' = t''$. It should be noted that t'' is the instant concerned when the force F is applied, it is therefore important to see what happens for $t < t''$ and $t > t''$, namely:

$$\langle v(t)F(t'') \rangle = \frac{A}{m} \exp\left[-\frac{\mu}{m}(t - t'')\right] \quad \text{for } t \geq t'', \quad (9.76)$$

$$= 0, \quad \text{for } t < t''. \quad (9.77)$$

These relations show that the velocity-force correlation function is discontinuous, and the velocity $v(t)$ is correlated only with the force $F(t'')$ from the time where it acts.

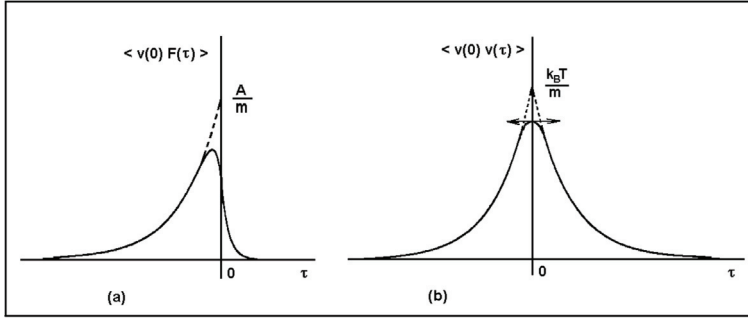


Figure 9.6: Schematic representations of (a) the velocity-force correlation function and (b) the velocity autocorrelation function. The dashed lines correspond to the conventional model of Langevin: since the velocity autocorrelation function has an exponential decay (the slope at the origin is nonzero), the velocity $v(t)$ has a Gaussian and Markovian character.

By putting $t'' - t = \tau$, we can easily see that the slope of the velocity-force correlation function (Fig. 9.6a), for $\tau < 0$, is:

$$\frac{d}{d\tau} \langle v(0)F(\tau) \rangle = \frac{A\mu}{m^2} \exp\left(\frac{\mu}{m}\tau\right). \quad (9.78)$$

In particular, the slope and the value of the velocity-force correlation function are, respectively, $\frac{A\mu}{m^2} = \frac{2\mu^2 k_B T}{m^2}$ and $\frac{A}{m} = \frac{2\mu k_B T}{m}$ when $\tau = 0$ (see Eq. 9.54).

Similarly, we calculate the velocity autocorrelation function in the Langevin model. With the help of equation (9.73), the following expression is obtained:

$$\langle v(t'')v(t) \rangle = \frac{1}{m} \int_{-\infty}^t \langle v(t'')F(t') \rangle \exp\left[-\frac{\mu}{m}(t-t')\right] dt', \quad (9.79)$$

in which the velocity-force correlation function $\langle v(t'')F(t') \rangle$, drawn from equation (9.75), reads after adjusting the variables:

$$\langle v(t'')F(t') \rangle = \frac{A}{m} \int_{-\infty}^{t''} \delta(t' - \tau) \exp\left[-\frac{\mu}{m}(t'' - \tau)\right] d\tau. \quad (9.80)$$

The substitution of the above relation in equation (9.79) provides the velocity autocorrelation function⁹:

$$\langle v(t'')v(t) \rangle = \frac{A}{2m\mu} \exp \left[-\frac{\mu}{m} (t'' - t) \right]. \quad (9.81)$$

If we express the constant $A (= 2\mu k_B T)$ and put $t'' - t = \tau$, the velocity autocorrelation function in the Langevin model is finally written as follows:

$$\langle v(0)v(\tau) \rangle = \frac{k_B T}{m} \exp \left(-\frac{\mu}{m} |\tau| \right). \quad (9.82)$$

Since the velocity is a stationary random function¹⁰, its autocorrelation function is an even function specified by the absolute value of τ . The velocity autocorrelation function is therefore subject to an exponential decay (Fig. 9.7a), and the slope whose expression is:

$$\frac{d}{d\tau} \langle v(0)v(\tau) \rangle = -\frac{k_B T \mu}{m^2} \exp \left(-\frac{\mu}{m} |\tau| \right) = -\frac{\mu}{m} \langle v(0)v(\tau) \rangle \quad (9.83)$$

also decreases exponentially (Fig. 9.6b). Moreover, if the suspended particle is in thermal equilibrium with the liquid, the value of the velocity autocorrelation function, at $\tau = 0^+$, is equal to the square

⁹The calculation is as follows:

$$\begin{aligned} \langle v(t'')v(t) \rangle &= \\ &= \frac{A}{m^2} \int_{-\infty}^t \left\{ \int_{-\infty}^{t''} \delta(t' - \tau) \exp \left[-\frac{\mu}{m} (t'' - \tau) \right] d\tau \right\} \exp \left[-\frac{\mu}{m} (t - t') \right] dt' \\ &= \frac{A}{m^2} \int_{-\infty}^t \exp \left[-\frac{\mu}{m} (t'' - t') \right] \exp \left[-\frac{\mu}{m} (t - t') \right] dt' \\ &= \frac{A}{m^2} \exp \left[-\frac{\mu}{m} (t'' + t) \right] \int_{-\infty}^t \exp \left[\frac{2\mu}{m} t' \right] dt' \\ &= \frac{A}{m^2} \exp \left[-\frac{\mu}{m} (t'' + t) \right] \frac{m}{2\mu} \left[\exp \left(\frac{2\mu}{m} t' \right) \right]_{-\infty}^t = \frac{A}{2m\mu} \exp \left[-\frac{\mu}{m} (t'' - t) \right]. \end{aligned}$$

¹⁰Having admitted that the random force $F(t)$ has a Gaussian character (section 9.1), the linearity of the Langevin equation imposes that the velocity $v(t)$ also has a Gaussian character. However, it has been shown [135] that a stationary random function with Gaussian character also has a Markovian character when its autocorrelation function is exponentially decreasing (Eq. 9.82). For a study of the Brownian motion in relation with the Markov process, see, for instance, the article by Wang and Uhlenbeck [136].

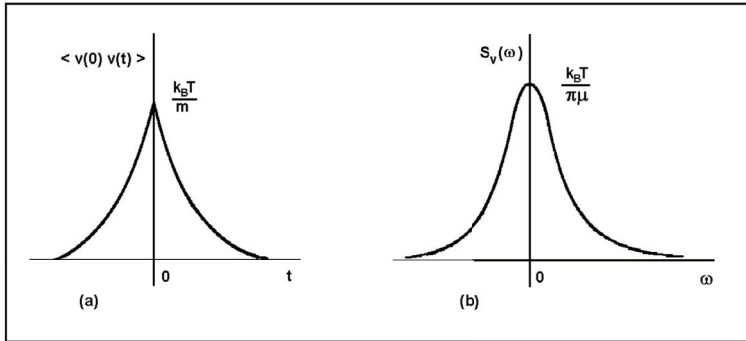


Figure 9.7: Schematic representation of (a) the velocity autocorrelation function and (b) the spectral density of the velocity in the conventional Langevin model.

of the thermal velocity $\langle v(0)v(0) \rangle = v_0^2 = \frac{k_B T}{m}$, and the initial slope is $-\frac{k_B T \mu}{m^2}$. Note that this value of the slope at the origin does not correspond to that which will be provided by a detailed study carried out in section (9.6).

9.5 The Fourier transform of the autocorrelation functions

The previous developments show that there is a link between the internal structure of a random process and the representation of the corresponding autocorrelation function. Yet another way to investigate the internal structure of a stationary random function is passing through its *spectral density* $S(\omega)$, which is completely determined by the autocorrelation function in using the Wiener–Khinchin theorem (section 9.3). Indeed, the spectral density of a random function is defined by the Fourier transform of the autocorrelation function of this function (Eq. 9.43).

For example, it is easy to obtain the spectral density $S_F(\omega)$ of the random force $F(t)$ in the conventional Langevin model by calculating the Fourier transform of the force autocorrelation function

$\langle F(0)F(t) \rangle = 2\mu k_B T \delta(t)$. In applying the definition of the spectral density (Eq. 9.43), we obtain immediately:

$$S_F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} 2\mu k_B T \delta(t) \exp(-i\omega t) dt = \frac{\mu k_B T}{\pi}, \quad (9.84)$$

for all values of ω . The spectral density $S_v(\omega)$ of the velocity can be obtained in the same way as the force by the expression:

$$S_v(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle v(0)v(t) \rangle \exp(-i\omega t) dt. \quad (9.85)$$

When equation (9.82) is used to express the velocity autocorrelation function in the above relation, it follows:

$$S_v(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{k_B T}{m} \exp\left(-\frac{\mu}{m} |t|\right) \exp(-i\omega t) dt, \quad (9.86)$$

or equivalently¹¹:

$$S_v(\omega) = \frac{\mu k_B T}{\pi (\mu^2 + m^2 \omega^2)}. \quad (9.87)$$

This relation is a Lorentzian function, centered at $\omega = 0$, with a width proportional to μ . As we know, the lower the coefficient of friction μ , the more slowly the autocorrelation function decreases and, simultaneously, the spectral density becomes sharper and the value at the origin higher (Fig. 9.7b). At the limit of $\mu \rightarrow 0$, the spectral density has a single line when $\omega = 0$. On the contrary, when the coefficient of friction increases, the velocity autocorrelation function

¹¹The above integral is calculated as follows:

$$\begin{aligned} S_v(\omega) &= \frac{k_B T}{2\pi m} \left\{ \int_{-\infty}^0 \exp\left[\left(\frac{\mu}{m} - i\omega\right)t\right] dt + \int_0^{\infty} \exp\left[-\left(\frac{\mu}{m} + i\omega\right)t\right] dt \right\} \\ &= \frac{k_B T}{2\pi m} \left\{ \int_0^{\infty} \exp\left[-\left(\frac{\mu}{m} - i\omega\right)t\right] dt + \int_0^{\infty} \exp\left[-\left(\frac{\mu}{m} + i\omega\right)t\right] dt \right\} \\ &= \frac{k_B T}{2\pi m} \left\{ \frac{1}{-\left(\frac{\mu}{m} - i\omega\right)} \exp\left[-\left(\frac{\mu}{m} - i\omega\right)t\right] + \frac{1}{-\left(\frac{\mu}{m} + i\omega\right)} \exp\left[-\left(\frac{\mu}{m} + i\omega\right)t\right] \right\}_0^{\infty} \\ &= \frac{k_B T}{2\pi m} \left[\frac{1}{\left(\frac{\mu}{m} - i\omega\right)} + \frac{1}{\left(\frac{\mu}{m} + i\omega\right)} \right] = \frac{k_B T}{2\pi m} \left[\frac{2\frac{\mu}{m}}{\left(\frac{\mu}{m}\right)^2 + \omega^2} \right] = \frac{\mu k_B T}{\pi (\mu^2 + m^2 \omega^2)}. \end{aligned}$$

decreases rapidly and the spectral density keeps a constant value with no dominant frequency (white noise).

The spectral density (often used in mechanics and electronics to perform the harmonic analysis of systems) is of paramount importance in the formalism of the *temporal correlation functions* because it describes the spectral distribution of variances for a stationary random process (section 9.2). In the case of the *spatial correlation functions*, the spectral density is also important because it is directly measurable. Indeed, it has been seen (Eq. 3.118) that the Fourier transform of the pair correlation function $g(r)$ is connected to the structure factor $S(q)$ which is nothing but a spectral density measured by *elastic scattering* experiments of X-rays or neutrons. Anticipating over what happens next, it is easy to imagine an *inelastic scattering* experiment – involving transfers of momentum $\hbar q$ and energy $\hbar\omega$ – capable of measuring the dynamic structure factor $S(\mathbf{q}, \omega)$ which represents the spectral density of a spatiotemporal correlation function to be defined.

9.6 The generalized Langevin equation

First recall that the results of the preceding section (in particular, the initial slope of the velocity autocorrelation function is *nonzero*) come from the fact that the force autocorrelation function is represented by the Dirac function $\langle F(t)F(t') \rangle = A\delta(t - t')$, with $A = 2\mu k_B T$ (Eq. 9.11).

Here we show that it is possible to *impose that the initial slope of the velocity autocorrelation function is zero* by writing the force autocorrelation function under the form:

$$\langle F(t)F(t') \rangle = k_B T M(t - t'), \quad (9.88)$$

where $M(t - t')$ is the *memory function* for the property of friction. The replacement of the Dirac function by the memory function amounts to assuming that the correlation time τ_c of the random force is not zero. In other words, this consists in considering that the friction does not appear immediately when the random force is applied, but after the time τ_c necessary for the response. To account for the

delay of the friction, it is sufficient to write the Langevin equation (Eq. 9.45) as follows:

$$m \frac{dv}{dt} = - \int_0^t M(t-t') v(t') dt' + F(t). \quad (9.89)$$

This expression is the *generalized Langevin equation* [137]. Incidentally, we note that, if the memory function was expressed in terms of the Dirac function as:

$$M(t-t') = 2\mu\delta(t-t'), \quad (9.90)$$

the force autocorrelation function should be equal to $\langle F(t)F(t') \rangle = 2\mu k_B T \delta(t-t')$,

i.e. a form that enables us to find again the conventional Langevin equation¹² (Eq. 9.45):

$$\begin{aligned} m \frac{dv}{dt} &= - \int_0^t 2\mu\delta(t-t') v(t') dt' + F(t) \\ &= -\mu v(t) + F(t). \end{aligned} \quad (9.91)$$

Equation (9.89) makes it possible, too, to determine of the correct value of the slope of the velocity autocorrelation function. In fact, the calculation of the derivative of $\langle v(0)v(\tau) \rangle$ is made by multiplying equation (9.89) by $v(0)$ and computing the mean value which gives:

$$m \left\langle v(0) \frac{d}{dt} v(t) \right\rangle = - \int_0^t M(t-t') \langle v(0)v(t') \rangle dt', \quad (9.92)$$

according to equation (9.76). However, in taking into account that $\langle v(0) \frac{d}{dt} v(t) \rangle = \frac{d}{dt} \langle v(0)v(t) \rangle$, the foregoing relation reduces to the expression:

$$m \frac{d}{dt} \langle v(0)v(t) \rangle = - \int_0^t M(t-t') \langle v(0)v(t') \rangle dt', \quad (9.93)$$

which is zero at the origin (Fig. 9.7b), whatever the form of the memory function, provided that it is different from the Dirac function (like in the conventional Langevin model).

¹²The factor 2 has been introduced because the Dirac function is integrated only over the positive values of time.

Equation (9.93) is an integro-differential Volterra equation. It shows that the velocity autocorrelation function is completely determined from the corresponding memory function. The relationships of the velocity-force correlation function (Eqs. 9.76 and 9.77) and the velocity autocorrelation function (Eq. 9.82) depend on the chosen memory function, and their representations (Fig. 9.7) differ from those of the conventional Langevin equation by the absence of discontinuity around the value $\tau = t - t' = 0$. These considerations suggest that there are two distinct time scales in the generalized Langevin model: the *correlation time* τ_c of the random force and the *relaxation time* $\tau_r = \frac{m}{\mu}$ of the average velocity. It is essential that the time interval Δt , during which there is a change in the velocity of the suspended particle, be much longer than the correlation time τ_c and much shorter than the relaxation time $\tau_r = \frac{m}{\mu}$, namely:

$$\tau_c \ll \Delta t \ll \frac{m}{\mu}. \quad (9.94)$$

It should be stressed that the generalized Langevin equation (Eq. 9.89) is an exact equation which can be demonstrated with the formalism of Mori [138]. This gives a particular importance to equation (9.93) because it is applicable to any correlation function $C(t)$ and its associated memory function $M(t)$ is related by the following expression:

$$\frac{d}{dt}C(t) = - \int_0^t M(t-t') C(t') dt'. \quad (9.95)$$

Note also that the relation between the velocity autocorrelation function (Eq. 9.93) and the memory function is simplified when its Fourier–Laplace transform is carried out¹³. This relation is expressed as:

$$\begin{aligned} m \int_0^\infty \frac{d}{dt} \langle v(0)v(t) \rangle \exp(-i\omega t) dt = \\ = - \int_0^\infty \left[\int_0^t M(t-t') \langle v(0)v(t') \rangle dt' \right] \exp(-i\omega t) dt. \end{aligned} \quad (9.96)$$

¹³The Laplace-Fourier transform is a Laplace transform in which the complex variable p reduces to the imaginary variable $-i\omega$. Unlike the Fourier transform, its domain of integration is $(0, \infty)$. It is useful when the functions to be integrated are zero for $t < 0$.

To evaluate the left hand side of the above relation, we perform an integration by parts:

$$\begin{aligned} \int_0^\infty \frac{d}{dt} \langle v(0)v(t) \rangle \exp(-i\omega t) dt &= \left[\langle v(0)v(t) \rangle \exp(-i\omega t) \right]_0^\infty \\ &+ i\omega \int_0^\infty \langle v(0)v(t) \rangle \exp(-i\omega t) dt. \end{aligned} \quad (9.97)$$

Then use is made of the Fourier–Laplace transform of the velocity autocorrelation function and the memory function ¹⁴:

$$C_v(\omega) = \int_0^\infty \langle v(0)v(t) \rangle \exp(-i\omega t) dt, \quad (9.98)$$

$$M(\omega) = \int_0^\infty M(\tau) \exp(-i\omega \tau) d\tau, \quad (9.99)$$

where $\tau = t - t'$. After inverting the integrations, the right hand side of equation (9.96) becomes¹⁵:

$$- \int_0^\infty \left[\int_0^t M(t-t') \langle v(0)v(t') \rangle dt' \right] \exp(-i\omega t) dt = -M(\omega)C_v(\omega). \quad (9.100)$$

By using equations (9.97) and (9.100) to express equation (9.96), it follows:

$$- \langle v(0)v(0) \rangle + i\omega C_v(\omega) = -M(\omega)C_v(\omega), \quad (9.101)$$

or:

$$C_v(\omega) = \frac{\langle v^2(0) \rangle}{i\omega + M(\omega)}. \quad (9.102)$$

This is the simplest relationship which can connect the Fourier–Laplace transform of the velocity autocorrelation function with that of

¹⁴Unless otherwise stated, the notation will be the same for the function $M(t)$ and its Fourier-Laplace transform denoted $M(\omega)$.

¹⁵With the change of variables $\tau = t - t'$, we find:

$$\begin{aligned} \int_0^\infty \left[\int_0^t M(t-t') \langle v(0)v(t') \rangle dt' \right] \exp(-i\omega t) dt &= \\ &= \int_0^\infty \left[\int_0^\infty M(\tau) \exp[-i\omega(\tau+t')] d\tau \right] \langle v(0)v(t') \rangle dt' \\ &= \int_0^\infty \left[\int_0^\infty M(\tau) \exp(-i\omega\tau) d\tau \right] \langle v(0)v(t') \rangle \exp(-i\omega t') dt' = M(\omega)C_v(\omega). \end{aligned}$$

the associated memory function. The general problem which arises is to deduce the memory function from the autocorrelation function. In some circumstances, it is possible, conversely, to extract the memory function from the autocorrelation function.

The rest of this section is devoted to the formal relationship connecting the autocorrelation function to the memory function. The general theoretical framework was laid down by Zwanzig [139] and Mori [138], and presented in detail by Berne et al. [140]. The essential content of the theory is contained in the integro-differential Volterra equation:

$$\frac{d}{dt} C(t) = - \int_0^t M(t-t') C(t') dt', \quad (9.103)$$

where $C(t)$ is the autocorrelation function of the dynamical variable $A(t)$, and $M(t-t')$ the kernel of the integral called the *memory function* and introduced by Zwanzig; the corresponding expression is:

$$M(t) = \langle i\mathcal{L}A \exp[i(1-\mathcal{P})\mathcal{L}t] i\mathcal{L}A \rangle, \quad (9.104)$$

where $\mathcal{L}$ is the Liouville operator and $\mathcal{P}$ the projection operator.

In practice, equation (9.104) is very difficult to be used. Hence, with a view to present the concept of memory function in the simplest way, we focus exclusively on equation (9.103) where $C(t)$ is the velocity autocorrelation function. This equation is identical to equation (9.93) involving the generalized Langevin equation, bearing in mind that such an equation (9.103) exists for each dynamical variable. To investigate the dynamics of *real liquids*, it is necessary for the correlation time of the random force $F(t)$ to be *finite*. One way to take account of this hypothesis is to write the mean value of $F(t)$ and the force autocorrelation function (Eq. 9.88) as:

$$\langle F(t) \rangle = 0 \quad (9.105)$$

and:

$$\langle F(0)F(t) \rangle = k_B T M(t), \quad (9.106)$$

where $M(t)$ is the memory function within the generalized Langevin equation (Eq. 9.89):

$$m \frac{dv}{dt} = - \int_0^t M(t-t') v(t') dt' + F(t). \quad (9.107)$$

Thus, in the generalized Langevin theory, the memory function $M(t)$ is proportional to the force autocorrelation function.

Incidentally, when writing $M(t) = 2\mu\delta(t)$, we note that the conventional Langevin equation (Eq. 9.45) and all related properties are recovered, especially the coefficient of friction (Eq. 9.64):

$$\mu = \frac{1}{2k_{\text{B}}T} \int_{-\infty}^{+\infty} \langle F(0)F(t) \rangle dt, \quad (9.108)$$

the velocity-force correlation function (Eqs. 9.76 and 9.77) and the velocity autocorrelation function (Eq. 9.82):

$$\langle v(0)v(t) \rangle = \frac{k_{\text{B}}T}{m} \exp\left(-\frac{\mu}{m} |t|\right). \quad (9.109)$$

Note that, in the conventional Langevin equation, it has been assumed that the force $F(t)$ is a stationary random function of *Gaussian* character with an *infinitely short* correlation time, unlike what we have in the general case where the memory function is frequently used under the exponential form:

$$M(t) = \gamma \exp(-\alpha t). \quad (9.110)$$

As a result, the force becomes a random function of *Gaussian* and *Markovian* character¹⁶ with a finite correlation time. Equation (9.110) is certainly not exact, but it nevertheless leads to an efficient and very useful expression of the velocity autocorrelation function, as will be shown in the following section.

9.7 Phenomenological model of memory functions

It is sufficient to observe equations (9.104) and (9.103) to see that the memory function $M(t)$ and the autocorrelation function $C(t)$ are very difficult to determine exactly. To easily comprehend the concept of memory function, an empirical approach can be used: it consists in choosing a functional form for the memory function, from which the autocorrelation function is derived with equation (9.103). Several expressions of $M(t)$ have been proposed (such as the exponential

¹⁶See footnote 10 in this chapter: a random function has a Gaussian and Markovian character when its autocorrelation function is an exponential decreasing function of time.

function [140], the Gaussian function [141], a combination¹⁷ between these functions) to calculate the velocity autocorrelation function with equation (9.93) and related properties (diffusion coefficient (Eq. 9.71), spectral density (Eq. 9.85)). The comparison of the results with those of molecular dynamics [57] showed that the exponential form (Eq. 9.110) is a pretty good choice, while being particularly well suited to mathematical treatment, as will be shown in the next paragraphs.

By substituting equation (9.110) in equation (9.103), it follows:

$$\frac{d}{dt} C(t) = - \int_0^t \gamma \exp[-\alpha(t-t')] C(t') dt'. \quad (9.111)$$

To solve this equation, we assume, without prejudging its final form, that the normalized velocity autocorrelation function is written $C(t) = C_1(t) \exp(-\alpha t)$, with the initial conditions $C(0) = 1$ and $\dot{C}(0) = 0$. After transferring the function $C(t)$ into equation (9.111), the integro-differential equation is reduced to:

$$\begin{aligned} \frac{d}{dt} C_1(t) \exp(-\alpha t) - \alpha C_1(t) \exp(-\alpha t) = \\ = -\gamma \int_0^t \exp[-\alpha(t-t')] C_1(t') \exp(-\alpha t') dt' \end{aligned} \quad (9.112)$$

$$\frac{d}{dt} C_1(t) - \alpha C_1(t) = -\gamma \int_0^t C_1(t') dt', \quad (9.113)$$

so that its differentiation with respect to the time yields the second order differential equation:

$$\ddot{C}_1(t) - \alpha \dot{C}_1(t) + \gamma C_1(t) = 0. \quad (9.114)$$

Searching for the solution $C_1(t)$ of this differential equation does not pose any problem. As regards the normalized velocity autocorrelation function $C(t) = C_1(t) \exp(-\alpha t)$, it depends on the initial conditions and values of the parameters α and γ . Three cases arise:

¹⁷Levesque and Verlet [143] suggested to use the functional form:

$$M(t) = \Omega_0^2 \exp\left(-\frac{t^2}{\tau^2}\right) + \gamma t^4 \exp(-\alpha t),$$

where Ω_0^2 , τ , γ and α are parameters adjusted on simulation results.

(1) If $\alpha^2 - 4\gamma > 0$, the solution is:

$$C(t) = \exp\left(-\frac{\alpha}{2}t\right) \left[\cosh\left(\frac{\sqrt{\alpha^2 - 4\gamma}}{2}t\right) + \frac{\alpha}{\sqrt{\alpha^2 - 4\gamma}} \sinh\left(\frac{\sqrt{\alpha^2 - 4\gamma}}{2}t\right) \right]. \quad (9.115)$$

(2) If $\alpha^2 - 4\gamma = 0$, the solution is:

$$C(t) = \exp\left(-\frac{\alpha}{2}t\right) \left(1 + \frac{\alpha}{2}t\right). \quad (9.116)$$

(3) if $\alpha^2 - 4\gamma < 0$, the solution is:

$$C(t) = \exp\left(-\frac{\alpha}{2}t\right) \left[\cos\left(\frac{\sqrt{4\gamma - \alpha^2}}{2}t\right) + \frac{\alpha}{\sqrt{4\gamma - \alpha^2}} \sin\left(\frac{\sqrt{4\gamma - \alpha^2}}{2}t\right) \right]. \quad (9.117)$$

In looking at the expressions of the force autocorrelation function (Eqs. 9.106 and 9.110) and the velocity autocorrelation function (Eqs. 9.115, 9.116 and 9.117), we see that the force is a random function of Gaussian and Markovian character (see footnote 10 of this chapter), in contrast to the velocity. In the following, we seek the special condition under which the velocity becomes a Markovian random function. To this end, we compare the quantities $1/\alpha$ and $1/\sqrt{\gamma}$, whose dimensions are those of time, in noting that they correspond to two different time scales (Eq. 9.94): $\tau_c \sim 1/\alpha$ and $\tau_r \sim 1/\sqrt{\gamma}$. If τ_c is very small compared to τ_r , it leads to the inequality $\alpha^2 - 4\gamma \gg 0$. In this case and taking the given initial conditions into account, the normalized velocity autocorrelation function (Eq. 9.115) reduces to the expression:

$$C(t) \simeq \exp\left(-\frac{\alpha}{2}t\right) \exp\left(\frac{\alpha}{2}\sqrt{1 - \frac{4\gamma}{\alpha^2}}t\right) \simeq \exp\left(-\frac{\gamma}{\alpha}t\right), \quad (9.118)$$

where the approximation $\sqrt{1 - 4\gamma/\alpha^2} \sim 1 - 2\gamma/\alpha^2$ has been used to obtain the last identity. Consequently, when $\tau_c \ll \tau_r$, the velocity autocorrelation function behaves as an exponential decreasing function, and the velocity becomes a random function of Gaussian and Markovian character. Of course, this situation applies to the diluted fluid. Moreover, in identifying equations (9.118) and (9.109), we can assign a physical meaning to the ratio of parameters γ and α , namely $\gamma/\alpha = \mu/m$. In contrast, for intermediate densities, the simulation

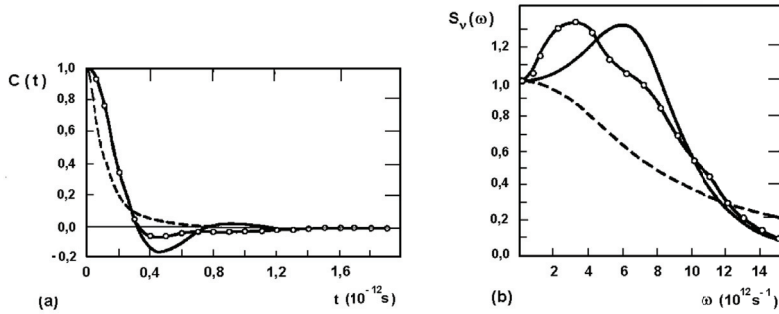


Figure 9.8: Representations of (a) the normalized autocorrelation function and (b) the normalized spectral density of the velocity in the model of Berne et al. [140] with the values of $\alpha = 8.06 \cdot 10^{12} \text{ s}^{-1}$ and $\gamma = 6.5 \cdot 10^{25} \text{ s}^{-2}$. The empty dots correspond to numerical simulation results. The solid curves are obtained with equations (9.117) and (9.162), and dashed curves with equations (9.118) and (9.164).

and kinetic theory [144, 145, 146, 147] have shown that the velocity autocorrelation function displays a gradual decrease proportional to $t^{-3/2}$, at long times (between 5τ and 30τ , where τ is the time interval between two collisions), and not an exponential decay. This is generally assigned to the fact that the memory function $M(t)$ exhibits two simultaneous collisional processes. The first process, associated with the *binary collisions* between atoms, has a small relaxation time whereas the second process, associated with a *coupling phenomenon*, has a relaxation time of 5 to 30 times longer.

The foregoing model, developed by Berne et al. [140], has been used to determine the normalized velocity autocorrelation function $C(t) = \frac{\langle v(0)v(t) \rangle}{\langle v^2(0) \rangle}$ of liquid argon, with the parameters α and γ adjusted on the results of molecular dynamics [57]. The process is clearly non-Markovian, considering that the best fit (Fig. 9.8a) is obtained by means of equation (9.117) with the values $\alpha = 8.06 \cdot 10^{12} \text{ s}^{-1}$ and $\gamma = 6.5 \cdot 10^{25} \text{ s}^{-2}$. Note that $C(t)$ makes it possible to determine the diffusion coefficient D . Its numerical value¹⁸ for liquid argon ($T = 94.4 \text{ K}$, $k_B = 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$ and $m = \frac{M}{N} = 6.64 \cdot 10^{-26} \text{ kg}$) is:

¹⁸The calculation of the diffusion coefficient D is made by substituting equation (9.117) in equation (9.71), i.e.:

$$D = \int_0^\infty \langle v(0)v(t) \rangle dt = \frac{k_B T}{m} \frac{\alpha}{\gamma} = 2.43 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}. \quad (9.119)$$

For liquids, it is remarkable that equation (9.117) reproduces qualitatively the results of molecular dynamics, with a significant increase in the amplitude of oscillations of the normalized velocity correlation function (Fig. 9.8a). The physical origin of the negative part of the velocity autocorrelation function can be interpreted in terms of *bounces* of an atom against the walls of the cage formed by its nearest neighbours [148]. Indeed, in the case of a liquid where each atom is trapped in such a cage, the time interval between two collisions ($\tau_c \sim 1/\alpha \sim 1.24 \cdot 10^{-13}$ s) is of the same order of magnitude as the duration of a collision ($\tau_r \sim 1/\sqrt{\gamma} \sim 1.24 \cdot 10^{-13}$ s).

9.8 Velocity autocorrelation function at short times

The frequency moments

In the previous section, it has been seen that the phenomenological model of Berne et al. [140] allows us to describe, at least qualitatively, the behaviour of the velocity autocorrelation function in the region of *intermediate times*, where it takes negative values. It has also

$$D = \langle v^2(0) \rangle \int_0^\infty \exp\left(-\frac{\alpha}{2}t\right) \left[\cos\left(\frac{\sqrt{4\gamma-\alpha^2}}{2}t\right) + \frac{\alpha}{\sqrt{4\gamma-\alpha^2}} \sin\left(\frac{\sqrt{4\gamma-\alpha^2}}{2}t\right) \right] dt.$$

In using the results of the integrals (I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, Acad. Press, New York (1965), p. 477):

$$\begin{aligned} \int_0^\infty \exp\left(-\frac{\alpha}{2}t\right) \cos(\Omega t) dt &= \frac{\frac{\alpha}{2}}{\left(\frac{\alpha}{2}\right)^2 + \Omega^2}, \\ \text{and} \quad \int_0^\infty \exp\left(-\frac{\alpha}{2}t\right) \sin(\Omega t) dt &= \frac{\Omega}{\left(\frac{\alpha}{2}\right)^2 + \Omega^2}, \end{aligned}$$

and in putting $\langle v^2(0) \rangle = \frac{k_B T}{m}$, the expression of D reduces to:

$$D = \langle v^2(0) \rangle \frac{\alpha}{\gamma} = \frac{k_B T}{m} \frac{\alpha}{\gamma}.$$

been noted that, in systems where a Markov process takes place, the autocorrelation functions undergo an exponential decay at *long times* (or more accurately an asymptotic behaviour in $t^{-3/2}$). Here, we seek to determine the behaviour of autocorrelation functions for *short times* by using the Maclaurin series about $t = 0$. For the autocorrelation function $C(t)$, this expansion is written:

$$C(t) = C(0) + t \frac{dC(t)}{dt} \Big|_{t=0} + \frac{t^2}{2!} \frac{d^2C(t)}{dt^2} \Big|_{t=0} + \frac{t^3}{3!} \frac{d^3C(t)}{dt^3} \Big|_{t=0} + \frac{t^4}{4!} \frac{d^4C(t)}{dt^4} \Big|_{t=0} + \dots \quad (9.120)$$

If the autocorrelation function $C(t)$ is supposed to be a function of the spectral density $S_C(\omega)$ of the corresponding dynamical variable (Eq. 9.156), i.e.:

$$C(t) = \int_{-\infty}^{\infty} S_C(\omega) \exp(i\omega t) d\omega, \quad (9.121)$$

then $C(0)$ can be evaluated as well as all the derivatives of $C(t)$ with respect to t , at time $t = 0$. These derivatives represent the frequency moments A_k associated with the autocorrelation function¹⁹:

$$C(0) = \int_{-\infty}^{\infty} S_C(\omega) d\omega = A_0, \quad (9.122)$$

$$\frac{dC(t)}{dt} \Big|_{t=0} = i \int_{-\infty}^{\infty} \omega S_C(\omega) d\omega = iA_1, \quad (9.123)$$

$$\frac{d^2C(t)}{dt^2} \Big|_{t=0} = - \int_{-\infty}^{\infty} \omega^2 S_C(\omega) d\omega = -A_2, \quad (9.124)$$

$$\frac{d^3C(t)}{dt^3} \Big|_{t=0} = -i \int_{-\infty}^{\infty} \omega^3 S_C(\omega) d\omega = -iA_3, \quad (9.125)$$

$$\frac{d^4C(t)}{dt^4} \Big|_{t=0} = \int_{-\infty}^{\infty} \omega^4 S_C(\omega) d\omega = A_4, \quad (9.126)$$

$$\dots = \dots;$$

$$\frac{d^kC(t)}{dt^k} \Big|_{t=0} = (i)^k \int_{-\infty}^{\infty} \omega^k S_C(\omega) d\omega = (i)^k A_k, \dots \quad (9.127)$$

¹⁹In terms of mathematical statistics, the normalized autocorrelation function $C(t)$ (with $C(0) = A_0 = 1$) behaves as a generating function, and the spectral density $S(\omega)$ as a probability density (Eq. 2.129).

As it will be explained at the beginning of the next section, both $C(t)$ and $S_C(\omega)$ are real and even functions. Therefore, the expansion of the autocorrelation function $C(t)$ contains only even powers of time, whose coefficients have the general expression:

$$\left. \frac{d^{2n} C(t)}{dt^{2n}} \right|_{t=0} = (-1)^n \int_{-\infty}^{\infty} \omega^{2n} S_C(\omega) d\omega = (-1)^n A_{2n}. \quad (9.128)$$

These relations are the sum rules used to write the autocorrelation function (Eq. 9.120) in terms of the frequency moments A_{2n} , as:

$$C(t) = \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n)!} A_{2n} t^{2n}. \quad (9.129)$$

However, what has been done for the autocorrelation function $C(t)$ may also be done for the memory function $M(t)$. Consequently, the sum rules and the expansion of the memory function can be written, respectively, in the following forms:

$$\left. \frac{d^{2n} M(t)}{dt^{2n}} \right|_{t=0} = (-1)^n \int_{-\infty}^{\infty} \omega^{2n} S_M(\omega) d\omega = (-1)^n B_{2n}, \quad (9.130)$$

$$\text{and} \quad M(t) = \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n)!} B_{2n} t^{2n}, \quad (9.131)$$

where B_{2n} are the frequency moments associated with the memory function.

Finally, a comprehensive study of the memory function formalism - not carried out here - shows that the frequency moments A_{2n} and B_{2n} are connected by the following relations:

$$\begin{aligned} B_0 &= A_2, \\ B_2 &= A_4 - A_2^2, \\ B_4 &= A_6 - 2A_4A_2 + A_2^3, \\ \dots &= \dots \end{aligned} \quad (9.132)$$

Analytical expressions of the frequency moments A_2 and A_4

Equations (9.129) and (9.131) allow an accurate determination of the autocorrelation function $C(t)$ and the memory function $M(t)$, provided that all the frequency moments A_{2n} are known. However, with the exception of the first two or three moments, the other ones are very difficult to calculate, so that it is not expected to make a precise dynamic description of liquids, except for the short times.

In what follows, we give, even though without proof, the expressions of the frequency moments A_2 and A_4 of the velocity autocorrelation function. Specifically for liquids, where the atoms interact by means of a continuous pair potential $u(r)$, it has been shown [149, 150] that the normalized velocity autocorrelation function can be expanded as:

$$\begin{aligned} C(t) &= \frac{\langle v(0)v(t) \rangle}{\langle v^2(0) \rangle} = \frac{m}{k_B T} \langle v(0)v(t) \rangle \\ &= 1 - \frac{m}{k_B T} \langle \dot{v}_x^2 \rangle \frac{t^2}{2} + \frac{m}{k_B T} \langle \ddot{v}_x^2 \rangle \frac{t^4}{4!} - \dots, \end{aligned} \quad (9.133)$$

where $\dot{v}_x$ and $\ddot{v}_x$ are the first and second derivatives of the unidirectional velocity, and their mean values are calculated on all the atoms. It can be observed that the slope of the velocity autocorrelation function is zero at $t = 0$, like in the generalized Langevin model (Fig. 9.6b). After identifying member to member the terms in the previous relation by comparing them with those of equation (9.129), we note that $A_0 = 1$ because the autocorrelation function is normalized. The frequency moment A_2 has been calculated by de Gennes [151] as a function of the pair potential $u(r)$ and the pair correlation function $g(r)$. The result is:

$$\begin{aligned} A_2 &= \frac{m}{k_B T} \langle \dot{v}_x^2 \rangle = \frac{\rho}{3m} \int g(r) \Delta_r u(r) dr \\ &= \frac{4\pi\rho}{3m} \int_0^\infty r^2 g(r) \left[u''(r) + \frac{2}{r} u'(r) \right] dr, \end{aligned} \quad (9.134)$$

where the term in brackets is the contribution of the radial Laplacian in spherical coordinates of the function $u(r)$. Equation (9.134) contains the particle density $\rho = N/V$, the atom mass m , the pair correlation function $g(r)$ and the first and second derivatives of the

pair potential $u(r)$. Since the frequency moment A_2 has the dimension of the square of a frequency, it is denoted $A_2 = \Omega_0^2$. For almost every continuous pair potential, the major contribution to the integral is given by the term $r^2 g(r) u''(r)$ which is precisely the square of the Einstein frequency:

$$\Omega_E^2 = \frac{4\pi\rho}{3m} \int_0^\infty r^2 g(r) u''(r) dr. \quad (9.135)$$

The calculation of the frequency moment A_4 is more difficult. It has been carried out by Nijboer and Rahman [149] and reads:

$$A_4 = \frac{m}{k_B T} \langle \ddot{v}_x^2 \rangle = A_{41} + A_{42}, \quad (9.136)$$

with

$$A_{41} = \frac{2\rho}{m^2} \int g(r) \frac{1}{3} \sum_{\alpha=x,y,z} \left[\nabla_r \frac{\alpha u'(r)}{r} \right]^2 dr \quad (9.137)$$

and

$$A_{42} = \frac{\rho^2}{m^2} \int g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \frac{1}{3} \sum_{\alpha=x,y,z} \left\{ \left[\nabla_{r_2} \frac{\alpha_2 u'_2}{r_2} \right] \left[\nabla_{r_3} \frac{\alpha_3 u'_3}{r_3} \right] \right\} d\mathbf{r}_2 d\mathbf{r}_3, \quad (9.138)$$

where the index α represents one of the coordinates (x , y or z) of the atoms. To calculate the integral in the expression of A_{42} , it is judicious to use the bipolar coordinates (Fig. 9.9) with $r_2 = r_{12}$, $r_3 = r_{13}$, $u'_2 = \frac{du(r_{12})}{dr_{12}}$ and $u'_3 = \frac{du(r_{13})}{dr_{13}}$ in order to simplify the notations.

After using the expansions of the gradients²⁰, the expression of A_{41} is written in the final form:

²⁰The expansion of the gradient in the expression A_{41} is written:

$$\begin{aligned} \nabla_r \frac{xu'(r)}{r} &= \frac{\partial}{\partial x} \left(\frac{xu'}{r} \right) \mathbf{i} + \frac{\partial}{\partial y} \left(\frac{xu'}{r} \right) \mathbf{j} + \frac{\partial}{\partial z} \left(\frac{xu'}{r} \right) \mathbf{k} \\ &= \left[\frac{u'}{r} + \frac{x^2}{r^2} \left(u'' - \frac{u'}{r} \right) \right] \mathbf{i} + \left[\frac{xy}{r^2} \left(u'' - \frac{u'}{r} \right) \right] \mathbf{j} + \left[\frac{xz}{r^2} \left(u'' - \frac{u'}{r} \right) \right] \mathbf{k}, \end{aligned}$$

$$\text{hence} \quad \left[\nabla_r \frac{xu'(r)}{r} \right]^2 = \frac{u'^2}{r^2} - \frac{x^2 u'^2}{r^4} + \frac{x^2 u''^2}{r^2},$$

and:

$$\sum_{\alpha=x,y,z} \left[\nabla_r \frac{\alpha u'(r)}{r} \right]^2 = 3 \frac{u'^2}{r^2} - (x^2 + y^2 + z^2) \frac{u'^2}{r^4} + (x^2 + y^2 + z^2) \frac{u''^2}{r^2} = 2 \frac{u'^2(r)}{r^2} + u''^2.$$

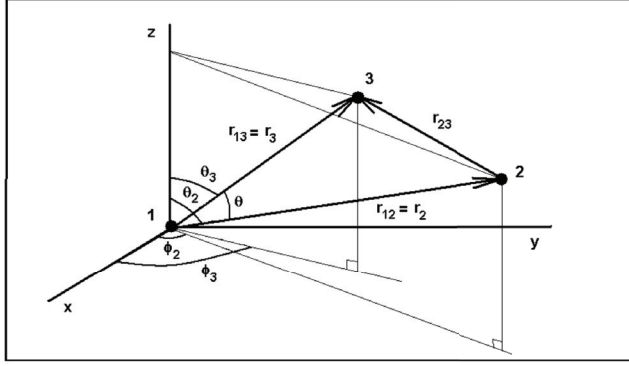


Figure 9.9: Bipolar coordinates of atoms 1, 2 and 3.

Regarding the product of gradients in the expression of A_{42} , it is:

$$\begin{aligned} \left[\nabla_{r_2} \frac{\alpha_2 u'_2}{r_2} \right] \left[\nabla_{r_3} \frac{\alpha_3 u'_3}{r_3} \right] &= \left[\frac{u'_2}{r_2} + \frac{x_2^2}{r_2^2} \left(u''_2 - \frac{u'_2}{r_2} \right) \right] \left[\frac{u'_3}{r_3} + \frac{x_3^2}{r_3^2} \left(u''_3 - \frac{u'_3}{r_3} \right) \right] \\ &+ \left[\frac{x_2 y_2}{r_2^2} \left(u''_2 - \frac{u'_2}{r_2} \right) \right] \left[\frac{x_3 y_3}{r_3^2} \left(u''_3 - \frac{u'_3}{r_3} \right) \right] + \left[\frac{x_2 z_2}{r_2^2} \left(u''_2 - \frac{u'_2}{r_2} \right) \right] \left[\frac{x_3 z_3}{r_3^2} \left(u''_3 - \frac{u'_3}{r_3} \right) \right] \\ &= \frac{u'_2}{r_2} \frac{u'_3}{r_3} + \frac{u'_2}{r_2} \frac{x_3^2}{r_3^2} \left(u''_3 - \frac{u'_3}{r_3} \right) + \frac{u'_3}{r_3} \frac{x_2^2}{r_2^2} \left(u''_2 - \frac{u'_2}{r_2} \right) + \frac{x_2 x_3}{r_2 r_3} \left(u''_2 - \frac{u'_2}{r_2} \right) \left(u''_3 - \frac{u'_3}{r_3} \right) \mu, \end{aligned}$$

where μ is an auxiliary variable defined by the scalar product $\mathbf{r}_2 \cdot \mathbf{r}_3 = r_2 r_3 \cos \theta = x_2 x_3 + y_2 y_3 + z_2 z_3$, i.e.:

$$\mu = \cos \theta = \frac{x_2 x_3 + y_2 y_3 + z_2 z_3}{r_2 r_3}.$$

By using two similar expressions for the indexes $\alpha_2 = y_2$ and z_2 , on one hand, and $\alpha_3 = y_3$ and z_3 , on the other hand, we deduce the following equation after some elementary calculations:

$$\begin{aligned} \sum_{\alpha_i=x,y,z} \left\{ \left[\nabla_{r_2} \frac{\alpha_2 u'_2}{r_2} \right] \left[\nabla_{r_3} \frac{\alpha_3 u'_3}{r_3} \right] \right\} &= \\ &= u''_2 u'_3 \mu^2 + \frac{u'_2}{r_2} \frac{u'_3}{r_3} (1 + \mu^2) + \left(\frac{u'_2 u''_3}{r_2} + \frac{u'_3 u''_2}{r_3} \right) (1 - \mu^2). \end{aligned}$$

$$\begin{aligned}
A_{41} &= \frac{2\rho}{m^2} \int g(r) \frac{1}{3} \sum_{\alpha=x,y,z} \left[\nabla_r \frac{\alpha u'(r)}{r} \right]^2 d\mathbf{r} \\
&= \frac{8\pi\rho}{3m^2} \int_0^\infty r^2 g(r) \left[u''^2(r) + \frac{2}{r^2} u'^2(r) \right] dr. \quad (9.139)
\end{aligned}$$

As far as the expression of A_{42} is concerned, it can be changed as follows using the results of the previous note:

$$\begin{aligned}
A_{42} &= \frac{\rho^2}{3m^2} \int g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \left[u_2'' u_3'' \mu^2 + \frac{u_2'}{r_2} \frac{u_3'}{r_3} (1 + \mu^2) \right. \\
&\quad \left. + \left(\frac{u_2' u_3''}{r_2} + \frac{u_3' u_2''}{r_3} \right) (1 - \mu^2) \right] d\mathbf{r}_2 d\mathbf{r}_3. \quad (9.140)
\end{aligned}$$

In order to calculate the two-centre integral in the above relation, we use equations (5.109) and (5.114) which provide dr_{23} as a function of $d\mu$, and the volume elements $d\mathbf{r}_2$ and $d\mathbf{r}_3$, respectively:

$$\mu = \cos \theta = \frac{r_{13}^2 + r_{12}^2 - r_{23}^2}{2r_{12}r_{13}}, \quad (9.141)$$

$$\text{hence} \quad d\mu = -\frac{r_{23}}{r_{12}r_{13}} dr_{23}, \quad (9.142)$$

as well as

$$d\mathbf{r}_2 = 4\pi r_{12}^2 dr_{12} \quad (9.143)$$

$$\text{and} \quad d\mathbf{r}_3 = 2\pi \frac{r_{13}r_{23}}{r_{12}} = -2\pi \frac{r_{13}r_{23}}{r_{12}} dr_{13} \frac{r_{12}r_{13}}{r_{23}} d\mu. \quad (9.144)$$

After substituting the integration element $d\mathbf{r}_2 d\mathbf{r}_3$ in equation (9.140), we obtain A_{42} :

$$\begin{aligned}
A_{42} &= \frac{\rho^2}{3m^2} \int_0^\infty \int_0^\infty \int_{-1}^1 f(\mu, r_2, r_3) \times 4\pi r_{12}^2 dr_{12} \times 2\pi \frac{r_{13}r_{23}}{r_{12}} dr_{13} \frac{r_{12}r_{13}}{r_{23}} d\mu \\
&= \frac{8\pi^2 \rho^2}{3m^2} \int_0^\infty \int_0^\infty r_{12}^2 dr_{12} r_{13}^2 dr_{13} \int_{-1}^1 f(\mu, r_2, r_3) d\mu, \quad (9.145)
\end{aligned}$$

with

$$\begin{aligned}
f(\mu, r_2, r_3) &= g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \left[u_2'' u_3'' \mu^2 + \frac{u_2'}{r_2} \frac{u_3'}{r_3} (1 + \mu^2) \right. \\
&\quad \left. + \left(\frac{u_2' u_3''}{r_2} + \frac{u_3' u_2''}{r_3} \right) (1 - \mu^2) \right]. \quad (9.146)
\end{aligned}$$

Without precise knowledge of the three-body correlation function $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, the integral is evaluated with the help of the Kirkwood superposition approximation (Eq. 5.107).

Let us take the dynamic properties of cesium with a metallic pair potential along the liquid-vapour coexistence curve as a relevant example. It has been shown [152] that the frequency moment A_2 increases with the density while the frequency moment A_4 remains practically constant, and this moment A_4 gives rise to oscillations on the VACF for high densities in the liquid metals. For this purpose, the empirical model of Tankeshwar et al. [153] has been used; it is based on the fact that the velocity autocorrelation function of a liquid at low density (or high temperature) is always positive, whereas it predicts negative correlations at high density.

9.9 Some useful relations and sum rules

The infinite continued fraction

The autocorrelation function $C(t)$ of a given dynamical variable is related to the memory function $M(t)$ by an integro-differential equation (Eq. 9.103), namely:

$$\frac{d}{dt}C(t) = - \int_0^t M(t-t')C(t')dt'. \quad (9.147)$$

Since $C(t)$ is a *real* function, the memory function $M(t)$ is likewise a *real* function. In addition, as the autocorrelation function depends on the values of the memory function at times t' earlier than t , the Fourier–Laplace transform $C(\omega)$ of $C(t)$ can be readily calculated. For a non-normalized autocorrelation function $C(t)$, the result is (Eq. 9.102):

$$C(\omega) = \frac{C(t=0)}{i\omega + M(\omega)}, \quad (9.148)$$

where the Fourier–Laplace transforms of $C(t)$ and $M(t)$ are complex functions defined by the expressions:

$$C(\omega) = \int_0^\infty C(t) \exp(-i\omega t) dt = C'(\omega) + iC''(\omega), \quad (9.149)$$

$$M(\omega) = \int_0^\infty M(t) \exp(-i\omega t) dt = M'(\omega) + iM''(\omega). \quad (9.150)$$

Since $C(t)$ is a *real* function, the real part $C'(\omega)$ of its Fourier transform is an *even* function and the imaginary part $C''(\omega)$ an *odd* function (see equations 10.67 and 10.68). If, moreover, the function $C(t)$ is *even*, its Fourier transform $C(\omega)$ is also a *real* and *even* function, as shown by calculating the spectral density of the velocity autocorrelation function (Eq. 9.87).

Equation (9.147), which links the autocorrelation function $C(t)$ with the memory function $M(t)$, can be regarded as the approximate equation of motion of a given dynamical variable. Mori [138] has shown that this approximate equation is all the better as the process is close to a Markov process, that is to say that the autocorrelation function undergoes a decay in $\exp(-\alpha t)$. Since this is not always the case, this author proposed to link the initial memory function $M^{(1)}(t)$ with a memory function $M^{(2)}(t)$ decreasing more rapidly and which is related to $M^{(1)}(t)$ by the equation:

$$\frac{d}{dt}M^{(1)}(t) = - \int_0^t M^{(2)}(t-t')M^{(1)}(t')dt'. \quad (9.151)$$

The author assumed that the memory function $M^{(2)}(t)$ has a memory function $M^{(3)}(t)$ of higher order, etc. in such a way that all together the equations form a coupled system of integro-differential equations, from which the respective Fourier–Laplace transforms are defined according to equation (9.148) by the expressions:

$$C(\omega) = \frac{C(t=0)}{i\omega + M^{(1)}(\omega)}, \quad (9.152)$$

$$M^{(1)}(\omega) = \frac{M^{(1)}(t=0)}{i\omega + M^{(2)}(\omega)}, \quad (9.153)$$

$$M^{(2)}(\omega) = \frac{M^{(2)}(t=0)}{i\omega + M^{(3)}(\omega)}, \quad (9.154)$$

$$\dots = \dots$$

By gradually replacing these expressions of the memory functions one in the other, we arrive at the infinite continued fraction:

$$C(\omega) = \frac{C(t=0)}{i\omega + \frac{M^{(1)}(t=0)}{i\omega + \frac{M^{(2)}(t=0)}{i\omega + \dots}}}, \quad (9.155)$$

which can be interrupted at any time by a procedure that will be described later.

The spectral density

When $C(t)$ is the non-normalized autocorrelation function of a given dynamical variable, the spectral density $S_C(\omega)$ of this dynamical variable is defined by the Fourier transform (Eq. 9.85):

$$S_C(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t) \exp(-i\omega t) dt, \quad (9.156)$$

where, according to the previous remarks, $C(t)$ and $S_C(\omega)$ are two *real* and *even* functions.

As the spectral density $S_C(\omega)$ is a real function, the comparison of equations (9.156) and (9.149) leads to the following expression for the spectral density $S_C(\omega)$:

$$S_C(\omega) = \frac{1}{\pi} \int_0^{\infty} C(t) \cos(\omega t) dt = \frac{C'(\omega)}{\pi}, \quad (9.157)$$

$$\text{or: } S_C(\omega) = \frac{1}{\pi} \text{Re} [C(\omega)], \quad (9.158)$$

so that, with the help of equations (9.148) and (9.150), the spectral density becomes:

$$S_C(\omega) = \frac{1}{\pi} \text{Re} \left[\frac{C(t=0)}{i\omega + M(\omega)} \right] = \frac{1}{\pi} \text{Re} \left\{ \frac{C(t=0)}{M'(\omega) + i[\omega + M''(\omega)]} \right\}, \quad (9.159)$$

or:

$$S_C(\omega) = \frac{1}{\pi} \frac{M'(\omega)C(t=0)}{M'^2(\omega) + [\omega + M''(\omega)]^2}. \quad (9.160)$$

This relation is of great interest because it allows the calculation of the spectral density of a dynamical variable from the memory function, without having to know the autocorrelation function itself. Thus, the spectral density can be calculated, either by using the memory function with equation (9.160), or by using the autocorrelation function with equation (9.157).

By way of illustration, let us calculate the spectral density of velocity $S_v(\omega)$ within the Berne et al. [140] model by using the velocity

autocorrelation function $\langle v(0)v(t) \rangle = \langle v^2(0) \rangle C(t)$, where $\langle v^2(0) \rangle = k_B T/m$ and $C(t)$ is given by equation (9.117). By putting $\Omega = \frac{1}{2}\sqrt{4\gamma - \alpha^2}$, the spectral density (Eq. 9.157) is:

$$\begin{aligned} S_v(\omega) &= \frac{1}{\pi} \int_0^\infty \frac{k_B T}{m} \exp\left(-\frac{\alpha}{2}t\right) \left\{ \cos(\Omega t) + \frac{\alpha}{2\Omega} \sin(\Omega t) \right\} \cos(\omega t) dt \\ &= \frac{k_B T}{m} \frac{1}{2\pi} \int_0^\infty \exp\left(-\frac{\alpha}{2}t\right) \left\{ \cos[(\Omega + \omega)t] + \cos[(\Omega - \omega)t] \right\} dt \\ &\quad + \frac{k_B T}{m} \frac{\alpha}{4\pi\Omega} \int_0^\infty \exp\left(-\frac{\alpha}{2}t\right) \left\{ \sin[(\Omega + \omega)t] + \sin[(\Omega - \omega)t] \right\} dt. \quad (9.161) \end{aligned}$$

After the calculations²¹, the spectral density becomes:

$$S_v(\omega) = \frac{k_B T}{m} \frac{1}{\pi} \frac{\alpha\gamma}{\gamma^2 + \omega^2(\alpha^2 - 2\gamma) + \omega^4}. \quad (9.162)$$

According to the above, equation (9.162) can equally be obtained with equation (9.160) by using the memory function (Eq. 9.110). Indeed, since the velocity autocorrelation function is not normalized,

²¹In using the results of the integrals (I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, Acad. Press, New York (1965), p. 477), i.e.:

$$\begin{aligned} \int_0^\infty \exp\left(-\frac{\alpha}{2}t\right) \cos[(\Omega \pm \omega)t] dt &= \frac{\frac{\alpha}{2}}{\frac{\alpha^2}{4} + (\Omega \pm \omega)^2}, \\ \text{and} \quad \int_0^\infty \exp\left(-\frac{\alpha}{2}t\right) \sin[(\Omega \pm \omega)t] dt &= \frac{\Omega \pm \omega}{\frac{\alpha^2}{4} + (\Omega \pm \omega)^2}, \end{aligned}$$

it follows:

$$S_v(\omega) = \frac{k_B T}{m} \frac{1}{2\pi} S_v^{(1)}(\omega) + \frac{k_B T}{m} \frac{\alpha}{4\pi\Omega} S_v^{(2)}(\omega),$$

$$\text{with} \quad S_v^{(1)}(\omega) = \frac{\frac{\alpha^3}{4} + \alpha(\Omega^2 + \omega^2)}{\left(\frac{\alpha^2}{4}\right)^2 + \frac{\alpha^2}{2}(\Omega^2 + \omega^2) + (\Omega + \omega)^2(\Omega - \omega)^2}$$

$$\text{and} \quad S_v^{(2)}(\omega) = \frac{\frac{\alpha^2\Omega}{2} + (\Omega + \omega)^2(\Omega - \omega) + (\Omega - \omega)^2(\Omega + \omega)}{\left(\frac{\alpha^2}{4}\right)^2 + \frac{\alpha^2}{2}(\Omega^2 + \omega^2) + (\Omega + \omega)^2(\Omega - \omega)^2}.$$

After simplifications, we get:

$$S_v(\omega) = \frac{k_B T}{m} \frac{1}{\pi} \frac{\alpha\gamma}{\gamma^2 + \omega^2(\alpha^2 - 2\gamma) + \omega^4}.$$

it follows that $C(t=0) = k_B T/m$ in equation (9.160). As regards the calculation of the Laplace–Fourier transform of the memory function $M(t) = \gamma \exp(-\alpha t)$, with equation (9.150), it gives:

$$M(\omega) = \gamma \int_0^\infty \exp(-\alpha t) \exp(-i\omega t) dt = \frac{\gamma\alpha - i\gamma\omega}{\alpha^2 + \omega^2}. \quad (9.163)$$

Therefore, when the real part $M'(\omega) = \frac{\gamma\alpha}{\alpha^2 + \omega^2}$ and the imaginary part $M''(\omega) = -\frac{\gamma\omega}{\alpha^2 + \omega^2}$ of the complex function $M(\omega) = M'(\omega) + iM''(\omega)$ are substituted into equation (9.160), the expression for the spectral density $S_v(\omega)$ is readily obtained as it coincides with equation (9.162).

Note that the spectral density of a Markov process (where the normalized autocorrelation function is that of equation (9.118) (and not that of equation (9.117)) is expressed as:

$$S_v(\omega) = \frac{k_B T}{m} \frac{1}{\pi} \frac{\alpha\gamma}{\gamma^2 + \omega^2\alpha^2}. \quad (9.164)$$

This result is obtained in taking the real part of equation (9.156), owing to the calculation already carried out in footnote 11 in this chapter. The spectral density of velocity $S_v(\omega)$ of liquid argon has been calculated with the Berne et al. [140] model for the parameters $\alpha = 8.06 \cdot 10^{12} \text{ s}^{-1}$ and $\gamma = 6.5 \cdot 10^{25} \text{ s}^{-2}$. The curves representing the normalized spectral density $\frac{S_v(\omega)}{S_v(0)}$ obtained with equations (9.162) and (9.164) have been plotted in figure (9.7b).

Numerical determination of the memory function

In the previous sections, the autocorrelation functions have been computed from the empirically modeled memory function. However, it is also possible to accurately determine the autocorrelation function $C(t)$ directly from the molecular dynamics simulation. In this case, it may be desirable to calculate the memory function $M(t)$ associated with this normalized autocorrelation function. For this purpose, it is necessary to solve numerically the Volterra equation (Eq. 9.103):

$$\frac{d}{dt}C(t) = - \int_0^t M(t-t')C(t')dt'. \quad (9.165)$$

As solving the above equation is not a major problem when searching for the autocorrelation function from the memory function, the

inverse problem of obtaining the memory function from the autocorrelation function is more subtle. In this case, it is advisable to tabulate the values of the autocorrelation function $C(t)$ resulting from the molecular dynamics calculations at equal time intervals:

$$t_i = i\Delta t \quad \text{with} \quad i = 0, 1, \dots, 499, \quad (9.166)$$

with $C(0) = 1$ and $\Delta t = 5 \cdot 10^{-15}$ s. After discretization of equation (9.165), the memory function obtained by the traditional methods of integrations (rectangles and trapezoids) presents intrusive oscillations and abnormalities at short times. So, to improve the stability of the method, Berne and Harp [154] recommended solving the Volterra equation by using the derivative of equation (9.165) with respect to the time²²:

$$\frac{d^2}{dt^2} C(t) = -M(t) - \int_0^t M(\tau) \frac{d}{dt} C(t - \tau) d\tau. \quad (9.167)$$

The most efficient numerical integration method for deducing the memory function from the autocorrelation function is given by Gregory [156]. By denoting the integrand in equation (9.167) by $z(t)$, i.e.:

$$z(t) = M(t) \dot{C}(t_i - t), \quad (9.168)$$

and using the variables $t_{i-1} = (i-1)\Delta t = t_i - t_1$ with the boundary conditions $t_0 = 0$, $C(t_0) = 1$ and $\dot{C}(t_0) = 0$, the integral reduces to²³:

²²Make first the change of variables $\tau = t - t'$ in equation (9.165) to write:

$$\frac{d}{dt} C(t) = - \int_0^t M(\tau) C(t - \tau) d\tau.$$

Then, compute the first derivative of the above equation with respect to t , using the formula given in footnote 3 in this chapter:

$$\frac{d^2}{dt^2} C(t) = - \int_0^t M(\tau) \frac{d}{dt} C(t - \tau) d\tau - M(\tau) C(t - \tau) \Big|_{\tau=t}.$$

Taking account that $C(0) = 1$ gives:

$$\frac{d^2}{dt^2} C(t) = - \int_0^t M(\tau) \frac{d}{dt} C(t - \tau) d\tau - M(t).$$

²³The Gregory formula estimates the integral in equation (9.167) as follows, by stopping at the second finite differences:

$$\begin{aligned}
\int_{t_0}^{t_i} M(t) \dot{C}(t_i - t) dt &= \Delta t \left[\frac{1}{2} M(t_0) \dot{C}(t_i) + \sum_{j=1}^{i-1} M(t_j) \dot{C}(t_{i-j}) \right] \\
&- \frac{\Delta t}{12} \left[-M(t_{i-1}) \dot{C}(t_1) - M(t_1) \dot{C}(t_{i-1}) + M(t_0) \dot{C}(t_i) \right] \\
&- \frac{\Delta t}{24} \left[-2M(t_{i-1}) \dot{C}(t_1) + M(t_{i-2}) \dot{C}(t_2) + M(t_2) \dot{C}(t_{i-2}) \right. \\
&\quad \left. - 2M(t_1) \dot{C}(t_{i-1}) + M(t_0) \dot{C}(t_i) \right]. \quad (9.169)
\end{aligned}$$

In order to solve equation (9.167), $M(t_i) = -\ddot{C}(t_i) - \int_{t_0}^{t_i} z(t) dt$, it is necessary to calculate the values of the first and second derivatives of the autocorrelation function $C(t_i)$ for all the values of i . For that purpose, it is convenient to use the Lagrange interpolation formula between five points that provides the values of $\dot{C}(t_i)$ and $\ddot{C}(t_i)$ at each point i by using the formula:

$$\begin{aligned}
\int_{t_0}^{t_i} z(t) dt &= \Delta t \left[\frac{1}{2} z(t_0) + z(t_1) + \dots + z(t_{i-1}) + \frac{1}{2} z(t_i) \right] \\
&- \frac{\Delta t}{12} \left[\Delta z(t_{i-1}) - \Delta z(t_0) \right] - \frac{\Delta t}{24} \left[\Delta^2 z(t_{i-2}) + \Delta^2 z(t_0) \right],
\end{aligned}$$

with the differences of order one:

$$\begin{aligned}
\Delta z(t_0) &= z(t_1) - z(t_0), \\
\Delta z(t_{i-1}) &= z(t_i) - z(t_{i-1})
\end{aligned}$$

and the differences of order two:

$$\begin{aligned}
\Delta^2 z(t_0) &= [z(t_2) - z(t_1)] - [z(t_1) - z(t_0)] = z(t_2) - 2z(t_1) + z(t_0), \\
\Delta^2 z(t_{i-2}) &= [z(t_i) - z(t_{i-1})] - [z(t_{i-1}) - z(t_{i-2})] = z(t_i) - 2z(t_{i-1}) + z(t_{i-2}).
\end{aligned}$$

The substitution of these differences in the expression of the integral leads to the formula:

$$\begin{aligned}
\int_{t_0}^{t_i} z(t) dt &= \Delta t \left[\frac{1}{2} z(t_0) + \sum_{j=1}^{i-1} z(t_j) + \frac{1}{2} z(t_i) \right] - \frac{\Delta t}{12} \left[z(t_i) - z(t_{i-1}) - z(t_1) + z(t_0) \right] \\
&- \frac{\Delta t}{24} \left[z(t_i) - 2z(t_{i-1}) + z(t_{i-2}) + z(t_2) - 2z(t_1) + z(t_0) \right].
\end{aligned}$$

$$\left. \frac{d^k C(t)}{dt^k} \right|_{t=t_i} \simeq \frac{k!}{m! \Delta t^k} \sum_{j=0}^m A_j C(t_j), \quad (9.170)$$

where k is the order of differentiation, $m (= 5)$ the number of points of the Lagrange interpolation formula and A_j the coefficients useful for the differentiation [157]. In addition, it is required to know the first four values of the memory function $M(t_0)$, $M(t_1)$, $M(t_2)$ and $M(t_3)$ to initialise the calculation with the Gregory formula as the Lagrange interpolation formula is used between five points. These initial values have to be drawn from the expansion of the memory function at short times (Eq. 9.131), where the values of the frequency moments B_0 and B_2 are calculated as a function of the pair potential with equations (9.134) and (9.136). Anyway, according to Berne and Harp [154], it is better to employ the Day method [158] which exploits the symmetry properties of the autocorrelation function (Eq. 9.129) and memory function (Eq. 9.131), and allows deducing the three following algebraic equations (see Ref. [157], p. 914):

$$M(t_1) = -\ddot{C}(t_1) - \frac{\Delta t}{24} \left[9M(t_0)\dot{C}(t_1) + 5M(t_2) - M(t_3)\dot{C}(t_2) \right], \quad (9.171)$$

$$M(t_2) = -\ddot{C}(t_2) - \frac{\Delta t}{3} \left[M(t_0)\dot{C}(t_2) + 4M(t_1)\dot{C}(t_1) \right], \quad (9.172)$$

$$M(t_3) = -\ddot{C}(t_3) - \frac{3\Delta t}{8} \left\{ M(t_0)\dot{C}(t_3) + 3[M(t_1)\dot{C}(t_2) + M(t_2)\dot{C}(t_1)] \right\}. \quad (9.173)$$

Solving this system of linear equations enables us to extract $M(t_1)$:

$$M(t_1) = \frac{-\ddot{C}(t_1) + \frac{\Delta t}{24}P + \frac{\Delta t^2}{72}Q + \frac{\Delta t^3}{64}\dot{C}(t_1)\dot{C}^2(t_2)M(t_0)}{D}, \quad (9.174)$$

with:

$$P = 5\dot{C}(t_1)\ddot{C}(t_2) - \dot{C}(t_2)\ddot{C}(t_3) - 9\dot{C}(t_1)M(t_0), \quad (9.175)$$

$$Q = \frac{27}{8}\dot{C}(t_1)\dot{C}(t_2)\ddot{C}(t_2) + 5\dot{C}(t_1)\dot{C}(t_2)M(t_0) - \frac{9}{8}\dot{C}(t_2)\dot{C}(t_3)M(t_0), \quad (9.176)$$

$$D = 1 - \Delta t^2 \left[\frac{5}{18}\dot{C}^2(t_1) - \frac{3}{64}\dot{C}^2(t_2) \right] - \frac{\Delta t^3}{16} \left[\dot{C}^2(t_1)\dot{C}(t_2) \right], \quad (9.177)$$

and to deduce successively the values of $M(t_2)$ and $M(t_3)$ in terms of $M(t_0) = B_0$. Having knowledge of the four initial values $M(t_0)$, $M(t_1)$,

$M(t_2)$ and $M(t_3)$ makes possible the continuation of the calculation of the memory function with the Gregory formula from the point $i = 4$. The best way to test the numerical calculations is to compare the results of $M(t_i)$ with the exact results of the analytical model of Berne et al. [140].

10 The linear response theory

10.1 Spatiotemporal correlation functions

The linear response theory has been developed to describe the phenomena occurring in non-equilibrium systems. It was aimed at finding exact expressions connecting the transport coefficients with the spatiotemporal correlation functions. Interestingly, the theory uses a formalism common to theorists and experimentalists that helps to explain the most relevant phenomena in order to extract valuable information about the atomic movement in liquids.

The diversity of the dynamic phenomena observed in fluids relies greatly on the type of fluid being studied. For instance, in dilute gases, the atoms undergo infrequent binary collisions during which the transfers of energy and momentum are perfectly described by the Boltzmann equation and the Chapman–Enskog theory. By contrast, the atoms interact in liquids so intricately by a potential repulsive at short distance and attractive at long distance that the theory of Chapman and Enskog ignores the details of the atomic motions and is ineffective. This explains why the microscopic theory of liquids has been developed later than the kinetic theory of gases.

The linear response theory applies to two types of seemingly different phenomena. The first category of phenomena involves systems which are initially *out-of-equilibrium* and relax toward *equilibrium*¹.

¹This type of phenomenon has been described for the first time in connection with the thermal noise in electrical circuits [159]. It has been examined later under the general form [161].

The second category is related to systems which are initially at *equilibrium* characterized by high symmetry and are submitted to an external strain. When a system at equilibrium is subjected to a time-dependent external action, the equilibrium is upset, the symmetries are broken and the system tries to adapt to its new environment. The macroscopic properties in a system at equilibrium are modified and their measurements can be used to deduce the response of the system to the external action. If this action is small, the measured quantities are assumed to be proportional to the external action and the proportionality coefficients are functionals depending on the intrinsic properties (microscopic) of the system at equilibrium. These two seemingly different phenomena are equivalent, because, if a system is out-of-equilibrium at a given moment, it is unclear whether this follows from spontaneous fluctuations (internal actions) or an external action. When the deviation from the equilibrium is small, the system evolves in the same manner towards a steady state within both cases [160].

The time correlation functions entering the calculation of macroscopic properties are extremely difficult to derive as a function of the interatomic interactions. Nevertheless, the dynamic properties are easier to explore after modelling the correlation functions. The numerous models developed for this purpose have proved to be very useful to understand the dynamic processes. Simultaneously, the physical content and the theoretical framework [162, 163, 138, 137, 164] of the dynamics of liquids have been supplemented by new concepts (such as the *linear response* theory, *fluctuation-dissipation* theorem, *memory function*, etc.) which were used to better understand the mechanisms governing the atomic motions in liquids. To introduce these notions, use has been made of some heuristic but physically sound arguments based upon the Brownian motion (chapter 9). The Brownian motion is the random motion of particles in liquids produced by the repeated impacts of neighbouring particles. They exert a *driving force* that maintains the motion of a test particle by giving rise simultaneously to a *frictional force* opposing its motion. The driving force is a *random function* produced by the fluctuations, and the frictional force that opposes the movement is an *ordinary function* stemming from the friction. Although they have different effects, the driving and frictional forces have a common origin that should emerge in a comprehensive study.

In a way, one can say that the time correlation functions establish a direct link between the experiment and the microscopic theory, in the sense that such relationships permit prediction of the transport coefficients of liquids likely to be measured by appropriate experiments. Historically, the first relation of this type was found by Einstein [133] when he deduced the *diffusion coefficient* D from the *velocity autocorrelation function* $\langle v(0)v(t) \rangle$ with the following integral (Eq. 9.71):

$$D = \int_0^\infty \langle v(0)v(t) \rangle dt. \quad (10.1)$$

This relation connecting the macroscopic property D to the microscopic quantity $\langle v(0)v(t) \rangle$ is true for any conventional liquid, regardless of its density, and for any type of interaction.

It has been clearly demonstrated throughout the previous chapter that the atomic motion in liquids can be described in terms of the correlation functions, and the results of experiments can be interpreted by using the time autocorrelation functions of some dynamical variables. As mentioned above, the diffusion coefficient is expressed with the velocity autocorrelation function (Eq. 10.1). The following sections will provide other examples of relationships linking dynamic properties of liquids to correlation functions of microscopic properties.

It is not wrong to say that what is applicable for the *time correlation function* towards the dynamic processes is likewise applicable for the *spatial correlation function* towards the static processes, except for an essential difference. Indeed, all the thermodynamic states of a liquid at equilibrium are well defined by its properties as a function of the pair correlation function $g(r)$ only. As an example, the isothermal compressibility χ_T is given by equation (5.85):

$$\frac{\rho}{\beta} \chi_T - 1 = \rho \int_V [g(r) - 1] d\mathbf{r}. \quad (10.2)$$

By contrast, the non-equilibrium states of a liquid, caused by external actions of different natures (mechanical or thermal), do not stem from a single time correlation function. When it was realized that the transport coefficients can be calculated by using the integral of a specific time correlation function, there has been a major breakthrough in the theory of the dynamic properties of liquids. When viewed more closely, we see that these integrals can have a more general form than

equation (10.1). For instance, the expression of the *electrical conductivity* $\sigma(\omega)$ of a metallic conductor subjected to an electric field of angular frequency ω is given by the integral:

$$\sigma(\omega) = \frac{1}{k_{\text{B}}T} \int_0^\infty \langle J(0)J(t) \rangle \exp(-i\omega t) dt, \quad (10.3)$$

where $\langle J(0)J(t) \rangle$ is the *autocorrelation function of the current density*. This relation, which contains the additional term $\exp(-i\omega t)$, is a better representative of the theory of time correlation functions than equation (10.1) as the diffusion coefficient D is merely the zero-frequency limit of a general formula of the same type as equation (10.3).

A better understanding of the dynamic properties of liquids has coincided with the advent of the neutron scattering experiments as means of investigation. The reason is that the wavelengths of slow neutrons are comparable to the interatomic distances and their energies are comparable to the energy transfers in play during the collisions between atoms. The theoretical basis of neutron scattering experiments is founded on the formalism of *spatiotemporal correlation functions* developed by van Hove [165]; it is a typical example of the equation (10.3). In fact, the *dynamic structure factor* $S(\mathbf{q}, \omega)$ is expressed through the *autocorrelation function of the particle density* $\langle \rho(-\mathbf{q}, 0)\rho(\mathbf{q}, t) \rangle$ by the integral (see chapter 11):

$$S(\mathbf{q}, \omega) = \frac{1}{\pi N} \int_0^\infty \langle \rho(-\mathbf{q}, 0)\rho(\mathbf{q}, t) \rangle \exp(-i\omega t) dt. \quad (10.4)$$

Like the diffusion coefficient D or the electrical conductivity $\sigma(\omega)$, the dynamic structure factor $S(\mathbf{q}, \omega)$ is an experimental quantity. It can be measured directly by neutron scattering and enjoys the advantage of giving the spectral distribution of its components. An experiment exploring extended ranges of frequencies and transfer vectors contributes far more to the understanding of the structural and dynamic processes than delivering a single value at $\omega = 0$ such as the diffusion coefficient. It should be remarked that the integral over ω of equation (10.4) represents the static structure factor defined by equation (3.118).

Even if the time correlation functions are very difficult to calculate in a way other than with molecular dynamics, the formalism of correlation functions (chapter 7) is, nevertheless, a very powerful tool for

analyzing the behaviour of liquids. The easiest way to perform this analysis is to choose an expression of the correlation function compatible with the theoretical model adopted, and to adjust the parameters on the dynamic properties determined experimentally or by simulation. The variety of the dynamic properties is of great benefit to test the validity of assumptions made in each specific theoretical model. Besides, it should be remembered that the theoretical framework of the dynamics of liquids enables us to link the autocorrelation function to the spectral density (section 9.5) and the memory function (section 9.6).

To set up the context of the discussion on the time correlation functions, we present in this chapter the essential notions of the linear response theory and generalized susceptibility, allowing to define the response function of a system, as well as the case of spatiotemporal correlation functions which make it possible to characterize the dynamic structure of liquids likely to be measured by neutron scattering.

10.2 Transformation of a stationary random function into a linear system

As already mentioned, the Brownian motion previously described above relates to a suspended particle subjected to a random driving force $F(t)$ and a systematic friction force $X(t) = -\mu \frac{dx}{dt}$. In this section, the particle will be submitted to an additional systematic external force $K(t)$. As a consequence, we are faced with the problem of a linear system governed by the conventional stochastic differential equation of Langevin, namely:

$$m \frac{d^2 x}{dt^2} = -\mu \frac{dx}{dt} + F(t) + K(t), \quad (10.5)$$

which provides the response to the excitation $K(t)$. In stationary state, the equation of mean values reduces to:

$$m \frac{d \langle v(t) \rangle}{dt} = -\mu \langle v(t) \rangle + K(t), \quad (10.6)$$

since $\langle F(t) \rangle = 0$. To determine the *frequency response* of the system, it is convenient to use the Fourier transforms:

$$K(t) = \int_{-\infty}^{\infty} K(\omega) \exp(i\omega t) d\omega, \quad (10.7)$$

$$v(t) = \int_{-\infty}^{\infty} v(\omega) \exp(i\omega t) d\omega, \quad (10.8)$$

$$\text{and} \quad \frac{dv(t)}{dt} = i\omega \int_{-\infty}^{\infty} v(\omega) \exp(i\omega t) d\omega. \quad (10.9)$$

After substituting these quantities in equation (10.6), we obtain²:

$$\langle v(\omega) \rangle = \chi(\omega) K(\omega), \quad (10.10)$$

$$\text{with} \quad \chi(\omega) = \frac{1}{\mu + im\omega}. \quad (10.11)$$

The complex function $\chi(\omega)$, called *admittance* or *susceptibility*, is the frequency response of the particle to the excitation $K(\omega)$. It is the relevant ingredient to calculate the mean velocity of the suspended particle for any excitation $K(\omega)$.

Here we show how the susceptibility $\chi(\omega)$ is related to the velocity autocorrelation function $\langle v(0)v(t) \rangle$ in the conventional Langevin model. For this, the Fourier-Laplace transform of the velocity autocorrelation function is carried out first. The result is³:

$$\int_0^{\infty} \langle v(0)v(t) \rangle \exp(-i\omega t) dt = \frac{k_B T}{\mu + im\omega}. \quad (10.12)$$

²Indeed:

$$m i\omega \int_{-\infty}^{\infty} \langle v(\omega) \rangle \exp(i\omega t) d\omega = -\mu \int_{-\infty}^{\infty} \langle v(\omega) \rangle \exp(i\omega t) d\omega + \int_{-\infty}^{\infty} K(\omega) \exp(i\omega t) d\omega,$$

$$\text{hence} \quad \langle v(\omega) \rangle = \frac{1}{\mu + im\omega} K(\omega).$$

³The Fourier-Laplace transform of equation (9.82) is evaluated simply as follows:

$$\begin{aligned} \int_0^{\infty} \langle v(0)v(t) \rangle \exp(-i\omega t) dt &= \frac{k_B T}{m} \int_0^{\infty} \exp\left[-\left(\frac{\mu}{m} + i\omega\right)t\right] dt \\ &= -\frac{k_B T}{m} \frac{1}{\left(\frac{\mu}{m} + i\omega\right)} \left\{ \exp\left[-\left(\frac{\mu}{m} + i\omega\right)t\right] \right\}_0^{\infty} = \frac{k_B T}{m} \frac{1}{\left(\frac{\mu}{m} + i\omega\right)} = \frac{k_B T}{\mu + im\omega}. \end{aligned}$$

Then, comparing equations (10.11) and (10.12) leads immediately to the expression:

$$\chi(\omega) = \frac{1}{k_B T} \int_0^\infty \langle v(0)v(t) \rangle \exp(-i\omega t) dt. \quad (10.13)$$

This formula connecting the susceptibility $\chi(\omega)$ to the velocity autocorrelation function $\langle v(0)v(t) \rangle$ is another aspect of the above mentioned fluctuation-dissipation theorem. Furthermore, by comparing equations (9.71) and (10.13), we can see that the diffusion coefficient D is related to $\chi(\omega = 0)$ by the relation:

$$D = k_B T \chi(\omega = 0). \quad (10.14)$$

This type of expression, introduced through the conventional Langevin model, will be examined more closely in the next sections.

When concluding this introduction to the linear response theory, it is worth keeping in mind that all applied functions (excitations) under the general rules of transformations of linear systems are governed by the same linear transformations. In the case of stationary random functions, the rule is: *when a stationary random function is applied to a linear system, the spectral density of the response of the system is equal to the product of the spectral density of the applied function by the squared modulus of the susceptibility.* This rule has an important consequence in the microscopic theory of liquids because, if it is assumed that the driving force $F(t)$ is a stationary random function, we pass from its spectral density (Eq. 9.84) to the spectral density of the velocity by the formula:

$$S_v(\omega) = |\chi(\omega)|^2 S_F(\omega) = \frac{1}{\mu^2 + m^2 \omega^2} \frac{\mu k_B T}{\pi}, \quad (10.15)$$

as confirmed by equation (9.87).

Finally, we should not overlook the resemblance between the expressions of the spectral density $S_v(\omega)$ (Eq. 9.85) and the susceptibility $\chi(\omega)$ (Eq. 10.13), since one is the Fourier transform of the velocity autocorrelation function while the other one is its Fourier-Laplace transform. This suggests the possibility of deducing remarkable properties of the correlation functions by a simple Fourier analysis.

10.3 Properties of the Liouville operator

Prior to presenting the linear response theory, we remind some important properties of the Liouville operator defined earlier. If a system consists of N classical particles, the Hamiltonian is $H(\mathbf{r}^N, \mathbf{p}^N, t)$ and its dynamic state is described by the distribution function $f(\mathbf{r}^N, \mathbf{p}^N, t)$ in the γ -space. The law of conservation of the distribution function $f(\mathbf{r}^N, \mathbf{p}^N, t)$ is given by the Liouville equation (Eq. 1.112):

$$\frac{\partial}{\partial t} f(\mathbf{r}^N, \mathbf{p}^N, t) = -i\mathcal{L} f(\mathbf{r}^N, \mathbf{p}^N, t), \quad (10.16)$$

where $\mathcal{L}$ is the Liouville operator defined by means of the Poisson brackets as follows:

$$\mathcal{L} = i[H, \] = i \sum_{i=1}^{3N} \left[\frac{\partial H}{\partial r_i} \frac{\partial}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial}{\partial r_i} \right]. \quad (10.17)$$

While the partial derivative on the left hand side of equation (10.16) acts on the time variable, the Liouville operator on the right hand side acts on the variables of phase space. The formal solution of equation (10.16) giving the evolution of $f(\mathbf{r}^N, \mathbf{p}^N, t)$ is merely:

$$f(\mathbf{r}^N, \mathbf{p}^N, t) = \exp(-i\mathcal{L}t) \cdot f(\mathbf{r}^N, \mathbf{p}^N, 0), \quad (10.18)$$

with :

$$f(\mathbf{r}^N, \mathbf{p}^N, 0) = \frac{1}{h^{3N} Q_N(V, T)} \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)], \quad (10.19)$$

where $Q_N(V, T)$ is the partition function of the canonical ensemble (Eq. 2.33).

Let us show that the evolution equation of any dynamical variable $A(\mathbf{r}^N, \mathbf{p}^N)$ can also be written using the Liouville operator. Indeed, given equation (1.35), namely:

$$\frac{\partial r_i}{\partial t} = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \frac{\partial p_i}{\partial t} = -\frac{\partial H}{\partial r_i}, \quad (10.20)$$

the partial derivative of the dynamical variable $A(\mathbf{r}^N, \mathbf{p}^N)$ with respect to the time is transformed as:

$$\frac{\partial A}{\partial t} = \sum_{i=1}^{3N} \left[\frac{\partial A}{\partial r_i} \frac{\partial r_i}{\partial t} + \frac{\partial A}{\partial p_i} \frac{\partial p_i}{\partial t} \right] = \sum_{i=1}^{3N} \left[\frac{\partial A}{\partial r_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial r_i} \right]. \quad (10.21)$$

Therefore, with the help of equation (10.17), equation (10.21) reads:

$$\frac{\partial A}{\partial t} = -[H, A] = i\mathcal{L}A, \quad (10.22)$$

or equivalently:

$$\dot{A} = i\mathcal{L}A, \quad (10.23)$$

and its formal solution is:

$$A(\mathbf{r}^N, \mathbf{p}^N, t) = \exp(i\mathcal{L}t) \cdot A(\mathbf{r}^N, \mathbf{p}^N, 0). \quad (10.24)$$

Note in passing the difference of sign in the arguments of the exponential function in equations (10.24) and (10.18).

Now, we present three important properties of the Liouville operator. In practice, we use frequently relations of the type $\iint B^*(\mathcal{L}A) d\mathbf{r}^N d\mathbf{p}^N$, where A and B are two real dynamical variables $A(=A^*)$ and $B(=B^*)$ of a Hilbert space⁴ and $\mathcal{L}$ is a Hermitian operator from which it results:

$$\iint B^*(\mathcal{L}A) d\mathbf{r}^N d\mathbf{p}^N = \iint B(\mathcal{L}A) d\mathbf{r}^N d\mathbf{p}^N. \quad (10.25)$$

Firstly, we show that the Liouville operator is a Hermitian operator⁵, satisfying the equation:

$$\iint B^*(\mathcal{L}A) d\mathbf{r}^N d\mathbf{p}^N = \iint (\mathcal{L}^*B^*) A d\mathbf{r}^N d\mathbf{p}^N. \quad (10.26)$$

⁴The set of all functions for which there is a *finite norm* is called Hilbert space. As an example, $\iint B^*B d\mathbf{r}^N d\mathbf{p}^N$ is always finite.

⁵To derive this relation, we write the following relation using equation (10.22):

$$\iint B^*(\mathcal{L}A) d\mathbf{r}^N d\mathbf{p}^N = i \iint B^* \left(-\frac{\partial A}{\partial t} \right) d\mathbf{r}^N d\mathbf{p}^N.$$

Then, we perform the integration by parts of the right hand side of the above relation. It results:

$$-i \iint B^* \left(\frac{\partial A}{\partial t} \right) d\mathbf{r}^N d\mathbf{p}^N = -i \iint (B^*A) d\mathbf{r}^N d\mathbf{p}^N + i \iint \frac{\partial B^*}{\partial t} A d\mathbf{r}^N d\mathbf{p}^N.$$

If it is now assumed that the dynamical variables A and B are cancelled on the surface of the integration domain (as functions belonging to a Hilbert space), the first term on the right hand side of the above equation vanishes. Furthermore, by explaining $\frac{\partial B^*}{\partial t}$ with equation (10.22) and using the complex conjugate Liouville operator $\mathcal{L}^* = -i[H, \]$, the second term on the right hand side is written:

$$i \iint \frac{\partial B^*}{\partial t} A d\mathbf{r}^N d\mathbf{p}^N = -i \iint [H, B^*] A d\mathbf{r}^N d\mathbf{p}^N = \iint (\mathcal{L}^*B^*) A d\mathbf{r}^N d\mathbf{p}^N.$$

As a consequence, the previous relation is transformed as:

$$\iint B(\mathcal{L}A) d\mathbf{r}^N d\mathbf{p}^N = \iint (\mathcal{L}^* B) A d\mathbf{r}^N d\mathbf{p}^N. \quad (10.27)$$

Secondly, since $\mathcal{L}$ is an Hermitian operator, the operator $\exp(i\mathcal{L}t)$ is unitary because the scalar product of two dynamical variables A and B is not changed after transformation by the exponential operator. It is proved by applying the operator $\exp(i\mathcal{L}t)$ to the two dynamical variables A and B . It is then found:

$$\begin{aligned} \iint [\exp(i\mathcal{L}t)B][\exp(i\mathcal{L}t)A] d\mathbf{r}^N d\mathbf{p}^N &= \\ &= \iint B \exp(-i\mathcal{L}t) \exp(i\mathcal{L}t) A d\mathbf{r}^N d\mathbf{p}^N = \iint BA d\mathbf{r}^N d\mathbf{p}^N. \end{aligned} \quad (10.28)$$

Thirdly, before turning to the linear response theory, we derive another useful relation connecting the dynamical variable A with the distribution function f written as:

$$[A, f] = -i\beta f \mathcal{L}A. \quad (10.29)$$

To prove this relationship, we write the left hand side of the above relation with the Poisson brackets:

$$[A, f] = \sum_{i=1}^{3N} \left[\frac{\partial A}{\partial r_i} \frac{\partial f}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial f}{\partial r_i} \right], \quad (10.30)$$

then, we clarify the partial derivatives of f in this relation by using equation (10.19). It follows:

$$\frac{\partial f}{\partial p_i} = \frac{\partial}{\partial p_i} \left\{ \frac{1}{h^{3N} Q_N(V, T)} \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)] \right\} = -\beta f \frac{\partial H}{\partial p_i}, \quad (10.31)$$

$$\begin{aligned} \text{and} \\ \frac{\partial f}{\partial r_i} = \frac{\partial}{\partial r_i} \left\{ \frac{1}{h^{3N} Q_N(V, T)} \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)] \right\} &= -\beta f \frac{\partial H}{\partial r_i}. \end{aligned} \quad (10.32)$$

After substitution of these quantities in equation (10.30) and a short look at equation (10.17), we obtain:

$$[A, f] = -\beta f \sum_{i=1}^{3N} \left[\frac{\partial A}{\partial r_i} \frac{\partial H}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial r_i} \right], \quad (10.33)$$

or equivalently:

$$[A, f] = \beta f [H, A] = -i\beta f \mathcal{L}A. \quad (10.34)$$

10.4 General theory of the linear response

Consider a system initially at thermal equilibrium. It is described by the Hamiltonian $H_0(\mathbf{r}^N, \mathbf{p}^N)$, and the evolution of the distribution function $f_0(\mathbf{r}^N, \mathbf{p}^N)$ is governed by the Liouville equation:

$$\frac{\partial f_0}{\partial t} = [H_0, f_0] = -i\mathcal{L}_0 f_0. \quad (10.35)$$

At time $t=0$, a weak perturbation is applied, thus causing a modification of the Hamiltonian H_0 by a small quantity H_1 written as:

$$H_1(\mathbf{r}^N, \mathbf{p}^N, t) = -A(\mathbf{r}^N, \mathbf{p}^N, 0)F(t), \quad (10.36)$$

where $F(t)$ is a function depending explicitly on the time, and $A(\mathbf{r}^N, \mathbf{p}^N, 0)$ is a dynamical variable depending implicitly on the time through the coordinates of phase space. Note that the dynamical variable $A(\mathbf{r}^N, \mathbf{p}^N, 0)$ characterizes an atomic property of the system, and $F(t)$ depends on the nature of the perturbation⁶ acting on the dynamical variable $A(\mathbf{r}^N, \mathbf{p}^N, 0)$. For example, in a system of permanent dipoles, we can consider that the dynamical variable is the total electric moment and the perturbation is the external electric field.

The perturbation $F(t)$ changes the values of all atomic properties of the system until a stationary regime is reached. To calculate the mean value of a dynamical variable $B(\mathbf{r}^N, \mathbf{p}^N, 0)$ (which can be the variable $A(\mathbf{r}^N, \mathbf{p}^N, 0)$ itself) affected by the perturbation $F(t)$, it is convenient to use the ensemble average:

$$\langle B(t) \rangle = \iint B(\mathbf{r}^N, \mathbf{p}^N, 0) f(\mathbf{r}^N, \mathbf{p}^N, t) d\mathbf{r}^N d\mathbf{p}^N, \quad (10.37)$$

knowing that, in the absence of any perturbation, $\langle B(t) \rangle = 0$. However, if the perturbation is small enough, it must slightly modify the distribution function to first-order approximation as:

$$f(\mathbf{r}^N, \mathbf{p}^N, t) = f_0(\mathbf{r}^N, \mathbf{p}^N, t) + f_1(\mathbf{r}^N, \mathbf{p}^N, t). \quad (10.38)$$

⁶It is considered here that the function $F(t)$ depends on the time and not on the position. It can obviously be assumed that it also depends on the position by writing $F(\mathbf{r}^N, t)$, in which case the calculation is more complicated. This will be made in section (10.8).

Since $f_1(\mathbf{r}^N, \mathbf{p}^N, t) = 0$ when $t \leq 0$, $f_0(\mathbf{r}^N, \mathbf{p}^N, t)$ is assumed to be equal to the equilibrium distribution function ($f_0(\mathbf{r}^N, \mathbf{p}^N, t) = f_0$) at any time.

The Liouville equation of the perturbed system is then:

$$\frac{\partial f}{\partial t} = -i\mathcal{L}f = \sum_{i=1}^{3N} \left[\frac{\partial H}{\partial r_i} \frac{\partial f}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial f}{\partial r_i} \right]. \quad (10.39)$$

By substituting the expressions of $f(= f_0 + f_1)$ and $H(= H_0 - AF(t))$ in the above relation, and keeping only the zero- and first-degree terms, we get:

$$\begin{aligned} \frac{\partial f}{\partial t} = & \sum_{i=1}^{3N} \left[\frac{\partial H_0}{\partial r_i} \frac{\partial f_0}{\partial p_i} - \frac{\partial H_0}{\partial p_i} \frac{\partial f_0}{\partial r_i} \right] + \sum_{i=1}^{3N} \left[\frac{\partial H_0}{\partial r_i} \frac{\partial f_1}{\partial p_i} - \frac{\partial H_0}{\partial p_i} \frac{\partial f_1}{\partial r_i} \right] \\ & - F(t) \sum_{i=1}^{3N} \left[\frac{\partial A}{\partial r_i} \frac{\partial f_0}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial f_0}{\partial r_i} \right], \end{aligned} \quad (10.40)$$

$$\text{or:} \quad \frac{\partial f}{\partial t} = [H_0, f_0] + [H_0, f_1] - F(t) [A, f_0]. \quad (10.41)$$

And, from equation (10.35) combined with the above relation, we deduce the partial derivative of the perturbative part of the distribution function with respect to the time:

$$\begin{aligned} \frac{\partial f_1}{\partial t} &= [H_0, f_1] - F(t) [A, f_0] \\ &= -i\mathcal{L}_0 f_1 - F(t) [A, f_0]. \end{aligned} \quad (10.42)$$

However, with the help of equation (10.29), this relation reads otherwise:

$$\frac{\partial f_1(\mathbf{r}^N, \mathbf{p}^N, t)}{\partial t} = -i\mathcal{L}_0 f_1(\mathbf{r}^N, \mathbf{p}^N, t) - F(t) [-i\beta f_0 \mathcal{L}_0 A(\mathbf{r}^N, \mathbf{p}^N, 0)]. \quad (10.43)$$

This is an operational inhomogeneous differential equation to first order whose formal solution is⁷:

$$\begin{aligned} f_1(\mathbf{r}^N, \mathbf{p}^N, t) = & \exp(-i\mathcal{L}_0 t) f_1(\mathbf{r}^N, \mathbf{p}^N, 0) \\ & + \exp(-i\mathcal{L}_0 t) \int_0^t \beta f_0 F(t') \exp(i\mathcal{L}_0 t') [i\mathcal{L}_0 A(\mathbf{r}^N, \mathbf{p}^N, 0)] dt'. \end{aligned} \quad (10.44)$$

⁷Its integration is performed in the same way as that of equation (9.46).

Since $f_1(\mathbf{r}^N, \mathbf{p}^N, t)$ is zero when $t \leq 0$, the first term on the right hand side of the above relation is zero, and the distribution function of the perturbed system (Eq. 10.38) is:

$$\begin{aligned} f(\mathbf{r}^N, \mathbf{p}^N, t) &= f_0(\mathbf{r}^N, \mathbf{p}^N, t) + f_1(\mathbf{r}^N, \mathbf{p}^N, t) \\ &= f_0 + \beta \int_0^t f_0 F(t') \exp[-i\mathcal{L}_0(t-t')] [i\mathcal{L}_0 A(\mathbf{r}^N, \mathbf{p}^N, 0)] dt'. \end{aligned} \quad (10.45)$$

This expression enables the calculation of the mean value of the dynamical variable $B(\mathbf{r}^N, \mathbf{p}^N, 0)$ thus written as (Eq. 10.37):

$$\begin{aligned} \langle B(t) \rangle &= \iint B(\mathbf{r}^N, \mathbf{p}^N, 0) f_0 d\mathbf{r}^N d\mathbf{p}^N + \beta \iint B(\mathbf{r}^N, \mathbf{p}^N, 0) \times \\ &\times \left[\int_0^t f_0 F(t') \exp[-i\mathcal{L}_0(t-t')] [i\mathcal{L}_0 A(\mathbf{r}^N, \mathbf{p}^N, 0)] dt' \right] d\mathbf{r}^N d\mathbf{p}^N. \end{aligned} \quad (10.46)$$

The first term on the right hand side corresponds to the mean value of $B(\mathbf{r}^N, \mathbf{p}^N, 0)$ in the absence of perturbation; therefore, it can be neglected in subsequent calculations. By interchanging the integrations in the second term on the right hand side and using equation (10.23), we obtain:

$$\begin{aligned} \langle B(t) \rangle &= \int_0^t F(t') \left[\beta \iint f_0 B(\mathbf{r}^N, \mathbf{p}^N, 0) \times \right. \\ &\times \exp[-i\mathcal{L}_0(t-t')] \dot{A}(\mathbf{r}^N, \mathbf{p}^N, t') d\mathbf{r}^N d\mathbf{p}^N \left. \right] dt'. \end{aligned} \quad (10.47)$$

This is the mathematical expression of the principle of causality which says that the effect cannot precede the cause. The perturbation acting only from time $t=0$, it is legitimate to push away the lower bound of integration to $-\infty$ and write the above relation as:

$$\langle B(t) \rangle = \int_{-\infty}^t F(t') \phi_{BA}(t-t') dt', \quad (10.48)$$

where the function $\phi_{BA}(t-t')$ is defined by the expression:

$$\begin{aligned} \phi_{BA}(t-t') &= \beta \iint f_0 \{ B(\mathbf{r}^N, \mathbf{p}^N, 0) \exp[-i\mathcal{L}_0(t-t')] \} \times \\ &\times \dot{A}(\mathbf{r}^N, \mathbf{p}^N, t') d\mathbf{r}^N d\mathbf{p}^N. \end{aligned} \quad (10.49)$$

The function $\phi_{BA}(t-t')$ is called the *after effect function* or *response function*. It connects the mean value of the dynamical variable

$B(\mathbf{r}^N, \mathbf{p}^N, 0)$ to the perturbation $F(t)$. It is remarkable that, if the perturbation is proportional to the Dirac function $F(t) = a\delta(t)$, the mean value of the dynamical variable is equal to:

$$\langle B(t) \rangle = \int_{-\infty}^t a\delta(t') \phi_{BA}(t-t') dt' = a \phi_{BA}(t). \quad (10.50)$$

In this case, the response function $\phi_{BA}(t)$ is the *Green function* of the system.

Since the exponential operator is unitary, we can further simplify equation (10.49) with equation (10.24) as:

$$\begin{aligned} \phi_{BA}(t-t') &= \beta \iint f_0 \left\{ \exp[i\mathcal{L}(t-t')] B(\mathbf{r}^N, \mathbf{p}^N, 0) \right\} \times \\ &\quad \times \dot{A}(\mathbf{r}^N, \mathbf{p}^N, t') d\mathbf{r}^N d\mathbf{p}^N \\ &= \beta \iint f_0 B(\mathbf{r}^N, \mathbf{p}^N, t-t') \dot{A}(\mathbf{r}^N, \mathbf{p}^N, t') d\mathbf{r}^N d\mathbf{p}^N, \end{aligned} \quad (10.51)$$

or equivalently:

$$\phi_{BA}(t-t') = \beta \langle \dot{A}(t') B(t-t') \rangle_0. \quad (10.52)$$

Being given that the mean value in the above relation is calculated in using the distribution function of the canonical ensemble at *equilibrium*, the dynamical variables A and B must satisfy the stationary conditions, indicating that there is no preferential origin of the time in the system at equilibrium. Under these conditions, the response function can still be written in one of the following forms⁸:

⁸To obtain these relations, begin by calculating the derivatives of the correlation function $\langle A(t') B(t-t') \rangle$ with respect to t and t' :

$$\begin{aligned} \frac{d}{dt} \langle A(t') B(t-t') \rangle &= \left\langle A(t') \frac{d}{dt} B(t-t') \right\rangle, \\ \text{and } \frac{d}{dt'} \langle A(t') B(t-t') \rangle &= \left\langle \frac{d}{dt'} A(t') B(t-t') \right\rangle + \left\langle A(t') \frac{d}{dt'} B(t-t') \right\rangle. \end{aligned}$$

For $t'=0$, the above relations are reduced respectively to:

$$\begin{aligned} \frac{d}{dt} \langle A(t') B(t-t') \rangle|_{t'=0} &= \langle A(0) \dot{B}(t) \rangle, \\ \text{and } \frac{d}{dt'} \langle A(t') B(t-t') \rangle|_{t'=0} &= \langle \dot{A}(0) B(t) \rangle + \langle A(0) \dot{B}(t) \rangle. \end{aligned}$$

If the dynamical variables A and B are stationary random functions (without

$$\phi_{BA}(t) = \beta \langle \dot{A}(0)B(t) \rangle_0 = -\beta \langle A(0)\dot{B}(t) \rangle_0 = -\beta \frac{d}{dt} \langle A(0)B(t) \rangle_0. \quad (10.53)$$

It should be stressed that the response of a system to a small uniform perturbation $F(t)$ is entirely determined by the temporal correlation of spontaneous fluctuations of the dynamical variables A and B in the system at equilibrium. Indeed, while the ensemble average (Eq. 10.37) is calculated with the distribution function of the system *out-of-equilibrium*, the time average (Eq. 10.48) uses only the distribution function of the system at *equilibrium*.

10.5 Generalized susceptibility

The expression of the mean value $\langle B(t) \rangle$ consists in a convolution integral that can be expressed in the reciprocal space. Before transforming equation (10.48), we perform the change of variables $t - t' = \tau$ that yields:

$$\langle B(t) \rangle = - \int_{-\infty}^0 F(t-\tau) \phi_{BA}(\tau) d\tau = \int_0^{\infty} F(t-\tau) \phi_{BA}(\tau) d\tau. \quad (10.54)$$

As the response function $\phi_{BA}(\tau)$ is zero when $\tau < 0$, it is more convenient to calculate the Fourier-Laplace transform of equation (10.54) than the Fourier transform, namely:

$$\int_0^{\infty} \langle B(t) \rangle \exp(-i\omega t) dt = \int_0^{\infty} \left[\int_0^{\infty} F(t-\tau) \phi_{BA}(\tau) d\tau \right] \exp(-i\omega t) dt. \quad (10.55)$$

Markovian character), the slope of the correlation function at the origin ($t' = 0$) is zero (see Fig. 9.6b):

$$\left. \frac{d}{dt'} \langle A(t')B(t-t') \rangle \right|_{t'=0} = 0.$$

Therefore, by combining the above relations, one arrives at the following identities:

$$\langle \dot{A}(0)B(t) \rangle = -\langle A(0)\dot{B}(t) \rangle = -\frac{d}{dt} \langle A(0)B(t) \rangle.$$

The Fourier–Laplace transforms of $\langle B(t) \rangle$, ϕ and F are then denoted:

$$\begin{aligned}\langle B(\omega) \rangle &= \int_0^\infty \langle B(t) \rangle \exp(-i\omega t) dt, \\ \chi_{BA}(\omega) &= \int_0^\infty \phi_{BA}(\tau) \exp(-i\omega\tau) d\tau, \\ F(\omega) &= \int_0^\infty F(s) \exp(-i\omega s) ds,\end{aligned}\tag{10.56}$$

where $s = t - \tau$. The permutation of the two integrals on the right hand side of equation (10.55) leads to⁹:

$$\langle B(\omega) \rangle = \chi_{BA}(\omega) F(\omega).\tag{10.57}$$

The Fourier–Laplace transform of the response function $\chi_{BA}(\omega) = FLT[\phi_{BA}(t)]$ is called the *generalized susceptibility*. Equation (10.57) is a generalization of equation (10.10). The expression of $\chi_{BA}(\omega)$, written by means of the response function (Eq. 10.56) is similar to equation (10.13) that directly links the susceptibility to the velocity autocorrelation function.

Furthermore, the generalized susceptibility $\chi_{BA}(\omega)$ has remarkable features which are due to the properties of the Fourier transform and to the fact that the response function $\phi_{BA}(t)$ is a real function subjected to the principle of causality ($\phi_{BA}(t < 0) = 0$). In what follows, we indicate some of these features by considering an arbitrary real function $F(t)$ and its Fourier transform:

$$F(\omega) = \frac{1}{2\pi} \int_{-\infty}^\infty F(t) \exp(-i\omega t) dt,\tag{10.58}$$

$$\text{with } F(t) = \int_{-\infty}^\infty F(\omega) \exp(i\omega t) d\omega.\tag{10.59}$$

⁹Indeed, we obtain:

$$\begin{aligned}\int_0^\infty \langle B(t) \rangle \exp(-i\omega t) dt &= \int_0^\infty \left[\int_0^\infty F(s) \exp[-i\omega(s+\tau)] ds \right] \phi_{BA}(\tau) d\tau \\ &= \int_0^\infty \left[\int_0^\infty F(s) \exp(-i\omega s) ds \right] \phi_{BA}(\tau) \exp(-i\omega\tau) d\tau, \\ \text{hence } \langle B(\omega) \rangle &= F(\omega) \int_0^\infty \phi_{BA}(\tau) \exp(-i\omega\tau) d\tau = F(\omega) \chi_{BA}(\omega).\end{aligned}$$

(1) The condition for the function $F(t)$ (that remains finite when $t \rightarrow \pm \infty$) is a real function which reads:

$$F(t) = F^*(t), \quad (10.60)$$

that is to say:

$$\int_{-\infty}^{\infty} F(\omega) \exp(i\omega t) d\omega = \int_{-\infty}^{\infty} F^*(\omega) \exp(-i\omega t) d\omega, \quad (10.61)$$

where only the complex functions $F(\omega)$ and $\exp(i\omega t)$ are provided with the sign of conjugation since ω is real. After making the change of variables $-\omega = \Omega$ in the integral on the right hand side of the above relation, we obtain the identity:

$$-\int_{\infty}^{-\infty} F^*(-\Omega) \exp(i\Omega t) d\Omega = \int_{-\infty}^{\infty} F^*(-\Omega) \exp(i\Omega t) d\Omega. \quad (10.62)$$

However, as Ω is a dummy variable, it can be replaced by ω , and this allows us to write equation (10.61) as:

$$\int_{-\infty}^{\infty} F(\omega) \exp(i\omega t) d\omega = \int_{-\infty}^{\infty} F^*(-\omega) \exp(i\omega t) d\omega, \quad (10.63)$$

so that the condition $F(t) = F^*(t)$ results in $F(\omega) = F^*(-\omega)$.

Given that $F(\omega)$ is a complex function (Eq. 10.58), it can be written with the help of the two real functions $F'(\omega)$ and $F''(\omega)$ defined in the algebraic form:

$$\begin{aligned} F(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} F(t) \cos(\omega t) dt - i \frac{1}{2\pi} \int_{-\infty}^{\infty} F(t) \sin(\omega t) dt \\ &= F'(\omega) - iF''(\omega), \end{aligned} \quad (10.64)$$

$$\text{with} \quad F'(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(t) \cos(\omega t) dt \quad (10.65)$$

$$\text{and} \quad F''(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(t) \sin(\omega t) dt. \quad (10.66)$$

The complex conjugate of $F(-\omega)$ being $F^*(-\omega) = F'(-\omega) + iF''(-\omega)$, it is deduced from the condition $F(\omega) = F^*(-\omega)$ that:

$$F'(-\omega) = F'(\omega), \quad (10.67)$$

$$F''(-\omega) = -F''(\omega). \quad (10.68)$$

Therefore, when $F(t)$ is a *real function*, the *real part* of its Fourier transform is an *even function* and the *imaginary part* is an *odd function*.

(2) In addition, the representation of $F(t)$ takes the trigonometric form:

$$\begin{aligned}
 F(t) &= \int_{-\infty}^{\infty} F(\omega) \exp(i\omega t) d\omega \\
 &= \int_{-\infty}^{\infty} [F'(\omega) - iF''(\omega)] [\cos(\omega t) + i \sin(\omega t)] d\omega \\
 &= \int_{-\infty}^{\infty} F'(\omega) \cos(\omega t) d\omega + \int_{-\infty}^{\infty} F''(\omega) \sin(\omega t) d\omega \\
 &\quad + i \int_{-\infty}^{\infty} F'(\omega) \sin(\omega t) d\omega - i \int_{-\infty}^{\infty} F''(\omega) \cos(\omega t) d\omega. \quad (10.69)
 \end{aligned}$$

According to equations (10.67) and (10.68), the last two integrals of the above relation are zero because their integrands are odd functions of ω . By contrast, the first two integrals are not zero because their integrands are even functions of ω . As a result, the real function $F(t)$ can be written as follows:

$$F(t) = 2 \int_0^{\infty} F'(\omega) \cos(\omega t) d\omega + 2 \int_0^{\infty} F''(\omega) \sin(\omega t) d\omega, \quad (10.70)$$

where the integrations are carried out over the positive angular frequencies.

10.6 Kramers–Kronig relations and the fluctuation-dissipation theorem

In this section, an important consequence of the principle of causality of the response function $\phi_{BA}(t)$ will be deduced. Given the properties of the response function mentioned in the preceding section, $\phi_{BA}(t)$ is a real function expressed through equation (10.70) as:

$$\phi_{BA}(t) = 2 \int_0^{\infty} \chi'_{BA}(\omega) \cos(\omega t) d\omega + 2 \int_0^{\infty} \chi''_{BA}(\omega) \sin(\omega t) d\omega, \quad (10.71)$$

and

$$\phi_{BA}(-t) = 2 \int_0^{\infty} \chi'_{BA}(\omega) \cos(\omega t) d\omega - 2 \int_0^{\infty} \chi''_{BA}(\omega) \sin(\omega t) d\omega \quad (10.72)$$

However, it follows from the principle of causality ($\phi_{BA}(-t) = 0$) that the two integrals of equation (10.72) are equal. Also, by combining equations (10.71) and (10.72), the response function takes one of two forms:

$$\phi_{BA}(t) = 4 \int_0^\infty \chi'_{BA}(\omega) \cos(\omega t) d\omega \quad (10.73)$$

$$\text{and} \quad \phi_{BA}(t) = 4 \int_0^\infty \chi''_{BA}(\omega) \sin(\omega t) d\omega, \quad (10.74)$$

and the inverse Fourier transforms are respectively¹⁰:

$$\chi'_{BA}(\omega) = \frac{1}{2\pi} \int_0^\infty \phi_{BA}(t) \cos(\omega t) dt, \quad (10.75)$$

$$\text{and} \quad \chi''_{BA}(\omega) = \frac{1}{2\pi} \int_0^\infty \phi_{BA}(t) \sin(\omega t) dt. \quad (10.76)$$

The last four relations are of great practical importance because they show that the real part $\chi'_{BA}(\omega)$ and imaginary part $\chi''_{BA}(\omega)$ of the generalized susceptibility are not independent of each other. Indeed, the knowledge of one of them makes it possible to determine the generalized susceptibility $\chi_{BA}(\omega)$. To obtain the expression that connects $\chi'_{BA}(\omega)$ with $\chi''_{BA}(\omega)$, it is sufficient to compute $\chi'_{BA}(\omega)$ with equation (10.75) by substituting $\phi_{BA}(t)$ drawn from equation (10.74). It is found that¹¹:

¹⁰As $\chi'_{BA}(\omega)$ is an even function, equation (10.73) reads:

$$\frac{\phi_{BA}(t)}{2} = \int_{-\infty}^\infty \chi'_{BA}(\omega) \cos(\omega t) d\omega,$$

and its Fourier transform is:

$$\chi'_{BA}(\omega) = \frac{1}{2\pi} \int_{-\infty}^\infty \frac{\phi_{BA}(t)}{2} \cos(\omega t) dt = \frac{1}{2\pi} \int_0^\infty \phi_{BA}(t) \cos(\omega t) dt.$$

¹¹First, consider the expression of $\chi'_{BA}(\omega)$ as a function of $\phi_{BA}(t)$:

$$\begin{aligned} \chi'_{BA}(\omega) &= \frac{1}{2\pi} \int_0^\infty \left[4 \int_0^\infty \chi''_{BA}(u) \sin(ut) du \right] \cos(\omega t) dt \\ &= \frac{2}{\pi} \int_0^\infty \left[\lim_{T \rightarrow \infty} \int_0^T \sin(ut) \cos(\omega t) dt \right] \chi''_{BA}(u) du \\ &= \frac{2}{\pi} \int_0^\infty \left[\lim_{T \rightarrow \infty} \int_0^T \frac{1}{2} \{ \sin[(u+\omega)t] + \sin[(u-\omega)t] \} dt \right] \chi''_{BA}(u) du \\ &= \frac{1}{\pi} \int_0^\infty \lim_{T \rightarrow \infty} \left\{ \frac{1 - \cos[(u+\omega)T]}{u+\omega} + \frac{1 - \cos[(u-\omega)T]}{u-\omega} \right\} \chi''_{BA}(u) du. \end{aligned}$$

$$\chi'_{BA}(\omega) = \frac{2}{\pi} \int_0^\infty \frac{u \chi''_{BA}(u)}{u^2 - \omega^2} du. \quad (10.77)$$

By a similar calculation, we obtain the relation:

$$\chi''_{BA}(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{\chi'_{BA}(u)}{u^2 - \omega^2} du. \quad (10.78)$$

Equations (10.77) and (10.78) are the *Kramers–Kronig dispersion relations*¹². They are very useful for experimentalists willing to exploit the results of spectroscopy experiments where the dynamical variable A is correlated with itself¹³. Indeed, they make it possible to deduce the real part $\chi'_{AA}(\omega)$ from the measurement of the imaginary part $\chi''_{AA}(\omega)$ over a sufficiently wide frequency range, and thus determine the generalized susceptibility $\chi_{AA}(\omega)$.

This integral contains functions which oscillate rapidly and whose positive part is almost neutralized by negative part, when T is large. To make an accurate estimation of the contribution in brackets, it is convenient to perform the integration by parts of the function of type $\int_0^\infty F(u, T) du = \int_0^\infty f(u, T) \cos(u \pm \omega) T du$. By neglecting the resulting integral whose order of magnitude is smaller than $(1/T)$, it can be shown that the final result is expressed as a function of $\frac{dF(u, T)}{du}$ in the form:

$$\int_0^\infty F(u, T) du \approx -\frac{1}{T^2} \left[\frac{dF}{du} \right]_0^\infty, \quad \text{for large values of } T.$$

From this formula, it is clear that the integral in cosine, in the expression of $\chi'_{BA}(\omega)$, is zero and it remains:

$$\chi'_{BA}(\omega) = \frac{1}{\pi} \int_0^\infty \left\{ \frac{1}{u+\omega} + \frac{1}{u-\omega} \right\} \chi''_{BA}(u) du = \frac{2}{\pi} \int_0^\infty \frac{u \chi''_{BA}(u)}{u^2 - \omega^2} du.$$

¹²For more information on the Kramers–Kronig formulas see, for instance, the article [166].

¹³Assuming that the dynamical variable A is correlated with itself, it implies that its mean value (Eq. 10.54) is:

$$\langle A(t) \rangle = \int_0^\infty F(t - \tau) \phi_{AA}(\tau) d\tau,$$

where the response function is defined by equation (10.52):

$$\phi_{AA}(t - t') = \beta \langle \dot{A}(t') A(t - t') \rangle_0,$$

and the generalized susceptibility by equation (10.56), i.e.:

$$\chi_{AA}(\omega) = \int_0^\infty \phi_{AA}(\tau) \exp(-i\omega\tau) d\tau.$$

Supposing that the dynamical variable A is correlated with itself, it can be shown with a simple example that the imaginary part $\chi''_{AA}(\omega)$ of the generalized susceptibility is related to the *dissipated energy* in the system. For this purpose, consider the process of radiation-matter interaction in which the system is subjected to the external harmonic field $F(t) = F_0 \cos \omega t$. The Hamiltonian of the system is modified by the quantity $H_1(\mathbf{r}^N, \mathbf{p}^N, t) = -A(\mathbf{r}^N, \mathbf{p}^N, 0)F(t)$ (Eq. 10.36) which has the dimensions of energy. Moreover, if we assume that the implicit variation in time of the dynamical variable A , through variations of the coordinates of phase space $\mathbf{r}^N$ and $\mathbf{p}^N$, is faster than that of the external field $F(t)$, the energy dissipated in the system per unit of time (instantaneous power) can be calculated by evaluating the expression:

$$\frac{dE}{dt} = -F(t) \frac{d}{dt} \langle A(t) \rangle, \quad (10.79)$$

where the mean value of the dynamical variable (Eq. 10.54) is:

$$\langle A(t) \rangle = \int_0^\infty F(t - \tau) \phi_{AA}(\tau) d\tau = \int_0^\infty F_0 \cos[\omega(t - \tau)] \phi_{AA}(\tau) d\tau, \quad (10.80)$$

or equivalently:

$$\langle A(t) \rangle = F_0 \operatorname{Re} \left\{ \exp(i\omega t) \int_0^\infty \exp(-i\omega\tau) \phi_{AA}(\tau) d\tau \right\}. \quad (10.81)$$

As the Fourier-Laplace transform of the response function $\phi_{AA}(\tau)$ is the generalized susceptibility $\chi_{AA}(\omega)$ (Eq. 10.56), the above relation can be put in the form¹⁴:

$$\langle A(t) \rangle = F_0 [\chi'_{AA}(\omega) \cos(\omega t) - \chi''_{AA}(\omega) \sin(\omega t)]. \quad (10.82)$$

Now, substituting this expression of $\langle A(t) \rangle$ in equation (10.79), we deduce the instantaneous power:

$$\frac{dE}{dt} = F_0^2 \cos \omega t [\omega \chi'_{AA}(\omega) \sin(\omega t) + \omega \chi''_{AA}(\omega) \cos(\omega t)], \quad (10.83)$$

¹⁴Equation (10.81) is transformed as follows:

$$\begin{aligned} \langle A(t) \rangle &= F_0 \operatorname{Re} \{ \exp(i\omega t) \chi_{AA}(\omega) \}, \\ &= F_0 \operatorname{Re} \{ [\cos(\omega t) + i \sin(\omega t)] [\chi'_{AA}(\omega) + i \chi''_{AA}(\omega)] \}, \\ &= F_0 [\chi'_{AA}(\omega) \cos(\omega t) - \chi''_{AA}(\omega) \sin(\omega t)]. \end{aligned}$$

and the mean energy, when dissipated irreversibly into the system during the period T , becomes:

$$\begin{aligned} \left\langle \frac{dE}{dt} \right\rangle = F_0^2 \omega \left\{ \chi'_{AA}(\omega) \frac{1}{T} \int_{-T/2}^{T/2} \cos(\omega t) \sin(\omega t) dt \right. \\ \left. + \chi''_{AA}(\omega) \frac{1}{T} \int_{-T/2}^{T/2} \cos^2(\omega t) dt \right\}, \end{aligned} \quad (10.84)$$

that is to say:

$$\left\langle \frac{dE}{dt} \right\rangle = F_0^2 \omega \frac{1}{2} \chi''_{AA}(\omega), \quad (10.85)$$

because:

$$\frac{1}{T} \int_{-T/2}^{T/2} \cos(\omega t) \sin(\omega t) dt = 0 \quad \text{and} \quad \frac{1}{T} \int_{-T/2}^{T/2} \cos^2(\omega t) dt = \frac{1}{2}. \quad (10.86)$$

This relation establishes the correspondence between the *mean dissipated power* in the system and the *imaginary part of the generalized susceptibility*. It is of great practical value because it allows us to determine directly the imaginary part of the generalized susceptibility $\chi''_{AA}(\omega)$ called the *dissipative part*, from the experimental measurement of the mean dissipated power $\langle \frac{dE}{dt} \rangle$. It is then easy to deduce the generalized susceptibility $\chi_{AA}(\omega)$ by using the Kramers–Kronig relations. The determination of the response function $\phi_{AA}(t)$ is also made possible by taking the inverse Fourier-Laplace transform (Eq. 10.56), as well as the autocorrelation function of the dynamical variable A with equation (10.53):

$$\phi_{AA}(t) = \beta \langle \dot{A}(0) A(t) \rangle_0 = -\beta \frac{d}{dt} \langle A(0) A(t) \rangle_0. \quad (10.87)$$

In summary, measuring the mean power $\langle \frac{dE}{dt} \rangle$ dissipated in the system permits the determination of the autocorrelation function of the dynamical variable A , i.e. its fluctuations $\langle A(0) A(t) \rangle_0$, in the system at equilibrium. Equation (10.85) is the exact definition of the fluctuation-dissipation theorem proved by Kubo [137], which has been obtained here in a particular case.

10.7 Application to the dielectric relaxation

As a direct application of the linear response theory, we examine the behaviour of permanent dipoles in a dielectric liquid submitted to a variable electric field [167]. As long as the frequency of the applied field is low, the dipoles remain permanently in line with the field direction, and, as the field frequency increases, the dipoles align with respect to the direction of the electric field with an increasing delay. This is the phenomenon of dielectric relaxation, which is accompanied with an energy absorption by the liquid.

Macroscopic aspect of the polarization. An external electric field applied to the dielectric substances gives rise to the electric polarization effect. The macroscopic polarization is a quantity produced by the formation of electric dipole moments at the microscopic level. Remind that the dipole moment of two point charges of opposite sign ($+q$ and $-q$), when separated by a distance r , is defined by the vector $\mathbf{p} = q\mathbf{r}$, where $\mathbf{r}$ is directed from the negative charge toward the positive one. In addition, the sum of the dipole moments per unit volume represents the *polarization vector* denoted $\mathbf{P}$:

$$\mathbf{P} = \frac{1}{V} \sum_i \mathbf{p}_i. \quad (10.88)$$

In the absence of an external field, the dipole moments in a dielectric substance have disordered orientations caused by the thermal agitation, and the polarization vector is zero. Otherwise, if an external field is applied to the dielectric, the dipoles tend to align in the direction of the field, so that the dielectric becomes polarized.

In fact, the polarization (formation of dipole moments) can come from three different mechanisms. It may be of *electronic* origin, with the deformation of electron shells in atoms. It may be of *ionic* origin, with the occurrence of a relative displacement of ions of opposite signs subject to an external field. The third mechanism, of *positional* origin, occurs in liquids and gases composed of molecules that possess permanent electric moments.

Without going into the details of the electrostatic theory of dielectrics [168], just recall that the introduction of a dielectric in an external electric field changes the arrangement of the charges generating the external field. In order to distinguish the characteristics of the field from those of the dielectric, the vector $\mathbf{D}$ is used to denote

the *electric induction field* and the vector $\mathbf{E}$ characterizing the *electric field*. While the electric induction field $\mathbf{D}$ depends only on the topological characteristics of the field produced by a given set of charges, the electric field $\mathbf{E}$ cumulates the characteristics of the dielectric.

In a dielectric of known electrical properties, the electric field $\mathbf{E}$ is related to the electric induction field $\mathbf{D}$ by the relation:

$$\mathbf{E} = \frac{\mathbf{D}}{\varepsilon}, \quad (10.89)$$

where ε is the *absolute dielectric permittivity* of the substance. Determining the electric field $\mathbf{E}_0$ in vacuum produced by the electric induction field $\mathbf{D}$ requires that:

$$\mathbf{E}_0 = \frac{\mathbf{D}}{\varepsilon_0}, \quad (10.90)$$

where ε_0 is *dielectric permittivity of vacuum*, $8.854 \cdot 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$. The electric field $\mathbf{E}$ is expressed in $\text{V} \cdot \text{m}^{-1}$ or in $\text{J} \cdot \text{C}^{-1} \cdot \text{m}^{-1}$, and the electric induction field $\mathbf{D}$ in $\text{C} \cdot \text{m}^{-2}$.

Thus, to determine the dielectric permittivity of a substance, it is sufficient to compare the electric field $\mathbf{E}$ at a point of the matter to the electric field $\mathbf{E}_0$ at the same point when the space is empty. By combining equations (10.89) and (10.90), we obtain the relative dielectric permittivity ε_r of the dielectric:

$$\varepsilon_r = \frac{\mathbf{E}_0}{\mathbf{E}} = \frac{\varepsilon}{\varepsilon_0}. \quad (10.91)$$

Moreover, the action of the electric induction field $\mathbf{D}$ on a dielectric produces a polarization that is made manifest by the appearance of surface charges on the faces of the dielectric. However, these charges give rise to an electric field $\mathbf{E}'$ inside the dielectric but against the field $\mathbf{E}_0$ existing in the absence of dielectric. Consequently, the resulting electric field is¹⁵:

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}'. \quad (10.92)$$

¹⁵The resulting electric field $\mathbf{E}$ is the macroscopic field used in Maxwell's equations. It should not be confused with the local electric field defined when a cavity is created in the dielectric in order to treat the interior of the cavity on a microscopic viewpoint, whereas the rest of the dielectric is treated under the macroscopic aspect.

The field $\mathbf{E}'$ is called the *depolarization field*, and it is connected to the polarization vector $\mathbf{P}$ by the relation:

$$\mathbf{E}' = -\frac{\mathbf{P}}{\varepsilon_0}, \quad (10.93)$$

so that, by substituting equations (10.90) and (10.93) in equation (10.92), we obtain:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}. \quad (10.94)$$

To measure the degree of polarization of a dielectric, it is necessary to express the depolarization field $\mathbf{E}'$ in terms of the macroscopic field $\mathbf{E}$ by the relation $\mathbf{E}' = -\chi_{el} \mathbf{E}$, where χ_{el} is the *electric susceptibility*. When combined with equation (10.93), it allows us to connect the polarization vector $\mathbf{P}$ with the macroscopic field $\mathbf{E}$ by the expression:

$$\mathbf{P} = \varepsilon_0 \chi_{el} \mathbf{E}. \quad (10.95)$$

Thus, to characterize the dielectric properties of a substance, we can use either the electric susceptibility χ_{el} , or the relative permittivity ε_r , with both being linked by a simple relation. Indeed, by putting the expression of $\mathbf{P}$ in equation (10.94) and with the help of equation (10.90), we note that:

$$\varepsilon_0 \mathbf{E}_0 = \varepsilon_0 \mathbf{E} + \varepsilon_0 \chi_{el} \mathbf{E}, \quad (10.96)$$

or:

$$\frac{\mathbf{E}_0}{\mathbf{E}} = \varepsilon_r = 1 + \chi_{el}. \quad (10.97)$$

Microscopic aspect of the polarization

Now that the macroscopic description of dielectric relaxation has been made, we apply the linear response theory by considering the Hamiltonian of the system:

$$H(\mathbf{r}^N, \mathbf{p}^N, t) = H_0(\mathbf{r}^N, \mathbf{p}^N) - P(\mathbf{r}^N) E(t), \quad (10.98)$$

where $H_0(\mathbf{r}^N, \mathbf{p}^N)$ is the Hamiltonian in the absence of external field, $E(t)$ the modulus of the macroscopic electric field, and $P(\mathbf{r}^N)$ (not to be confused with the probability density) is the projection of the sum of the dipole moments $\mathbf{P}(\mathbf{r}^N) = \sum_i \mathbf{p}_i$ onto the field direction. By comparing the above relation with equation (10.36), we see that the

electric field $E(t)$ corresponds to the function $F(t)$ and the polarization $P(\mathbf{r}^N)$ to the dynamical variable $A(\mathbf{r}^N, \mathbf{p}^N, 0)$. If, moreover, we assume that the dynamical variable $B(\mathbf{r}^N, \mathbf{p}^N, 0)$ is assimilated to the polarization $P(\mathbf{r}^N)$, the mean value $\langle P(t) \rangle$ is written (Eq. 10.48):

$$\langle P(t) \rangle = \int_{-\infty}^t E(t') \phi(t-t') dt', \quad (10.99)$$

where the response function $\phi(t-t')$ is defined by the expression (Eqs. 10.52 and 10.53):

$$\phi(t-t') = \beta \langle \dot{P}(t') P(t-t') \rangle_0, \quad (10.100)$$

or:

$$\phi(t) = -\beta \frac{d}{dt} \langle P(0) P(t) \rangle_0. \quad (10.101)$$

As regards the generalized susceptibility (Eq. 10.56), whose explicit form is:

$$\chi(\omega) = -\beta \int_0^\infty \frac{d}{dt} \langle P(0) P(t) \rangle \exp(-i\omega t) dt, \quad (10.102)$$

it helps to link $\langle P(\omega) \rangle$ to $E(\omega)$ by equation (10.57):

$$\langle P(\omega) \rangle = \chi(\omega) E(\omega). \quad (10.103)$$

After comparing equation (10.103) with equation (10.95), it is easy to see that the generalized susceptibility $\chi(\omega)$ is related to the electric susceptibility $\chi_{el}(\omega)$ by the relation:

$$\chi(\omega) = \varepsilon_0 \chi_{el}(\omega). \quad (10.104)$$

For fluids consisting of dipolar molecules, the calculations of the response function and the generalized susceptibility are very difficult. By contrast, in the case of dilute fluids, the calculations are simplified if the two following assumptions are made:

(1) The dipole moments on different sites are uncorrelated. Therefore, the autocorrelation function of the dipole moments $\langle P(0) P(t) \rangle = \sum_{i,j} \langle p_i(0) p_j(t) \rangle$ can be simplified by neglecting the terms $i \neq j$ and

keeping only the terms $i = j$. The response function (Eq. 10.101) is then:

$$\begin{aligned}\phi(t) &= -\beta \frac{d}{dt} \langle P(0)P(t) \rangle = -\beta \frac{d}{dt} \sum_{i=1}^N \langle p_i(0)p_i(t) \rangle, \\ &\simeq -\beta N \frac{d}{dt} \langle p(0)p(t) \rangle,\end{aligned}\quad (10.105)$$

where N is the number of dipole moments in the system.

(2) The autocorrelation function of the dipole moments undergoes an exponential decay:

$$\langle p(0)p(t) \rangle \simeq p^2 \exp\left(-\frac{t}{\tau}\right), \quad (10.106)$$

where p^2 is the value of the autocorrelation function of the dipole moments at the initial time, and τ the relaxation time. According to footnote 10, this approximation means that the dipole moment is a random variable with the Markovian character.

With these two assumptions, the response function (Eq. 10.105) reads:

$$\phi(t) = \beta \frac{N}{\tau} p^2 \exp\left(-\frac{t}{\tau}\right), \quad (10.107)$$

and the generalized susceptibility (Eq. 10.56) becomes:

$$\begin{aligned}\chi(\omega) &= \int_0^\infty \phi(t) \exp(-i\omega t) dt \\ &= \beta \frac{N}{\tau} p^2 \left[\int_0^\infty \exp\left(-\frac{t}{\tau}\right) \cos(\omega t) dt \right. \\ &\quad \left. - i \int_0^\infty \exp\left(-\frac{t}{\tau}\right) \sin(\omega t) dt \right],\end{aligned}\quad (10.108)$$

namely:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega) \quad (10.109)$$

with¹⁶:

$$\chi'(\omega) = \beta \frac{N}{\tau} p^2 \int_0^\infty \exp\left(-\frac{t}{\tau}\right) \cos(\omega t) dt = \beta N p^2 \frac{1}{1 + \tau^2 \omega^2}, \quad (10.110)$$

$$\chi''(\omega) = \beta \frac{N}{\tau} p^2 \int_0^\infty \exp\left(-\frac{t}{\tau}\right) \sin(\omega t) dt = \beta N p^2 \frac{\tau \omega}{1 + \tau^2 \omega^2}. \quad (10.111)$$

¹⁶It is easy to verify whether the integration by parts of the two quantities X

Equations (10.97) and (10.104) can be used in conjunction with the above expressions to determine the complex dielectric constant $\varepsilon_r(\omega) = \varepsilon'_r(\omega) + i\varepsilon''_r(\omega)$. Indeed, by combining these equations, we derive:

$$\varepsilon_r(\omega) - 1 = \chi_{el}(\omega) = \frac{\chi(\omega)}{\varepsilon_0}, \quad (10.112)$$

or:

$$\varepsilon'_r(\omega) - 1 + i\varepsilon''_r(\omega) = \frac{\chi'(\omega)}{\varepsilon_0} + i\frac{\chi''(\omega)}{\varepsilon_0}, \quad (10.113)$$

so that, by identifying simultaneously the real parts and the imaginary parts of each side in the above relation, we acquire:

$$\varepsilon'_r(\omega) = 1 + \frac{\beta N p^2}{\varepsilon_0} \frac{1}{1 + \tau^2 \omega^2} \quad (10.114)$$

$$\text{and} \quad \varepsilon''_r(\omega) = \frac{\beta N p^2}{\varepsilon_0} \frac{\tau \omega}{1 + \tau^2 \omega^2}. \quad (10.115)$$

These formulas have been obtained by Debye [169], by a direct route. They mean that the real part of dielectric constant is decreasing from the initial value $\varepsilon'_r(0)$ to unity, when the angular frequency of the external field is increasing. In addition, the imaginary part passes by the maximum value $\omega = \frac{1}{\tau}$ in the vicinity of the spot where the decay of the real part is the fastest (Fig. 10.1).

It follows that the mean power dissipated in the dielectric (Eq. 10.85) increases drastically up to the value $\omega = 1/\tau$ of the frequency, before slowly decreasing. A comprehensive study of the dielectric relaxation shows that the higher the frequency increases, the more the dipoles are struggling to align in the direction of the field.

As the Debye relations are similar to the Kramers–Kronig relations, it is not necessary to carry out the measurements of $\varepsilon'_r(\omega)$ and

and Y defined below gives the following results:

$$\begin{aligned} X &= \int_0^\infty \exp\left(-\frac{t}{\tau}\right) \cos(\omega t) dt = \frac{1}{\tau \omega} Y, \\ Y &= \int_0^\infty \exp\left(-\frac{t}{\tau}\right) \sin(\omega t) dt = \frac{1}{\omega} - \frac{1}{\tau \omega} X, \end{aligned}$$

from which the following relations can be deduced:

$$X = \frac{\tau}{1 + \tau^2 \omega^2}, \quad Y = \frac{\tau^2 \omega}{1 + \tau^2 \omega^2}.$$

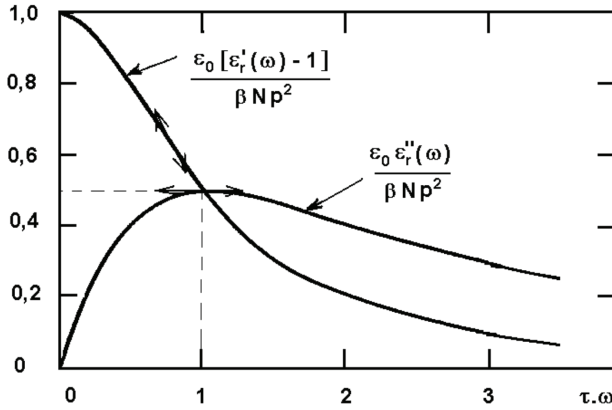


Figure 10.1: Representation of real and imaginary parts of the dielectric constant.

$\epsilon''_r(\omega)$ to determine the complex dielectric constant. According to the fluctuation-dissipation theorem, it is sufficient to measure the mean power dissipated in the dielectric in order to obtain directly the imaginary part $\epsilon''_r(\omega)$, then to deduce the real part $\epsilon'_r(\omega)$ with the Kramers–Kronig relations and the expression of the complex dielectric constant $\epsilon_r(\omega) = \epsilon'_r(\omega) - i\epsilon''_r(\omega)$. However, given the rough assumptions made to derive the Debye formulas, the theoretical results are not expected to coincide precisely with the experimental data.

10.8 Response of a system to a non-uniform field

In section (10.4), we considered a system at equilibrium submitted to a perturbation varying over time but spatially constant. In this section, the perturbation is supposed to be dependent on the time and the positions of the particles. If $F(\mathbf{r}, t)$ stands for the external field, the Hamiltonian of the perturbation is written by generalizing equation (10.36) as:

$$H_1(t) = - \int_V A(\mathbf{r}, 0) F(\mathbf{r}, t) d\mathbf{r}, \quad (10.116)$$

where $A(\mathbf{r}, 0)$ is the local dynamical variable coupled to the external field $F(\mathbf{r}, t)$ and the integration is performed over the volume V of

the system. The external field giving rise to the perturbation can be a scalar or vector function. For instance, in an electron system perturbed by the electric field $\mathbf{E}(\mathbf{r}, t)$, the function $F(\mathbf{r}, t)$ represents the electrostatic potential [$\mathbf{E}(\mathbf{r}, t) = -\mathbf{grad}F(\mathbf{r}, t)$], and the dynamical variable $A(\mathbf{r}, 0)$ corresponds to the charge density $e \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$. By contrast, in a system of neutral particles in interaction, it is customary to equate the function $F(\mathbf{r}, t)$ to the potential energy of interaction and the dynamical variable $A(\mathbf{r}, 0)$ to the density of particles $\rho(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$. This case will be discussed in the following subsection parallel to the van Hove correlation function.

Generally, when a system is submitted to a non-uniform external field $F(\mathbf{r}, t)$ associated with the dynamical variable $A(\mathbf{r}, 0)$, the mean value of the dynamical variable $B(\mathbf{r}, t)$ is written by analogy with equation (10.48) as¹⁷:

$$\langle B(\mathbf{r}, t) \rangle = \int_V \left\{ \int_{-\infty}^t F(\mathbf{r}', t') \phi_{BA}(\mathbf{r} - \mathbf{r}', t - t') dt' \right\} d\mathbf{r}', \quad (10.117)$$

where $\phi_{BA}(\mathbf{r} - \mathbf{r}', t - t')$ is the spatiotemporal response function. In writing the above relation, it has been assumed that the response function is invariant under translation in time (as for a uniform perturbation) as well as in space so that, by taking $\mathbf{r}' = \mathbf{0}$ and $t' = 0$, the response function can be denoted $\phi_{BA}(\mathbf{r}, t)$. Thus the mean value of the dynamical variable $B(\mathbf{r}, t)$ at point $\mathbf{r}$ and time t depends on all the positions $\mathbf{r}'$ and the times t' earlier than t .

As regards the generalized susceptibility, it is written by analogy to equation (10.56) in the form:

$$\chi_{BA}(\mathbf{q}, \omega) = \int_V \left\{ \int_0^\infty \phi_{BA}(\mathbf{r}, t) \exp(-i\omega t) dt \right\} \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}. \quad (10.118)$$

It should be stressed that the spatial integration over $\mathbf{r}$ is a genuine Fourier transform because it is performed on the system volume. By contrast, the temporal integration over t is a Fourier-Laplace transform due to the principle of causality. In continuing the analogy by generalizing equation (10.57), the expression of the mean value of the dynamical variable $B(\mathbf{r}, t)$ can be written in the space of transfer vectors and angular frequency:

¹⁷At this stage, the interested reader is advised to consult the article by B. J. Berne [170].

$$\langle B(\mathbf{q}, \omega) \rangle = \chi_{BA}(\mathbf{q}, \omega) F(\mathbf{q}, \omega). \quad (10.119)$$

Finally, as the response function $\phi_{BA}(\mathbf{r}, t)$ is real, the real and imaginary parts of the generalized susceptibility have the following properties (section 10.5):

$$\chi'_{BA}(-\mathbf{q}, -\omega) = \chi'_{BA}(\mathbf{q}, \omega); \quad (10.120)$$

$$\chi''_{BA}(-\mathbf{q}, -\omega) = -\chi''_{BA}(\mathbf{q}, \omega), \quad (10.121)$$

and the Kramers–Kronig relations (Eqs. 10.77 and 10.78) remain valid.

11 Dynamic structure factor

11.1 The van Hove correlation function

Although the correlation function of van Hove [165] has been introduced as a consequence of the study of the inelastic neutron scattering, it is possible to define it intuitively by means of the autocorrelation function of the particle density. The van Hove correlation function is a natural extension of the pair correlation function $g(\mathbf{r})$. It describes the correlation between a particle at the point $\mathbf{r}'$, at time t' , and another particle at the point $\mathbf{r}''$, at time t'' , averaged over the space. As it will be seen later, the van Hove function denoted $G(\mathbf{r}, t)$ reduces to $\rho g(\mathbf{r})$ when $t=0$, where $\rho = N/V$ is the average density of particles.

Before presenting the van Hove function, let us introduce a dynamical variable, i.e. the *density of particles* $\rho(\mathbf{r}, t)$ at the point $\mathbf{r}$ and time t , as defined by the Dirac function:

$$\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{r}_i(t)] . \quad (11.1)$$

In agreeing that the vector $\mathbf{r}_i(t)$ stands for the position of the particle i at time t , it can be seen that $\delta[\mathbf{r} - \mathbf{r}_i(t)] = 0$ when the radius vector $\mathbf{r}$ does not coincide with the vector $\mathbf{r}_i(t)$. Obviously, the integral of the density of particles on the volume is equal to the total number of particles N :

$$\int \rho(\mathbf{r}, t) d\mathbf{r} = \sum_{i=1}^N \int \delta[\mathbf{r} - \mathbf{r}_i(t)] d\mathbf{r} = \sum_{i=1}^N 1 = N . \quad (11.2)$$

By omitting the time dependence in the above relation, it can be observed that the mean density of particles in the canonical ensemble is written as (section 3.4):

$$\langle \rho(\mathbf{r}) \rangle = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle = \frac{1}{Z_N} \int \int \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N. \quad (11.3)$$

If the Dirac function is used, the previous integral is equal to N times the integral of a single particle over one of the N variables ($\mathbf{r}_1$ for instance). Accordingly, the mean density of particles reads:

$$\langle \rho(\mathbf{r}) \rangle = \frac{1}{Z_N} N \int \int \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (11.4)$$

However, this expression is exactly the generic first-order distribution function $\rho_N^{(1)}(\mathbf{r})$ (Eq. 3.83). For a homogeneous and isotropic fluid, it is reduced to the mean density of particles:

$$\langle \rho(\mathbf{r}) \rangle = \rho_N^{(1)}(\mathbf{r}) = \rho = \frac{N}{V}. \quad (11.5)$$

A similar calculation can be carried out to obtain the following mean value:

$$\begin{aligned} \left\langle \sum_i^N \sum_{j \neq i}^N \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \right\rangle &= \\ &= \frac{1}{Z_N} \int \int \sum_i^N \sum_{j \neq i}^N \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}^N \\ &= \frac{1}{Z_N} N(N-1) \int \int \exp[-\beta U(\mathbf{r}^N)] d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N. \end{aligned} \quad (11.6)$$

This expression refers to the generic second-order distribution function $\rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ (Eq. 3.89). For a homogeneous and isotropic fluid, it is linked to the pair correlation function $g(r)$ by the relation:

$$\left\langle \sum_i^N \sum_{j \neq i}^N \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \right\rangle = \rho_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 g(r), \quad (11.7)$$

which is proportional to the probability of finding a particle at distance r from another particle fixed at an arbitrary place. Note that

equation (11.7) also corresponds to the spatial autocorrelation function of the particle density $\langle \rho(r_1)\rho(r_2) \rangle$.

Now, if we are interested in the probability of finding the particle j at the point $\mathbf{r}''$ and time t'' , while the particle i was at the point $\mathbf{r}' = \mathbf{r}'' - \mathbf{r}$ at time $t' = t'' - t$, we have to consider the two time-dependent density of particles:

$$\rho(\mathbf{r}', t') = \sum_{i=1}^N \delta[\mathbf{r}' - \mathbf{r}_i(t')] \quad (11.8)$$

$$\text{and } \rho(\mathbf{r}'', t'') = \sum_{j=1}^N \delta[\mathbf{r}'' - \mathbf{r}_j(t' + t)] . \quad (11.9)$$

Assuming that the origin of time is $t' = 0$, the van Hove correlation function is defined by the expression:

$$\begin{aligned} G(\mathbf{r}, t) &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] d\mathbf{r}' \right\rangle \\ &= \frac{1}{N} \int \langle \rho(\mathbf{r}'', t) \rho(\mathbf{r}', 0) \rangle d\mathbf{r}' , \end{aligned} \quad (11.10)$$

where the integration on $\mathbf{r}'$ arises because the origin of the radius vector $\mathbf{r}$ is arbitrary (Fig. 11.1). It should be noted that the above relation represents the spatiotemporal autocorrelation function of the particle density:

$$G(\mathbf{r}, t) = \frac{1}{\rho} \langle \rho(\mathbf{0}, 0) \rho(\mathbf{r}, t) \rangle. \quad (11.11)$$

Equation (11.10) is applicable to all systems (quantum and classical). For classical liquids, where the scales of time and distance in the diffusion process are large¹, the operators $\mathbf{r}_i(0)$ and $\mathbf{r}_j(t)$ commute. In this case, the direct integration over $\mathbf{r}'$ can be performed, giving the expression:

$$G_{cl}(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)] \right\rangle . \quad (11.12)$$

¹Quantum effects do not manifest themselves in systems where the distances between particles are much larger than the de Broglie wavelength $\Lambda = \hbar \left(\frac{\beta}{2\pi M} \right)^{1/2} \sim 10^{-12}$ m and for time intervals much larger than $\frac{\hbar}{\beta} \sim 10^{-12}$ s. Except for helium and neon, most of the simple liquids are classical (see Egelstaff [171], p. 106).

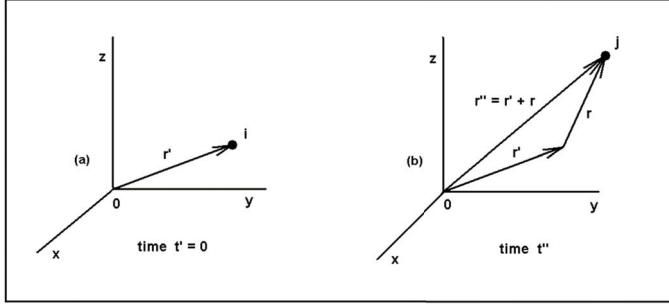


Figure 11.1: Positions of (a) the particle i at time $t' = 0$ and (b) the particle j at time $t'' = t' + t$.

By following the presentation of van Hove, we distinguish between the term $i=j$ and the terms $i \neq j$ in the double sum that allows the decomposition of equation (11.10) as:

$$G(\mathbf{r}, t) = G_s(\mathbf{r}, t) + G_d(\mathbf{r}, t), \quad (11.13)$$

where :

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_i(t)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] d\mathbf{r}' \right\rangle, \quad (11.14)$$

$$G_d(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] d\mathbf{r}' \right\rangle. \quad (11.15)$$

The function $G_s(\mathbf{r}, t)$ describes the correlation of one particle with itself, and the quantity $G_s(\mathbf{r}, t)d\mathbf{r}$ can be regarded as the probability of finding the particle i confined in the volume element $d\mathbf{r}$ located at the point $\mathbf{r}$ at time t , while it was at the point $\mathbf{r} = 0$ at time $t = 0$. As far as the function $G_d(\mathbf{r}, t)$ is concerned, it describes the correlation between two different particles, and the quantity $G_d(\mathbf{r}, t)d\mathbf{r}$ can be interpreted as the probability of finding the particle j in the volume element $d\mathbf{r}$ located at the point $\mathbf{r}$ at time t , while the particle i was at the point $\mathbf{r} = 0$ at time $t = 0$ (Fig. 11.1).

At $t = 0$, it is easy to see that the functions $G_s(\mathbf{r}, 0)$ and $G_d(\mathbf{r}, 0)$

are reduced respectively to:

$$\begin{aligned} G_s(\mathbf{r}, 0) &= \frac{1}{N} \left\langle \sum_{i=1}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_i(0)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] d\mathbf{r}' \right\rangle \\ &= \frac{1}{N} \left\langle \sum_{i=1}^N \delta(\mathbf{r}) \right\rangle = \delta(\mathbf{r}), \end{aligned} \quad (11.16)$$

and:

$$G_d(\mathbf{r}, 0) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(0)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] d\mathbf{r}' \right\rangle. \quad (11.17)$$

In homogeneous and isotropic fluids, the integration over the volume V of the system does not depend on the choice of the integration variables. After posing $\mathbf{r}' = \mathbf{r}_1$ and $\mathbf{r}' + \mathbf{r} = \mathbf{r}_2$, and using equation (11.7), the expression of $G_d(\mathbf{r}, 0)$ becomes:

$$\begin{aligned} G_d(\mathbf{r}, 0) &= \frac{1}{N} \int \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \delta[\mathbf{r}_2 - \mathbf{r}_j(0)] \delta[\mathbf{r}_1 - \mathbf{r}_i(0)] \right\rangle d\mathbf{r}' \\ &= \frac{1}{N} \int \rho^2 g(r) d\mathbf{r}' = \frac{V}{N} \rho^2 g(r) = \rho g(r). \end{aligned} \quad (11.18)$$

When the time is increasing ($t \rightarrow \infty$), the correlations between particles continue to diminish so that $G_s(\mathbf{r}, t) \rightarrow 0$ and $G_d(\mathbf{r}, t) \rightarrow \rho$, whatever the values of $\mathbf{r}$. In fact, there is no correlation between the particles (Fig. 11.2) at the limit of long distances and large times, so that:

$$\lim_{r \rightarrow \infty} G_s(\mathbf{r}, t) = \lim_{t \rightarrow \infty} G_s(\mathbf{r}, t) = \frac{1}{V} \sim 0, \quad (11.19)$$

$$\lim_{r \rightarrow \infty} G_d(\mathbf{r}, t) = \lim_{t \rightarrow \infty} G_d(\mathbf{r}, t) = \rho. \quad (11.20)$$

It is worthwhile mentioning that the normalization of $G_d(\mathbf{r}, t)$ is different from that of the pair correlation function $g(r)$ which is conventionally equal to unit at large values of r . In addition, according to equation (11.16), the dimension of $G_s(\mathbf{r}, t)$ is the same as that of $\delta(\mathbf{r})$, that is to say V^{-1} . Hence, it follows that the dimension of the van Hove function is the inverse of a volume.

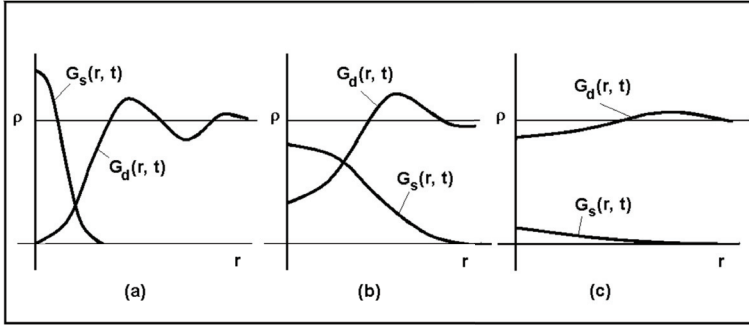


Figure 11.2: Schematic representations of the correlation functions $G_s(r, t)$ and $G_d(r, t)$ at (a) short times, (b) intermediate times and (c) long times.

11.2 The intermediate scattering function and dynamic structure factor

After having defined the van Hove function $G(\mathbf{r}, t)$ as the spatiotemporal autocorrelation function of the particle density, and examined some properties of the functions $G_s(\mathbf{r}, t)$ and $G_d(\mathbf{r}, t)$ we give their representations in the reciprocal spatial and temporal spaces (as a function of $\mathbf{q}$ and ω) because these new functions are directly related to the experimental results of neutron scattering.

As a matter of fact, the key function arising from the inelastic neutron scattering experiments is the *dynamic structure factor* $S(\mathbf{q}, \omega)$ which is the spatiotemporal Fourier transform of the van Hove function, namely:

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\int G(\mathbf{r}, t) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \right] \exp(-i\omega t) dt \quad (11.21)$$

with

$$G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int \left[\int_{-\infty}^{\infty} S(\mathbf{q}, \omega) \exp(i\omega t) d\omega \right] \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q}. \quad (11.22)$$

Traditionally, the dynamic structure factor is evaluated through the *intermediate scattering function* $F(\mathbf{q}, t)$ that is the spatial Fourier transform of the van Hove function:

$$F(\mathbf{q}, t) = \int G(\mathbf{r}, t) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \quad (11.23)$$

$$\text{with} \quad G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int F(\mathbf{q}, t) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q}. \quad (11.24)$$

Thus, the dynamic structure factor $S(\mathbf{q}, \omega)$ is related to the intermediate scattering function $F(\mathbf{q}, t)$ by the temporal Fourier transform as:

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\mathbf{q}, t) \exp(-i\omega t) dt, \quad (11.25)$$

$$\text{with} \quad F(\mathbf{q}, t) = \int_{-\infty}^{\infty} S(\mathbf{q}, \omega) \exp(i\omega t) d\omega. \quad (11.26)$$

To justify the intermediate character of the function $F(\mathbf{q}, t)$ and assign a physical meaning to it, let us calculate its expression by substituting equation (11.10) in equation (11.23). The result of the calculations is²:

$$F(\mathbf{q}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp[i\mathbf{q} \cdot \mathbf{r}_j(t)] \exp[-i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle. \quad (11.27)$$

After noting that the mean value in the above relationship is the *autocorrelation function* of the particle density in the reciprocal space³,

²With the changes of variables $\mathbf{r}_1 = \mathbf{r}'$ and $\mathbf{r}_2 = \mathbf{r}' + \mathbf{r}$, where $|J| = 1$, and the use of the Dirac function, the intermediate scattering function $F(\mathbf{q}, t)$ is transformed as follows:

$$\begin{aligned} F(\mathbf{q}, t) &= \frac{1}{N} \int \left\langle \sum_{i=1}^N \sum_{j=1}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] d\mathbf{r}' \right\rangle \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} \\ &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \int \int \delta[\mathbf{r}_2 - \mathbf{r}_j(t)] \delta[\mathbf{r}_1 - \mathbf{r}_i(0)] \exp[i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] d\mathbf{r}_1 d\mathbf{r}_2 \right\rangle \\ &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp[i\mathbf{q} \cdot \mathbf{r}_j(t)] \exp[-i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle. \end{aligned}$$

³Indeed, the spatial Fourier transform of the particle density (Eq. 11.1) is:

$$\begin{aligned} \rho(\mathbf{q}, t) &= \int \rho(\mathbf{r}, t) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \\ &= \int \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{r}_i(t)] \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = \sum_{i=1}^N \exp[i\mathbf{q} \cdot \mathbf{r}_i(t)]. \end{aligned}$$

the intermediate scattering function $F(\mathbf{q}, t)$ can also be written:

$$F(\mathbf{q}, t) = \frac{1}{N} \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle. \quad (11.28)$$

It represents the conditional probability of having a density fluctuation of transfer vector $\mathbf{q}$ at time t , whereas there was a density fluctuation of transfer vector $-\mathbf{q}$ at time 0. Besides, since the van Hove correlation function $G(\mathbf{r}, t)$ has the dimension of the inverse volume, it follows that the intermediate scattering function $F(\mathbf{q}, t)$ is dimensionless and the dynamic structure factor $S(\mathbf{q}, \omega)$ has the dimension of time.

By separating the term $i = j$ from the terms $i \neq j$ in the double sum of equation (11.27), the latter is written as:

$$F(\mathbf{q}, t) = F_s(\mathbf{q}, t) + F_d(\mathbf{q}, t), \quad (11.29)$$

with

$$F_s(\mathbf{q}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \exp[i\mathbf{q} \cdot \mathbf{r}_i(t)] \exp[-i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle \quad (11.30)$$

and

$$F_d(\mathbf{q}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \exp[i\mathbf{q} \cdot \mathbf{r}_j(t)] \exp[-i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle. \quad (11.31)$$

Like the van Hove function $G(\mathbf{r}, t)$, the intermediate scattering function $F(\mathbf{q}, t)$ and the dynamic structure factor $S(\mathbf{q}, \omega)$ can be split into a part related to the correlation of one particle with itself – respectively $F_s(\mathbf{q}, t)$ and $S_s(\mathbf{q}, \omega)$ – and a part related to the correlation between different particles – respectively $F_d(\mathbf{q}, t)$ and $S_d(\mathbf{q}, \omega)$. Therefore, equations (11.23) and (11.25) are equally valid with the indices “ s ” and “ d ”. These relations allow the inference of some important formulas, especially in the case where $t = 0$. For example, equation (11.26) yields directly:

$$F(\mathbf{q}, 0) = \int_{-\infty}^{\infty} S(\mathbf{q}, \omega) d\omega. \quad (11.32)$$

Moreover, substituting successively equations (11.16) and (11.18) in equation (11.23), we obtain the intermediate scattering functions $F_s(\mathbf{q}, 0)$, $F_d(\mathbf{q}, 0)$ and $F(\mathbf{q}, 0)$ in terms of the pair correlation function:

$$F_s(\mathbf{q}, 0) = \int G_s(\mathbf{r}, 0) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = \int \delta(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = 1, \quad (11.33)$$

$$F_d(\mathbf{q}, 0) = \int G_d(\mathbf{r}, 0) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} = \rho \int g(r) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}, \quad (11.34)$$

and

$$F(\mathbf{q}, 0) = F_s(\mathbf{q}, 0) + F_d(\mathbf{q}, 0) = 1 + \rho \int g(r) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}. \quad (11.35)$$

By extracting the singularity in the previous integral, we find again equation (3.116):

$$F(\mathbf{q}, 0) = 1 + \rho \int [g(r) - 1] \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r} + \rho(2\pi)^3 \delta(\mathbf{q}), \quad (11.36)$$

that is to say the identity between the intermediate scattering function at $t = 0$ and the static structure factor $S(q)$, namely:

$$F(\mathbf{q}, 0) = \int_{-\infty}^{\infty} S(\mathbf{q}, \omega) d\omega = S(q) + \rho(2\pi)^3 \delta(\mathbf{q}). \quad (11.37)$$

This definition is consistent with the treatment of the static structure factor given in section (3.5). The static structure factor $S(q)$ results from the integration of the dynamic structure factor $S(\mathbf{q}, \omega)$ over the difference in energy $\hbar\omega$ between the radiations of scattered and incident neutrons.

11.3 Properties of the functions $F(\mathbf{q}, t)$ and $S(\mathbf{q}, \omega)$

To determine the main properties of the intermediate scattering function $F(\mathbf{q}, t)$, we write it with the autocorrelation function of the particle density in reciprocal space by means of equation (11.28). Since this autocorrelation function is stationary, it depends only on the time interval t . As a consequence, if an arbitrary origin t_0 is chosen, it is also expressed under the following form:

$$F(\mathbf{q}, t) = \frac{1}{N} \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle = \frac{1}{N} \langle \rho(\mathbf{q}, t_0 + t) \rho(-\mathbf{q}, t_0) \rangle, \quad (11.38)$$

hence, by assigning $t_0 = -t$, it reduces to:

$$F(\mathbf{q}, t) = \frac{1}{N} \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle = \frac{1}{N} \langle \rho(\mathbf{q}, 0) \rho(-\mathbf{q}, -t) \rangle. \quad (11.39)$$

In addition, by using equation (11.27), it is easy to see that the complex conjugate of the autocorrelation function of the particle density is:

$$\begin{aligned} F^*(\mathbf{q}, t) &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp[-i\mathbf{q} \cdot \mathbf{r}_j(t)] \exp[i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle \\ &= \frac{1}{N} \langle \rho(-\mathbf{q}, t) \rho(\mathbf{q}, 0) \rangle. \end{aligned} \quad (11.40)$$

However, by definition (Eq. 11.28), $F^*(\mathbf{q}, t)$ can also be written:

$$F^*(\mathbf{q}, t) = \frac{1}{N} \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle^*. \quad (11.41)$$

Thus the comparison of equations (11.40) and (11.41) leads to the identity:

$$F^*(\mathbf{q}, t) = \frac{1}{N} \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle^* = \frac{1}{N} \langle \rho(-\mathbf{q}, t) \rho(\mathbf{q}, 0) \rangle. \quad (11.42)$$

Equations (11.39) and (11.42) sum up on their own the properties of the autocorrelation function of the particle density in reciprocal space.

Now we show the real character of the dynamic structure factor by taking the complex conjugate of equation (11.25). After substituting equation (11.42), it becomes:

$$\begin{aligned} S^*(\mathbf{q}, \omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} F^*(\mathbf{q}, t) \exp(i\omega t) dt \\ &= \frac{1}{2\pi N} \int_{-\infty}^{\infty} \langle \rho(-\mathbf{q}, t) \rho(\mathbf{q}, 0) \rangle \exp(i\omega t) dt. \end{aligned} \quad (11.43)$$

However, by replacing t by $-t$ in the integral, we get:

$$S^*(\mathbf{q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{\infty} \langle \rho(-\mathbf{q}, -t) \rho(\mathbf{q}, 0) \rangle \exp(-i\omega t) dt, \quad (11.44)$$

and, owing to equations (11.39) and (11.25), $S^*(\mathbf{q}, \omega)$ becomes:

$$S^*(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\mathbf{q}, t) \exp(-i\omega t) dt = S(\mathbf{q}, \omega). \quad (11.45)$$

The relation $S^*(\mathbf{q}, \omega) = S(\mathbf{q}, \omega)$ shows that the dynamic structure factor is a *real* function for all types of systems (quantum or classical). In addition, for a *homogeneous classical fluid* (with translational invariance in space), the dynamic structure factor $S(\mathbf{q}, \omega)$ is, not only a real quantity, but also an even function⁴ of ω . This is valid for the van Hove function $G(\mathbf{r}, t)$ and the intermediate scattering function $F(\mathbf{q}, t)$ which are *real* and *even* functions of $\mathbf{r}$ and t , and of $\mathbf{q}$ and t , respectively. Therefore, in a homogeneous classical fluid, the dynamic structure factor $S(\mathbf{q}, \omega)$ (Eq. 11.45) is written simply as:

$$S(\mathbf{q}, \omega) = \frac{1}{\pi} \int_0^\infty F(\mathbf{q}, t) \cos(\omega t) dt = \frac{1}{\pi} \text{Re} \{FLT[F(\mathbf{q}, t)]\}, \quad (11.46)$$

which is nothing less than the real part of the Fourier–Laplace transform of the intermediate scattering function $F(\mathbf{q}, t)$.

Let us conclude this section by showing the link between the inelastic neutron scattering process and the linear response theory presented in section (10.4). Recall first that the dynamic structure factor can be expressed in terms of the autocorrelation function of the particle density, substituting equation (11.28) in equation (11.25), namely:

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi N} \int_{-\infty}^\infty \langle \rho(\mathbf{q}, t) \rho(-\mathbf{q}, 0) \rangle \exp(-i\omega t) dt. \quad (11.47)$$

Then, consider the Hamiltonian of the perturbation applied to the system of N particles confined in the volume V :

$$H_1(t) = -\frac{1}{V} \rho(\mathbf{q}, 0) F(t), \quad (11.48)$$

where $\rho(\mathbf{q}, 0)$ is the spatial Fourier transform of the density of particles. It corresponds to the dynamical variable $A(\mathbf{q}, 0)$ coupled to the external field $F(t)$ (Eqs. 10.36 and 10.116). According to equation (10.54), if $\rho(-\mathbf{q}, t)$ stands for the dynamical variable $B(\mathbf{q}, t)$, its mean value is:

$$\langle \rho(-\mathbf{q}, t) \rangle = \frac{1}{V} \int_0^\infty F(t-\tau) \phi(\tau) d\tau, \quad (11.49)$$

⁴In fact, a real liquid is never entirely classical. This is why $S(\mathbf{q}, \omega)$ is always more or less asymmetrical and the processes of radiation-matter interaction can reach thermal equilibrium.

where $\phi(t)$ is the response function written in accordance with equation (10.53) as:

$$\phi(t) = \beta \langle \dot{\rho}(\mathbf{q}, 0) \rho(-\mathbf{q}, t) \rangle_0 = -\beta \frac{d}{dt} \langle \rho(\mathbf{q}, 0) \rho(-\mathbf{q}, t) \rangle_0. \quad (11.50)$$

Following the calculation carried out to derive equation (10.57), the Fourier–Laplace transform of equation (11.49) is expressed by:

$$\langle \rho(-\mathbf{q}, \omega) \rangle = \chi(\mathbf{q}, \omega) F(\omega), \quad (11.51)$$

where the generalized susceptibility is $\chi(\mathbf{q}, \omega) = \chi(-\mathbf{q}, \omega)$ because the system has the inversion symmetry $\mathbf{r} \rightarrow -\mathbf{r}$. According to equation (10.56), the generalized susceptibility is written:

$$\begin{aligned} \chi(\mathbf{q}, \omega) &= \frac{1}{V} \int_0^\infty \phi(t) \exp(-i\omega t) dt \\ &= -\frac{\beta}{V} \int_0^\infty \frac{d}{dt} \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle_0 \exp(-i\omega t) dt. \end{aligned} \quad (11.52)$$

After the integration by parts, $\chi(\mathbf{q}, \omega)$ reduces to⁵:

$$\chi(\mathbf{q}, \omega) = \chi'(\mathbf{q}, \omega) + i\chi''(\mathbf{q}, \omega), \quad (11.53)$$

$$\begin{aligned} \text{with } \chi'(\mathbf{q}, \omega) &= \frac{\beta}{V} \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle_0 \\ &\quad - \frac{\omega\beta}{V} \int_0^\infty \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle \sin(\omega t) dt \end{aligned} \quad (11.54)$$

$$\text{and } \chi''(\mathbf{q}, \omega) = -\frac{\omega\beta}{V} \int_0^\infty \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle_0 \cos(\omega t) dt, \quad (11.55)$$

⁵Indeed:

$$\begin{aligned} \chi(\mathbf{q}, \omega) &= -\frac{\beta}{V} \left\{ \left[\langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle \exp(-i\omega t) \right]_0^\infty \right. \\ &\quad \left. - \int_0^\infty (-i\omega) \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle \exp(-i\omega t) dt \right\} \\ &= \frac{\beta}{V} \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle - i\frac{\omega\beta}{V} \int_0^\infty \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle \exp(-i\omega t) dt \\ &= \frac{\beta}{V} \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle - i\frac{\omega\beta}{V} \int_0^\infty \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle [\cos(\omega t) - i \sin(\omega t)] dt \\ &= \frac{\beta}{V} \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle - \frac{\omega\beta}{V} \int_0^\infty \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle \sin(\omega t) dt \\ &\quad - i\frac{\omega\beta}{V} \int_0^\infty \langle \rho(-\mathbf{q}, 0) \rho(\mathbf{q}, t) \rangle \cos(\omega t) dt. \end{aligned}$$

or, with equation (11.28):

$$\chi''(\mathbf{q}, \omega) = -\frac{\omega\beta}{V} \int_0^\infty NF(\mathbf{q}, t) \cos(\omega t) dt. \quad (11.56)$$

However, in comparing the imaginary component $\chi''(\mathbf{q}, \omega)$ to the expression of the dynamic structure factor (Eq. 11.46), it follows merely that:

$$\chi''(\mathbf{q}, \omega) = -\pi\rho\omega\beta S(\mathbf{q}, \omega). \quad (11.57)$$

Finally, we show that the generalized susceptibility at zero angular frequency $\chi(\mathbf{q}, 0)$ can be expressed as a function of the static structure factor $S(q)$. Of course, when $\omega = 0$, it means that $\chi''(\mathbf{q}, 0) = 0$, and the use of the Kramers-Kronig relations (Eq. 10.77) provides the following expression:

$$\begin{aligned} \chi(\mathbf{q}, 0) &= \lim_{\omega \rightarrow 0} [\chi'(\mathbf{q}, \omega) + i\chi''(\mathbf{q}, \omega)] \\ &= \lim_{\omega \rightarrow 0} \frac{2}{\pi} \int_0^\infty [-\pi\rho\omega'\beta S(\mathbf{q}, \omega')] \frac{\omega'}{\omega'^2 - \omega^2} d\omega', \end{aligned} \quad (11.58)$$

hence it results, taking account of equation (11.37):

$$\chi(\mathbf{q}, 0) = -2\rho\beta \int_0^\infty S(\mathbf{q}, \omega') d\omega' = -\rho\beta [S(q) + \rho(2\pi)^3 \delta(\mathbf{q})]. \quad (11.59)$$

This expression, which is similar to equation (6.97), justifies the previous calculation.

11.4 Thermal neutron scattering in liquids

Historically, the experimental determination of the atomic structure of condensed matter was first performed by X-ray diffraction. The wavelength of X-rays is comparable to the interatomic distance (~ 0.2 nm) and the energy transfers are small compared to the energy of incident photons, so that the X-rays enable us to measure the static structure. By contrast, they do not give access to the dynamic behaviour of liquids because of their radiation frequency far from the vibration frequency of the atoms in liquids (10^{13} s $^{-1}$).

It is quite different with the neutron scattering. With an energy of about 20 meV, corresponding to a frequency $\nu(= E/h)$ around

10^{13} s^{-1} and a wavelength $\lambda (= h/\sqrt{2mE})$ of the order of the interatomic distance, the neutrons⁶ are particularly suitable for studying the atomic structure of liquids and their dynamic properties by the same token.

In a neutron scattering experiment, the neutron-nucleus interaction is quite well localized and the interaction potential is traditionally represented by the Fermi pseudopotential:

$$u_l(\mathbf{r}) = \frac{2\pi\hbar^2}{m} b_l \delta(\mathbf{r} - \mathbf{r}_l), \quad (11.60)$$

where b_l is the characteristic scattering length of the nuclei l . Moreover, the energy of a neutron is $\frac{\hbar^2 k^2}{2m}$ and the associated wave is the plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$. When the modulus of wave vector $\mathbf{k}'$ of the scattered neutron is equal to that of the wave vector $\mathbf{k}$ of the incident neutron, the scattering is *elastic*: this is the type of scattering originally used to measure the static structure factor $S(q)$. In the opposite case ($|\mathbf{k}'| \neq |\mathbf{k}|$), an exchange of energy takes place between the neutrons and the nuclei, and the scattering is *inelastic*. The latter makes possible the measurement of the dynamic structure factor $S(\mathbf{q}, \omega)$.

If we agree that φ_i and φ_f are the wave functions of the *nucleus* before and after diffusion, and E_i and E_f are the energies before and after diffusion, the initial state (i) and final state (f) of the *neutron-nucleus* system are described by the product of the wave functions and the sum of the energies of the neutron-nucleus system, i.e., in

$$\text{initial state: } \phi_i = \varphi_i \exp(i\mathbf{k}\cdot\mathbf{r}) \quad \text{with} \quad E_i^{tot} = E_i + \frac{\hbar^2 k^2}{2m}, \quad (11.61)$$

$$\text{final state: } \phi_f = \varphi_f \exp(i\mathbf{k}'\cdot\mathbf{r}) \quad \text{with} \quad E_f^{tot} = E_f + \frac{\hbar^2 k'^2}{2m}. \quad (11.62)$$

To simplify the notations, we introduce the transfer vector $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ and the energy variation of a neutron during the collision:

$$\hbar\omega = \frac{\hbar^2}{2m} (\mathbf{k}'^2 - \mathbf{k}^2). \quad (11.63)$$

According to the theory of quantum transitions, the differential scattering cross section [172] is proportional to:

⁶The mass m of neutron is 1.00898 atomic mass unit, i.e. $\approx 1.68 \times 10^{-27} \text{ kg}$.

– the square of the modulus of the matrix element of the neutron-nucleus pseudopotential between the initial and final states:

$$\left| \left\langle \varphi_f \exp(-i\mathbf{k}' \cdot \mathbf{r}) \left| \sum_l \frac{2\pi\hbar^2}{m} b_l \delta(\mathbf{r} - \mathbf{r}_l) \right| \varphi_i \exp(i\mathbf{k} \cdot \mathbf{r}) \right\rangle \right|^2, \quad (11.64)$$

– the Dirac function that ensures the conservation of energy of the neutron-nucleus system during the collision:

$$\delta(E_i^{tot} - E_f^{tot}) = \delta(E_i - E_f - \hbar\omega), \quad (11.65)$$

– the probability that the initial state, at the thermal equilibrium, is occupied (Eq. 2.33):

$$p_i = \frac{1}{h^3 Q} \exp(-\beta H), \quad (11.66)$$

– the velocity ratio of the neutron $v'/v (= k'/k)$ before and after the collision.

The differential scattering cross section, per units of energy and solid angle, is calculated by taking the product of these four terms averaged over all initial and final states compatible with the energy conservation, namely:

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} &\propto \frac{k'}{k} \sum_i \sum_f p_i \times \\ &\times \left| \left\langle \varphi_f \exp(-i\mathbf{k}' \cdot \mathbf{r}) \left| \sum_l \frac{2\pi\hbar^2}{m} b_l \delta(\mathbf{r} - \mathbf{r}_l) \right| \varphi_i \exp(i\mathbf{k} \cdot \mathbf{r}) \right\rangle \right|^2 \times \\ &\times \delta(E_i - E_f - \hbar\omega). \end{aligned} \quad (11.67)$$

To reduce this expression, we develop the matrix element of the pseudopotential, which can be written⁷:

$$\begin{aligned} |\langle \dots \rangle|^2 &= \left(\frac{2\pi\hbar^2}{m} \right)^2 \times \\ &\times \sum_l \sum_p \langle \varphi_i | b_l \exp(-i\mathbf{q} \cdot \mathbf{r}_l) | \varphi_f \rangle \langle \varphi_f | b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) | \varphi_i \rangle. \end{aligned} \quad (11.68)$$

⁷The transformation of the matrix element of the pseudopotential is performed

Then, equation (11.68) is substituted in equation (11.67) with the aim of writing the differential scattering cross section as:

$$\frac{d^2\sigma}{d\Omega dE} \propto \frac{k'}{k} \sum_i \sum_f p_i \left(\frac{2\pi\hbar^2}{m} \right)^2 \sum_l \sum_p \langle \varphi_i | b_l \exp(-i\mathbf{q} \cdot \mathbf{r}_l) | \varphi_f \rangle \times \\ \langle \varphi_f | b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) | \varphi_i \rangle \delta(E_i - E_f - \hbar\omega). \quad (11.69)$$

The integral form of the Dirac function⁸, whose expression is

$$\delta(E_i - E_f - \hbar\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp\left[i\frac{t}{\hbar}(E_i - E_f - \hbar\omega)\right] dt, \quad (11.70)$$

makes it possible to transform the latter part of equation (11.69):

$$\langle \varphi_f | b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) | \varphi_i \rangle \delta(E_i - E_f - \hbar\omega) = \\ = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle \varphi_f | b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) | \varphi_i \rangle \exp\left[i\frac{t}{\hbar}(E_i - E_f - \hbar\omega)\right] dt. \quad (11.71)$$

As $\exp\left[i\frac{t}{\hbar}(E_i - E_f - \hbar\omega)\right]$ is a scalar quantity, we can place it to the right or left side of the operator and write equation (11.71) in the following explicit form:

$$\langle \varphi_f | b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) | \varphi_i \rangle \delta(E_i - E_f - \hbar\omega) = \quad (11.72) \\ = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\langle \varphi_f \left| \exp\left(i\frac{t}{\hbar}E_i\right) b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) \exp(-i\frac{t}{\hbar}E_f) \right| \varphi_i \right\rangle \exp(-it\omega) dt.$$

as follows [171]:

$$|\langle \dots \rangle|^2 = \left\langle \varphi_i \left| \int \exp(i\mathbf{k} \cdot \mathbf{r}) \sum_l \frac{2\pi\hbar^2}{m} b_l \delta(\mathbf{r} - \mathbf{r}_l) \exp(-i\mathbf{k}' \cdot \mathbf{r}) d\mathbf{r} \right| \varphi_f \right\rangle \times \\ \times \left\langle \varphi_f \left| \int \exp(i\mathbf{k}' \cdot \mathbf{r}) \sum_p \frac{2\pi\hbar^2}{m} b_p \delta(\mathbf{r} - \mathbf{r}_p) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \right| \varphi_i \right\rangle \\ = \left\langle \varphi_i \left| \frac{2\pi\hbar^2}{m} \sum_l b_l \int \delta(\mathbf{r} - \mathbf{r}_l) \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] d\mathbf{r} \right| \varphi_f \right\rangle \times \\ \times \left\langle \varphi_f \left| \frac{2\pi\hbar^2}{m} \sum_p b_p \int \delta(\mathbf{r} - \mathbf{r}_p) \exp[i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}] d\mathbf{r} \right| \varphi_i \right\rangle \\ = \left(\frac{2\pi\hbar^2}{m} \right)^2 \left\langle \varphi_i \left| \sum_l b_l \exp(-i\mathbf{q} \cdot \mathbf{r}_l) \right| \varphi_f \right\rangle \left\langle \varphi_f \left| \sum_p b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) \right| \varphi_i \right\rangle.$$

⁸By taking advantage of the properties of Dirac's function mentioned in footnote 7 of chapter 3, we have the relation:

$$\delta(\hbar x) = \frac{1}{|\hbar|} \delta(x) = \frac{1}{2\pi|\hbar|} \int_{-\infty}^{\infty} \exp(itx) dt.$$

Next, we express the operator $\exp(i\mathbf{q} \cdot \mathbf{r}_p)$ as a function of the time in the above relation. This issue is related to the transformation of the matrix element stemming from the Schrödinger representation written as $\langle \varphi_f(t) | b_p \exp[i\mathbf{q} \cdot \mathbf{r}_p(0)] | \varphi_i(t) \rangle$, into the Heisenberg representation⁹ dinger representation, turns into the Heisenberg representation as follows (see p. 169 of [172]):

$$\begin{aligned} \langle \varphi_f(t) | X(0) | \varphi_i(t) \rangle &= \left\langle \varphi_f(0) \left| \exp\left(i\frac{t}{\hbar}H\right) X(0) \exp\left(-i\frac{t}{\hbar}H\right) \right| \varphi_i(0) \right\rangle \\ &= \langle \varphi_f(0) | X(t) | \varphi_i(0) \rangle. \end{aligned}$$

written as $\langle \varphi_f(0) | b_p \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] | \varphi_i(0) \rangle$.

With this change of representation, equation (11.72) is transformed in terms of the wave functions at time zero:

$$\begin{aligned} \langle \varphi_f | b_p \exp(i\mathbf{q} \cdot \mathbf{r}_p) | \varphi_i \rangle \delta(E_i - E_f - \hbar\omega) &= \\ = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \langle \varphi_f | b_p \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] | \varphi_i \rangle \exp(-it\omega) dt. \end{aligned} \quad (11.73)$$

Then, this expression is substituted in equation (11.69) in order to write the differential scattering cross section as:

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} &\propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m}\right)^2 \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \sum_l \sum_p \left\{ \sum_i \sum_f p_i \times \right. \\ &\quad \left. \times \langle \varphi_i | b_l \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] | \varphi_f \rangle \langle \varphi_f | b_p \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] | \varphi_i \rangle \right\} \exp(-it\omega) dt. \end{aligned} \quad (11.74)$$

⁹With the Dirac notation, the time-dependent Schrödinger equation is:

$$i\hbar \frac{\partial}{\partial t} |\varphi(t)\rangle = H |\varphi(t)\rangle.$$

If the Hamiltonian H is independent of time, the formal solution of the Schrödinger equation is:

$$|\varphi(t)\rangle = \exp\left(-i\frac{t}{\hbar}H\right) |\varphi(0)\rangle,$$

where $|\varphi(t)\rangle$ is the wavefunction at time t and $|\varphi(0)\rangle$ the wave function at time zero. The eigenvalue equation for the energy is:

$$H |\varphi_i\rangle = E_i |\varphi_i\rangle,$$

$$\text{with } |\varphi_i(t)\rangle = \exp\left(-i\frac{t}{\hbar}H\right) |\varphi_i(0)\rangle \quad \text{and} \quad \langle \varphi_i(t) | = \langle \varphi_i(0) | \exp\left(i\frac{t}{\hbar}H\right).$$

However, the matrix element of the operator X , which is written $\langle \varphi_f(t) | X(0) | \varphi_i(t) \rangle$ in the Schrö

By taking account of the closure relation $\sum_f |\varphi_f\rangle\langle\varphi_f| = 1$, the remaining summation in brackets on the initial states is equal to the thermal average at equilibrium of the product of the two operators, one of which is set at time t and the other one at time zero, i.e.:

$$\begin{aligned} \sum_i \sum_f p_i \langle\varphi_i| b_l \exp[-i\mathbf{q}\cdot\mathbf{r}_l(0)] |\varphi_f\rangle\langle\varphi_f| b_p \exp[i\mathbf{q}\cdot\mathbf{r}_p(t)] |\varphi_i\rangle = \\ = \langle b_l b_p \exp[-i\mathbf{q}\cdot\mathbf{r}_l(0)] \exp[i\mathbf{q}\cdot\mathbf{r}_p(t)] \rangle. \end{aligned} \quad (11.75)$$

Ultimately, the expression of the differential scattering cross section is simplified to:

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE} \propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m} \right)^2 \frac{1}{2\pi\hbar} \times \\ \times \int_{-\infty}^{\infty} \sum_l \sum_p \langle b_l b_p \exp[-i\mathbf{q}\cdot\mathbf{r}_l(0)] \exp[i\mathbf{q}\cdot\mathbf{r}_p(t)] \rangle \exp(-it\omega) dt. \end{aligned} \quad (11.76)$$

In this formulation, the neutron scattering can be seen as resulting from the interference between the wave scattered by the nucleus l , located at the point $\mathbf{r}_l$ at time $t=0$, and the wave scattered by the nucleus p , located at the point $\mathbf{r}_p$ at time t . If all the nuclei are assumed to be identical, the scattering length b can be extracted from the sum. It follows that equation (11.76) is written explicitly with the intermediate scattering function $F(\mathbf{q}, t)$ (Eq. 11.27) in the form:

$$\frac{d^2\sigma}{d\Omega dE} \propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m} \right)^2 \frac{b^2}{2\pi\hbar} N \int_{-\infty}^{\infty} F(\mathbf{q}, t) \exp(-it\omega) dt. \quad (11.77)$$

However, with the help of equation (11.25), the differential scattering cross section is also expressed as a function of the dynamic structure factor $S(\mathbf{q}, \omega)$ as:

$$\frac{d^2\sigma}{d\Omega dE} \propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m} \right)^2 \frac{Nb^2}{\hbar} S(\mathbf{q}, \omega). \quad (11.78)$$

11.5 Coherent and incoherent scatterings

At this stage of the presentation, it should be stressed that the scattering length b plays a major role in neutron scattering experiments.

It is important to distinguish the case where the nuclei are chemically identical, isotopically pure and of spin zero, from the case where the nuclei differ from each other by the isotope and spin effects. In the first case, correlations take place between the nuclei and interferences occur between the scattered waves: this corresponds to the *coherent scattering*. In the second case, there is no correlation between the nuclei of different nature and no interference between the scattered waves: this corresponds to the *incoherent scattering*. In practice, all the elements contain a proportion of coherent scattering and incoherent scattering [173].

In order to treat these two forms of scattering, we write the mean value in the integral of equation (11.76) by separating the terms $l=p$ from the terms $l \neq p$ in the double sum. This gives:

$$\begin{aligned} \left\langle \sum_l \sum_p b_l b_p \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] \right\rangle &= \\ &= \left\langle \sum_l b_l^2 \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_l(t)] \right\rangle \quad (11.79) \\ &+ \left\langle \sum_l \sum_{p \neq l} b_l b_p \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] \right\rangle. \end{aligned}$$

The first contribution on the right hand side of equation (11.79) corresponds to the coherent scattering because the scattering lengths b_l are identical. The meaning of this contribution is evident when $t=0$. It becomes:

$$\left\langle \sum_l b_l^2 \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_l(0)] \right\rangle = N \langle b^2 \rangle. \quad (11.80)$$

As regards the second contribution on the right hand side, it can be written under the form :

$$\begin{aligned} \left\langle \sum_l \sum_{p \neq l} b_l b_p \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_p(0)] \right\rangle &= \\ &= N \langle b \rangle^2 \left\langle \sum_l \sum_{p \neq l} \exp\{-i\mathbf{q} \cdot [\mathbf{r}_l(0) - \mathbf{r}_p(0)]\} \right\rangle, \quad (11.81) \end{aligned}$$

by the fact that the nuclei of different nature are not correlated.

Incidentally, we note that equation (11.79) generalizes equation (3.108) which allows to deduce the static structure factor $S(q)$ through

the *elastic scattering*. In the case of the *inelastic scattering*, equation (11.79) can be written using the intermediate scattering functions (Eqs. 11.30 and 11.31) as:

$$\begin{aligned} \left\langle \sum_l \sum_p b_l b_p \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] \right\rangle = \\ = N \langle b^2 \rangle F_s(\mathbf{q}, t) + N \langle b \rangle^2 F_d(\mathbf{q}, t). \end{aligned} \quad (11.82)$$

But this decomposition is not appropriate to the experimental study of neutron scattering in liquids. For practical reasons, it is better to rearrange the terms as follows:

$$\begin{aligned} \left\langle \sum_l \sum_p b_l b_p \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] \right\rangle = \\ = N \langle b^2 \rangle F_s(\mathbf{q}, t) + N \langle b \rangle^2 F_d(\mathbf{q}, t) + N \langle b \rangle^2 F_s(\mathbf{q}, t) - N \langle b \rangle^2 F_s(\mathbf{q}, t), \end{aligned} \quad (11.83)$$

or equivalently:

$$\begin{aligned} \left\langle \sum_l \sum_p b_l b_p \exp[-i\mathbf{q} \cdot \mathbf{r}_l(0)] \exp[i\mathbf{q} \cdot \mathbf{r}_p(t)] \right\rangle = \\ N \langle b \rangle^2 F(\mathbf{q}, t) + N [\langle b^2 \rangle - \langle b \rangle^2] F_s(\mathbf{q}, t), \end{aligned} \quad (11.84)$$

in order to write equation (11.76) with the intermediate scattering functions $F(q, t)$ and $F_s(q, t)$ as:

$$\begin{aligned} \frac{d^2 \sigma}{d\Omega dE} \propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m} \right)^2 \frac{N}{2\pi\hbar} \int_{-\infty}^{\infty} \left\{ \langle b \rangle^2 F(\mathbf{q}, t) \right. \\ \left. + [\langle b^2 \rangle - \langle b \rangle^2] F_s(\mathbf{q}, t) \right\} \exp(-it\omega) dt, \end{aligned} \quad (11.85)$$

or:

$$\begin{aligned} \frac{d^2 \sigma}{d\Omega dE} \propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m} \right)^2 \frac{N}{\hbar} \left\{ \langle b \rangle^2 \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\mathbf{q}, t) \exp(-it\omega) dt \right. \\ \left. + [\langle b^2 \rangle - \langle b \rangle^2] \frac{1}{2\pi} \int_{-\infty}^{\infty} F_s(\mathbf{q}, t) \exp(-it\omega) dt \right\}. \end{aligned} \quad (11.86)$$

Finally, the differential scattering cross section is expressed in terms of the dynamic structure factors $S(\mathbf{q}, \omega)$ and $S_s(\mathbf{q}, \omega)$ (Eq. 11.25) as:

$$\frac{d^2 \sigma}{d\Omega dE} = \left(\frac{d^2 \sigma}{d\Omega dE} \right)_{coh} + \left(\frac{d^2 \sigma}{d\Omega dE} \right)_{incoh}, \quad (11.87)$$

with:

$$\left(\frac{d^2\sigma}{d\Omega dE} \right)_{coh} \propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m} \right)^2 \frac{N}{\hbar} \langle b \rangle^2 S(\mathbf{q}, \omega), \quad (11.88)$$

$$\left(\frac{d^2\sigma}{d\Omega dE} \right)_{incoh} \propto \frac{k'}{k} \left(\frac{2\pi\hbar^2}{m} \right)^2 \frac{N}{\hbar} [\langle b^2 \rangle - \langle b \rangle^2] S_s(\mathbf{q}, \omega). \quad (11.89)$$

In equations (11.88) and (11.89), the quantities $4\pi\langle b \rangle^2 = \sigma_{coh}$ and $4\pi[\langle b^2 \rangle - \langle b \rangle^2] = \sigma_{incoh}$, which are respectively the *coherent scattering cross section* and the *incoherent scattering cross section* per atom, are determined experimentally. Some elements, such as argon 36, carbon and oxygen, are fully coherent. Other elements, such as hydrogen and vanadium, have spin effects which are so important that they are almost totally incoherent. Note that the coherent scattering cross sections of almost all elements have been measured accurately, whereas the understanding of incoherent scattering cross sections is generally not so clear¹⁰.

11.6 Further additional remarks

Equations (11.88) and (11.89) show that $S(\mathbf{q}, \omega)$ suits the *coherent scattering* and $S_s(\mathbf{q}, \omega)$ the *incoherent scattering*, respectively. The dynamic structure factor $S_s(\mathbf{q}, \omega)$ associated with the incoherent scattering cross section σ_{incoh} provides information about the *individual motion* of atoms because of the absence of interference between the scattering centres. Concerning the dynamic structure factor $S(\mathbf{q}, \omega)$, it is associated with the coherent scattering cross section σ_{coh} which gives information about the *collective motion* and *individual motion* of atoms because $S(\mathbf{q}, \omega) = S_s(\mathbf{q}, \omega) + S_d(\mathbf{q}, \omega)$. Consequently, for an element such as oxygen, for which the diffusion is only *coherent* ($\sigma_{incoh} = 0$), $S(\mathbf{q}, \omega)$ is directly extracted providing information about the *individual* and *collective* motions of atoms. By contrast, for an element where the scattering is essentially *incoherent* ($\sigma_{coh} = 0$), only $S_s(\mathbf{q}, \omega)$ is extracted gaining information about the *individual motion* of atoms. The very low value of the ratio $\sigma_{coh}/\sigma_{incoh}$ ($\sim 2/80$) for hydrogen explains why, in this element, it is easier to observe the individual motion of atoms than collective motion.

¹⁰For instance: $\sigma_{coh} = 4, 2$ barns and $\sigma_{incoh} = 0$ barn for oxygen, and $\sigma_{coh} = 1, 8$ barn and $\sigma_{incoh} = 79, 7$ barns for hydrogen – see p. 296 of [174].

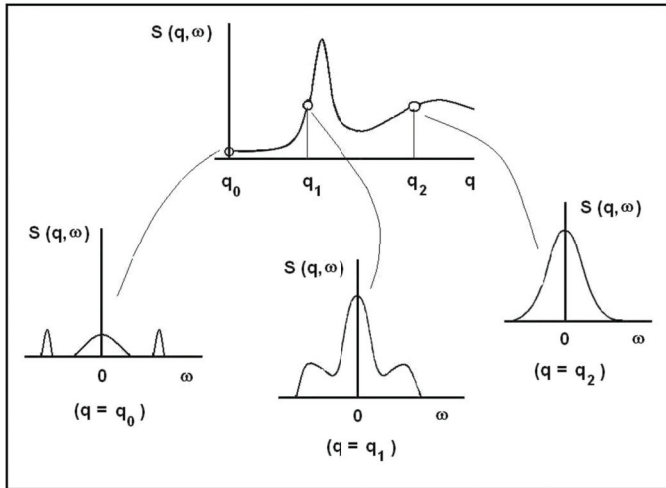


Figure 11.3: Qualitative behavior of the dynamic structure factor $S(\mathbf{q}, \omega)$ for three values of $\mathbf{q}$.

If some elements have several isotopes, it is possible to measure separately the dynamic structure factors $S(\mathbf{q}, \omega)$ and $S_s(\mathbf{q}, \omega)$ by performing two separate experiments. The first experiment, being conducted with the isotopically pure element, gives $S(\mathbf{q}, \omega)$ and the second experiment, being conducted with a combination of isotopes chosen to maximize the incoherent scattering, gives $S_s(\mathbf{q}, \omega)$. Therefore, the experiments of inelastic neutron scattering provide separate access to the individual behaviour of atoms with $S_s(\mathbf{q}, \omega)$ and their collective behaviour thanks to the difference between $S(\mathbf{q}, \omega)$ and $S_s(\mathbf{q}, \omega)$. In the domain of large values of q and ω , i.e. for low values of r and t , the general characteristics of the functions $S(\mathbf{q}, \omega)$ and $S_s(\mathbf{q}, \omega)$ differ slightly from each other because the interference effects between the scattered waves are weak. By contrast, for low values of q and ω , the difference between the functions $S(\mathbf{q}, \omega)$ and $S_s(\mathbf{q}, \omega)$ is stronger but, practically, the collective and individual motions of atoms are mixed. Figure (11.3) reproduces – very schematically – the variation of the dynamic structure factor $S(\mathbf{q}, \omega)$ as a function of $\mathbf{q}$ and ω . In this figure, the bottom curves correspond to sections of the function $S(\mathbf{q}, \omega)$ for three particular values of $\mathbf{q}$. For the value q_0 , where there is a clear distinction between the individual and collective motions

of atoms, we observe a central peak (Rayleigh peak) and two satellite peaks (Brillouin peaks). Regarding the value q_1 the central peak is increasing while the satellite peaks become blurred and, regarding the large values of q , where individual and collective motions of atoms cannot be discriminated, there remains only a broad central peak.

It should be recalled that the dynamic structure factors $S_s(\mathbf{q}, \omega)$ and $S(\mathbf{q}, \omega)$ depend only on the dynamic properties of atoms and not on the radiation. Therefore, the measurement of the dynamic structure factors can, in principle, be done with all available scattering techniques (neutrons, electrons, X rays, electromagnetic radiations... – see p. 99 of [171]). However, each type of radiation makes it possible only to explore the domain (q, ω) for which the scattering angle θ is between 0 and π . As it is seen in figure (11.4a), the variations of energy $\hbar\omega$ and the modulus of the transfer vector $\mathbf{q}$ during the collision are:

$$\hbar\omega = E_i - E_f = \frac{\hbar^2}{2m} \mathbf{k}_i^2 - \frac{\hbar^2}{2m} \mathbf{k}_f^2, \quad (11.90)$$

$$\text{and} \quad q = |\mathbf{k}_f - \mathbf{k}_i|, \quad (11.91)$$

where q is related to the scattering angle θ by the relation:

$$q^2 = |\mathbf{k}_f - \mathbf{k}_i|^2 = k_f^2 + k_i^2 - 2k_f k_i \cos \theta. \quad (11.92)$$

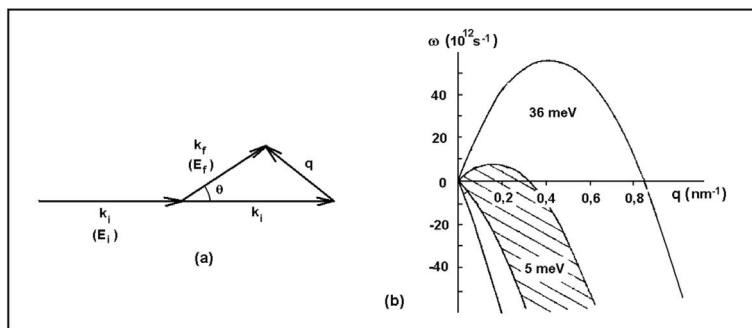


Figure 11.4: (a) Schematic representation of the wave vectors of a neutron. (b) Domains accessible with neutrons of energies 36 meV and 5 meV (the hatched area is for the neutrons of energies 5 meV).

The limits of q^2 for $\theta = 0$ and $\theta = \pi$ are respectively:

$$q^2 = (k_f - k_i)^2 = \frac{2m}{\hbar^2} \left(\sqrt{E_i} - \sqrt{E_f} \right)^2 \quad \text{if } \theta = 0 \quad (11.93)$$

$$= (k_f + k_i)^2 = \frac{2m}{\hbar^2} \left(\sqrt{E_i} + \sqrt{E_f} \right)^2 \quad \text{if } \theta = \pi. \quad (11.94)$$

For example, with a incident neutron beam of energy $E_i = \frac{\hbar^2}{2m} \mathbf{k}_i^2 = 36 \text{ meV}$, corresponding to the wavelength $\lambda (= h/\sqrt{2mE}) \sim 0.15 \text{ nm}$, the possible measurements of q and ω (Fig. 11.4b) are located between the curves of equations:

$$q_{\text{inf}} = \frac{\sqrt{2m}}{\hbar} \left(\sqrt{E_i} - \sqrt{E_i - \hbar\omega} \right), \quad (11.95)$$

$$\text{and} \quad q_{\text{sup}} = \frac{\sqrt{2m}}{\hbar} \left(\sqrt{E_i} + \sqrt{E_i - \hbar\omega} \right). \quad (11.96)$$

It is easy to see that the accessible domain (q, ω) is much larger when the energy of the neutron beam is large, i.e. when the wavelength is small. Unfortunately, one cannot use energetic neutron beams because the resolution is too poor. Therefore, the measurements are practically restricted to the lowest energies of about 5 meV.

Before neutron scattering was used intensively, the visible light was employed with its advantages and disadvantages. Specifically, it provides additional information about the domain of wavelengths ($\sim 400 \text{ nm}$) which differs from that of neutrons ($\sim 1 \text{ nm}$). Thus, the light scattering is appropriate to explore the dynamic behaviour of liquids in the hydrodynamic regime (at very low values of q and ω). It is particularly useful for studying fluids near the critical point [175, 176] where the atomic fluctuations have large amplitudes.

The visible light can also bring information about colloidal suspensions whose dimensions are much larger than those of atoms. The static and dynamic properties of colloidal suspensions share many common features with those of atomic liquids such as, for example, liquid–amorphous–solid transitions when the concentration of particles increases. Although the thermodynamics and transport properties in colloidal and atomic systems have formal analogies, the time scales are considerably different as the relaxation time of density fluctuations is estimated around 10^{-12} s in atomic systems and around 1 s in colloidal solutions. Moreover, the diameter of the colloidal particles

(~ 200 nm) is typically 10^3 times larger than that of the atoms. As a result, the main peak of the static structure factor $S(q)$ is located near $q_m \simeq \frac{2\pi}{d} < 0,05 \text{ nm}^{-1}$, instead of 50 nm^{-1} for liquids. Therefore, the movements of colloidal particles (Brownian motion) are extremely slow and the structure of colloidal solutions can be measured by light scattering. By illuminating the sample with a krypton laser of a power of some mW operating in the wavelength around 500 nm, it is possible to measure the static and dynamic structure factors of colloidal suspensions [177, 178].

It should be noted that, in the atomic systems, the light scattering does not allow measuring $S_s(\mathbf{q}, \omega)$, because the electromagnetic radiation scattered by the atoms is always coherent. Conversely, in the colloidal suspensions, the visible light does not allow measuring $S(\mathbf{q}, \omega)$ because of the strong dispersion of the particle size destroying the interferences between the scattered waves. Therefore, only the static structure factor $S(q)$ and the dynamic structure factor $S_s(\mathbf{q}, \omega)$ of colloidal suspensions are accessible by visible light scattering.

The dynamic structure factors $S_s(\mathbf{q}, \omega)$ and $S(\mathbf{q}, \omega)$ can be calculated by using molecular dynamics and theoretical models specific to the microscopic theory of liquids when the interaction potential $u(r)$ is known. While the comparison between the simulation results and those of a model allows essentially testing the theoretical model, the comparison of simulation results with experimental results is the most effective way to test the interaction potential.

The mathematical models for the dynamic structure factor have been developed mainly for classical systems. However, it has been mentioned in footnote 4 of this chapter that real systems are never entirely classical, and the quantum effects are necessary for reaching the thermal equilibrium between radiation and matter. To compare theory with experiment, either a quantum correction to the model must be carried out, or a specific treatment of the experimental result has to be applied in order to make it compatible with the calculated result. Both methods are equivalent. Without going into details, we mention that the quantum correction is based on the detailed balance condition [179] which is seen in the asymmetry of the experimental dynamic structure factor $S(\mathbf{q}, \omega)$. This is reflected by the relation:

$$S(\mathbf{q}, \omega) = S(\mathbf{q}, -\omega) \exp\left(\frac{\hbar\omega}{k_B T}\right). \quad (11.97)$$

In practice, the comparison between theory and experiment is made by using the *symmetrized dynamic structure factor* $S_{sym}(\mathbf{q}, \omega)$ obtained from the arithmetic or geometric means of $S(\mathbf{q}, \omega)$ and $S(\mathbf{q}, -\omega)$. This amounts to taking one of the following relations:

$$S_{sym1}(\mathbf{q}, \omega) = \frac{S(\mathbf{q}, \omega) + S(\mathbf{q}, -\omega)}{2} = \frac{S(\mathbf{q}, \omega)}{2} \left[1 + \exp\left(-\frac{\hbar\omega}{k_B T}\right) \right], \quad (11.98)$$

and

$$S_{sym2}(\mathbf{q}, \omega) = [S(\mathbf{q}, \omega)S(\mathbf{q}, -\omega)]^{1/2} = S(\mathbf{q}, \omega) \exp\left(-\frac{\hbar\omega}{2k_B T}\right). \quad (11.99)$$

Many theoretical models have been developed over the last thirty years to calculate the dynamic structure factors $S(\mathbf{q}, \omega)$ and $S_s(\mathbf{q}, \omega)$. As they are applicable only in fairly restrictive conditions, none is sufficient in itself to predict the dynamic structure on the whole domain (q, ω) . This is why the numerical simulation is used as an indispensable complement to the interpretation of experimental results, insofar as it helps to fill in the domains (q, ω) unexplored by theoretical models.

By developing the models in the 1960's for calculating the dynamic structure factor, the theorists hashed out the problem of extracting information on individual and collective motions of atoms, from the functions $S_s(\mathbf{q}, \omega)$ and $S(\mathbf{q}, \omega)$ presented in the next sections. Whereas it is easy to imagine how an atom diffuses into a liquid, it seems to be more difficult to relate its individual motion to the measurement of $S_s(\mathbf{q}, \omega)$, and also very importantly to get a clear-cut representation of the collective motion of atoms.

The dynamic structure factor is seldom measured over a large range of energy $\hbar\omega$ and transfer vector $\mathbf{q}$. Furthermore, the theoretical models are applicable only to domains of ω and $\mathbf{q}$ which do not necessarily correspond to those of the measurements. However, the theoretical analysis of the results of $S_s(\mathbf{q}, \omega)$ and $S(\mathbf{q}, \omega)$ performed with the models, together with the experimental results, enables a better understanding of the atomic motion in liquids. To perform this analysis, the intermediate scattering functions $F_s(\mathbf{q}, t)$ and $F(\mathbf{q}, t)$ are usually modeled and provide the dynamic structure factors $S_s(\mathbf{q}, \omega)$ and $S(\mathbf{q}, \omega)$ which are derived by temporal Fourier transform, and then compared with those of the experiment or simulation.

As the results of the *incoherent scattering* $S_s(\mathbf{q}, \omega)$ are inherently easier to interpret than those of the *coherent scattering* $S(\mathbf{q}, \omega)$, we first present some models of the dynamic structure factor $S_s(\mathbf{q}, \omega)$ likely to provide information on the individual motion of atoms. Then, we consider more elaborated models for the dynamic structure factor $S(\mathbf{q}, \omega)$.

11.7 Models for incoherent scattering

The ideal gas model

The *ideal gas model* is the simplest model used to describe the individual motion of atoms on time intervals less than the time between two collisions, that is to say, for *high values of energy* $\hbar\omega$ and *transfer vector* $\mathbf{q}$. With such short time intervals, we can expect that the atoms in fluids will behave as free particles (like in the ideal gas), where the position of each atom is written:

$$\mathbf{r}_1(t) = \mathbf{r}_1(0) + \mathbf{v}_1 t = \mathbf{r}_1(0) + \frac{\mathbf{p}_1}{m} t. \quad (11.100)$$

As the positions of atoms in the ideal gas are not correlated, the intermediate scattering function $F_d(\mathbf{q}, t)$ (Eq. 11.31) is zero, and the intermediate scattering function $F_s(\mathbf{q}, t)$ (Eq. 11.30) simplifies to:

$$F_s(\mathbf{q}, t) = \langle \exp \{ i \mathbf{q} \cdot [\mathbf{r}_1(t) - \mathbf{r}_1(0)] \} \rangle = \left\langle \exp \left(i \frac{\mathbf{q} \cdot \mathbf{p}_1}{m} t \right) \right\rangle. \quad (11.101)$$

However, in the above relation, the ensemble average can be evaluated with the correlation function for one particle as¹¹:

$$F_s(\mathbf{q}, t) = \frac{\int \exp \left(i \frac{\mathbf{q} \cdot \mathbf{p}_1}{m} t \right) \exp \left(-\frac{\beta p_1^2}{2m} \right) d\mathbf{p}_1}{\int \exp \left(-\frac{\beta p_1^2}{2m} \right) d\mathbf{p}_1} = \exp \left(-\frac{q^2 t^2}{2\beta m} \right). \quad (11.102)$$

¹¹If the vector $\mathbf{q}$ is oriented in the x -direction, it is found that $\mathbf{q} \cdot \mathbf{p}_1 = qp_{1x}$ and the expression of $F_s(\mathbf{q}, t)$ is:

$$\begin{aligned} F_s(\mathbf{q}, t) &= \frac{\int \exp \left(i \frac{qp_{1x}}{m} t \right) \exp \left(-\frac{\beta p_{1x}^2}{2m} \right) \exp \left(-\frac{\beta p_{1y}^2}{2m} \right) \exp \left(-\frac{\beta p_{1z}^2}{2m} \right) dp_{1x} dp_{1y} dp_{1z}}{\int \exp \left(-\frac{\beta p_{1x}^2}{2m} \right) \exp \left(-\frac{\beta p_{1y}^2}{2m} \right) \exp \left(-\frac{\beta p_{1z}^2}{2m} \right) dp_{1x} dp_{1y} dp_{1z}} \\ &= \frac{\int \exp \left(i \frac{qp_{1x}}{m} t \right) \exp \left(-\frac{\beta p_{1x}^2}{2m} \right) dp_{1x} \times \int \exp \left(-\frac{\beta p_{1y}^2}{2m} \right) dp_{1y} \times \int \exp \left(-\frac{\beta p_{1z}^2}{2m} \right) dp_{1z}}{\int \exp \left(-\frac{\beta p_{1x}^2}{2m} \right) dp_{1x} \times \int \exp \left(-\frac{\beta p_{1y}^2}{2m} \right) dp_{1y} \times \int \exp \left(-\frac{\beta p_{1z}^2}{2m} \right) dp_{1z}}. \end{aligned}$$

In substituting the expression of $F_s(\mathbf{q}, t)$ in equations (11.24) and (11.25), we obtain respectively the van Hove correlation function $G_s(r, t)$ and the dynamic structure factor $S_s(\mathbf{q}, \omega)$ in the following forms¹²:

$$G_s(r, t) = \frac{1}{(2\pi)^3} \int F_s(q, t) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q} = \left(\frac{\beta m}{2\pi}\right)^{3/2} \frac{1}{t^3} \exp\left(-\frac{\beta m r^2}{2 t^2}\right), \quad (11.103)$$

and¹³:

The first integral in the numerator of the above expression is calculated as follows:

$$\begin{aligned} \int \exp\left(i \frac{qp_{1x}}{m} t - \frac{\beta p_{1x}^2}{2m}\right) dp_{1x} &= \int \exp\left\{-\frac{\beta}{2m} \left[\left(p_{1x} - i \frac{q}{\beta} t\right)^2 - i^2 \frac{q^2}{\beta^2} t^2\right]\right\} dp_{1x} \\ &= \exp\left(i^2 \frac{q^2}{2m\beta} t^2\right) \int \exp\left[-\frac{\beta}{2m} \left(p_{1x} - i \frac{q}{\beta} t\right)^2\right] dp_{1x} \\ &= \exp\left(-\frac{q^2}{2\beta m} t^2\right) \int \exp\left(-\frac{\beta X^2}{2m}\right) dX. \end{aligned}$$

However, in putting this result in its place, it can be seen that the three integrals in the numerator are equal and can be simplified with the three integrals in the denominator, so that $F_s(\mathbf{q}, t) = \exp\left(-\frac{q^2}{2\beta m} t^2\right)$.

¹²The spatial Fourier transform is calculated with the following relation:

$$G_s(r, t) = \frac{1}{(2\pi)^3} \int F_s(q, t) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q} = \frac{4\pi}{(2\pi)^3} \int_0^\infty \exp\left(-\frac{q^2 t^2}{2\beta m}\right) \frac{\sin(qr)}{qr} q^2 dq.$$

This integral has the known form (I. S. Gradshteyn et I. M. Ryzhik, *Table of Integrals, Series and Products*, Acad. Press, New York (1965), p. 495):

$$\int_0^\infty x \exp(-b^2 x^2) \sin(ax) dx = \frac{a\sqrt{\pi}}{4b^3} \exp\left(-\frac{a^2}{4b^2}\right).$$

By writing $x = q$, $a = r$ and $b^2 = \frac{t^2}{2\beta m}$, we obtain:

$$G_s(r, t) = \frac{1}{2\pi^2 r} \int_0^\infty q \exp\left(-\frac{t^2}{2\beta m} q^2\right) \sin(qr) dq = \left(\frac{\beta m}{2\pi}\right)^{3/2} \frac{1}{t^3} \exp\left(-\frac{\beta m r^2}{2 t^2}\right).$$

¹³The temporal Fourier transform is calculated as follows:

$$\begin{aligned} S_s(q, \omega) &= \frac{1}{2\pi} \int_{-\infty}^\infty \exp\left(-\frac{q^2}{2\beta m} t^2\right) \exp(-i\omega t) dt \\ &= \frac{1}{2\pi} \int_{-\infty}^\infty \exp\left\{-\frac{q^2}{2\beta m} \left[\left(t + i \frac{\omega\beta m}{q^2}\right)^2 - \frac{\omega^2 \beta^2 m^2}{q^4}\right]\right\} dt, \\ &= \frac{1}{2\pi} \exp\left(-\frac{\omega^2 \beta m}{2q^2}\right) \int_{-\infty}^\infty \exp\left[-\frac{q^2}{2\beta m} \left(t + i \frac{\omega\beta m}{q^2}\right)^2\right] dt. \end{aligned}$$

By writing $a = \frac{q^2}{2\beta m}$ and $T = \left(t + i \frac{\omega\beta m}{q^2}\right)$, the integral in the above relation is equal to:

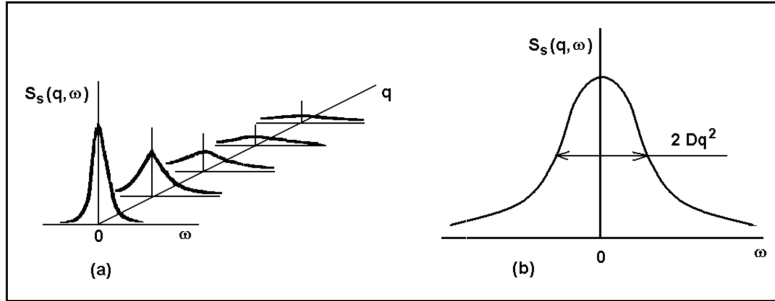


Figure 11.5: Schematic representations of the dynamic structure factor $S_s(q, \omega)$ (a) in the ideal gas model and (b) in the diffusion model.

$$S_s(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_s(q, t) \exp(-i\omega t) dt = \sqrt{\frac{\beta m}{2\pi}} \frac{1}{q} \exp\left(-\frac{\beta m \omega^2}{2 q^2}\right). \quad (11.104)$$

The expressions for $F_s(q, t)$, $G_s(r, t)$ and $S_s(q, \omega)$ are those of the ideal gas model in which the atoms behave like free particles. This is plausible because their motions are observed for times shorter than the time between two collisions and over very short distances. The intermediate scattering function $F_s(q, t)$ is a Gaussian depending on t and q , and the van Hove correlation function $G_s(r, t)$ a Gaussian of r , while the dynamic structure factor $S_s(q, \omega)$ is a Gaussian of ω , whose amplitude at the origin gradually diminishes as q increases (Fig. 11.5a). Moreover, its standard deviation ($\sigma = \frac{q}{\sqrt{\beta m}}$) increases with q .

$$\int_{-\infty}^{\infty} \exp(-aT^2) dT = \sqrt{\frac{\pi}{a}},$$

and the expression for the dynamic structure factor becomes:

$$S_s(q, \omega) = \sqrt{\frac{\beta m}{2\pi}} \frac{1}{q} \exp\left(-\frac{\beta m \omega^2}{2 q^2}\right).$$

The diffusion model

Unlike the ideal gas model, the *diffusion model* applies to large scales of distance and time, that is to say to *low values* of ω and q . The diffusion model results from the *Gaussian approximation* for the intermediate scattering function proposed by Rahman et al. [180]. These authors showed that the intermediate scattering function $F_s(\mathbf{q}, t)$ can be assumed to be a power series expansion in q^2 , in which the coefficients are expressed in terms of the velocity autocorrelation function. Here, we give an outline of the proof by considering the intermediate scattering function $F_s(\mathbf{q}, t)$ (Eq. 11.30) at long times which supposes the lack of correlation between the positions of an atom at time t and at time 0. In this case, the intermediate scattering function is simplified to:

$$F_s(\mathbf{q}, t) = \langle \exp \{ i\mathbf{q} \cdot [\mathbf{r}_1(t) - \mathbf{r}_1(0)] \} \rangle. \quad (11.105)$$

The fact that the vector $\mathbf{q}$ is directed in the x -direction amounts to writing:

$$F_s(q, t) = \langle \exp \{ iq [x(t) - x(0)] \} \rangle, \quad (11.106)$$

$$\text{with } x(t) - x(0) = \int_0^t v(t') dt'. \quad (11.107)$$

However, using the cumulant method (see footnote 2 in chapter 5), the authors showed that the power series expansion of the intermediate scattering function was:

$$F_s(q, t) = 1 - q^2 \gamma_1(t) + q^4 \gamma_2(t) + \dots \quad (11.108)$$

$$\text{with } \gamma_1(t) = \frac{1}{2} \langle [x(t) - x(0)]^2 \rangle = \frac{1}{2} \int_0^t \int_0^t \langle v(t') v(t'') \rangle dt' dt''. \quad (11.109)$$

Equation (11.108) results from the fact that the intermediate scattering function is a real and even function (section 11.3). The coefficient $\gamma_2(t)$ and the next coefficients in equation (11.108) involve the velocity autocorrelation functions of higher orders. Here, they are not very useful, unlike the coefficient $\gamma_1(t)$ whose expression is given by equation (9.70):

$$\gamma_1(t) = t \int_0^t \langle v(0) v(\tau) \rangle \left(1 - \frac{\tau}{t} \right) d\tau. \quad (11.110)$$

As the model involves what is happening at long times, the coefficient $\gamma_1(t)$ can be evaluated as a function of the diffusion coefficient (Eq. 9.71) as:

$$\gamma_1(t) = t \lim_{t \rightarrow \infty} \int_0^t \langle v(0) v(\tau) \rangle \left(1 - \frac{\tau}{t}\right) d\tau = Dt. \quad (11.111)$$

In the Gaussian approximation, Rahman et al. [180] assumed that the intermediate scattering function (Eq. 11.108) coincides approximately with the series expansion of the following exponential function:

$$F_s(q, t) \simeq \exp[-q^2 \gamma_1(t)], \quad (11.112)$$

which is valid for all values of t . However, as we are interested in the long times, it is legitimate to replace $\gamma_1(t)$ by Dt in equation (11.112). With these assumptions, it is easy to see that the van Hove correlation function $G_s(r, t)$ and the dynamic structure factor $S_s(q, \omega)$ of the diffusion model have respectively the expressions¹⁴:

$$G_s(r, t) = \frac{1}{(2\pi)^3} \int F_s(q, t) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{q} = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \quad (11.113)$$

and:

$$S_s(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_s(q, t) \exp(-i\omega t) dt = \frac{1}{\pi} \frac{Dq^2}{\omega^2 + (Dq^2)^2}. \quad (11.114)$$

Similarly to what is done with the ideal gas model, the van Hove correlation function $G_s(r, t)$ of the diffusion model is a Gaussian of r . By contrast, the dynamic structure factor $S_s(q, \omega)$ behaves as a Lorentzian, whose shape is portrayed in figure (11.5b) for a given value of q . It is easy to check whether the peak width at half height is $\Delta\omega = 2Dq^2$ thus enabling a priori the graphical deduction of the diffusion coefficient D from the measurement of dynamic structure factor $S_s(q, \omega)$. The results of the diffusion coefficient obtained in this way are very imprecise. Moreover, experiments show that the diffusion model is applicable only to values of $q < 5 \text{ nm}^{-1}$, i.e. for weak scattering angles. With a beam of thermal neutrons of wavelength in

¹⁴The spatiotemporal Fourier transforms are calculated without difficulty, in the same way as equations (11.103) and (11.104). Just remember that the dynamic structure factor is an even function (see section 11.3).

the range of the interatomic distance ($\lambda \sim 0, 2$ nm), and given the fact that $q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$, the value of the scattering angle θ corresponding to $q = 5 \text{ nm}^{-1}$ is in the order of $\theta \sim 9^\circ$.

When it is over large time intervals, an atom undergoes so many collisions that the microscopic details of the collisions are irrelevant. However, in so far as the diffusion coefficient is founded on a phenomenological concept, which is valid at long times and large distances, it seems that the description of the motion of an atom is based on a quasi-macroscopic approach in assuming that the diffusional behaviour of liquids is provided by the diffusion equation (Eq. 8.122). Helfand [181] suggested that the macroscopic equation for the probability $G_s(\mathbf{r}, t)d\mathbf{r}$ to find an atom in the volume element $d\mathbf{r}$, at distance $\mathbf{r}$ and time t , is given by the diffusion equation:

$$\begin{aligned} \frac{\partial G_s(\mathbf{r}, t)}{\partial t} &= D \nabla^2 G_s(\mathbf{r}, t), \\ \text{with } G_s(\mathbf{r}, 0) &= \delta(\mathbf{r}). \end{aligned} \quad (11.115)$$

Without taking the time to solve the diffusion equation, we can easily make sure¹⁵ that the solution is given by equation (11.113).

¹⁵The time derivative of equation (11.113) is:

$$\frac{\partial G_s(\mathbf{r}, t)}{\partial t} = \frac{1}{(4\pi D)^{3/2}} \left[-\frac{3}{2} t^{-5/2} + t^{-3/2} \left(\frac{r^2}{4Dt^2} \right) \right] \exp\left(-\frac{r^2}{4Dt}\right),$$

and the spatial derivative is:

$$\begin{aligned} \frac{\partial G_s(\mathbf{r}, t)}{\partial x} &= \frac{1}{[4\pi Dt]^{3/2}} \left[-\frac{2x}{4Dt} \exp\left(-\frac{r^2}{4Dt}\right) \right], \\ \frac{\partial^2 G_s(\mathbf{r}, t)}{\partial x^2} &= \frac{1}{[4\pi Dt]^{3/2}} \left[-\frac{1}{2Dt} \exp\left(-\frac{r^2}{4Dt}\right) \right. \\ &\quad \left. + \left(-\frac{x}{2Dt}\right) \left(-\frac{2x}{4Dt}\right) \exp\left(-\frac{r^2}{4Dt}\right) \right] \\ &= \frac{1}{[4\pi D]^{3/2}} \left[-\frac{1}{2D} t^{5/2} + t^{-3/2} \left(\frac{x^2}{4D^2 t^2} \right) \right] \exp\left(-\frac{r^2}{4Dt}\right), \end{aligned}$$

or

$$\begin{aligned} \frac{\partial^2 G_s(\mathbf{r}, t)}{\partial x^2} + \frac{\partial^2 G_s(\mathbf{r}, t)}{\partial y^2} + \frac{\partial^2 G_s(\mathbf{r}, t)}{\partial z^2} &= \\ &= \frac{1}{[4\pi D]^{3/2}} \frac{1}{D} \left[-\frac{3}{2} t^{5/2} + t^{-3/2} \left(\frac{r^2}{4Dt^2} \right) \right] \exp\left(-\frac{r^2}{4Dt}\right), \end{aligned}$$

so that equation (11.115) is verified by comparing both results.

To summarize what the individual motion of atoms in real fluids actually is, it should be noted that the representation of the dynamic structure factor $S_s(q, \omega)$ is changing from a Lorentzian (diffusion model), for small values of q and ω , to a Gaussian (ideal gas model) for large values. At the same time, the van Hove function $G_s(r, t)$ has the same dependence on r for the two models (Eqs. 11.103 and 11.113). Therefore, it has been postulated [182] that the functional form of the van Hove function $G_s(r, t)$ should be written, whatever the scale of time, as:

$$G_s(r, t) = \frac{1}{[4\pi w(t)]^{3/2}} \exp\left[-\frac{r^2}{4w(t)}\right], \quad (11.116)$$

where the function $w(t)$, characterizing the width of the Gaussian distribution, is determined by adjusting the dynamic structure factor (obtained by inverse Fourier transform) on the experimental symmetrized dynamic structure factor $S_s(q, \omega)$ (see section 11.6).

11.8 Models for coherent scattering

Vineyard approximation

Assuming that there is no correlation between the atoms, the expression for the intermediate scattering function $F(\mathbf{q}, t)$ (Eq. 11.27) is considerably simplified. Indeed, the lack of correlation between the positions of atoms enables the writing of equation (11.31) as:

$$F_d(\mathbf{q}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \exp[i\mathbf{q} \cdot \mathbf{r}_j(t)] \exp[-i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle = 0, \quad (11.117)$$

so that the following identity holds:

$$F(\mathbf{q}, t) = F_s(\mathbf{q}, t). \quad (11.118)$$

In first approximation, it follows that the dynamic structure factor $S(\mathbf{q}, \omega)$, corresponding to the coherent scattering, merges into the dynamic structure factor $S_s(\mathbf{q}, \omega)$:

$$S(\mathbf{q}, \omega) = S_s(\mathbf{q}, \omega). \quad (11.119)$$

But this approximation can be improved by including partial correlations between the positions of atoms. To do this, we transform equation (11.27) as:

$$\begin{aligned}
 F(\mathbf{q}, t) &= F_s(\mathbf{q}, t) + \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \exp[i\mathbf{q} \cdot \mathbf{r}_j(t)] \exp[-i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle \\
 &= F_s(\mathbf{q}, t) + \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \exp[i\mathbf{q} \cdot \mathbf{r}_j(t)] \exp[-i\mathbf{q} \cdot \mathbf{r}_j(0)] \times \right. \\
 &\quad \left. \times \exp[i\mathbf{q} \cdot \mathbf{r}_j(0)] \exp[-i\mathbf{q} \cdot \mathbf{r}_i(0)] \right\rangle. \quad (11.120)
 \end{aligned}$$

However, in replacing the thermal average in the above equation by the product of two thermal averages, namely:

$$\begin{aligned}
 F(\mathbf{q}, t) &\simeq F_s(\mathbf{q}, t) + \frac{1}{N} \left\langle \sum_{j=1}^N \exp\{i\mathbf{q} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\} \right\rangle \times \\
 &\quad \times \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \exp\{i\mathbf{q} \cdot [\mathbf{r}_j(0) - \mathbf{r}_i(0)]\} \right\rangle \quad (11.121)
 \end{aligned}$$

a less rough approximation which does not totally ignore the correlations between the positions of atoms is achieved. The product of thermal averages in the above relation simplifies to¹⁶:

$$F(\mathbf{q}, t) \simeq F_s(\mathbf{q}, t) + F_s(\mathbf{q}, t) [F(\mathbf{q}, 0) - 1] = F_s(\mathbf{q}, t) F(\mathbf{q}, 0). \quad (11.122)$$

¹⁶Indeed, the thermal averages are written as a function of $F_s(\mathbf{q}, t)$ and $F_d(\mathbf{q}, 0)$ with respectively equations (11.30) and (11.31). They read:

$$\begin{aligned}
 F_s(\mathbf{q}, t) &= \frac{1}{N} \left\langle \sum_{j=1}^N \exp\{i\mathbf{q} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\} \right\rangle, \\
 F_d(\mathbf{q}, 0) &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j \neq i}^N \exp\{i\mathbf{q} \cdot [\mathbf{r}_j(0) - \mathbf{r}_i(0)]\} \right\rangle \\
 &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \exp\{-i\mathbf{q} \cdot [\mathbf{r}_i(0) - \mathbf{r}_j(0)]\} - \sum_{i=1}^N \exp\{-i\mathbf{q} \cdot [\mathbf{r}_i(0) - \mathbf{r}_i(0)]\} \right\rangle \\
 &= F(\mathbf{q}, 0) - 1.
 \end{aligned}$$

Moreover, in using equation (11.37), we deduce the approximation $F(q, t) \simeq F_s(q, t)S(q)$ and the following relation between the structure factors:

$$S(q, \omega) \simeq S(q)S_s(q, \omega). \quad (11.123)$$

It is the well known Vineyard approximation [182] which provides an estimate of the dynamic structure factor $S(q, \omega)$ in terms of the dynamic structure factor $S_s(q, \omega)$ and the static structure factor $S(q)$. Given the gross simplification made in calculating the thermal average, the Vineyard approximation does not apply in the domain of *low values of q and ω* , where $S(q, \omega)$ and $S_s(q, \omega)$ differ considerably from each other. This approximation also has significant shortcomings in the range of *intermediate values of q and ω* . Nevertheless, its accuracy can be slightly improved by replacing the transfer vector q by $q/\sqrt{S(q)}$ in the intermediate scattering function [183], so that:

$$F(q, t) \simeq F_s\left[\frac{q}{\sqrt{S(q)}}, t\right]S(q). \quad (11.124)$$

Hydrodynamic model

Like the diffusion model, the *hydrodynamic model* is used to explore the region of *low values of q and ω* . The diffusion and hydrodynamic models are both best suited to interpret the diffraction experiments in which the wavelength of the radiation is large compared to the atomic sizes.

Contrary to the diffusion model enabling the investigation of the individual properties of atoms, the hydrodynamic model gives information on individual and collective properties of atoms as well. The hydrodynamic model uses the equations of continuum mechanics [184]. It is based on the laws of conservation of matter (Eq. 8.159), energy (Eq. 8.161) and momentum (Eq. 8.160). These three equations enable us to calculate the particle density $\rho(\mathbf{q}, t)$ from which it is possible to deduce the intermediate scattering function $F(\mathbf{q}, t)$ (Eq. 11.28) and the dynamic structure factor $S(\mathbf{q}, \omega)$ (Eq. 11.25).

In what follows, we give an outline of the proof [162, 175] to find the expression of $S(\mathbf{q}, \omega)$, after the linearization of the three conservation equations has been carried out.

(1) The equation of mass conservation (Eq. 8.159) is the following:

$$\frac{D\rho_m}{Dt} = \frac{\partial\rho_m}{\partial t} + (\mathbf{v}\cdot\nabla)\rho_m = -\rho_m\nabla\cdot\mathbf{v}, \quad (11.125)$$

where $\rho_m = m\rho(\mathbf{r}, t)$ is the local density of mass¹⁷ and $\mathbf{v}$ its velocity. It then leads to the relationship:

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot(\rho\mathbf{v}). \quad (11.126)$$

To linearize the above equation, it is stated that the local density of particles is $\rho(\mathbf{r}, t) = \rho_0 + \rho_1(\mathbf{r}, t)$, where ρ_0 is the number density of a volume element in local equilibrium and $\rho_1(\mathbf{r}, t)$ the fluctuation of local density. By neglecting the second order contributions, the linearized equation is written:

$$\frac{\partial\rho_1}{\partial t} = -\rho_0\nabla\cdot\mathbf{v}. \quad (11.127)$$

(2) In the absence of external force, the equation of energy conservation (Eq. 8.161) reads:

$$\rho m \frac{De}{Dt} = \bar{\bar{t}}\nabla\cdot\mathbf{v} - \nabla\cdot\mathbf{Q}, \quad (11.128)$$

where m is the mass of the particle, e the energy per mass unit, $\bar{\bar{t}}$ the stress tensor, $\mathbf{v}$ the velocity and $\mathbf{Q}$ the heat flux density. The linearization of this expression is carried out as for equation (11.127), by writing $e(\mathbf{r}, t) = e_0 + e_1(\mathbf{r}, t)$, where e_0 is the energy at equilibrium and $e_1(\mathbf{r}, t)$ the fluctuation of energy. It is directly related to the fluctuation of temperature $T_1(\mathbf{r}, t)$ by equation $e_1(\mathbf{r}, t) = c_V T_1(\mathbf{r}, t)$, where c_V is the specific heat at constant volume (in $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$). Then, neglecting the viscosity enables the replacement of the stress tensor (Eq. 8.101) by the hydrostatic pressure ($\bar{\bar{t}} = -p\bar{\delta}$). If, at this stage, the heat flux density is given by the Fourier law $\mathbf{Q} = -\lambda\nabla T_1$, where λ the thermal conductivity (in $\text{J}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), the equation of energy conservation is linearized as follows:

$$\rho_0 m c_V \frac{\partial T_1}{\partial t} = -p\nabla\cdot\mathbf{v} + \lambda\nabla^2 T_1. \quad (11.129)$$

¹⁷The local density of mass $\rho_m = m\rho(\mathbf{r}, t)$ is defined by the product of the mass of one particle m times the local density of particles $\rho(\mathbf{r}, t)$ (see section 8.7).

For a stationary fluid, it should be noted that the above relationship is reduced to the equation of heat propagation $\frac{\partial T_1}{\partial t} = \frac{\lambda}{\rho_0 m c_V} \nabla^2 T_1$, where the coefficient of the right hand side is connected to the thermal diffusivity $D_T = \frac{\lambda}{\rho_0 m c_p} = \frac{\lambda}{\rho_0 m c_V} \frac{1}{\gamma}$ (in $\text{m}^2 \cdot \text{s}^{-1}$) with $\gamma = c_p/c_V$.

(3) With regard to the linearized equation of momentum conservation, in the absence of the force $\mathbf{F}$, it is reduced to the Navier–Stokes equation (Eq. 8.141):

$$\rho_0 m \frac{\partial \mathbf{v}}{\partial t} = -\nabla p + (\eta_v + \frac{4\eta}{3}) \nabla(\nabla \cdot \mathbf{v}), \quad (11.130)$$

where ρ_0 is the number density at equilibrium, η the shear viscosity and η_v the bulk viscosity (in $\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$).

Hereafter, we follow the proposal of Mountain to substitute the equation of mass conservation (Eq. 11.127) in equations (11.129) and (11.130), in order to form a system of partial differential equations where the unknown functions are the independent thermodynamical variables $\rho_1(\mathbf{r}, t)$ and $T_1(\mathbf{r}, t)$. We start to express the pressure in equation (11.129) as a function of the calorimetric coefficients¹⁸:

$$p = \frac{Nm(c_p - c_V)}{V\alpha} = \frac{\rho_0 m(c_p - c_V)}{\alpha}. \quad (11.131)$$

This gives the simplification of equation (11.129) as follows:

$$\rho_0 m c_V \frac{\partial T_1}{\partial t} + \frac{\rho_0 m(c_p - c_V)}{\alpha} \nabla \cdot \mathbf{v} - \lambda \nabla^2 T_1 = 0. \quad (11.132)$$

After eliminating $\nabla \cdot \mathbf{v}$ in the above relation, owing to equation (11.127), the equation of energy conservation is written:

$$\rho_0 m c_V \frac{\partial T_1}{\partial t} - \frac{m(c_p - c_V)}{\alpha} \frac{\partial \rho_1}{\partial t} - \lambda \nabla^2 T_1 = 0. \quad (11.133)$$

¹⁸The difference of heat capacities ($c_p - c_V$) is written using the classical thermodynamic relation:

$$Nm(c_p - c_V) = \left[p + \left(\frac{\partial E}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_p \sim pV\alpha,$$

where $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p$ is the thermal expansion coefficient. It may seem unwise to neglect the second term in square brackets, the contribution of which is working against the cohesive forces and which can be important in liquids, but this is nevertheless what is generally done.

Then, in order to express the pressure in equation (11.130), we transform the term ∇p by noting that its component along the x -axis is:

$$\frac{\partial p}{\partial x} = \left(\frac{\partial p}{\partial \rho_1} \right)_T \frac{\partial \rho_1}{\partial x} - \left(\frac{\partial p}{\partial \rho_1} \right)_T \left(\frac{\partial \rho_1}{\partial T_1} \right)_p \frac{\partial T_1}{\partial x}, \quad (11.134)$$

with¹⁹:

$$\left(\frac{\partial p}{\partial \rho_1} \right)_T = \frac{v_s^2 m}{\gamma}, \quad (11.135)$$

$$\left(\frac{\partial \rho_1}{\partial T_1} \right)_p = -\alpha \rho_0, \quad (11.136)$$

where v_s is the sound velocity and α the thermal expansion coefficient. Taking into account these simplifications, ∇p is expressed in terms of $\nabla \rho_1$ and ∇T_1 as:

$$\nabla p = \frac{v_s^2 m}{\gamma} \nabla \rho_1 + \frac{\alpha \rho_0 v_s^2 m}{\gamma} \nabla T_1, \quad (11.137)$$

and the Navier–Stokes equation (Eq. 11.130) reduces to:

$$\rho_0 m \frac{\partial \mathbf{v}}{\partial t} + \frac{v_s^2 m}{\gamma} \nabla \rho_1 + \frac{\alpha \rho_0 v_s^2 m}{\gamma} \nabla T_1 - \left(\eta_v + \frac{4\eta}{3} \right) \nabla (\nabla \cdot \mathbf{v}) = \mathbf{0}. \quad (11.138)$$

In the procedure used by Mountain, the velocity in the above equation is converted by substituting $\nabla \cdot \mathbf{v}$ with equation (11.127) and calculating the divergence of each term. Then the two coupled equations (Eqs. 11.133 and 11.138) are solved after their transformations into algebraic equations by using the spatial Fourier transform and the temporal Fourier–Laplace transform, defined as:

$$\rho(\mathbf{q}, s) = \int_V \int_0^\infty \rho_1(\mathbf{r}, t) \exp(-i\mathbf{q} \cdot \mathbf{r}) \exp(-st) dt d\mathbf{r}, \quad (11.139)$$

$$T(\mathbf{q}, s) = \int_V \int_0^\infty T_1(\mathbf{r}, t) \exp(-i\mathbf{q} \cdot \mathbf{r}) \exp(-st) dt d\mathbf{r}. \quad (11.140)$$

¹⁹The sound velocity v_s in liquids is defined in terms of the pressure derivative with respect to the density, at constant entropy, by equation (Eq. 4.105):

$$v_s = \sqrt{\left(\frac{\partial p}{\partial (\rho m)} \right)_S} = \sqrt{\frac{\gamma}{m} \left(\frac{\partial p}{\partial \rho} \right)_T},$$

where the last equality follows from the Reech formula (section 2.5).

When the temporal Fourier–Laplace transform is performed, we are faced with a problem of initial conditions in which it is not necessary to include the term $T(\mathbf{q}, 0)$ as there is no instantaneous correlations between the fluctuations of density and temperature. The lengthy calculation will not be detailed here. At the end of this calculation, the two simultaneous linear algebraic equations to be solved are:

$$\left[-\frac{m(c_p - c_V)}{\alpha} s \right] \rho(\mathbf{q}, s) + [\rho_0 m c_v s + \lambda q^2] T(\mathbf{q}, s) = - \left[\frac{m(c_p - c_V)}{\alpha} \right] \rho(\mathbf{q}, 0), \quad (11.141)$$

$$\left[s^2 + \frac{v_s^2}{\gamma} q^2 + \left(\eta_v + \frac{4\eta}{3} \right) \frac{q^2}{\rho_0 m} s \right] \rho(\mathbf{q}, s) + \left[\frac{\alpha \rho_0 v_s^2}{\gamma} q^2 \right] T(\mathbf{q}, s) = \left[s + \left(\eta_v + \frac{4\eta}{3} \right) \frac{q^2}{\rho_0 m} \right] \rho(\mathbf{q}, 0). \quad (11.142)$$

It remains to analyse the nature of the poles of $\rho(\mathbf{q}, s)$ by solving the cubic equation provided by the principal determinant of the above system of equations. This study will not be shown here. From the calculations, an expression follows for $\rho(\mathbf{q}, s)$ as a function of $\rho(\mathbf{q}, 0)$ from which $\rho(\mathbf{q}, t)$ is inferred by inverse Laplace transform. Then, using equation (11.39), we deduce the following relationship in terms of the intermediate scattering function :

$$\frac{F(q, t)}{F(q, 0)} = \left(\frac{\gamma - 1}{\gamma} \right) \exp(-D_T q^2 t) + \frac{1}{\gamma} \exp(-\Gamma q^2 t) \cos(v_s q t), \quad (11.143)$$

where most of the parameters have been previously defined, with the exception of the attenuation parameter of sound:

$$\Gamma = \frac{1}{2} \left[\frac{1}{\rho_0 m} \left(\eta_v + \frac{4\eta}{3} \right) + D_T (\gamma - 1) \right]. \quad (11.144)$$

Therefore, after performing the temporal Fourier-Laplace transform of equation (11.143), we obtain the following expression for the

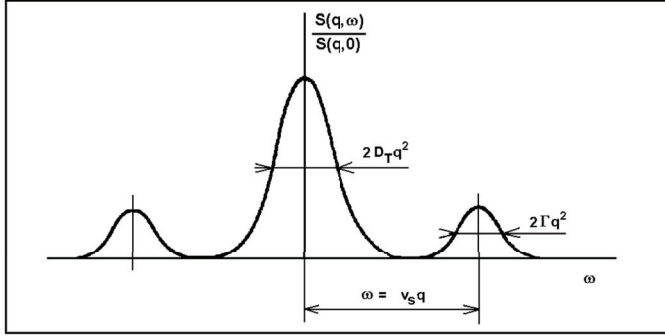


Figure 11.6: Positions of the Brillouin peaks and the Rayleigh peak.

dynamic structure factor $S(q, \omega)$ of the hydrodynamic model:

$$\frac{2\pi S(q, \omega)}{S(q)} = \frac{2(\gamma-1)}{\gamma} \frac{D_T q^2}{\omega^2 + (D_T q^2)^2} + \frac{1}{\gamma} \left[\frac{\Gamma q^2}{(\omega + v_s q)^2 + (\Gamma q^2)^2} + \frac{\Gamma q^2}{(\omega - v_s q)^2 + (\Gamma q^2)^2} \right]. \quad (11.145)$$

This expression contains three terms depending on q and ω . Their frequency dependence is given by a Lorentzian of general form:

$$f(\omega) = \frac{X}{(\omega - \omega')^2 + X^2}, \quad (11.146)$$

centered at the frequency ω' , with a width at half height of $2X$. The first term on the right hand side of equation (11.145) is a Lorentzian centered on $\omega = 0$; it is represented by the *Rayleigh central peak* whose width at half height is $2D_T q^2$. As regards the second term, it consists of two Lorentzian shifted symmetrically on both sides of the origin by the quantities $\omega = \pm v_s q$, with a width at half height of $2\Gamma q^2$; it is represented by the *Brillouin satellite peaks*. In practice, the parameters D_T and Γ are very small compared to v_s , so that the peaks are well separated from each other (Fig. 11.6).

It may be noted that the area under the Rayleigh peak is²⁰:

²⁰Indeed, the result of the integral is:

$$\int_{-\infty}^{\infty} \frac{a}{\omega^2 + a^2} d\omega = \left[\arctan\left(\frac{\omega}{a}\right) \right]_{-\infty}^{\infty} = \pi.$$

$$A_R = \frac{2(\gamma-1)}{\gamma} \int_{-\infty}^{\infty} \frac{D_T q^2}{\omega^2 + (D_T q^2)^2} d\omega = \frac{2\pi(\gamma-1)}{\gamma}, \quad (11.147)$$

and the area under the Brillouin peaks is $A_B = \frac{2\pi}{\gamma}$. It follows that the ratio of the two areas $\frac{A_R}{A_B}$ is $(\gamma-1)$. This is the *Landau-Placzek ratio*. When the critical point is approached, c_p is abnormally large and, as $c_p \propto \gamma$, $\frac{A_R}{A_B}$ becomes very important. The height of the Rayleigh peak is magnified, whereas its width at half height undergoes a substantial shrinkage. In return and far below the critical point, the Brillouin doublet is predominant over the Rayleigh peak.

In the hydrodynamic limit, the values of the macroscopic physical properties (λ , c_p , c_V , v_s , η) entering equation (11.145) are considered as constants and must be drawn from the literature to predict the dynamic structure factor $S(q, \omega)$. Conversely, we can adjust the parameters D_T , Γ and v_s in equation (11.145) from the experimental curve of $S(q, \omega)$, and infer the atomic transport coefficients. In addition, if the experimental conditions are such that the hydrodynamic model is not applicable (for the values of q being too large), the expression given by equation (11.145) can be left unchanged. So, the quantities D_T , Γ and v_s , fitted on the experimental results of $S(q, \omega)$, have to be considered as parameters dependent on q and ω .

It has been established (see p. 243 of [185]), through studies on the light scattering in liquids, that the density fluctuations are produced by the superposition of *mechanical fluctuations*, associated with the local variations of pressure, and *thermal fluctuations*, associated with the local variations of temperature (or entropy). More specifically, it has been found that these results are contained in the expression of $S(q, \omega)$ (Eq. 11.145), insofar as the presence of the Brillouin peaks comes from the pressure fluctuations, at entropy constant (spreading through the fluid at the sound velocity, like the acoustic phonons propagate in solids), whereas the presence of the Rayleigh peak is due to the entropy fluctuations, at constant pressure (remaining at the place where they occur, but falling into decay under the effect of the thermal conductivity).

11.9 Viscoelastic model

The viscoelastic model is noticeably more elaborate than the previous ones; it is based on the use of the memory function and the frequency moments (section 9.8) of the intermediate scattering function $F(\mathbf{q}, t)$. The intermediate scattering function $F(\mathbf{q}, t)$, i.e. the autocorrelation function of the particle density, can be (1) written by means of the memory function with the Volterra equation (Eq. 9.147), and (2) expressed in terms of the frequency moments by using its series expansion around $t = 0$ (Eq. 9.120).

Like any autocorrelation function, the intermediate scattering function $F(\mathbf{q}, t)$ is related to a memory function $M^{(1)}(\mathbf{q}, t)$ by the Volterra integro-differential equation (Eq. 9.147):

$$\frac{\partial F(\mathbf{q}, t)}{\partial t} = - \int_0^t M^{(1)}(\mathbf{q}, t-t') F(\mathbf{q}, t') dt'. \quad (11.148)$$

This convolution integral shows that the variation of $F(\mathbf{q}, t)$, over any time interval, depends on its past history via the memory function $M^{(1)}(\mathbf{q}, t)$. However, the memory function $M^{(1)}(\mathbf{q}, t)$ has its own memory function $M^{(2)}(\mathbf{q}, t)$ which is linked to $M^{(1)}(\mathbf{q}, t)$ by a relationship similar to equation (11.148). Then, $M^{(2)}(\mathbf{q}, t)$ is related to the memory function $M^{(3)}(\mathbf{q}, t)$ and so on, so that equation (11.148) is the first one of a chain of hierarchically coupled equations. Consequently, the calculations of the Fourier-Laplace transforms of these equations, followed by their successive substitutions one into the other, lead to the continued fraction (Eq. 9.155):

$$F(\mathbf{q}, \omega) = \frac{F(\mathbf{q}, t=0)}{i\omega + \frac{M^{(1)}(\mathbf{q}, t=0)}{i\omega + \frac{M^{(2)}(\mathbf{q}, t=0)}{i\omega + M^{(3)}(\mathbf{q}, \omega)}}}, \quad (11.149)$$

which has been interrupted arbitrarily at the memory function of order three.

The viscoelastic approximation consists in postulating that the memory function $M^{(2)}(\mathbf{q}, \omega)$ is a decreasing exponential function of time (see p. 544 of [186]), with a characteristic time $\tau(q)$, according to the standard expression:

$$M^{(2)}(\mathbf{q}, t) = M^{(2)}(\mathbf{q}, t=0) \exp\left(-\frac{t}{\tau(q)}\right), \quad (11.150)$$

so that the Fourier–Laplace transform of the above relation is²¹:

$$M^{(2)}(\mathbf{q}, \omega) = \frac{M^{(2)}(\mathbf{q}, t=0)}{i\omega + \frac{1}{\tau(q)}}. \quad (11.151)$$

However, by comparing equations (11.149) and (11.151), we note that the memory function $M^{(3)}(\mathbf{q}, \omega)$ can be identified with the function $1/\tau(q)$ which will be determined later. If we replace $M^{(3)}(\mathbf{q}, \omega)$ by $1/\tau(q)$, and write $M^{(2)}(\mathbf{q}, t=0) = M^{(2)}$ and $M^{(1)}(\mathbf{q}, t=0) = M^{(1)}$ in order to simplify the notations, equation (11.149) turns without difficulty into:

$$F(\mathbf{q}, \omega) = F(\mathbf{q}, t=0) \frac{\tau(q) [M^{(2)} - \omega^2] + i\omega}{[M^{(1)} - \omega^2] + i\omega\tau(q) [M^{(2)} + M^{(1)} - \omega^2]}. \quad (11.152)$$

Then, this expression allows us to deduce the dynamic structure factor $S(\mathbf{q}, \omega)$ with equation (11.46), namely:

$$\begin{aligned} S(\mathbf{q}, \omega) &= \frac{1}{\pi} \text{Re} [F(\mathbf{q}, \omega)] = \frac{F(\mathbf{q}, t=0)}{\pi} \times \\ &\times \frac{\tau(q) [M^{(2)} - \omega^2] [M^{(1)} - \omega^2] + \omega^2 \tau(q) [M^{(2)} + M^{(1)} - \omega^2]}{[M^{(1)} - \omega^2]^2 + \omega^2 \tau^2(q) [M^{(2)} + M^{(1)} - \omega^2]^2}. \end{aligned} \quad (11.153)$$

To completely determine the dynamic structure factor, we have now to express all the terms of equation (11.153), and specially the memory functions $M^{(1)}$ and $M^{(2)}$ as a function of the frequency moments of $F(\mathbf{q}, t)$. However, at this stage of the presentation, it is important to distinguish the case of the coherent dynamic structure factor $S(\mathbf{q}, \omega)$ from that of the incoherent dynamic structure factor $S_s(\mathbf{q}, \omega)$, and to recall that, at $t = 0$, the coherent intermediate scattering function is $F(\mathbf{q}, t=0) = S(q)$ (Eq. 11.37) whereas the incoherent intermediate scattering function is $F_s(\mathbf{q}, t=0) = 1$ (Eq. 11.33).

²¹Indeed,

$$\begin{aligned} M^{(2)}(\mathbf{q}, \omega) &= \int_0^\infty M^{(2)}(\mathbf{q}, t) \exp(-i\omega t) dt \\ &= M^{(2)}(\mathbf{q}, t=0) \int_0^\infty \exp\left\{-\left[i\omega + \frac{1}{\tau(q)}\right]t\right\} dt = \frac{M^{(2)}(\mathbf{q}, t=0)}{i\omega + \frac{1}{\tau(q)}}. \end{aligned}$$

Coherent structure factor $S(\mathbf{q}, \omega)$

The finding of the memory functions $M^{(1)}$ and $M^{(2)}$ can be performed by considering the series expansion about $t = 0$ (Eq. 9.120) of the intermediate scattering function $F(\mathbf{q}, t)$. Since $F(\mathbf{q}, t)$ is a real and even function, the only powers of t present in the Maclaurin formula are the even ones²²:

$$F(\mathbf{q}, t) = F(\mathbf{q}, 0) + \frac{t^2}{2!} \left. \frac{\partial^2 F(\mathbf{q}, t)}{\partial t^2} \right|_{t=0} + \frac{t^4}{4!} \left. \frac{\partial^4 F(\mathbf{q}, t)}{\partial t^4} \right|_{t=0} + \dots, \quad (11.154)$$

where the successive partial derivatives of $F(\mathbf{q}, t)$ with respect to t are obtained by differentiation of equation (11.26), in accordance with the relations:

$$\left. \frac{\partial^2 F(\mathbf{q}, t)}{\partial t^2} \right|_{t=0} = - \int_{-\infty}^{\infty} \omega^2 S(\mathbf{q}, \omega) d\omega = \langle \omega^2 \rangle, \quad (11.155)$$

$$\left. \frac{\partial^4 F(\mathbf{q}, t)}{\partial t^4} \right|_{t=0} = \int_{-\infty}^{\infty} \omega^4 S(\mathbf{q}, \omega) d\omega = \langle \omega^4 \rangle, \quad (11.156)$$

$$\dots = \dots$$

The expressions of the frequency moments to second and fourth orders for the coherent scattering²³ have been derived by de Gennes [189], namely:

$$\langle \omega^2 \rangle = \frac{k_B T}{m S(q)} q^2, \quad (11.157)$$

$$\langle \omega^4 \rangle = \langle \omega^2 \rangle \left[\frac{3k_B T}{m} q^2 + \Omega_0^2 - \Omega_q^2 \right], \quad (11.158)$$

while those related to the incoherent scattering are:

$$\langle \omega_s^2 \rangle = \frac{k_B T}{m} q^2, \quad (11.159)$$

$$\langle \omega_s^4 \rangle = \langle \omega_s^2 \rangle \left[\frac{3k_B T}{m} q^2 + \Omega_0^2 \right], \quad (11.160)$$

²²Note that, for the hard-sphere potential with a discontinuity at $r = \sigma$, the expansion of $F(\mathbf{q}, t)$ contains, in addition, the first derivative responsible for the non-zero slope at the origin [187]. In fact, it appears that the continued fraction representation in its original form is inadequate for discontinuous potentials – see p. 529 of [186].

²³The frequency moment to sixth order has also been calculated by Bansal and Pathak [188], but its expression is very complicated and not decisive for calculating the dynamic structure factor of liquids.

with

$$\Omega_0^2 = \frac{4\pi\rho}{3m} \int_0^\infty r^2 g(r) \left[u''(r) + \frac{2}{r} u'(r) \right] dr \quad (11.161)$$

and

$$\begin{aligned} \Omega_q^2 = & \frac{4\pi\rho}{m} \int_0^\infty r^2 g(r) \left\{ u''(r) \left[\frac{\sin(qr)}{qr} + \frac{2\cos(qr)}{(qr)^2} - \frac{2\sin(qr)}{(qr)^3} \right] \right. \\ & \left. + \frac{2}{r} u'(r) \left[\frac{\sin(qr)}{(qr)^3} - \frac{\cos(qr)}{(qr)^2} \right] \right\} dr, \end{aligned} \quad (11.162)$$

where Ω_0^2 coincides with the second-order moment of frequency A_2 (Eq. 9.134). The first three memory functions written below without demonstration [138, 150] are expressed as a function of the frequency moments $\langle \omega^2 \rangle$ and $\langle \omega^4 \rangle$:

$$M^{(1)} = M^{(1)}(\mathbf{q}, t=0) = \langle \omega^2 \rangle, \quad (11.163)$$

$$M^{(2)} = M^{(2)}(\mathbf{q}, t=0) = \frac{\langle \omega^4 \rangle}{\langle \omega^2 \rangle} - \langle \omega^2 \rangle = \omega_l^2 - \langle \omega^2 \rangle \quad (11.164)$$

$$M^{(3)} = M^{(3)}(\mathbf{q}, t=0) = \frac{1}{M^{(2)}} \left[\frac{\langle \omega^6 \rangle}{\langle \omega^2 \rangle} - \left(\frac{\langle \omega^4 \rangle}{\langle \omega^2 \rangle} \right)^2 \right]. \quad (11.165)$$

Therefore, when the static structure factor $S(q)$ and the memory functions $M^{(1)}$ and $M^{(2)}$ are known from the microscopic theory of liquids, it becomes possible to deduce the expression for the coherent dynamic structure factor $S(q, \omega)$. Indeed, after simplifications, equation (11.153) is written in the operational form:

$$S(q, \omega) = \frac{S(q)}{\pi} \frac{\tau(q) [\omega_l^2 - \langle \omega^2 \rangle] \langle \omega^2 \rangle}{[\langle \omega^2 \rangle - \omega^2]^2 + \omega^2 \tau^2(q) [\omega_l^2 - \omega^2]^2}. \quad (11.166)$$

The only unknown function in equation (11.166) is $\tau(q)$. The later can be estimated, either empirically by adjusting $S(q, \omega)$ on the experimental dynamic structure factor [190], or theoretically [191] by assessing the approximate relation:

$$\frac{1}{\tau(q)} \simeq M^{(3)}(\mathbf{q}, \omega=0) = \int_0^\infty M^{(3)}(\mathbf{q}, t) dt. \quad (11.167)$$

Among the possible approximations, one of the most frequently used is:

$$\tau(q) = \frac{1}{2} \sqrt{\frac{\pi}{\omega_l^2 - \langle \omega^2 \rangle}}. \quad (11.168)$$

Incoherent structure factor $S_s(\mathbf{q}, \omega)$

The corresponding expression [192] is obtained in the same manner as that of $S(\mathbf{q}, \omega)$. By simple analogy, let us write all the terms of equation (11.152) with the index s . It results in:

$$F_s(\mathbf{q}, \omega) = F_s(\mathbf{q}, t=0) \frac{\tau_s(q) [M_s^{(2)} - \omega^2] + i\omega}{[M_s^{(1)} - \omega^2] + i\omega\tau_s(q) [M_s^{(2)} + M_s^{(1)} - \omega^2]}. \quad (11.169)$$

Then, we calculate the incoherent dynamic structure factor, $S_s(\mathbf{q}, \omega) = \frac{1}{\pi} \text{Re} [F_s(\mathbf{q}, \omega)]$ (see Eq. 11.46), after having provided each term thanks to the following relations:

$$F_s(\mathbf{q}, t=0) = 1, \quad (11.170)$$

$$M_s^{(1)} = \langle \omega_s^2 \rangle = \frac{k_B T}{m} q^2, \quad (11.171)$$

and

$$\begin{aligned} M_s^{(2)} &= \frac{\langle \omega_s^4 \rangle}{\langle \omega_s^2 \rangle} - \langle \omega_s^2 \rangle = \left[\frac{3k_B T}{m} q^2 + \Omega_0^2 \right] - \langle \omega_s^2 \rangle \\ &= 2 \langle \omega_s^2 \rangle + \Omega_0^2. \end{aligned} \quad (11.172)$$

After simplifications, the incoherent dynamic structure factor turns into²⁴:

$$S_s(\mathbf{q}, \omega) = \frac{1}{\pi} \frac{\tau_s(q) \langle \omega_s^2 \rangle [2 \langle \omega_s^2 \rangle + \Omega_0^2]}{[\langle \omega_s^2 \rangle - \omega^2]^2 + \omega^2 \tau_s^2(q) [3 \langle \omega_s^2 \rangle + \Omega_0^2 - \omega^2]^2}. \quad (11.173)$$

²⁴The incoherent dynamic structure factor $S_s(\mathbf{q}, \omega)$ has a form similar to that of equation (11.153), i.e.:

$$\begin{aligned} S_s(\mathbf{q}, \omega) &= \frac{1}{\pi} \frac{\tau_s(q) [M_s^{(2)} - \omega^2] [M_s^{(1)} - \omega^2] + \omega^2 \tau_s(q) [M_s^{(2)} + M_s^{(1)} - \omega^2]}{[M_s^{(1)} - \omega^2]^2 + \omega^2 \tau_s^2(q) [M_s^{(2)} + M_s^{(1)} - \omega^2]^2} \\ &= \frac{\tau_s(q)}{\pi} \frac{M_s^{(1)} M_s^{(2)}}{[M_s^{(1)} - \omega^2]^2 + \omega^2 \tau_s^2(q) [M_s^{(2)} + M_s^{(1)} - \omega^2]^2} \\ &= \frac{\tau_s(q)}{\pi} \frac{2 \langle \omega_s^2 \rangle^2 + \Omega_0^2 \langle \omega_s^2 \rangle}{[\langle \omega_s^2 \rangle - \omega^2]^2 + \omega^2 \tau_s^2(q) [3 \langle \omega_s^2 \rangle + \Omega_0^2 - \omega^2]^2}. \end{aligned}$$

As for the coherent dynamic structure factor defined in the previous paragraph, the only unknown function is $\tau_s(q)$. The quickest and most efficient manner to find the function $\tau_s(q)$ is to adjust the expression of the dynamic structure factor $S_s(\mathbf{q}, \omega)$ for $\omega = 0$ to that obtained with the diffusion model (Eq. 11.114). Identifying the two expressions gives:

$$\frac{\tau_s(q) [2 \langle \omega_s^2 \rangle + \Omega_0^2]}{\langle \omega_s^2 \rangle} \equiv \frac{1}{Dq^2}, \quad (11.174)$$

from which it follows:

$$\tau_s(q) = \frac{\langle \omega_s^2 \rangle}{Dq^2 [2 \langle \omega_s^2 \rangle + \Omega_0^2]}. \quad (11.175)$$

By the fact that $\langle \omega_s^2 \rangle \ll \Omega_0^2$ when $q \rightarrow 0$, the value of $\tau_s(q)$, at $q=0$, is merely deduced under the form:

$$\tau_s(0) = \frac{\frac{k_B T}{m} q^2}{Dq^2 [2 \frac{k_B T}{m} q^2 + \Omega_0^2]} \sim \frac{k_B T}{mD \Omega_0^2}. \quad (11.176)$$

In summary, the viscoelastic model permits the calculation of the coherent dynamic structure factor $S(\mathbf{q}, \omega)$ and the incoherent dynamic structure factor $S_s(\mathbf{q}, \omega)$ with a minimum of adjustable parameters. The model is based on the use of the continued fraction representation of the intermediate scattering functions $F(\mathbf{q}, \omega)$ and $F_s(\mathbf{q}, \omega)$, and the frequency moments. Note that the viscoelastic model requires adequate knowledge of the second and fourth frequency moments which must be calculated with the microscopic theory of liquids, and the approximations are solely those of the functions $\tau(q)$ and $\tau_s(q)$. With the most efficient among these functions, the viscoelastic model gives a correct description of the dynamic structure factors over a wide range of the domain (q, ω) , for systems as diverse as argon [143, 192] and liquid metals (see p. 548 of [186]).

12 Ordering in complex fluids

12.1 Introduction

Over the last three decades, many theoretical and experimental studies have been devoted to the understanding of order in complex fluids. The study of two categories of systems is particularly interesting: (i) the supercooled liquid phases of glass formers and (ii) a certain class of soft materials.

Neutron scattering is a valuable tool for studying the dynamic structure factor of supercooled liquids and providing detailed information on the liquid-glass transition. When the liquids are cooled below their melting temperature, they sometimes do not solidify immediately, but remain in supercooled state up to temperatures far below the melting point. Then, they can solidify into the form of amorphous solids without crystallizing.

To study the dynamic properties of supercooled liquids and predict the liquid-glass transition [193, 194, 195], the models for the coherent scattering presented in section (11.8) have been used intensively since the 1980s. In particular, the mode-coupling theories [196, 197], which are based on a consistent treatment of the time autocorrelation functions, predict two regimes of relaxation in the supercooled liquids as well as the kinetic liquid-glass transition [198, 199, 200]. The dynamic state of an atom is affected by its environment even more than in the liquid, and the individual motion of each atom is strongly coupled to the density fluctuations in the system.

The liquid-glass transition is not well defined experimentally, but it can also be studied by molecular dynamic simulations for systems of particles interacting with various types of pair potentials [15]. Even if the results of these simulations are limited by the small system size

and the short time intervals, they can provide detailed information on the dynamic properties of supercooled liquids and glasses. A supercooled liquid and an amorphous solid are metastable phases which are not fully understood in terms of structural arrangement and thermodynamic behaviour. However, the most interesting feature in the liquid-glass transition is by far the manifestation of a dynamic event into which a dramatic dynamic arrest intervenes [201].

Contrary to glass-forming liquids where the range of interaction is comparable to the particle size in soft materials, the range of interaction is smaller than the particle size. The complexity of these systems increases by the presence of dissolved ions, surfactant or polymer molecules and other small solutes in the solvent [202, 203]. Of particular interest are the colloidal suspensions and the globular proteins in aqueous solutions, as well as the microemulsions and diblock copolymer systems. Consequently, the nanometer-sized particles form ordered arrangements of particles and microphase separated systems with periodic density modulation widely depending on concentration, temperature, solvent composition, chemical constituents, etc. [204, 205, 206]. Thus, the stability of soft materials results from the balance between attractive and repulsive interactions which are exerted on the particles.

From an experimental point of view, confocal microscopy and small angle neutron scattering reveal the degree of order in these complex fluids. Soft materials are scientifically important for testing and improving our understanding of sophisticated self-assembly hypotheses needed to describe the molecular ordering [207, 208]. Self-assembly is a process in which components spontaneously form ordered aggregates without human intervention. From a theoretical viewpoint, the cornerstone of our understanding of these complex fluids is the interparticle potential, which is treated rigorously with the statistical mechanical theory [209].

For the supercooled liquids, the interactions are frequently modelled by purely repulsive potentials in inverse power of the distance or by Lennard–Jones potentials. For soft materials, the potential models consist of an attractive well at short distances – beyond the collision diameter – followed by a long-range repulsion [14]. The short-range attraction favoring the aggregation is frustrated by the long-range repulsion which prohibits further growth and changes drastically the phase diagram of purely attractive potentials at long distances. More

explicitly, with a long-range attraction between colloids, the colloidal dispersions exhibit a stable liquid-vapour transition while, with a long-range repulsion, a metastable fluid-fluid transition occurs which complicates the description of the thermodynamic phase transitions [210, 211, 212, 213].

12.2 Experimental evidence of liquid-glass transition

If the liquids are cooled *slowly* (or packaged as droplets in an emulsion [214]), they can reach a freezing temperature T_f of about a third of the melting temperature ($T_f \sim 1/3 T_m$) before crystallising. In contrast, if they are cooled *rapidly* ($10^6 \text{ K}\cdot\text{s}^{-1}$) (or are compressed) by *ad hoc* methods, they can solidify into the form of amorphous solids (glasses) without crystallising. In the amorphous state, the solids have *mechanical* properties similar to those of crystalline solids and *thermodynamic* properties similar to those of liquids. From an experimental point of view, the viscosity η which varies drastically in the supercooled liquid is often used to estimate the temperature T_g of the *liquid-glass transition*. It is conventionally assumed that the transition temperature T_g is what corresponds to the value of viscosity of $10^{12} \text{ N}\cdot\text{m}^{-2}\cdot\text{s}$. The amorphous state whose viscosity follows the Arrhenius law, $\eta(T) \sim b \exp(aT_g/T)$, is called *strong glass*, while the amorphous state of which $\eta(T)$ deviates from Arrhenius behaviour is said to be *fragile* [215]. As an example, the experimental curve of the viscosity of silica can be adjusted by the Arrhenius law with the values of $T_g \sim 1446 \text{ K}$, $a \sim 41.5$ and $b \sim 10^{-6} \text{ N}\cdot\text{m}^{-2}\cdot\text{s}$. Figure (12.1) represents $\log \eta$ as a function of T_g/T . While the slope in this curve is constant for strong glasses, it changes at the temperature $T_c \sim T_g/0.8$ for fragile glasses. This change of regime at T_c is the mark of the *kinetic glass transition* [216] in fragile glasses. More specifically, at temperature $T_c \sim T_g/0.8$, the viscosity drops to $\eta \sim 1 \text{ N}\cdot\text{m}^{-2}\cdot\text{s}$ and the relaxation time is about $\tau_M \sim 10^{-9} \text{ s}$. This timescale is quite satisfactory for an experimental investigation by neutron diffraction and light scattering, and for the theoretical study [217, 218].

Among the physical properties under investigation, the static structure factor $S(q)$ is not of great help for a precise study of supercooled liquids and of the liquid-glass transition because it does not undergo drastic changes as a function of temperature. This is not surprising,

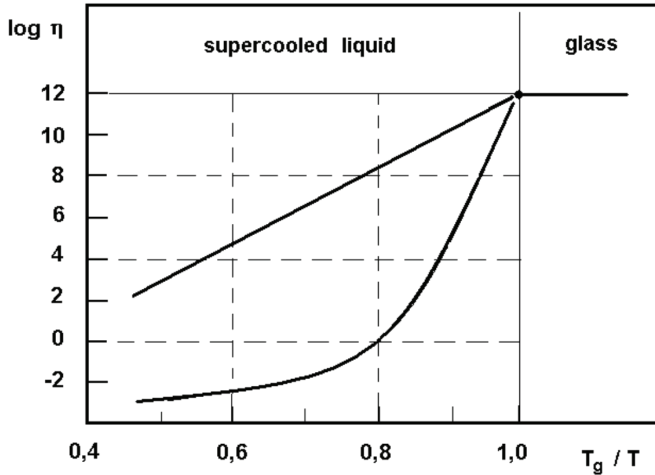


Figure 12.1: Viscosity of the supercooled liquids as a function of reduced inverse temperature. The viscosity is expressed in $\text{N}\cdot\text{m}^{-2}\cdot\text{s}$.

since the liquid–glass transition is purely dynamic by nature. Even if we could think that the splitting of the second peak of the pair correlation function $g(r)$ is an essential feature of the amorphous solids, we realize that it already appears above T_g .

Regarding the thermodynamic properties, they are not affected by particular anomalies, except the specific heat at constant pressure c_p when undergoing a significant decrease with temperature in the transition region. This suggests that supercooled liquids remain in a metastable state and the ergodic–non-ergodic transition occurs at a temperature below T_g . The entropy $S(T)$ is also an advantageous property to be observed in various temperature regimes encountered during supercooling (Fig. 12.2).

We note the linear variation of $S(T)$ above T_g . The highest characteristic temperature is the melting temperature T_m which corresponds to the first-order phase transition between the crystal and the liquid. The relaxation time ($\sim 10^{-13}$ s) is that of the liquid. Then comes the temperature T_c where the kinetic glass transition takes place. The corresponding relaxation time is of the order of 10^{-9} s. Below this temperature, the only way to avoid crystallization is forcing the system to transform into a metastable state through physical mechanisms

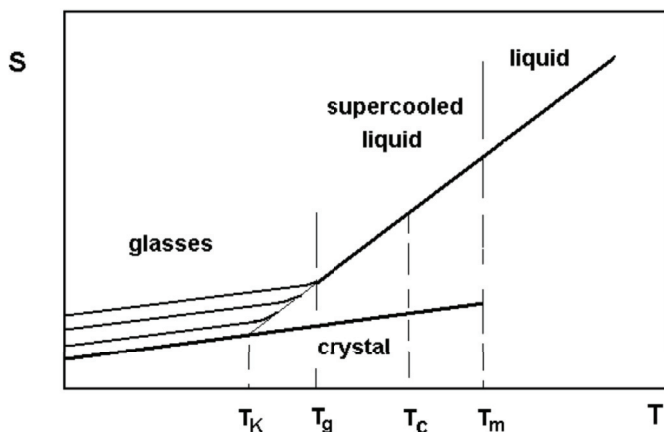


Figure 12.2: Schematic representation of the entropy as a function of temperature for a liquid which can both crystallize and form a glass. Typical values for the relaxation time $\tau(T_g) \sim 10^2$ s; $\tau(T_c) \sim 10^{-9}$ s; $\tau(T_m) \sim 10^{-13}$ s.

which are still poorly understood. Afterwards, if the existence of the liquid is guaranteed against any undesirable crystallization, the temperature of the liquid–glass transition T_g can be reached, at which the relaxation time ($\sim 10^2$ s) increases considerably. From here, the system reaches a non-equilibrium state (glass) defined by the history of the sample and the rate of cooling. It must be understood that, if the existence of the liquid was not guaranteed against crystallization below T_g , then the entropy should decrease linearly down to the temperature T_K , called Kauzmann’s temperature [219], where the entropy of the supercooled liquid becomes equal to that of the crystal. According to some theories, there is a thermodynamic phase transition at T_K . However, it is currently considered that this transition does not exist because the liquid–glass transition opportunely occurs, thus avoiding the Kauzmann temperature to be reached.

The dynamic properties, such as the autocorrelation functions of velocity, stress, density of particles, etc., can preferentially be calculated by molecular dynamics. As far as the stress autocorrelation function $\langle \sigma_{xy}(t)\sigma_{xy}(0) \rangle$ is concerned, it can be used to calculate the viscosity with the Green–Kubo relation [220, 221]:

$$\eta = \frac{\beta}{V} \int_0^\infty \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle dt. \quad (12.1)$$

When T is decreasing, η increases and calculating it becomes very difficult. The mode-coupling theories (MCTs) are well known as being highly suitable to better understand the kinetic glass transition. The early computations of the autocorrelation function for the density of particles $F(q, t)$ show a gradual transition [222] beginning when the value of $f(q) = \lim_{t \rightarrow \infty} F(q, t)$ becomes non-zero over the observation time. This behaviour is usually interpreted as the beginning of the structural arrest, which is the precursor signal of non-ergodicity. In recent years, the MCTs have been frequently tested by numerical simulations and through real experiments, the most conclusive results being obtained for colloidal solutions by light scattering [175, 176].

In the foregoing, the control variable used to study the behaviour of amorphous solids is the temperature. However, beginning with the studies by Bernal [223] on hard spheres, a large number of such studies has been developed to establish a hierarchy of order in physical systems including liquids, glasses, colloids, granular materials, etc. In this case, the control variable is no longer the temperature, but rather the density ρ . Note that, for a regular stack of hard spheres in the FCC structure, the volume available for each sphere is $\nu_0 = 1/\rho = \sigma^3 \cdot \sqrt{2}$, where σ is the hard-sphere diameter, and the packing fraction is $\eta = \pi \rho \sigma^3 / 6 = 0.74$. But when the spheres are randomly tipped into a container and shaken down, there is a dispersion of the values of the packing fraction in the interval $[0.52 - 0.74]$, according to the distribution of a large number of real and numerical experiments using various algorithms [224, 225, 226], whose mean value is invariably $\eta \sim 0.64$. This value ($\eta_{\text{RCP}} = 0.64$), corresponding to the random closely packed state, is about 15% lower than the regular stack ($\eta_{\text{FCC}} = 0.74$) where the pressure diverges.

Figure (12.3), representing the variation of the compressibility factor ($P/\rho k_B T$) as a function of η , displays a first-order transition between the liquid phase and the FCC crystal clearly demonstrated by numerical simulation [227, 228]. It should be noted that the portion of curve corresponding to the liquid phase ($\eta < 0.494$) is correctly described by the Carnahan–Starling [42] equation of state. In contrast, the extrapolation of this equation of state at infinite pressure is definitely incorrect since it takes place at the nonphysical value of

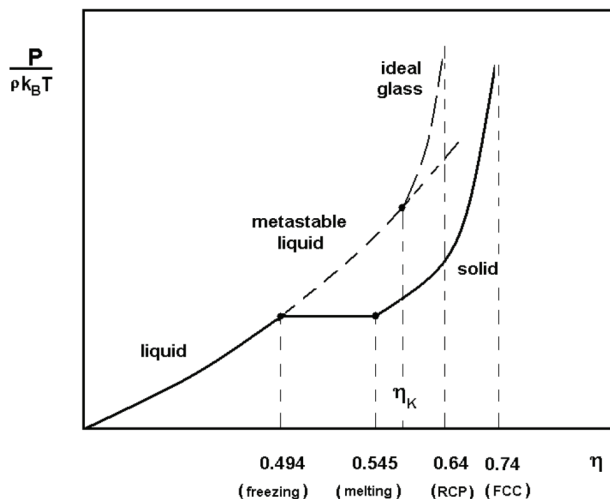


Figure 12.3: Schematic phase diagram of hard spheres. Expected behavior in stable and metastable liquids, as well as in the ideal glass and the solid.

$\eta = 1$, i.e. well above $\eta_{\text{FCC}} = 0.74$. However, as liquids can easily be supercooled, there is no objection to using the equation of state of liquids in the metastable phase up to the threshold η_0 to be determined [229]. It cannot be ruled out that the branch continues to develop up to the value $\eta_{\text{RCP}} = 0.64$, by using a suitable equation of state. Much work [230] has been devoted to the study of packing fraction η in the interval between 0.545 and 0.64. It will be noted from the available results that a transition between the metastable liquid phase and the amorphous state (ideal glass) could take place at the value η_K as indicated by a jump in the compressibility.

12.3 The Goldstein picture for the metastable states

In this section, the liquid-glass transition is analysed in terms of local minima of the potential energy landscape (PEL). The paradigm of the PEL has been introduced by Goldstein [231] to provide a consistent description of the relaxational dynamics of supercooled liquids in $3N$ -dimensional configuration space, rather than in 3-dimensional

ordinary space (section 1.3). While each point is assigned to one particle in ordinary space and to its potential energy in $3N$ -dimensional configuration space, the single point of coordinate vector $\mathbf{r}^N$ represents the microscopic state of the system moving on the potential energy landscape $V(\mathbf{r}^N)$. In fact, the potential energy $V(\mathbf{r}^N)$ of the system describes an hypersurface in $(3N+1)$ dimensions with quite well-defined local minima. The aim of the PEL is to estimate the number of minima and their distribution in energy, and to determine the height and shape of these minima.

At a given temperature, the microscopic state of the system vibrates in a particular minimum whose level of the bottom is V_{min} . Note that each local minimum V_{min} of the PEL is identified with an inherent structure (IS) [232] which forms a metastable state. In terms of energy density, an inherent structure is defined as $e_{IS} = V_{min}/3N$, where $3N$ is the number of degrees of freedom. Thus, the potential energy function $V(\mathbf{r}_i^N)$ in a particular basin is expressed as the sum of the inherent structure $3Ne_{IS}$ and the vibrational component $3Nk_B T/2$, i.e. $V(\mathbf{r}_i^N) = 3N(e_{IS} + k_B T/2)$. Stillinger and Weber [232] provided a formally exact partitioning of the configuration space and an algorithm appropriate for numerical determination of the PEL properties. The PEL formalism has been extensively used to show how changes in the dynamic [233, 234] and mechanical [235] properties are related to the changes of the PEL of the glassy materials. In this section, we take the topological point of view developed by Goldstein [231] which is suitable to give an interpretation of the configurational entropy in supercooled liquids.

The liquid state within a basin is assumed to be in a (local) equilibrium state, which is a metastable state compared to the stable crystal form. The topology of the hypersurface allows us to make difference between liquid, crystal and glass, and give access to the slow dynamics of supercooled liquids. Roughly speaking, for a liquid, there are many basins that can easily be explored whereas, for crystal the hypersurface presents a single deep absolute minimum, i.e. the ground state where the system remains trapped. The supercooled liquid and the glass are characterized by local minima separated by potential energy barriers, thus forming a rough PEL.

Here, we give the three statements required in the Goldstein picture to define two regimes on both sides of the crossover temperature T_x .

(i) The first statement assumes that a supercooled liquid below T_x explores the configuration space thanks to jumps between various minima of the PEL. It should be mentioned that the microscopic state of the system can switch to lower or higher energy minima, provided that the basins have depths similar in size, even if the potential energy barriers are large with respect to the thermal energy. In that case, the system can be considered as quasi-ergodic.

(ii) The second statement stipulates that, when the state of the system crosses a potential energy barrier from one minimum to another, only a small number n of particles are involved in the activated process, whereas the positions of the other $(N - n)$ particles change very little in the system. Thus, even if the entire system undergoes a transition, only a small part of it, in a limited region of the system, is affected by the jump from a minimum to another. As an interesting result, it is found that the potential energy barrier V separating two minima in $3N$ -dimensional configuration space is proportional to the number of particles n that participate in the rearrangement ($V \propto n$).

(iii) The third statement supposes that the number n of particles participating in the activated process *decreases as the temperature increases*. As a consequence, when T increases, n and V decrease in such a way that the heights of potential energy barriers V become comparable to the thermal energies $k_B T$. At higher temperatures, in the fluid regime, the system is perfectly ergodic as it visits the entire $3N$ -configuration space. The reverse situation where T decreases is more relevant. Indeed, at the same time when the thermal energy $k_B T$ decreases, the potential energy barriers V (and the number of particles n) increase, so that the system is in a local minimum surrounded by large potential energy barriers compared to $k_B T$. In that case, it is useful to think in terms of the localization of the microscopic state in a particular minimum for some time, followed by an activated transition to another next neighbour minimum. The activated process allowing the system to jump across a barrier starts to take place around the crossover temperature T_x which makes a difference between the non-activated high-temperature regime and the activated low-temperature regime¹. Goldstein [231] proposed to define T_x with respect to the value of the relaxation time $\tau(T_x) \sim 10^{-9}$ s. When compared to the value of the relaxation time at melting $\tau(T_m) \sim 10^{-13}$ s and to that

¹The temperature T_x is close to kinetic glass transition T_c , defined from the viscosity of fragile glasses.

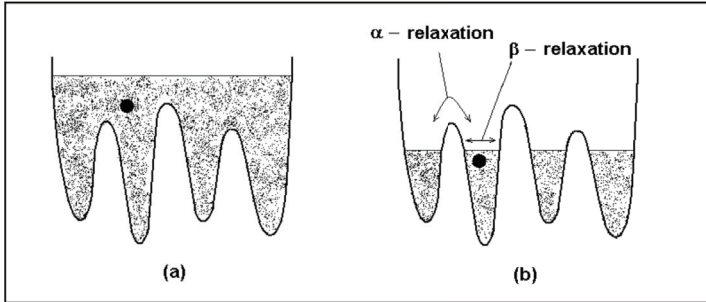


Figure 12.4: Goldstein picture: schematic representation of the potential energy landscape to one dimension of (a) a liquid and (b) a glass (each minimum represents a possible configuration).

of the conventional liquid-glass transition $\tau(T_g) \sim 10^2$ s (Fig. 12.2), it results that $T_g < T_x < T_m$.

Above this somewhat arbitrary temperature T_x , the particle diffusion proceeds by usual small displacements involved in the well-known mechanism of the liquid theory i.e. the Brownian motion. By contrast, below T_x , in the activated low-temperature regime, the Goldstein scenario provides a natural description in terms of two timescale characteristics of the activated process. The physical picture is that of a system stuck in a minimum within a high-frequency vibrational motion (β -relaxation), followed by a low-frequency transition (α -relaxation) into a next minimum after the system has been sufficiently activated. The simplest image likely to show the difference between liquid and glass states in the PEL is that of a set of lakes between mountains. When the level of water is high, all the lakes are easily visited by a 'fish' (liquid-state system) without an activated process: the system is ergodic. When the water level is decreasing, some lakes are isolated from the other ones, so that a 'fish' can (1) remain trapped in its own lake (glass-state system) if the energy barrier is high or (2) jump towards another lake within an activated process if the energy barrier is small (Fig. 12.4).

The original Goldstein picture also allows us to give an interpretation of the entropy crisis and the Kauzmann temperature T_K . The entropy crisis can be summarized as follows: after plotting the liquid-crystal difference of some quantities like entropy, enthalpy, specific

volume, etc., Kauzmann [219] observed that these differences vanish at finite temperatures different from one property to another. For the sake of comparison, it should be remembered that the free-energy difference ΔF between liquid and crystal is zero at T_m and increases when the temperature decreases. In the case of entropy (Fig. 12.2), it amounts to stating that the entropy of the supercooled liquid should become lower than that of the crystal at T_K . When returning to the Goldstein picture, the particles in crystals stay trapped almost without any interruption in their cage. Consequently, it can be assumed that the entropy of a crystal is equal to the vibrational entropy ($S_{\text{cry}} \sim S_{\text{vib}}$). In contrast, the entropy of a locally equilibrated supercooled liquid is composed of the vibrational entropy S_{vib} which is supposed to be approximately the same as in the crystal, plus the configurational entropy S_{con} , i.e. $S_{\text{liq}} = S_{\text{con}} + S_{\text{vib}}$. The configurational entropy is defined [236] as a function of the number of minima $\mathcal{N}$ in the PEL as $S_{\text{con}} = Nk_B s_c$, where $s_c = \frac{1}{N} \log \mathcal{N}$ is the dimensionless configurational entropy per particle. Thus, entropies of the crystal and the liquid increase with the temperature, and entropy variation of the liquid is more rapid than that of the crystal because both vibrational and configurational contributions increase with the temperature (Fig. 12.2). As a result, the liquid and crystal entropies should meet at the temperature T_K , in agreement with the Kauzmann observation. The importance of the configurational entropy in the study of supercooled liquids appears in the calculation of the liquid-crystal difference, which reads:

$$S_{\text{liq}} - S_{\text{cry}} \sim (S_{\text{con}} + S_{\text{vib}}) - S_{\text{vib}} = k_B \log \mathcal{N}. \quad (12.2)$$

When the temperature decreases, the number of minima $\mathcal{N}$ decreases to the value $\mathcal{N} = 1$ at which the crystal occurs. At the same time, the Kauzmann temperature T_K is reached and the configurational entropy $S_{\text{con}} = 0$. Thus, the phase transition from the supercooled liquid to the “last” amorphous phase appears conveniently at T_K , just before the entropy of the liquid falls below the entropy of the solid. Since it is generally accepted that $S_{\text{liq}} - S_{\text{cry}} \geq 0$, this transition is usually called the *ideal glass transition*, which is not experimentally accessible.

However, it should be mentioned that recent theoretical predictions [237, 238, 239] have suggested that a new phase transition (Gardner transition) is supposed to occur below T_K . The Gardner transition is

apparently not limited to spin glasses [240] and other model glasses [241, 242], but is nevertheless of prime importance in a variety of disordered systems [243]. Although there is no clear evidence of such a transition in glass formers, the first experimental confirmation seems to attest to the existence of the Gardner transition in a granular two-dimensional glass [244]. It was shown that beyond a specific density, basins are divided into several sub-basins in which collisions occur in most cases. The local minimum of free energy corresponding to glass decomposes into a large number of minima as the density increases [245].

12.4 Mode-coupling theories

The mode-coupling theories (MCTs) have been designed to calculate the temporal correlation functions in liquids, their particularity being to show how the collective motions of atoms can significantly affect their individual motions [33]. These theories have been developed in the 1970s, when it was found that the asymptotic behaviour of the autocorrelation functions depends on the atomic transport coefficients. This result followed another important one as it indicates that the autocorrelation functions in gases undergo an exponential decay at short times and a slow $t^{-3/2}$ decrease at long times. In particular, it was shown that the velocity autocorrelation function (from which the diffusion coefficient is calculated) depends on the diffusion coefficient D itself, and on the viscosity coefficient η by the following relation [246]:

$$\langle v(0)v(t) \rangle \sim \left[\pi \left(D + \frac{\eta}{\rho m} \right) t \right]^{-3/2}. \quad (12.3)$$

The presence of the two transport coefficients, D and η , in this relation reflects the simultaneous action of two processes that occur on different timescales: the diffusion of an individual atom (individual mode) and the viscosity of the surrounding environment (collective excitations). The physical origin of this phenomenon is explained by invoking (1) the individual motion of each atom, and (2) the swirling flow of surrounding atoms which propels a given atom by hitting it from behind.

Similar arguments can be used for liquids by considering the auto-correlation function of the density of particles $\langle \rho(q, t) \rho(-q, 0) \rangle$ which is the intermediate scattering function $F(q, t)$. For simplicity, consider the expression of the intermediate scattering function in the hydrodynamic limit given by equation (11.143), i.e.:

$$F(q, t) = S(q) \left[\left(\frac{\gamma-1}{\gamma} \right) \exp(-D_T q^2 t) + \frac{1}{\gamma} \exp(-\Gamma q^2 t) \cos(v_s q t) \right], \quad (12.4)$$

where the thermal diffusivity D_T and the sound attenuation Γ determine, respectively, the width of the Rayleigh peak and that of the Brillouin peaks on the dynamic structure factor $S(q, \omega)$, while the sound velocity v_s determines the position of the Brillouin peaks. The presence of these three peaks in the measured dynamic structure factor is the result of a coupling between the neutron beam and three of the modes of the linearised hydrodynamic equations: the Rayleigh peak corresponds to the thermal (or entropic) mode and the Brillouin peaks to the mechanical (or sonic) modes.

The early MCTs have been developed along two distinct routes, both founded on the use of the Zwanzig [139] projection operator formalism. The first route is based on a generalized form of the Boltzmann kinetic equation (in terms of collision integral). The second one makes use of the Mori [138] formalism, with an expression supplemented by approximations for the phenomenological memory functions of the velocity autocorrelation function and the particle density autocorrelation function [33]. The functional forms of the memory functions were those of the hydrodynamic regime (for long times) and the ideal gas regime (for short times). The MCTs have also been extensively used when the calculation of the memory functions became possible and when similarities between the two approaches were noted (i.e. when the collision integral in the Boltzmann equation was expressed in terms of the memory function) [247, 248]. Without dwelling on what makes the difference between the various versions of the MCTs, it is sufficient to note that the Zwanzig–Mori formalism is valid for a long list of autocorrelation functions depending on time. At the outset, the MCTs are based on the important following identity for the dynamic variable $A(t)$:

$$\frac{d}{dt} A(t) = i\Omega A(t) - \int_0^t M(t-t') A(t') dt' + f(t), \quad (12.5)$$

where the first term on the right-hand side stands for the collective motion of atoms associated with the variable $A(t)$. The second term corresponds to the friction term with the memory kernel $M(t)$, and the third term to the random force. After multiplying equation (12.5) by $A(0)$ and calculating the thermal average, the following Mori equation for the autocorrelation function $\langle A(0)A(t) \rangle$ is obtained:

$$\frac{d}{dt} \langle A(0)A(t) \rangle = i\Omega \langle A(0)A(t) \rangle - \int_0^t M(t-t') \langle A(0)A(t') \rangle dt'. \quad (12.6)$$

The difficulty of finding the solution of this exact equation is transferred onto the calculations of Ω and the memory function $M(t)$. This last one is generally a complicated function of the intermediate scattering function as well as of the interatomic potential and of the three-body correlation function [249, 250]. When applied to the velocity autocorrelation function for which the initial slope is $\Omega = \frac{\langle \dot{v}(0)v(0) \rangle}{\langle v(0)v(0) \rangle} = \frac{d}{dt} \langle v(0)v(t) \rangle|_{t=0} = 0$, it is seen that equation (12.6) coincides with the Langevin equation (Eq. 9.103).

All the recent approaches used to study the liquid–glass transition involve the particle density autocorrelation function, i.e. the intermediate scattering function $F(q, t)$, at long times. The starting point of these approaches is equation (9.167), i.e.:

$$\frac{d^2 F(q, t)}{dt^2} + M(q, t) + \int_0^t M(q, t-t') \frac{dF(q, t)}{dt} dt' = 0, \quad (12.7)$$

in which the memory function $M(q, t)$ itself is expressed approximately in terms of the intermediate scattering function $F(q, t)$. One of the simplest approximations for the memory function is $M(q, t) = \frac{k_B T q^2}{m S(q)} F(q, t)$, which calls for the calculation of the static structure factor $S(q)$ with the atomic interaction potential $u(r)$ [251, 252, 253].

It should be mentioned that the early MCTs predicted a sudden ergodic–non-ergodic transition at $T = T_d$, which was not observed neither experimentally, nor by simulation. Accordingly, the original MCTs have been modified [254] to preserve the ergodicity of systems for temperatures significantly below T_d . The MCTs are complicated and will not be discussed here. Only the most important results schematised in figure (12.5) should be summarized as follows:

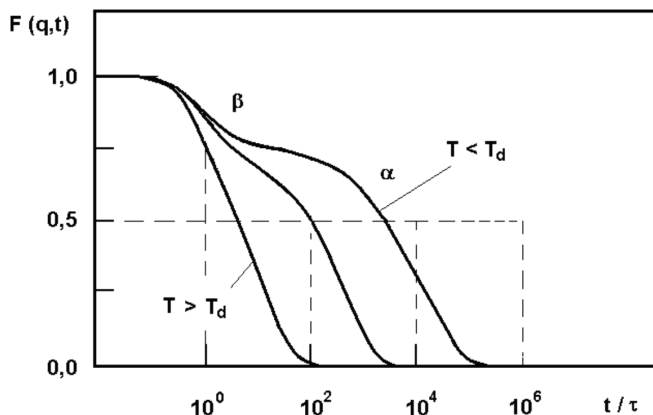


Figure 12.5: Schematic representation of the time dependence of the intermediate scattering function in the supercooled liquids, from MCT.

(1) When the temperature decreases, the transition occurs at a temperature T_d above which the system is ergodic (with the intermediate scattering function $F(q, t)$ tending rapidly to zero as time increases), and below which the system becomes non-ergodic with a long-lived intermediate scattering function $F(q, t)$.

(2) For temperatures around T_d , the variation of $F(q, t)$ with time occurs in three steps. The first one happens over a short timescale (fast relaxation) corresponding to the phonon frequencies. The second one (β -relaxation) takes place on the timescale $\tau_\beta \sim (T - T_d)^{-\delta}$ and the third one (α -relaxation or slow process) on the timescale $\tau_\alpha \sim (T - T_d)^{-\gamma}$. This latter timescale is longer and enables the study of the behaviour of the atomic transport properties.

(3) The loss of ergodicity below T_d is accompanied by freezing of the structure of the system (structural arrest). Consequently, $F(q, t)$ could be seen as the measure of the amount of density fluctuations frozen in the system.

For temperatures below T_d , the first relaxation is very rapid and almost invisible at the scale of the graph contrarily to the β and α relaxations. Between the β and α relaxations, the intermediate scattering function describes a plateau becoming larger as the temperature

decreases. Thus, the α -relaxation depends to a larger extent on the temperature than the β -relaxation.

In summary, MCTs have been widely used to investigate the dynamic properties of liquids (particle density autocorrelation functions in Ar, Rb, Al, ...) and atomic transport properties near the critical point [249, 246, 255]. Then, they have also been extended to study the supercooled liquids and describe the glass transition [254, 251, 253]. During such a transition, the dynamic state of an atom is affected by its environment even more significantly than in the liquid, and the individual motion of each atom is strongly coupled to the density fluctuations in the system. Moreover, beyond a certain density, the freezing of the structure develops, preventing the atom from escaping the cage formed by its nearest neighbours. In the framework of MCTs, the kinetic transition is not an ordinary thermodynamic transition because the ensemble average does not coincide with the time average in the ensemble at work; as a consequence, it is rather an ergodic–non-ergodic transition [256].

More recently, a new approach of the liquid-glass transition has developed, leading to a significant contribution to the understanding of the nature of glasses. This approach, known as Random First Order Transition (RFOT) (or Replica Symmetry Breaking, RSB), was inspired by the pioneering work of Edward and Anderson [257], whose object was to build a thermodynamic description for a class of magnetic alloys with a small amount of magnetic impurity substituted into a nonmagnetic metallic host. They used the concept of an order parameter in conjunction with that of *replicas*, that is to say many strictly identical systems with an infinitesimal extensive attraction between each other. Applying these ideas to a solvable model, Sherrington and Kirkpatrick [258] obtained an ill-defined solution with a negative entropy at very low temperatures, though giving some insights into the thermodynamics of spin glasses. Then, Parisi [259] discovered a new symmetry breaking of great importance, enabling to solve the negative entropy conundrum and give a unified view on the spin glass physics. Later, a close analogy was noticed between the phenomenology of some RSB models and that of structural glasses [260]. In the following years, a great deal of work allowed a deep understanding of the spin-glass models and glass-forming liquids, giving rise to the so-called RFOT theory of the glass transition [261].

This transition is quite unusual in the Erhenfest classification since it presents two apparently contradictory features. As far as the thermodynamic properties are concerned, the transition is of second order because the internal energy and the entropy variations are continuous, whereas the specific heat jumps discontinuously from its liquid value to a value very close to that of the crystal phase. In contrast, regarding the order parameter used in replica theory, the glass transition is of first order because it jumps discontinuously from 0 in the liquid phase to a finite value in the glass phase.

The RFOT provides useful groundwork in order to study glass-forming liquids and spin glasses by gathering many different approaches [262, 263, 264], i.e. mode-coupling theories, mean-field spin glass theories, replica recipe, mosaic picture, etc. They allow to define a series of specific temperatures roughly localized as follows $T_K < T_g < T_x < T_d < T_m$.

12.5 Soft materials: microemulsions, colloids, globular proteins

Of particular interest is the spontaneous microphase formation in systems of spherical symmetric particles lying at the interface of two simple liquids. These systems, known as **microemulsions**, are of industrial importance because they produce very low interfacial tensions (by cosolubilizing specific elements in the medium) and are of scientific interest because the formation of their microstructures is not yet well understood. A *microemulsion* is a thermodynamically *stable* dispersion of two immiscible liquids, optically isotropic and stabilized by one surfactant (amphiphilic molecules). Since the typical sizes of mesophases (few nanometers) are smaller than the light wavelength, the microemulsions are generally transparent. In contrast, the *macroemulsions* made of large droplets, with a diameter greater than $1\text{ }\mu\text{m}$, are thermodynamically *unstable* in the sense that the droplets sediment or float, depending on the densities of the dispersed phases.

A microemulsion contains a polar solvent (water), a nonpolar solvent (oil) and a surfactant, composed of long amphiphilic molecules having at one end a hydrophilic polar segment and at the other end a hydrophobic segment. Usually, a second amphiphilic component (cosurfactant) is introduced in order to ensure the flexibility of the interface and favour the microemulsion formation. By its tendency

to locate between water and oil regions, the surfactant reduces the interfacial tension by several orders of magnitude and imposes a topological order in the microemulsions and a geometric disorder of the mesophases [265]. The specificity of the surfactant is to leave the dispersion macroscopically homogeneous and to arrange the mesophases on a microscopic scale. The microstructure has been examined by various techniques including light scattering, conductivity, diffusion by NMR, etc. as a function of temperature [266, 267]. It appears now to be admitted that, at low volume fraction of one component (water or oil) in the other, the picture of a microemulsion structure is made of discrete swollen micelles whose long-range order remains stochastic. At intermediate volume fraction of water and oil, microemulsions can organize themselves into spatially periodic mesophases separated by equilibrium bicontinuous structures like sheets between water-rich and oil-rich domains [268, 269, 270].

As in microemulsions, many exotic geometries have been observed in **diblock copolymers** consisting of two types of monomers. The monomers A and B are set out to form a single copolymer chain, e.g. a diblock of two monomers, a triblock of three monomers, etc. Ternary mixtures of A, B homopolymers and AB diblock copolymers are similar in some respects to mixtures of water, oil and surfactant. Above a certain temperature, the large collection of diblock copolymers is equally distributed in a disordered state as they are in liquids. Below that temperature, when entropy is dominated by enthalpy, the diblock copolymers form regular structures common to the microemulsions [271, 272]. The copolymer acts as a surfactant for the A and B homopolymer mixture, decreasing the surface tension between the A-rich and B-rich domains when it accumulates on the interface, and maintaining a topological order between the domains. In spite of this similarity, the diblock copolymer is generally not a solubilizer of homopolymers as efficient as a good amphiphile in the mixture of oil and water [273].

The phenomenon of microphase separation observed in microemulsions and diblock copolymers is also common to other physical systems exhibiting diverse microstructures at two- and three-dimensions known as **modulated phases**. Most of the observed phenomena and available experimental data (lamellar structures, diverse arrays of cylinders and spheres...) have stimulated a strong theoretical effort [207, 274]. In particular, the microscopic inhomogeneities in microemulsions or copolymers are characterized by two length scales

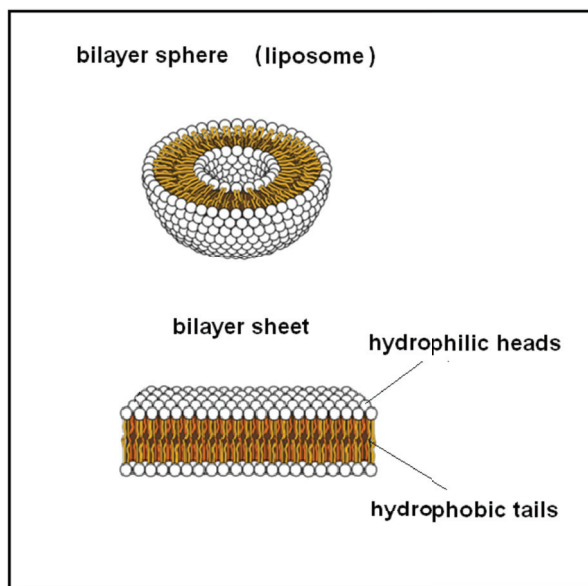


Figure 12.6: Colloidal solutions: cross section views of liposome and bilayer sheet.

which are related to the temperature, the chemical constituents and the range of volume fractions. From phenomenological and microscopic approaches, it is now understood that frustration when arising from competing interactions over different length scales, plays a crucial role in microphase separation [275].

Colloidal suspensions are involved in many phenomena (precipitation, flocculation, sedimentation, ...) playing an important role in the formation of clusters and the transport of specific substances [276, 277, 278, 279]. For instance, it is of great interest for the environment to regulate sedimentation in estuaries silted up with sand, clay and silt, or to control the transport of toxic metals in water or soil.

Certain colloidal suspensions are rich in micelles (spheroidal aggregates) of nanometric size formed of molecules having a hydrophilic polar head directed towards the solvent and a hydrophobic tail directed towards the core. In some cases, the molecules can self-assemble in

aqueous medium to form liposomes or bilayer sheets (Fig. 12.6). Liposomes are micelles consisting of concentric lipid bilayers enclosing aqueous compartments. Liposomes are increasingly used in pharmaceutical research (to carry drugs and monitor their accumulation) and in medical imaging by introducing fluorescent-labeled substances.

As already mentioned, attractive interactions promote ordered phases, whereas long-range repulsions inhibit this tendency. At low density, long-range repulsions combined with short-range attractions, may lead to a variety of states as glassy states of clusters [280, 281]. For small ranges of interaction compared to the particle size, simulation computations have disclosed the presence of a Wigner glass of clusters observed in charged colloidal dispersions for very low concentration [282], in analogy with the Wigner crystals produced by long-range Coulombic interactions in the electron gas [283]. When the density is increasing, clusters become more and more anisotropic and lead, at the end, to gelation by forming a network with chainlike local structure [210, 284].

Globular proteins in aqueous solutions have been widely studied. A protein is a biological macromolecule formed of one or more polypeptide chains, with each of them consisting of small subunits (amino acids) linked together which constitute their elementary structure. With different chemical properties, the amino acids determine the spatial arrangement of proteins along the polypeptide chain. The spherical globular proteins are a special case as they are highly soluble in the solvent (Fig. 12.7). They play an important role in metabolism.

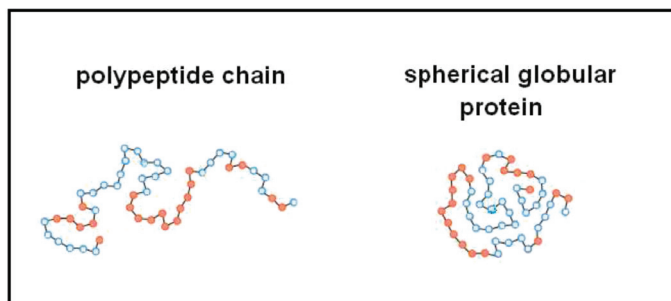


Figure 12.7: A polypeptide chain made of amino acids and a spherical globular protein.

Albumins and globulins, being abundant in animal cells and blood serum, are representative of globular proteins. Hemoglobin is also a protein whose primary function is to transport oxygen in humans and other vertebrates, and which is responsible for the color of red blood cells. Lysozyme is encountered in a number of secretions (tears, saliva, breast milk, mucus, ...) and egg white in many animal species. Enzyme is another protein acting in lowering the activation energy of a chemical reaction, thereby increasing reaction rate.

A number of techniques have been designed to produce protein crystals. Systematic investigation of the process is difficult due to the slow time scale: the growth of a regular crystal can take weeks or months. Aside from the crystallization of dense colloidal suspensions, spherical clusters of proteins can also be formed at lower concentrations. Recent experiments indicate that clusters formed in dilute solutions exhibit no tendency of bulk phase transition [285, 286]. In contrast, a liquid-liquid phase separation occurs when a protein solution is cooled below its cloud point temperature. This is the temperature above which the aqueous solution remains practically homogeneous and transparent whereas, below it separates into two coexisting liquids, one being rich in proteins, and the other one being poor in proteins [276]. Contrary to the crystallization, the onset of the liquid-liquid phase separation (sometimes called coacervation) takes only few minutes. It should be mentioned that liquid-liquid transition can be metastable because the equilibration and demixing into two clear liquid phases separated by a sharp meniscus can take many days. The clusters formation is different from the critical nucleus occurring during the liquid-vapour phase separation.

12.6 Phase transitions

It is fascinating that a small variation of a parameter, such as temperature, causes in some cases a spectacular modification of the system and the appearance of new phases of matter whose collective behaviour bears little resemblance to that of a few particles. The theory aims to identify both range and strength of the interactions among particles in terms of experimentally accessible parameters, such as molecular length, density and temperature. But it is rare to find an interacting many-particle system likely to be easily described by a microscopic approach near the critical points. More useful is the macroscopic

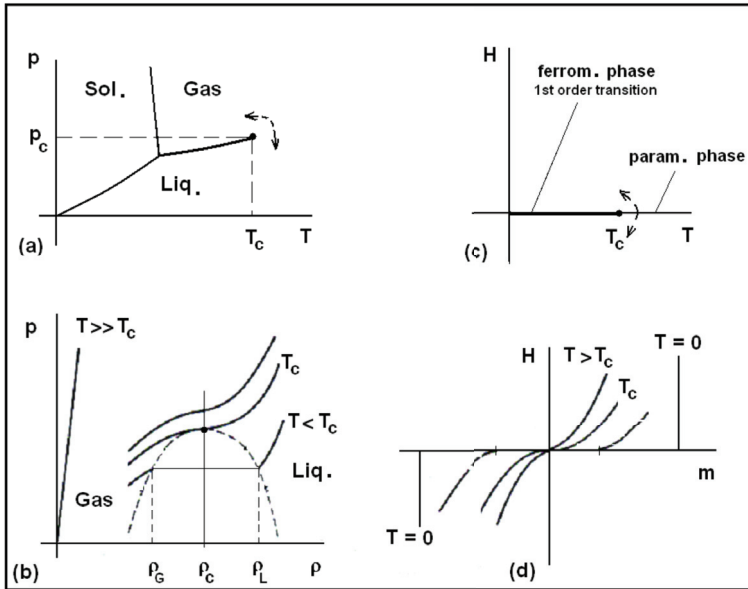


Figure 12.8: Phase diagram of a liquid-gas transition (a) $p(T)$ and (b) $p(\rho)$. Phase diagram of a ferromagnetic transition (c) $H(T)$ and (d) $H(m)$, where H is the magnetic field and m the magnetisation density. Note the similarity between p and H and between ρ and m .

approach having its origin in the thermodynamic theory of critical phenomena, which ignores the interactions between particles. Since all macroscopic properties can be deduced from the free energy, their dramatic changes involved in phase transitions correspond to singularities in the free energy. As with any thermodynamic system, there is a competition between entropy and enthalpy whose balance corresponds to the minimization of free energy. Hence, the study of phase transitions is related to finding the origin of these singularities and the identification of new phases.

Among the numerous phase transitions, the liquid-gas transition is well known with the line in the (p, T) plane (Fig. 12.8a) which ends up at the critical point (T_c, p_c) , and the coexistence interval containing a mixture of gas and liquid of densities $\rho_G = 1/v_G$ and $\rho_L = 1/v_L$ at $T < T_c$, in the (p, ρ) plane (Fig. 12.8b). Since the curve $p(T)$ terminates at a critical point, there is a possibility to convert a

liquid into a gas continuously without crossing the phase transition line, contrary to the liquid-solid transition line.

Another interesting phase transition occurs in the Ising ferromagnetic system. The system is in a paramagnetic (disordered) phase for a temperature higher than the critical temperature (Curie temperature T_c), while it remains in a ferromagnetic (ordered) phase below T_c (Fig. 12.8c). If a magnetic field H is applied to a ferromagnetic material (Fig. 12.8d), a discontinuity occurs in magnetization density $m = M/V$ as the magnetic field H goes to zero for $T < T_c$. It can be seen from these figures that the isotherms $p(\rho)$ and $H(m)$ have much in common, due to the similarity between H and p and between m and ρ , respectively. Note that jumps in the magnetization m and the density ρ decrease when the temperature increases towards T_c .

In spite of the apparent similarities between these two phase transitions, they differ by some specific features. Generally, to distinguish two phases of a material, it is possible to use an *order parameter* which is equal to zero in the disordered phase and non-zero in the ordered phase (usually the phase of low temperature). For the liquid-gas transition, the order parameter ($\rho - \rho_c$) is defined as the difference between the density ρ and the critical density ρ_c , and, for the ferromagnetic transition, the role of the order parameter is played by the magnetization density m . In the case of the liquid-gas transition, the order parameter has the dimensionality $n = 1$ since the density is a scalar, while the order parameter for the ferromagnetic transition has the dimension $n = 3$ because of the vectorial character of the magnetization M . Figure (12.9) displays the phase diagram of the Ising ferromagnetic system representing the magnetization density m as a function of temperature T and the magnetic field H .

There are two ways in which the transition can appear when H varies. For temperatures $T < T_c$, the system undergoes a *first-order phase transition* with magnetization passing abruptly from a positive value to a negative value. In contrast, near the critical point, the system undergoes a continuous or *second-order phase transition* with magnetization varying continuously. It is reported that a second-order phase transition is accompanied by a spontaneous symmetry breaking in which the system chooses to be in either an up or down-spin phase.

When a system is divided in a small number of domains, keeping the thermodynamic variables constant, the macroscopic properties of each domain remain usually unchanged with regard to the whole.

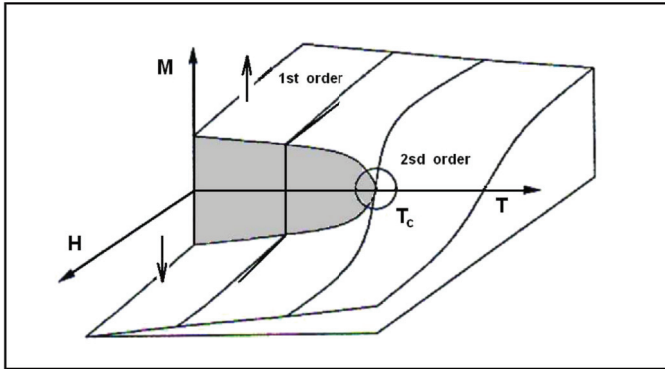


Figure 12.9: Isotherms in the phase diagram of the ferromagnetic system. First-order transition when the magnetisation density m changes abruptly for $T < T_c$, and second-order transition when m changes continuously around T_c .

Nevertheless, if the number of domains becomes important, in such a way that the size of each domain is lower than a certain length ξ , the properties of each domain differ from those of the original system. The typical length scale ξ is known as the *correlation length*, i.e. the length over which the *fluctuations* of microscopic variables are correlated. At the critical point, the system is divided into locally ordered domains scattered in the bulk, whose mean size corresponds to the correlation length ξ and the mean lifetime to the correlation time τ . The experiments indicate that the correlation and the correlation time increase as the critical point is approached from the low temperatures. In particular, it is observed that the correlation length ξ remains finite for a first-order phase transition, while it becomes infinite for a second-order phase transition. When T tends to T_c , the correlation length diverges according to the simple form $\xi \sim (T_c - T)^{-\nu}$, where ν is known as a *critical exponent*. As a consequence of large fluctuations, which become correlated over all distances near the critical point, the system is in a single phase, as the disordered phase has a stability similar to the ordered phase.

It is well known that the singular behaviour of various thermodynamic functions, in the vicinity of the critical point, is governed by a set of critical exponents for transitions as different as those of liquid-gas and ferromagnetic. In addition to the exponent ν , the most

commonly encountered critical exponents are : (i) β which describes the order parameter m below T_c as $m \sim (T_c - T)^\beta$, (ii) γ describing the susceptibility (i.e. the response of the order parameter m to its conjugate field H), $\chi = \frac{\partial m}{\partial H}|_{H=0} \sim |T - T_c|^{-\gamma}$, (iii) α describing the heat capacity (i.e. the thermal response function) $C = \frac{\partial E}{\partial T} \sim |T - T_c|^{-\alpha}$, etc. It is remarkable that the critical phenomena of very different physical systems show the same temperature dependence, with roughly similar values of the critical exponents. For a liquid-gas transition $\alpha \simeq 0.11$, $\beta \simeq 0.32$, $\gamma \simeq 1.24$, $\nu \simeq 0.63$, and for a ferromagnetic transition $\alpha \simeq -0.1$, $\beta \simeq 0.34$, $\gamma \simeq 1.4$, $\nu \simeq 0.7$, linked by the relationship $\alpha + 2\beta + \gamma \simeq 2$. Detailed studies of this universality applied to critical phenomena go beyond the scope of this review [287].

The divergence of the correlation length near a second-order phase transition indicates that the thermodynamical properties are insensitive to most microscopic details of the system. This is a motivation to search for a phenomenological description of critical phenomena capable of describing a wide variety of model systems. In the next section, we introduce such a phenomenological approach of second-order phase transitions, known as the Landau–Ginzburg [288] theory, in which the order parameter goes continuously to zero. It should be noted that this theory is of quite general meaning, so that it can be used for a great number of systems with various dimensionalities: three-dimensional systems (fluids, ferromagnetic systems...), two-dimensional systems (films, emulsions...), one-dimensional systems (polymers, chains of weakly coupled atoms, etc.).

12.7 A phenomenological approach: the Landau–Ginzburg theory

The Landau–Ginzburg theory [288] has been first developed to investigate the charged superfluids. Later on, the calculations started with the free-energy functional under a form that generalizes Eq. (5.227) and the results were obtained from its minimization. Now, the expansion of the free-energy functional applied to complex fluids near the critical point is written as an integral over all space of an appropriate function of the order parameter and its spatial deviations as:

$$F[m(\mathbf{r})] = \int \left\{ a[m(\mathbf{r})]^2 + b[m(\mathbf{r})]^4 + c[\nabla m(\mathbf{r})]^2 + d[\nabla^2 m(\mathbf{r})]^2 + \dots \right\} d\mathbf{r}, \quad (12.8)$$

where the order parameter noted $m(\mathbf{r}) = \rho(\mathbf{r}) - \rho_c$ is the difference between the local density $\rho(\mathbf{r})$ and the critical density ρ_c . It can be noted that the odd powers of $m(\mathbf{r})$ are absent in the integrand (free-energy density) by virtue of the conservation law of particles, and the third and fourth terms are the square gradient and square Laplacian of the order parameter, respectively. Depending on the system under study, other terms can be added or dropped in the expansion. Whereas the spatial derivatives are expected for inhomogeneous fluids, all the spatial derivatives of the order parameter are neglected for homogeneous fluids, although $m(\mathbf{r})$ is subject to fluctuations at the microscopic level². Thus, the Ornstein–Zernike theory can be re-derived [289] with equation (12.8), when only the coefficients a and c are kept. By stability consideration, both parameters a and c must be positive, whereas a vanishes at the critical point.

In other circumstances, such as those in microemulsions [268, 290] and homopolymer–diblock copolymer blends [291, 292], the terms pertinent to a study of the critical behaviour are those with the coefficients a , c and d , with a positive value of a so that the free energy has a minimum. In that case, it has been argued that the stability condition imposes $c^2 - 4ad < 0$, so that d is positive and c is positive or negative. It should be mentioned that, during the change of sign of c by varying an appropriate parameter, the system undergoes a phase separation into a bulk phase or a spatially modulated phase. The condition $c = 0$, referred to as the Lifshitz point, was first introduced into the context of ferromagnetic systems [293], but it is also known to exist in other systems such as liquid crystals [294], microemulsions [268], [290], block copolymers [291], [292].

In the Landau–Ginzburg theory, it is convenient to write the free-energy functional $F[m(\mathbf{r})]$ in an alternative form by expanding the order parameter and its spatial deviations in Fourier series as:

$$m(\mathbf{r}) = \sum_{\mathbf{q}} m_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}) \quad (12.9)$$

$$\text{with } m_{\mathbf{q}} = \frac{1}{V} \int m(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r},$$

²This local inhomogeneity assumption has been discussed by Landau in his theory of the spatial correlation functions, see L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon, London (1968).

$$\nabla m(\mathbf{r}) = \sum_{\mathbf{q}} (i\mathbf{q}) m_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}), \quad (12.10)$$

$$\nabla^2 m(\mathbf{r}) = \sum_{\mathbf{q}} -\mathbf{q}^2 m_{\mathbf{q}} \exp(i\mathbf{q} \cdot \mathbf{r}). \quad (12.11)$$

After substituting these relations in equation (12.8) and integrating them, all the terms of the form $m_{\mathbf{q}} m_{\mathbf{q}'}$ vanish when $\mathbf{q}' \neq -\mathbf{q}$, and are equal to $|m_{\mathbf{q}}|^2$ when $\mathbf{q}' = -\mathbf{q}$, so that $F[m_{\mathbf{q}}]$ reads:

$$F[m_{\mathbf{q}}] = V \sum_{\mathbf{q}} (a + cq^2 + dq^4) |m_{\mathbf{q}}|^2. \quad (12.12)$$

It should be noted that each term of the sum in equation (12.12) depends only on single density modes $m_{\mathbf{q}}$ contributing additively to the free energy. Consequently, the various $m_{\mathbf{q}}$ are statistically independent, i.e. noninteracting. Because of the truncation of the Fourier series, equation (12.12) is only valid for small q , where the wavelength $1/q$ is great compared to the interparticle distance.

12.8 Density fluctuations near the critical point

To link the Landau–Ginzburg phenomenological approach to the microscopic approach, it should be pointed out that the free energy can be written as a function of the density fluctuations under the form [289]:

$$\frac{\beta F[m_{\mathbf{q}}]}{N} = \sum_{\mathbf{q}} \frac{1}{S(q)} \left| \frac{m_{\mathbf{q}}}{\rho} \right|^2, \quad (12.13)$$

where $S(q)$ is the static structure factor, i.e. the linear response of the system with respect to the particle density. This relation results from the fluctuation-dissipation theorem (Eq. 6.97) indicating that the structure factor $S(q)$ of the system is directly proportional to the susceptibility $\chi(q)$ given by the formula $\chi^{-1}(q) = -(\frac{\delta^2 F[m_{\mathbf{q}}]}{\delta m_{\mathbf{q}}^2})$. Comparing equation (12.12) with equation (12.13) allows us to deduce the following expression for the structure factor at small q :

$$S(q) \simeq \frac{1}{\beta \rho (a + cq^2 + dq^4)}. \quad (12.14)$$

A point of particular interest is the correlation of the density fluctuations in complex fluids near the critical point. To gain an insight into the density fluctuations in fluids, the total correlation function $h(r)$ can be investigated directly by X-rays or light scattering experiments, with its Fourier transform $h(q)$ that is related to the structure factor $S(q)$ by equation (6.128):

$$S(q) = 1 + \rho h(q). \quad (12.15)$$

The microscopic nature of density fluctuations can also be studied in terms of the Fourier transform of the direct correlation function $c(r)$ by the Ornstein–Zernike relation (Eq. 6.126):

$$S(q) = 1 + \rho h(q) = \frac{1}{1 - \rho c(q)}, \quad (12.16)$$

This relation shows that the correlation functions depend on a set of the arbitrary phenomenological parameters a , c and d , which are non-universal functions of microscopic interactions. The understanding of the physical origin of long-range character of $h(r)$ is a major problem of complex fluids near the critical point. The slower the attenuation of correlations, the greater the characteristic size of fluctuations. In an attempt to explain the asymptotic behaviour of $h(r)$ for large r , calculating the inverse FT of equation (12.14) is possible.

It should be stressed that the Ornstein–Zernike (OZ) theory can be rederived by considering only of the terms with the coefficients a and c in equation (12.14). Considering that this well-known theory predicts a large isothermal compressibility χ_T at the critical point of simple fluids, the structure factor for small values of q is:

$$S(q) \simeq \frac{1}{\beta \rho (a + cq^2)}. \quad (12.17)$$

Far away from the critical point, the structure factor at $q = 0$ is $S(0) = (\beta \rho a)^{-1} = \frac{\rho \chi_T}{\beta}$. However, when reaching the critical point, a tends to zero as a consequence of the divergence of the isothermal compressibility. Taking the inverse FT of the Lorentzian representation of equation (12.17), presumably adequate for small wave vectors, provides the total correlation function where the leading term at large distances is:

$$h(r) \simeq \frac{1}{4\pi\beta\rho^2c} \frac{\exp(-r/\xi)}{r}, \quad (12.18)$$

with the correlation length $\xi = \sqrt{c/a}$. This is in agreement with the fluctuation theorem for the isothermal compressibility:

$$\rho k_B T \chi_T = S(0) = 1 + 4\pi\rho \int h(r)r^2 dr, \quad (12.19)$$

which predicts that $h(r)$ must vanish asymptotically to zero at large distances more rapidly than $1/r^3$. The thermodynamic stability in the OZ theory requires positive values of a and c , and at the critical point, where $a \rightarrow 0$, the correlation length tends to infinity, so that $h(r)$ is no longer exponentially damped at the critical point. The asymptotic behaviour of $h(r)$ given by equation (12.18) is only correct for moderately large values of the isothermal compressibility, away from the critical point, whereas it behaves as $1/r$ at the critical point.

Equation (12.14) deduced from the Landau–Ginzburg expansion of the free-energy functional has been used for the structure factors of microemulsions [268] and diblock copolymers [295, 296]. In this case, a , c and d are arbitrary phenomenological parameters fit accurately on experimental scattering data of these systems up to a small microscopic cutoff compared to the inverse of the interparticle distance. Additional information about the disordered phases may be extracted from the structure factor when the discriminant Δ of the polynomial in equation (12.14) changes of sign.

With the conditions $\Delta = c^2 - 4ad > 0$, $a > 0$ and $d > 0$, the inverse FT of equation (12.14) and straightforward algebra leads to [268, 211]:

$$h(r) \simeq \left(\frac{1}{4\pi\beta\rho^2\Delta^{1/2}} \right) \frac{1}{r} [\exp(-r/\xi_1) - \exp(-r/\xi_2)], \quad (12.20)$$

with the two correlation lengths:

$$\xi_1 = \sqrt{\frac{2d}{c - \Delta^{1/2}}}, \quad (12.21)$$

$$\xi_2 = \sqrt{\frac{2d}{c + \Delta^{1/2}}}. \quad (12.22)$$

With the conditions $\Delta = c^2 - 4ad < 0$, $a > 0$ and $d > 0$, the inverse FT of equation (12.14) reads:

$$h(r) \simeq \left(\frac{1}{4\pi\beta\rho^2|\Delta|^{1/2}} \right) \frac{1}{r} \exp(-r/\xi) \sin(r/\delta), \quad (12.23)$$

with the two correlation lengths :

$$\xi = 2 \sqrt{\frac{d}{2(ad)^{1/2} + c}}, \quad (12.24)$$

$$\delta = 2 \sqrt{\frac{d}{2(ad)^{1/2} - c}}. \quad (12.25)$$

Depending on the values of the parameters a , c and d in equation (12.14), the total correlation function $h(r)$ may present either a decay resulting from a combination of two Yukawa functions, with the correlation lengths ξ_1 and ξ_2 , or a damped oscillatory behaviour with a periodic spatial variation δ , generating modulated phases in the system.

To obtain more information on how the surfactant in microemulsions (or the copolymer in mixtures of homopolymers) tends to order the mesophases and also to order itself, it is useful to introduce the disorder line and the Lifshitz line.

The *disorder line* of the system is the locus of points in the phase diagram at which the oscillatory behaviour appears in the total correlation function $h(r)$, when $(c^2 - 4ad)$ is negative. The total correlation function is presented in figure (12.10) for a system with $a = d = 1$ and several values of c . The discriminant $(c^2 - 4ad)$ is negative when $-2 < c < 2$, and it can be seen that the largest amplitude of the oscillations of the total correlation function $h(r)$ is for $c = -1.99$. Then, when c increases, the oscillations of $h(r)$ undergoes a fast attenuation which becomes invisible beyond $c = 1.8$.

The *Lifshitz line* is the locus of points at which the peak in the structure factor $S(q)$ just starts to move out of zero wave vector towards a nonzero value (Fig. 12.11). Its localization is given by $\frac{\partial S^2(q)}{\partial q^2} \big|_{q=0} = 0$, i.e. $c = 0$. In other words, it corresponds to the point where the structure factor ceases to decay monotonously, in contrast to the disorder line for which oscillatory behaviour occurs in the total correlation function $h(r)$. It should be noted that the position of the peak in $S(q)$ moves to large wave vectors when c decreases and its divergence takes place for $c = -2$.

In the context of diblock copolymer blends, equation (12.23) with $\Delta < 0$ is required to describe the disordered phase with the correlation length ξ and the wavelength δ . From an experimental point of view,

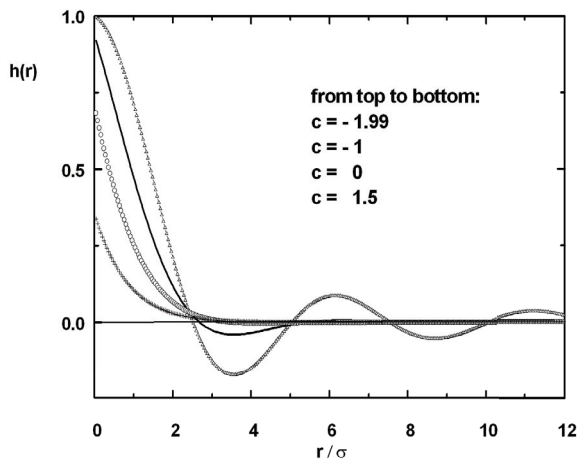


Figure 12.10: Total correlation function $h(r)$ for the system with $a=d=1$ and different values of $c = (-1.99, -1, 0, 1, 1.5)$, from top to bottom. The disorder line appears around $c = 1.8$.

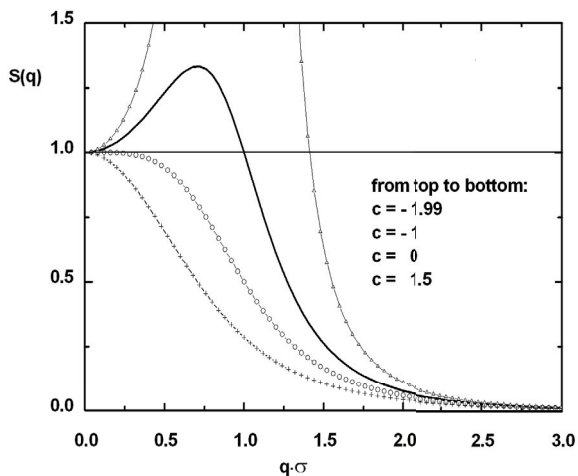


Figure 12.11: Structure factor $S(q)$ for the system with $a = d = 1$ and different values of $c = (-1.99, -1, 0, 1.5, 2.5)$, from top to bottom. The Lifshitz line appears for $c = 0$.

the oscillation in $h(r)$ reflects the tendency of the copolymer to order the A and B monomers in space. It depends on the temperature [296] and the concentration of diblock copolymers [297]. At low copolymer density, when the parameter c is positive, the total correlation function $h(r)$ and the structure factor $S(q)$ decrease monotonously with the distance as shown in figures (12.10) and (12.11), respectively. As the copolymer density increases and the temperature remains constant, we can expect the wavelength δ to decrease and enforce the order over shorter distances. When the amount of copolymer continues to increase, c changes its sign at the composition of the Lifshitz line. Then, for larger copolymer content, it remains negative up to the divergence of the peak in $S(q)$ ($c = -2$). The divergence of the fluctuations at $q = q_c$ means an instability of the homogeneous phase leading to microphase separation. The wavelength of the fluctuations where the instability of the homogeneous phase is realized is indeed $\delta = 2\pi/q_c$. It should be noted that the parameter c depends on the copolymer density and the question arises meanwhile whether it varies with the temperature [298].

12.9 The structure factor of complex liquids

As already mentioned, the structure factor is an essential property of liquids measured by X-ray or neutron scattering, and calculated by various methods from the interparticle potential. The structure factor $S(q)$ describes the arrangement of the particles in the reciprocal space for any system. In the case of simple liquids, the principal peak in $S(q)$, at $q = q_p$, gives an indication on the mean distance between particles. More relevant for the purpose is the value of $S(q)$ at $q = 0$ as it increases drastically when the first-order liquid-vapour transition occurs, due to the increase of the density fluctuations in vapour state. Besides, in more complex liquids, a pre-peak can emerge in the structure factor at the small wave vector q_c ($0 < q_c < q_p$) when the long-range repulsion in the pair potential is sufficiently large; this pre-peak is the signature of the formation of clusters in the system. In some circumstances, the pre-peak in $S(q)$ grows, indicating a disordered-pattern of clusters, with the possibility to display spontaneous modulated phases when the pre-peak is diverging. This transition (modulated phases) observed in $S(q)$ at $q = q_c$ displays an analogy with the liquid-vapour transition expected from the divergence of $S(q)$ at

$q=0$. Both transitions are indeed the consequence of instabilities of the uniform phase with respect to the density fluctuations. In simple liquids with long-range attraction of the van der Waals type, the long-wavelength fluctuations dominate, whereas in complex liquids, with a long-range slightly repulsive interaction, the density fluctuations of the microscopic wavelength $2\pi/q_c$ are predominant, thus leading to the microphase separation.

To illustrate the concept of density fluctuations in complex liquids, we investigate the structure factor $S(q)$ and focus attention on the magnitude and the position of the pre-peak on $S(q)$. When using the MD simulation, the results are accurate and depend only on the potential model. In contrast, when the liquid theory methods are employed, the results also depend on the approximation used. For instance, with the simplest random phase approximation (RPA) (section 6.6), the structure factor is given by equation (6.253) or equivalently by:

$$S_{RPA}(q) = \frac{1}{1 - \rho c_{HS}(q) - \rho c_{lr}(q)}, \quad (12.26)$$

where $S^{HS}(q)$ is the hard-sphere structure factor (Eq. 6.181) whose expression is known accurately under the analytical form [74, 75]:

$$1 - \rho c_{HS}(q) = \frac{1}{S_{HS}(q)} = 1 + 24\eta[\alpha J_1(q\sigma) + \delta J_2(q\sigma) + \gamma J_3(q\sigma)], \quad (12.27)$$

$$\begin{aligned} \text{with} \quad \eta &= \frac{\pi}{6}\rho\sigma^3; \quad Q = q\sigma; \quad \alpha = \frac{(1+2\eta)^2}{(1-\eta)^4}; \\ \delta &= -6\eta \frac{\left(1+\frac{\eta}{2}\right)^2}{(1-\eta)^4}; \quad \gamma = \frac{\eta(1+2\eta)^2}{2(1-\eta)^4}, \end{aligned} \quad (12.28)$$

and

$$J_1(q\sigma) = \frac{1}{(q\sigma)^3} \{ \sin(q\sigma) - (q\sigma) \cos(q\sigma) \}, \quad (12.29)$$

$$J_2(q\sigma) = \frac{1}{(q\sigma)^4} \{ 2(q\sigma) \sin(q\sigma) - [(q\sigma)^2 - 2] \cos(q\sigma) - 2 \}, \quad (12.30)$$

$$\begin{aligned} J_3(q\sigma) &= \frac{1}{(q\sigma)^6} \left\{ [4(q\sigma)^3 - 24(q\sigma)] \sin(q\sigma) \right. \\ &\quad \left. - [(q\sigma)^4 - 12(q\sigma)^2 + 24] \cos(q\sigma) + 24 \right\}. \end{aligned} \quad (12.31)$$

The function $\rho c_{lr}(q)$ in equation (12.26) is the FT of the direct correlation function $\rho c_{lr}(r) \simeq -\rho \beta u_{lr}(r)$ (with $u_{lr}(r)$ being the long-range part of the potential) which is defined as:

$$\rho c_{lr}(q) = \frac{4\pi}{q} \int [-\rho \beta u_{lr}(r)] \sin(qr) r dr. \quad (12.32)$$

For mathematical convenience, the potential $u(r)$ is taken to be the temperature-independent double Yukawa (2Y) potential [299], namely

$$\beta u(r) = -K_a \frac{\sigma}{r} \exp\left[-z_a \left(\frac{r}{\sigma} - 1\right)\right] + K_r \frac{\sigma}{r} \exp\left[-z_r \left(\frac{r}{\sigma} - 1\right)\right]. \quad (12.33)$$

If the direct correlation function $\rho c_{lr}(r) \simeq -\rho \beta u(r)$ is selected to be extended inside the core [300, 301], the FT of the direct correlation function $\rho c_{lr}(q)$ is expressed directly in terms of the model parameters under the analytical form:

$$\rho c_{lr}(q) = 24\eta \left[\frac{K_a \exp(z_a)}{(q\sigma)^2 + z_a^2} - \frac{K_r \exp(z_r)}{(q\sigma)^2 + z_r^2} \right]. \quad (12.34)$$

However, the $c_{lr}(r)$ in the RPA inside the core is sometimes taken to be $c_{lr}(r < \sigma) = \lambda (K_a - K_r)$, where λ is a fitting parameter. Various choices for $c_{lr}(r < \sigma)$ are possible by changing the parameter λ , with $\lambda = 0$ or $\lambda = 1$ being often used among them. In addition, with an appropriate polynomial for $c_{lr}(r < \sigma)$ into the hard core whose parameters are chosen by determining the free energy, the optimized random phase approximation (ORPA) brings an appreciable improvement to the structure factor [39, 101]. As an example, the ORPA has been proven to be an efficient tool to predict the particularities of the structure factor of the divalent liquid metals [302]. It should be mentioned that the structure factor determined by RPA (with $c_{lr}(r)$ rigorously equal to $-\beta u(r)$ at all distances) is not as accurate as those of simulation or integral equations calculations because the $c_{lr}(r)$ in the hard core is not equal to that of the HS potential; the $c_{lr}(r)$ can be corrected by an additional contribution [104].

Figure (12.12) displays the structure factor $S(q)$ of the 2Y potential for $z_a = 1$, $z_r = 0.5$ and various values of K_a , K_r and ρ . It can be seen that $S(q)$ develops a pre-peak at q_c when K_a is increasing, thus revealing a propensity towards cluster formation in the system [303]. Some experiments [285, 286] suggested that the presence of a pre-peak in $S(q)$ indicated the occurrence of a generic Intermediate

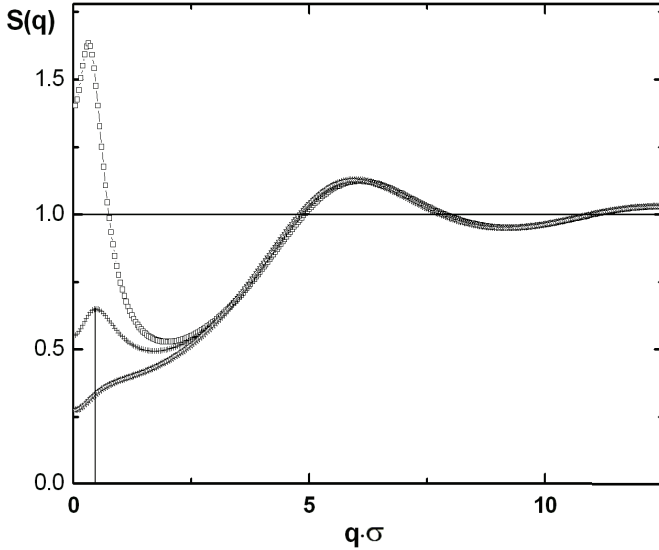


Figure 12.12: Structure factor $S(q)$ calculated for the double Yukawa potential, with the values $\rho^* = \rho\sigma^3$ (reduced density) = 0.25, $z_a = 1$, $z_r = 0.5$, $K_r = 0.08$, for $K_a = 0.58$ (squares), $K_a = 0.35$ (crosses), $K_a = 0.10$ (stars).

Range Order (IRO) within the fluid. An IRO witnesses a locally inhomogeneous region characterized by the appearance of aggregates with sizes dispatched up into dimers, trimers and so on, rather than sets of clusters of preferred finite size s . Clusters at equilibrium are just a peculiar case of IRO. In addition to the pre-peak developing in $S(q)$, the cluster formation has been investigated [304, 305] regarding the pair correlation function $g(r)$. The Monte-Carlo simulations performed for the 2Y potential to extract $g(r)$ and $S(q)$ show that the attractive strength K_a stabilizes an outmost shell of neighbours around the existing aggregation seeds. By using recent structural criteria [306, 307] to identify the threshold of appearance of the IRO, various regimes are identified, starting from a homogeneous state for low values of K_a , up to the IRO with increasing K_a . Long-range oscillations in $g(r)$ – typical of patterns formation – undergo peculiar modifications at intermediate distances.

Simultaneously, in the phase diagram $K_a^{-1}(\rho)$, we observe a curve denoted λ -line [213] that is generated by the locus of points where

$S(q_c)$ diverges. The λ -line marks the boundary between the homogeneous phase (above) and the modulated phase (below). It can be compared with the binodal, for which $p(\rho_L) = p(\rho_G)$ at a given temperature, and the spinodal, for which the isothermal compressibility diverges ($\chi_T = \frac{S(0)}{\rho k_B T}$). In fact, for a pair potential of the van der Waals type, consisting of a short-range repulsion and a long-range attraction, the theory predicts a first-order liquid-vapour transition at the critical temperature, with a diverging value of $S(0)$. Both the binodal and spinodal have the vortex at the critical point C . When the ranges of the repulsive and attractive interactions are interchanged, giving a small long-range repulsion beyond the attractive well, various phase behaviours can exist. On the other hand, the λ -line intersects the binodal at two points A and B , indicating that the liquid-vapour transition is preempted by a microphase separation in the range of densities between A and B . This phenomenon happens for a particular choice of potential parameters giving rise to the competition between the short-range attraction and long-range repulsion. It should be noted that the location of the λ -line is very sensitive to the choice of the approximation used to calculate the structure factor [213].

The formation and growth of equilibrium clusters in suspensions of weakly charged colloidal particles and/or small non-adsorbing polymers can also be examined with the potential composed of the Lennard-Jones and the repulsive Yukawa potentials (LJY):

$$\beta u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{2\alpha} - \left(\frac{\sigma}{r} \right)^\alpha \right] + A \frac{\exp\left(-\frac{r}{\xi}\right)}{\frac{r}{\xi}}, \quad (12.35)$$

with $\alpha > 6$ to ensure a very short-range attraction. Various choices of the parameters ε and α as well as ξ and A lead to different scenarios such as crystal made of finite-sized clusters, lamellar phases [308] and elongated structures forming a connected network (gel) [309].

In order to extend our purpose, we show in figure (12.13) the cluster-size distribution $N(s)$ calculated for the LJY potential (Eq. 12.35) with the following values of parameters: $\alpha = 50$, $A = 2$, $\xi = 1.794$. Calculations have been performed by Molecular Dynamics in a cubic box ($L_x = L_y = L_z$) containing 1372 particles in the NVT ensemble, at the reduced density $\rho\sigma^3 = 0.1$. The reduced temperature in all the simulations is kept unchanged, whereas only the strength of the short-range attraction ε is diverse and varies from 2

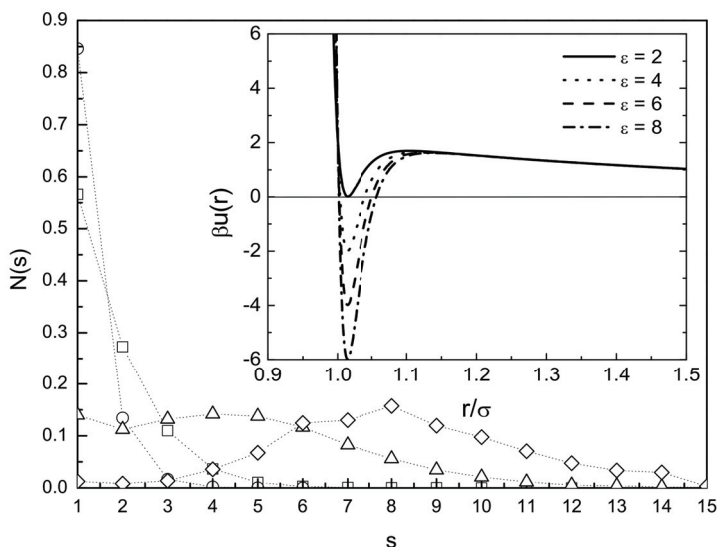


Figure 12.13: Distribution of cluster sizes, $N(s)$, for the density $\rho\sigma^3 = 0.1$. The symbols correspond to various values of ε : $\varepsilon = 2$ (empty squares), $\varepsilon = 4$ (circles), $\varepsilon = 6$ (stars), $\varepsilon = 8$ (full squares).

to 8. Equilibration and production runs are performed with $\sim 10^8$ steps each. The distance criterion to define a cluster is as follows: two particles are considered as bounded if the centre-to-centre distance is lower than a cut-off distance which is the location of the maximum of $u(r)$ (inset of figure 12.13). As seen, for low ε values, $N(s)$ decreases monotonously with increasing s , so that the system is in a mono-dispersed fluid phase. A maximum in $N(s)$ is observed as ε increases, showing that the system is in an equilibrium-cluster phase. Figure (12.14) displays a typical snapshot of representative clusters at equilibrium for $\varepsilon = 8$. It is found that most of clusters are made of $7 \sim 9$ particles.

To summarize, the possibility that a delicate balance between short-range attraction and long-range repulsion can stabilize equilibrium clusters has been discussed in many theoretical works [310, 275, 284, 282, 286]. There are clear-cut evidence at low densities for the existence of a fluid phase of clusters, whose size and shape are expected to be sensitive to the respective ranges and strengths of the

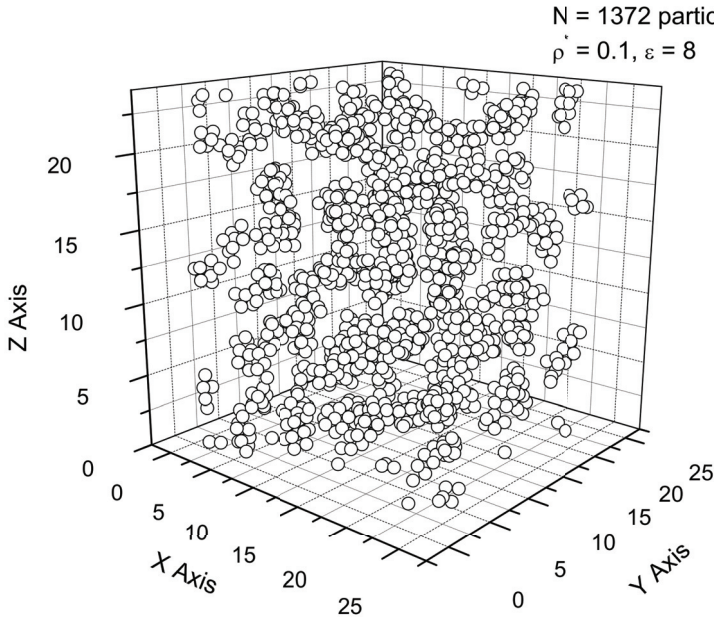


Figure 12.14: Simulation snapshot of microscopic configuration for the LJY potential with 1372 particles, $\rho\sigma^3 = 0.1$ and $\epsilon = 8$.

attractive and repulsive contributions of the pair potential. Upon increasing the density, the competition between the repulsive and attractive contributions can produce new particle arrangements. The presence of long-range repulsive interactions in colloidal suspensions highly alters the formation of clusters giving rise to stable chainlike clusters coalescing into elongated structures which, eventually, will form a connected network at gelation [284, 274]. In other systems, such as aqueous surfactants and mixtures of block copolymers, competing interactions can lead to the formation of modulated phases [265, 311, 290, 267].

Bibliography

- [1] J. W. Gibbs, *Elementary principles in statistical mechanics*, Charles Scribner's sons, New York (1902).
- [2] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular theory of gases and liquids*, Wiley, New York, (1954).
- [3] T. L. Hill, *Statistical Mechanics*, McGraw-Hill, New York (1956).
- [4] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon, London (1968).
- [5] A. I. Khinchin, *Mathematical foundations of Statistical Mechanics*, Dover, New York (1949).
- [6] K. Huang, *Statistical Mechanics*, John Wiley, New York (1963).
- [7] J. E. Mayer and M. Goppert-Mayer, *Statistical Mechanics*, John Wiley, New York (1977).
- [8] J. E. Mayer and E. Montroll, *Molecular distribution*, J. Chem. Phys. **9**, 2 (1941).
- [9] P. Debye and E. Hückel, *The theory of electrolytes. I. Lowering of freezing point and related phenomena*, Phys. Z., **24**, 185 (1923).
- [10] L. H. Thomas, *The calculation of atomic fields*, Proc. Camb. Phil. Soc. **23**, 542 (1927).
- [11] E. Fermi, *Eine Statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente*, Z. für Phys. **48**, 73 (1928).

- [12] N. F. Mott, *The electrical resistance of dilute solid solutions*, Proc. Camb. Phil. Soc. **32**, 281 (1936). N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, Dover Publ., New York (1958), p. 86.
- [13] D. A. McQuarrie, *Statistical Mechanics*, Harper and Row, New York (1976).
- [14] C. N. Likos, *Effective interactions in soft condensed matter physics*, Phys. Rep. **348**, 267 (2001).
- [15] J. L. Barrat and J. P. Hansen, *Basic Concepts for Simple and Complex Liquids*, Cambridge U. Press, New York (2003).
- [16] J. L. Bretonnet, *Competing interactions in colloidal suspensions*, AIMS Materials Science, **6**, 509 (2019). <http://www.aimspress.com/journal/Materials>
- [17] R. Zwanzig, *High-Temperature Equation of State by a Perturbation Method. I. Nonpolar Gases*, J. Chem. Phys. **22**, 1420 (1954).
- [18] J. G. Kirkwood, *Statistical Mechanics of Fluid Mixtures*, J. Chem. Phys. **3**, 300 (1935). J. G. Kirkwood and E. Monroe, *Statistical Mechanics of Fusion*, J. Chem. Phys. **9**, 514 (1941).
- [19] R. E. Nettleton and M. S. Green, *Expression in Terms of Molecular Distribution Functions for the Entropy Density in an Infinite System*, J. Chem. Phys. **29**, 1365 (1958).
- [20] H. J. Raveché, *Entropy and Molecular Correlation Functions in Open Systems. I. Derivation*, J. Chem. Phys. **55**, 2242 (1971).
- [21] B. M. Axilrod and E. Teller, *Interaction of the van der Waals Type Between Three Atoms*, J. Chem. Phys. **11**, 299 (1943).
- [22] L. L. Lee, *Molecular Thermodynamics of Nonideal Fluids*, Butterworths, London (1988).
- [23] D. C. Wallace, *On the role of density fluctuations in the entropy of a fluid*, J. Chem. Phys. **87**, 2282 (1987).
- [24] P. Attard, *Pair-hypernetted-chain closure for three-body potentials: Results for argon with the Axilrod-Teller triple-dipole potential*, Phys. Rev. A **45**, 3659 (1992).

- [25] G. S. Rushbrooke and M. Silbert, *On triplet potentials in the theory of classical fluids*, Mol. Phys. **12**, 505 (1967).
- [26] D. A. Copeland and N. R. Kestner, *Accurate "Effective" Intermolecular Pair Potentials in Gaseous Argon*, J. Chem. Phys. **49**, 5214 (1968).
- [27] G. Casanova, R. J. Dulla, D. A. Jonah, J. S. Rowlinson and G. Saville, *Effective pair potentials in fluids in the presence of three-body forces*, Mol. Phys. **18**, 589 (1970).
- [28] N. Jakse and J. L. Bretonnet, *Use of state-dependent pair potentials in describing the structural and thermodynamic properties of noble gases*, J. Phys.: Condens. Matter, **15**, S3455 (2003).
- [29] A. A. Louis, *Beware of density dependent pair potentials*, J. Phys.: Condens. Matter, **14**, 9187 (2002).
- [30] A. J. Greenfield, J. Wellendorf and N. Wiser, *X-Ray Determination of the Static Structure Factor of Liquid Na and K*, Phys. Rev. A **4**, 1607 (1971).
- [31] N. W. Ashcroft and J. Lekner, *Structure and Resistivity of Liquid Metals*, Phys. Rev. **145**, 83 (1966).
- [32] L. Verlet, *Computer "Experiments" on Classical Fluids. II. Equilibrium Correlation Functions*, Phys. Rev. **165**, 201 (1968).
- [33] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Acad. Press, London (3rd edition, 2006).
- [34] R. Kubo, *Generalized Cumulant Expansion Method*, J. Phys. Soc. Japan, **17**, 1100 (1962).
- [35] J. A. Barker and D. Henderson, *Perturbation Theory and Equation of State for Fluids: The Square-Well Potential*, J. Chem. Phys. **47**, 2856 (1967).
- [36] G. A. Mansoori and F. B. Canfield, *Variational approach to the equilibrium thermodynamic properties of simple liquids*, J. Chem. Phys. **51**, 4958 (1969).
- [37] G. A. Mansoori and F. B. Canfield, *Variational approach to melting*, J. Chem. Phys. **51**, 4967 (1969). G. A. Mansoori, J.

- A. Provine and F. B. Canfield, *Note on the Perturbation Equation of State of Barker and Henderson*, **51**, 5295 (1969). G. A. Mansoori and F. B. Canfield, *Inequalities for the Helmholtz Free Energy*, **53**, 1618 (1970).
- [38] J. A. Barker and D. Henderson, *Theories of liquids*, Annu. Rev. Phys. Chem. **23**, 439 (1972).
- [39] J. D. Weeks, D. Chandler and H. C. Andersen, *Role of repulsive forces in determining the equilibrium structure of simple liquids*, J. Chem. Phys. **54**, 5237 (1971). J. D. Weeks and D. Chandler, *Perturbation theory of the thermodynamic properties of simple liquids*, **55**, 5422 (1971).
- [40] F. H. Ree and W. G. Hoover, *Fifth and Sixth Virial Coefficients for Hard Spheres and Hard Disks*, J. Chem. Phys. **40**, 939 (1964).
- [41] B. J. Alder and T. E. Wainwright, *Phase Transition in Elastic Disks*, Phys. Rev. **127**, 359 (1962).
- [42] N. F. Carnahan and K. E. Starling, *Equation of State for Nonattracting Rigid Spheres*, J. Chem. Phys. **51**, 635 (1969).
- [43] R. P. Feynman, *Statistical Mechanics*, 01 Lectures. Frontiers in Physics, W. A. Benjamin (1972).
- [44] J. S. Rowlinson, *The thermodynamic theory of capillarity under the hypothesis of a continuous variation of density* (English translation of the original paper by J. D. van der Waals), J. Stat. Phys. **20**, 197 (1979).
- [45] J. W. Cahn and J. E. Hilliard, *Free Energy of a Nonuniform System. I. Interfacial Free Energy*, J. Chem. Phys. **28**, 258 (1958).
- [46] P. Mr. W. Cornelisse, C. J. Peters and J. de Swaan Arons, *On the fundamentals of the gradient theory of van der Waals*, J. Chem. Phys. **106**, 9820 (1997).
- [47] A. J. M. Yang, P. D. Fleming and J. H. Gibbs, *Molecular theory of surface tension*, J. Chem. Phys. **64**, 3732 (1976).
- [48] R. Evans, *The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids*, Adv. Phys. **28**, 143 (1979).

- [49] D. Bonn and D. Ross, *Wetting transitions*, Rep. Prog. Phys. **64**, 1085 (2001).
- [50] G. T. Dee and B. B. Sauer, *The surface tension of polymer liquids*, Adv. Phys. **47**, 161 (1998).
- [51] J. Z. Wu and Z. D. Li, *Density-functional theory for complex fluids*, Annu. Rev. Phys. Chem. **58**, 85 (2007).
- [52] J. M. Bomont, J. L. Bretonnet, D. J. Gonzales and L. E. Gonzales, *Computer simulation calculations of the free liquid surface of mercury*, Phys. Rev. B **79**, 144202 (2009).
- [53] R. Evans, *Density Functional Theory for Inhomogeneous Fluids I*, Lectures at 3rd Warsaw School of Statistical Physics (2009).
http://www.phy.bris.ac.uk/people/evans_r/papers/Evans194.pdf
.
- [54] J. Yvon, *Actualités scientifiques et industrielles*, Hermann, Paris (1935), p. 203.
- [55] M. Born and H. S. Green, *A general kinetic theory of liquids. II. Equilibrium properties*, Proc. Roy. Soc, **A189**, 103 (1947).
- [56] B. J. Alder, *Triplet Correlations in Hard Spheres*, Phys. Rev. Lett. **12**, 317 (1964).
- [57] A. Rahman, *Triplet Correlations in Liquids*, Phys. Rev. Lett. **12**, 575 (1964); *Correlations in the Motion of Atoms in Liquid Argon*, Phys. Rev. **136**, A405 (1964).
- [58] E. E. Salpeter, *On Mayer's theory of cluster expansions*, Ann. Phys., **5**, 183 (1958).
- [59] J. E. Mayer, *Integral equations between distribution functions of molecules*, J. Chem. Phys. **15**, 187 (1947).
- [60] J. G. Kirkwood and Z. Salsburg, *The statistical mechanical theory of molecular distribution functions in liquids*, Disc. Faraday Soc. **15**, 28 (1953).
- [61] J. K. Percus and G. J. Yevick, *Analysis of Classical Statistical Mechanics by Means of Collective Coordinates*, Phys. Rev. **110**, 1 (1958).

- [62] G. Stell, *The Percus-Yevick equation for the radial distribution function of a fluid*, Physica, **29**, 517 (1963).
- [63] J. K. Percus, *Approximation Methods in Classical Statistical Mechanics*, Phys. Rev. Lett. **8**, 462 (1962).
- [64] L. S. Ornstein and F. Zernike, *Accidental deviations of density and opalescence at the critical point of a single substance*, Proc. Akad. Sci. (Amsterdam), **17**, 793 (1914).
- [65] V. Volterra, *Theory of Functionals*, Dover, New-York (1959).
- [66] R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics*, Wiley, New-York (1975), p. 251.
- [67] G. S. Rushbrooke, *Physics of Simple Liquids*, North-Holland Publishing Company, Amsterdam (1968), p. 25.
- [68] P. Hohenberg and W. Kohn, *Inhomogeneous Electron Gas*, Phys. Rev. **136**, B 864 (1964).
- [69] W. Kohn and L. J. Sham, *Self-Consistent Equations Including Exchange and Correlation Effects*, Phys. Rev. **140**, A1133 (1965).
- [70] J. L. Bretonnet, *Basics of the density functional theory*, AIMS Materials Science, **4**, 1372 (2017). <http://www.aimspress.com/journal/Materials>
- [71] C. Ebner, W. F. Saam and D. Stroud, *Density-functional theory of simple classical fluids. I. Surfaces*, Phys. Rev. A **14**, 2264 (1976).
- [72] Y. Rosenfeld, *Free-energy model for the inhomogeneous hard-sphere fluid mixture and density-functional theory of freezing*, Phys. Rev. Lett. **63**, 980 (1989).
- [73] R. Evans, *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson, Marcel Dekker, New-York (1992), p. 85.
- [74] M. S. Wertheim, *Exact Solution of the Percus-Yevick Integral Equation for Hard Spheres*, Phys. Rev. Lett. **10**, 321 (1963).
- [75] E. Thiele, *Equation of State for Hard Spheres*, J. Chem. Phys. **39**, 474 (1963).

- [76] H. Reiss, H. L. Frisch and J. L. Lebowitz, *Statistical mechanics of rigid spheres*, J. Chem. Phys. **31**, 369 (1959).
- [77] E. Meeron and A. J. F. Siegert, *Statistical Mechanics of Hard-Particle Systems*, J. Chem. Phys. **48**, 3139 (1968).
- [78] L. Verlet and J. J. Weis, *Perturbation theory for the thermodynamic properties of simple liquids*, Mol. Phys. **24**, 1013 (1972).
- [79] J. S. Rowlinson, *Self-consistent approximations for molecular distribution functions*, Mol. Phys. **9**, 217 (1965).
- [80] C. Croxton, *Introduction to Liquid State Physics*, Wiley, New York (1975), p. 76.
- [81] J. de Boer, *Development of probability densities in power series of the density*, Physica **15**, 680 (1949).
- [82] G. S. Rushbrooke and H. I. Scoins, *On the theory of fluids*, Proc. Roy. Soc. **A216**, 203 (1953).
- [83] M. Klein and M. S. Green, *Numerical solution of the convolution-hypernetted chain integral equation for the pair correlation function of a fluid. I. The Lennard-Jones (12,6) potential*, J. Chem. Phys. **39**, 1367 (1963).
- [84] G. A. Martynov, *Fundamental Theory of Liquids*, Adam Hilger, Bristol (1997). The notations adopted in this book are different from the more classical one.
- [85] B. R. A Nijboer and L. van Hove, *Radial distribution function of a gas of hard spheres and the superposition approximation*, Phys. Rev. **85**, 777 (1952).
- [86] P. Attard and G. N. Patey, *Hypernetted-chain closure with bridge diagrams. Asymmetric hard sphere mixtures*, J. Chem. Phys. **92**, 4970 (1990).
- [87] L. Verlet, *Integral equations for classical fluids: I. The hard sphere case*, Mol. Phys. **41**, 183 (1980).
- [88] F. J. Rogers and D. A Young, *New, thermodynamically consistent, integral equation for simple fluids*, Phys. Rev. A **30**, 999 (1984).

- [89] G. Zerah and J. P. Hansen, *Self-consistent integral equations for fluid pair distribution functions: Another attempt*, J. Chem. Phys. **84**, 2336 (1986).
- [90] D. M. Duh and D. Henderson, *Integral equation theory for Lennard-Jones fluids: The bridge function and applications to pure fluids and mixtures*, J. Chem. Phys. **104**, 6746 (1996).
- [91] J. M. Bomont and J. L. Bretonnet, *A self-consistent integral equation: Bridge function and thermodynamic properties for the Lennard-Jones fluid*, J. Chem. Phys. **119**, 2188 (2003).
- [92] J. M. Bomont, *Recent advances in the field of integral equation theories: bridge functions and applications to classical fluids*, Advances in Chemical Physics, **139**, 1 (2008).
- [93] L. L. Lee, *The potential distribution-based closures to the integral equations for liquid structure: The Lennard-Jones fluid*, J. Chem. Phys. **107**, 7360 (1997).
- [94] L. L. Lee, *Chemical potentials based on the molecular distribution functions. An exact diagrammatical representation and the star function*, J. Chem. Phys. **97**, 8606 (1992).
- [95] R. Kjellander and S. Sarman, *The chemical potential of simple fluids in a common class of integral equation closures*, J. Chem. Phys. **90**, 2768 (1989).
- [96] X. S. Chen, F. Forstmann and M. Kasch, *The free energy and the chemical potential of molecular fluids*, J. Chem. Phys. **95**, 2832 (1991).
- [97] O. E. Kiselyov and G. A. Martynov, *Free energy in the statistical theory of fluids*, J. Chem. Phys. **93**, 1942 (1990).
- [98] J. M. Bomont and J. L. Bretonnet, *Approximative "one particle" bridge function $B^{(1)}(r)$ for the theory of simple fluids*, J. Chem. Phys. **126**, 214504 (2007).
- [99] A. A. Broyles, H. L. Sahlin and D. D. Carley, *Radial distribution functions for long-range forces*, J. Math. Phys. **4**, 216 (1963). P. C. Hemmer, *On the van der Waals Theory of the Vapor-Liquid Equilibrium. IV. The Pair Correlation Function and Equation of State for Long-Range Forces*, J. Math. Phys. **5**, 75 (1964).

- [100] J. L. Lebowitz, G. Stell and S. Baer, *Separation of the Interaction Potential into Two Parts in Treating Many-Body Systems. I. General Theory and Applications to Simple Fluids with Short-Range and Long-Range Forces*, J. Math. Phys. **6**, 1282 (1965).
- [101] D. Chander and H. C. Andersen, *Mode expansion in equilibrium statistical mechanics. II. A rapidly convergent theory of ionic solutions*, J. Chem. Phys. **54**, 26 (1971).
- [102] F. Lado, *Perturbation correction to the radial distribution function*, Phys. Rev. **135**, A1013 (1964).
- [103] J. L. Lebowitz and J. K. Percus, *Mean spherical model for lattice gases with extended hard cores and continuum fluids*, Phys. Rev. **144**, 251 (1966).
- [104] E. Waisman, *The radial distribution function for a fluid of hard spheres at high densities*, Mol. Phys. **25**, 45 (1973).
- [105] J. S. Hoyer and G. Stell, *Ornstein-Zernike equation with core condition and direct correlation function of Yukawa form*, Mol. Phys. **32**, 195 (1976).
- [106] M. J. Gillan, *A new method of solving the liquid structure integral equations*, Mol. Phys. **38**, 1781 (1979).
- [107] S. Labik, A. Malijevsky and P. Vonka, *A rapidly convergent method of solving the OZ equation*, Mol. Phys. **56**, 709 (1985).
- [108] T. Dauxois, M. Peyrard and S. Ruffo, *The Fermi–Pasta–Ulam ‘numerical experiment’: history and pedagogical perspectives*, Eur. J. Phys. **26**, S3 (2005).
- [109] G. P. Berman and F. M. Izrailev, *The Fermi–Pasta–Ulam problem: fifty years of progress*, Chaos **15**, 015104 (2005).
- [110] H. W. Broer, *KAM theory: the legacy of Kolmogorov’s 1954 paper*, Bull. Amer. Math. Soc. **41**, 507 (2004).
- [111] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller and E. Teller, *Equation of state calculations by fast computing machines*, J. Chem. Phys. **21**, 1087 (1953). N. Metropolis and S. Ulam, *The Monte Carlo Method*, J. Amer. Stat. Assoc. **44**, 335 (1949).

- [112] W. W. Wood, *Physics of Simple Liquids*, North-Holland Publishing Compagny, Amsterdam (1968), p. 115.
- [113] S. Nosé, *A unified formulation of the constant temperature molecular dynamics methods*, J. Chem. Phys. **81**, 511 (1984).
- [114] H. C. Andersen, *Molecular dynamics simulations at constant pressure and/or temperature*, J. Chem. Phys. **72**, 2384 (1980).
- [115] L. Verlet, *Computer "experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules*, Phys. Rev. **159**, 98 (1967); *Computer "experiments" on classical fluids. II. equilibrium correlation functions*, Phys. Rev. **165**, 201 (1968).
- [116] B. Quentrec and C. Brot, *New method for searching for neighbors in molecular dynamics computations*, J. of Comput. Phys. **13**, 430 (1975).
- [117] M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids*, Clarendon Press, Oxford, (1990).
- [118] D. W. Heermann, *Computer Simulation Methods in Theoretical Physics*, Springer, Berlin (1990).
- [119] J. M. Haile, *Molecular Dynamics Simulation: Elementary Methods*, John Wiley, New York (1992).
- [120] J. M. G. Vilar and J. M. Rubi, *Thermodynamics beyond local equilibrium*, in arXiv:cond-mat/0110614v1
- [121] J. F. Nye, *Physical properties of crystals*, Clarendon Press, Oxford (1957).
- [122] L. E. Malvern, *Introduction to the mechanics of a continuous medium*, Prentice-Hall, Inc. Englewood Cliffs, New Jersey (1969).
- [123] M. R. von Smoluchovski, *Drei vortrage uber diffusion. Brownsche bewegung und koagulation von kolloidteilchen*, Phys. Zeits. **17**, 557 (1916); *Three discourses on diffusion, Brownian movements, and the coagulation of colloid particles*, **17**, 585 (1916).
- [124] A. Einstein, *On the Motion of Small Particles Suspended in Liquids at Rest Required by the Molecular-Kinetic Theory of Heat*, Annalen der Physik **17**, 549 (1905).

- [125] W. Sutherland, *A dynamical theory of diffusion for non-electrolytes and the molecular mass of albumin*, Phil. Mag. **9**, 781 (1905).
- [126] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, London (1939), reedited in 1970 and 1995.
- [127] C. F. Curtis and J. O. Hirschfelder, *Transport properties of multicomponent gas mixtures*, J. Chem. Phys. **17**, 550 (1949).
- [128] A. Brongniart, *Mémoire sur la génération et le développement de l'embryon dans les végétaux phanérogames*, Ann. Sci. Naturelles **12**, 41 (1827).
- [129] R. Brown, Ann. Sci. Naturelles **14**, 341 (1828).
- [130] L. G. Gouy, *Note sur le Mouvement Brownien*, J. Physique (Paris) **7**, 561 (1888); *Sur le mouvement brownien*, C. R. Acad. Sci. (Paris) **109**, 102 (1889).
- [131] M. Smoluchowski, *The kinetic theory of Brownian molecular motion and suspensions*, Annalen der Physik **21**, 756 (1906).
- [132] P. Langevin, *Sur la théorie du mouvement brownien*, C. R. Acad. Sci. (Paris), **146**, 530 (1908).
- [133] A. Einstein, Annalen der Physik **19**, 371 (1906), in *Investigations on the theory of the Brownian movement*, Ed. F. Fürth, Dover Publications, London (1956).
- [134] J. Perrin, *L'agitation moléculaire et le mouvement brownien*, C. R. Acad. Sci. (Paris) **146**, 967 (1908) and the book *Les atomes*, Félix Alcan, Paris (1913), reprinted at Champs Flammarion, Paris (1991).
- [135] J. L. Domb, Ann. Math. **43**, 351 (1942).
- [136] M. C. Wang and G. E. Uhlenbeck, *On the Theory of the Brownian Motion II*, Rev. Mod. Phys. **17**, 323 (1945).
- [137] R. Kubo, *The fluctuation-dissipation theorem*, Rep. Prog. Phys. **29**, 255 (1966).

- [138] H. Mori, *Transport, Collective Motion, and Brownian Motion*, Prog. Theor. Phys. **33**, 423 (1965); *A Continued-Fraction Representation of the Time-Correlation Functions*, **34**, 399 (1965).
- [139] R. Zwanzig, *Lectures in Theoretical Physics*, Interscience, New York (1961) Vol. 3, p. 106.
- [140] B. J. Berne, J. P. Boon and S. A. Rice, *On the calculation of autocorrelation functions of dynamical variables*, J. Chem. Phys. **45**, 1086 (1966).
- [141] K. S. Singwi and M. P. Tosi, *On the Velocity Autocorrelation in a Classical Fluid*, Phys. Rev. **157**, 153 (1967).
- [142] P. K. Kahol, R. Bansal, and K. N. Pathak, *Collective excitations in liquid rubidium*, Phys. Rev. A **14**, 408 (1976).
- [143] D. Levesque and L. Verlet, *Computer" Experiments" on Classical Fluids. III. Time-Dependent Self-Correlation Functions*, Phys. Rev. A **2**, 2514 (1970).
- [144] B. J. Alder and T. E. Wainwright, *Velocity Autocorrelations for Hard Spheres*, Phys. Rev. Lett. **18**, 988 (1969).
- [145] M. H. Ernst, E. H. Hauge and J. M. J. van Leeuwen, *Asymptotic Time Behavior of Correlation Functions*, Phys. Rev. Lett. **25**, 1254 (1970).
- [146] J. R. Dorfman and E. G. D. Cohen, *Velocity Correlation Functions in Two and Three Dimensions*, Phys. Rev. Lett. **25**, 1257 (1970).
- [147] R. Zwanzig and M. Bixon, *Hydrodynamic Theory of the Velocity Correlation Function*, Phys. Rev. A **2**, 2005 (1970).
- [148] E. G. D. Cohen, *Fifty years of kinetic theory*, Physica A, **194**, 229 (1993).
- [149] B. R. A. Nijboer and A. Rahman, *Time expansion of correlation functions and the theory of slow neutron scattering*, Physica **32**, 415 (1966).
- [150] U. Balucani and M. Zoppi, *Dynamics of the Liquid State*, Clarendon Press, Oxford (1994).

- [151] P. G. de Gennes, *Liquid dynamics and inelastic scattering of neutrons*, Physica **25**, 825 (1959).
- [152] R. Albaki, J. F. Wax and J. L. Bretonnet, *Dynamic properties of expanded liquid cesium*, J. Non-Cryst. Solids **312-314**, 153 (2002).
- [153] K. Tankeshwar, B. Singla and K. N. Pathak, *A simple model for the calculation of self-diffusion*, J. Phys.: Condens. Matter **3**, 3173 (1991).
- [154] B. J. Berne and G. D. Harp, *On the calculation of time correlation functions*, Advan. Chem. Phys. **17**, 63 (1970).
- [155] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, Acad. Press, New York (1965).
- [156] C. Jordan, *Calculus of Finite Differences*, New York, Chelsea, (1965).
- [157] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover Publications, New York (1965).
- [158] J. T. Day, *On the numerical solution of linear Volterra integral equations*, Bit. **7**, 71 (1967).
- [159] H. Nyquist, *Thermal Agitation of Electric Charge in Conductors*, Phys. Rev. **32**, 110 (1928).
- [160] L. Onsager, *Reciprocal Relations in Irreversible Processes. I.*, Phys. Rev. **37**, 405 (1931).
- [161] H. B. Callen and T. A. Welton, *Irreversibility and Generalized Noise*, Phys. Rev. **83**, 34 (1951).
- [162] L. P. Kadanoff and P. C. Martin, *Hydrodynamic equations and correlation functions*, Ann. Phys. (New York) **24**, 419 (1963).
- [163] R. Zwanzig, *Time-Correlation Functions and Transport Coefficients in Statistical Mechanics*, Annu. Rev. Phys. Chem. **16**, 67 (1965).
- [164] N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids*, Macmillan Press, London (1976).

- [165] L. van Hove, *Correlations in Space and Time and Born Approximation Scattering in Systems of Interacting Particles*, Phys. Rev. **95**, 249 (1954).
- [166] J. R. Macdonald and M. K. Brachman, *Linear-System Integral Transform Relations*, Rev. Mod. Phys. **28**, 393 (1956).
- [167] S. H. Glarum, *Dielectric relaxation of polar liquids*, J. Chem. Phys. **33**, 1371 (1960).
- [168] C. Kittel, *Introduction to solid state physics*, John Wiley and Sons, Inc., New York (1968).
- [169] P. Debye, Ver. Deut. Phys. Gesell. **15**, 777 (1913); reprinted in *The Collected Papers of Peter J. W. Debye*. Interscience Publishers, Inc., New York, (1954).
- [170] B. J. Berne, *Time Correlation Functions in Condensed Media*, in Physical Chemistry, Vol. VIIIB, pp. 539-716. Eds. H. Eyring, D. Henderson and W. Jost, Academic Press, New York (1971), available at the address: <http://www.columbia.edu/cu/chemistry/groups/berne/papers/Physical-Chemistry-VIIIB-539-716.pdf>
- [171] P. A. Egelstaff, *An Introduction to the Liquid State*, Acad. Press, London (1967).
- [172] L. I. Schiff, *Quantum Mechanis*, McGraw-Hill, New York (1968).
- [173] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Harcourt College Publisher, New York (1976).
- [174] *Chemical Applications of Thermal Neutron Scattering*, edited by B. T. M. Willis, Oxford University Press, (1973).
- [175] R. D. Mountain, *Spectral Distribution of Scattered Light in a Simple Fluid*, Rev. Mod. Phys. **38**, 205 (1966).
- [176] D. McIntyre and J. V. Singers, *Physics of Simple Liquids*, North-Holland Publishing Company, Amsterdam (1968), p. 447.
- [177] W. van Megen and P. N. Pusey, *Dynamic light-scattering study of the glass transition in a colloidal suspension*, Phys. Rev A **43**, 5429 (1991).

- [178] W. van Meegen, *Freezing, melting and the glass transition in a suspension of hard spheres*, J. Phys.: Condens. Matter **14**, 7699 (2002).
- [179] P. Schofield, *Space-Time Correlation Function Formalism for Slow Neutron Scattering*, Phys. Rev. Lett. **4**, 239 (1960).
- [180] A. Rahman, K. S. Singwi and A. Sjölander, *Theory of Slow Neutron Scattering by Liquids. I*, Phys. Rev. **126**, 986 (1962).
- [181] E. Helfand, *Transport Coefficients from Dissipation in a Canonical Ensemble*, Phys. Rev. **119**, 1 (1960).
- [182] G. H. Vineyard, *Scattering of Slow Neutrons by a Liquid*, Phys. Rev. **110**, 999 (1958).
- [183] K. Sköld, *Small Energy Transfer Scattering of Cold Neutrons from Liquid Argon*, Phys. Rev. Lett. **19**, 1023 (1967).
- [184] J. P. Boon and S. Yip, *Molecular Hydrodynamics*, McGraw-Hill, New York (1980).
- [185] J. Frenkel, *Kinetic Theory of Liquids*, Dover Publications, New York (1955).
- [186] J. R. D. Copley and S. W. Lovesey, *The dynamic properties of monatomic liquids*, Rep. Prog. Phys. **38**, 461 (1975).
- [187] H. C. Longuet-Higgins and J. A. Pople, *Transport properties of a dense fluid of hard spheres*, J. Chem. Phys. **25**, 884 (1956).
- [188] R. Bansal and K. N. Pathak, *Sum rules and atomic correlations in classical liquids*, Phys. Rev. A **9**, 2773 (1974).
- [189] P. G. de Gennes, *Liquid dynamics and inelastic scattering of neutrons*, Physica **25**, 825 (1959).
- [190] N. K. Ailawadi, A. Rahman and R. Zwanzig, *Generalized Hydrodynamics and Analysis of Current Correlation Functions*, Phys. Rev. A **4**, 1616 (1971).
- [191] A. Z. Akcasu and E. Daniels, *Fluctuation Analysis in Simple Fluids*, Phys. Rev. A **2**, 962 (1970).
- [192] S. W. Lovesey, *Single-particle motion in classical monatomic liquids*, J. Phys. C : Solid State Phys. **6**, 1856 (1973).

- [193] T. Geszti, *Pre-vitrification by viscosity feedback*, J. Phys. C; Solid State Phys. **16**, 5805 (1983).
- [194] E. Leutheusser, *Dynamical model of the liquid-glass transition*, Phys. Rev. A **29**, 2765 (1984).
- [195] L. Berthier and G. Biroli, *Theoretical perspective on the glass transition and amorphous materials*, Rev. Mod. Phys. **83**, 587 (2011).
- [196] W. Götze and L. Sjögren, *Relaxation processes in supercooled liquids*, Rep. Prog. Phys. **55**, 241 (1992).
- [197] W. Götze, *Recent tests of the mode-coupling theory for glassy dynamics*, J. Phys.: Condens. Matter **11** A1 (1999).
- [198] B. Bernu, Y. Hiwatari and J. P. Hansen, *A molecular dynamics study of the glass transition in binary mixtures of soft spheres*, J. Phys. C **18**, L371 (1985).
- [199] S. P. Das, *Mode-coupling theory and the glass transition in supercooled liquids*, Rev. Mod. Phys. **76**, 785 (2004).
- [200] D. R. Reichman and P. Charbonneau, *Mode-coupling theory*, J. Stat. Mech. P05013 (2005).
- [201] L. Berthier, G. Biroli, P. Charbonneau, E. I. Corwin, S. Franz and F. Zamponi, *Gardner physics in amorphous solids and beyond*, J. Chem. Phys. **151**, 010901 (2019).
- [202] A. P. Gast and W. B. Russel, *Simple Ordering in Complex Fluids*, Phys. Today **51**, 24 (1998).
- [203] V. J. Anderson and H. N. W. Lekkerkerker, *Insights into phase transition kinetics from colloid science*, Nature **416**, 811 (2002).
- [204] D. F. Evans, H. Wennerström, *The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet*, Wiley, New York (1999).
- [205] J. M. Lehn and P. Ball, in *The New Chemistry*, Ed. Hall N., Cambridge Univ Press: 300-351 (2000).
- [206] P. N. Pusey and R. J. A. Tough, *Dynamic Light Scattering with Applications to Chemistry and Biology*, Ed. Pecora R., Plenum Press, New York (1985).

- [207] M. Seul and D. Andelman, *Domain Shapes and Patterns: The Phenomenology of Modulated Phases*, Science **267**, 476 (1995).
- [208] G. M. Whitesides and M. Boncheva, *Beyond molecules: Self-assembly of mesoscopic and macroscopic components*, PNAS **99**, 4769 (2002).
- [209] J. N. Israelachvili, *Intermolecular and Surface Forces*, Elsevier, Amsterdam, third edition (2011).
- [210] F. Sciortino, P. Tartaglia and E. Zaccarelli, *One-Dimensional Cluster Growth and Branching Gels in Colloidal Systems with Short-Range Depletion Attraction and Screened Electrostatic Repulsion*, J. Phys. Chem. B **109**, 21942 (2005).
- [211] D. Pini, A. Parola and L. Reatto, *Freezing and correlations in fluids with competing interactions*, J. Phys.; Condens. Matter **18**, S2305 (2006).
- [212] A. J. Archer, D. Pini, R. Evans and L. Reatto, *Model colloidal fluid with competing interactions: Bulk and interfacial properties*, J. Chem. Phys. **126**, 014104 (2007).
- [213] A. J. Archer and N. B. Wilding, *Phase behavior of a fluid with competing attractive and repulsive interactions*. Phys. Rev. E **76**, 031501 (2007).
- [214] J. H. Perepezko and J. S. Paik, *Thermodynamic properties of undercooled liquid metals*, J. Non-Cryst. Solids **61-62**, 113 (1984).
- [215] C. A. Angel, *Perspective on the glass transition*, J. Phys. Chem. Solids **49**, 863 (1988).
- [216] R. Richert and C. A. Angel, *Dynamics of glass-forming liquids. V. On the link between molecular dynamics and configurational entropy*, J. Chem. Phys. **108**, 9016 (1998).
- [217] F. F. Abraham, *An isothermal-isobaric computer simulation of the supercooled-liquid/glass transition region: Is the short-range order in the amorphous solid fcc?*, J. Chem. Phys. **72**, 359 (1980).
- [218] W. Kob, *Computer simulations of supercooled liquids and glasses*, J. Phys.: Condens. Matter **11**, R85 (1999).

- [219] W. Kauzmann, *The Nature of the Glassy State and the Behavior of Liquids at Low Temperatures*, Chem. Rev. (Washington, D. C.) **43**, 219 (1948).
- [220] M. S. Green, *Markoff random processes and the statistical mechanics of time-dependent phenomena. II. Irreversible processes in fluids*, J. Chem. Phys. **22**, 398 (1954).
- [221] R. Kubo, *Statistical-mechanical theory of irreversible processes. I. General theory and simple applications to magnetic and conduction problems*, J. Phys. Soc. Japan **12**, 570 (1957).
- [222] J. J. Ullo and S. Yip, *Dynamical Transition in a Dense Fluid Approaching Structural Arrest*, Phys. Rev. Lett. **54**, 1509 (1985).
- [223] J. D. Bernal and J. Mason, *Packing of spheres: co-ordination of randomly packed spheres*, Nature **188**, 910 (1960).
- [224] S. Torquato, T. M. Truskett, P. G. Debenedetti, *Is Random Close Packing of Spheres Well Defined?*, Phys. Rev. Lett. **84**, 2064 (2000).
- [225] C. S. O'Hern, S. A. Langer, A. J. Liu and S. R. Nagel, *Random Packings of Frictionless Particles*, Phys. Rev. Lett. **88**, 075507 (2002).
- [226] T. Aste, M. Saadatfar and T. J. Senden, *Geometrical structure of disordered sphere packings*, Phys. Rev. E **71**, 061302 (2005).
- [227] B. J. Alder and T. E. Wainwright, *Phase transition for a hard sphere system*, J. Chem. Phys. **27**, 1208 (1957).
- [228] W. W. Wood and J. D. Jacobson, *Preliminary results from a recalculation of the Monte Carlo equation of state of hard spheres*, J. Chem. Phys. **27**, 1207 (1957).
- [229] J. M. Bomont and J. L. Bretonnet, *Thermodynamics and dynamics of the hard-sphere system: From stable to metastable states*, Chem. Phys. **439**, 85 (2014).
- [230] G. Parisi and F. Zamponi, *Mean-field theory of hard sphere glasses and jamming*, Rev. Mod. Phys., **82**, 789 (2010) and references herein.

- [231] M. Goldstein, *Viscous liquids and the glass transition: a potential energy barrier picture*, J. Chem. Phys. **51**, 3728 (1969).
- [232] F. H. Stillinger and T. A. Weber, *Hidden structure in liquids*, Phys. Rev. A **25**, 978 (1982).
- [233] S. Sastry, P. G. Debenedetti and F. H. Stillinger, *Signatures of distinct dynamical regimes in the energy landscape of a glass-forming liquid*, Nature **393**, 554 (1998). P. G. Debenedetti and F. H. Stillinger, *Supercooled liquids and the glass transition*, Nature **410**, 259 (2001).
- [234] F. H. Stillinger and P. G. Debenedetti, *Glass transition thermodynamics and kinetics*, Annu. Rev. Condens. Matter Phys. **4**, 263 (2013).
- [235] D. L. Malandro and D. J. Lacks, *Volume dependence of potential energy landscapes in glasses*, J. Chem. Phys. **107**, 5804 (1997); *Relationships of shear-induced changes in the potential energy landscape to the mechanical properties of ductile glasses*, J. Chem. Phys. **110**, 4593 (1999).
- [236] G. Adam and J. H. Gibbs, *On the temperature dependence of cooperative relaxation properties in glass-forming liquids*, J. Chem. Phys. **43**, 139 (1965).
- [237] A. Montanari and F. Ricci-Tersenghi, *On the nature of the low-temperature phase in discontinuous mean-field spin glasses*, Eur. Phys. J. B **33**, 339 (2003).
- [238] P. Charbonneau, J. Kurchan, G. Parisi, P. Urbani, and F. Zamponi, *Fractal free energy landscapes in structural glasses*, Nat. Commun. **5**, 3725 (2014).
- [239] G. Biroli and P. Urbani, *Breakdown of elasticity in amorphous solids*, Nat. Phys. **12**, 1130 (2016).
- [240] E. Gardner, *Spin glasses with p-spin interactions*, Nucl. Phys. B **257**, 747 (1985).
- [241] J. Kurchan, G. Parisi, P. Urbani, and F. Zamponi, *Exact theory of dense amorphous hard spheres in high dimension. II. The high density regime and the Gardner transition*, J. Phys. Chem. B **117**, 12979 (2013).

- [242] P. Charbonneau, Y. Jin, G. Parisi, C. Rainone, B. Seoane, and F. Zamponi, *Numerical detection of the Gardner transition in a mean-field glass former*, Phys. Rev. E **92**, 012316 (2015).
- [243] P. Urbani and G. Biroli, *Gardner transition in finite dimensions*, Phys. Rev. B **91**, 100202(R) (2015).
- [244] A. Seguin and O. Dauchot, *Experimental Evidence of the Gardner Phase in a Granular Glass*, Phys. Rev. Lett. **117**, 228001 (2016).
- [245] K. Geirhos, P. Lunkenheimer and A. Loidl, *Johari-Goldstein relaxation far below T_g : experimental evidence for the Gardner Transition in structural glasses?*, Phys. Rev. Lett. **120**, 085705 (2018).
- [246] A. Sjölander and L. A. Turski, *On the properties of supercooled classical liquids*, J. Phys. C: Solid State Phys. **11**, 1973 (1978).
- [247] K. Kawasaki, *Correlation-Function Approach to the Transport Coefficients near the Critical Point. I*, Phys. Rev. **150**, 291 (1966).
- [248] A. Z. Akcasu and J. J. Duderstadt, *Derivation of Kinetic Equations from the Generalized Langevin Equation*, Phys. Rev. **188**, 479 (1969).
- [249] J. Bosse, W. Götze and M. Lücke, *Mode-coupling theory of simple classical liquids*, Phys. Rev. A **17**, 434 (1978). J. Bosse, W. Götze and A. Zippelius, *Velocity-autocorrelation spectrum of simple classical liquids*, Phys. Rev. A **18**, 1214 (1978).
- [250] L. Sjögren and A. Sjölander, *Density fluctuations in liquid aluminium*, J. Phys. C: Solid State Phys. **11**, 1493 (1978); *Kinetic theory of self-motion in monatomic liquids*, **12**, 4369 (1979).
- [251] J. L. Barrat and A. Latz, *Mode coupling theory for the glass transition in a simple binary mixture*, J. Phys. Condens. Matter **2**, 4289 (1990).
- [252] W. Götze, *Liquids, Freezing, and the Glass Transition* (North-Holland, Amsterdam, 1991), p. 287.

- [253] J. Bosse and S. D. Wilke, *Low-Density Ionic Glass*, Phys. Rev. Lett. **80**, 1260 (1998). S. D. Wilke and J. Bosse, *Relaxation of a supercooled low-density Coulomb fluid*, Phys. Rev. E **59**, 1968 (1999).
- [254] W. Kob and H. C. Andersen, *Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture I: The van Hove correlation function*, Phys. Rev. E **51**, 4626 (1995); *Testing mode-coupling theory for a supercooled binary Lennard-Jones mixture. II. Intermediate scattering function and dynamic susceptibility*, Phys. Rev. E **52**, 4134 (1995).
- [255] G. Wahnstrom and L. Sjogren, *Incoherent scattering function in simple classical liquids*, J. Phys. C: Sol. Stat. Phys. **15**, 401 (1982). W. Gotze and L. Sjogren, *Relaxation processes in supercooled liquids*, Rep. Prog. Phys. **55**, 241 (1992).
- [256] G. F. Mazenko, *Smoluchowski dynamics and the ergodic-nonergodic transition*, Phys. Rev. E **83**, 041125 (2011).
- [257] S. F. Edwards and P. W. Anderson, J. Phys. F: Liq. Met. **5**, 965 (1975).
- [258] D. Sherrington and S. Kirkpatrick, *Solvable Model of a Spin-Glass*, Phys. Rev. Lett. **35**, 1792 (1975).
- [259] G. Parisi, *Infinite Number of Order Parameters for Spin-Glasses*, Phys. Rev. Lett. **43**, 1754 (1979); *Order Parameter for Spin-Glasses*, Phys. Rev. Lett. **50**, 1946 (1983).
- [260] T. Kirkpatrick and P. Wolynes, *Connections between some kinetic and equilibrium theories of the glass transition*, Phys. Rev. A **35**, 3072 (1987). T. Kirkpatrick, D. Thirumalai and P. Wolynes, *Scaling concepts for the dynamics of viscous liquids near an ideal glassy state*, Phys. Rev. A **40**, 1045 (1989).
- [261] G. Biroli and J. Bouchaud, *The random first-order transition theory of glasses: a critical assessment*, arXiv:cond-mat/0912.2542 (2009).
- [262] A. Cavagna, *Supercooled liquids for pedestrians*, Phys. Rep. **476**, 51 (2009).

- [263] G. L. Hunter and E. R. Weeks, *The physics of the colloidal glass transition*, Rep. Prog. Phys. **75** 066501 (2012).
- [264] J. L. Bretonnet, *Glass-forming liquids*, Mol. Phys. **114**, 2868 (2016).
- [265] E. W. Kaler, K. E. Bennett, H. T. Davis and L. E. Scriven, *Analysis of small angle neutron scattering spectra from polydisperse interacting colloids*, J. Chem. Phys. **79**, 5673 (1983).
- [266] M. Kotlarchyk and S. H. Chen, *Analysis of small angle neutron scattering spectra from polydisperse interacting colloids*, J. Chem. Phys. **79**, 2461 (1983).
- [267] K. V. Schubert and R. Strey, *Small-angle neutron scattering from microemulsions near the disorder line in water/formamide-octane- $C_{12}E_6$ systems*, J. Chem. Phys. **95**, 8532 (1991).
- [268] M. Teubner and R. Strey, *Origin of the scattering peak in microemulsions*, J. Chem. Phys. **87**, 3195 (1987).
- [269] H. J. Woo, C. Carraro and D. Chandler, *Quantitative molecular interpretation of mesoscopic correlations in bicontinuous microemulsions*, Phys. Rev. E **52**, 6497 (1995).
- [270] S. Wu, H. Westfahl Jr., J. Schmalian and P. G. Wolynes, cond-mat/0105308v1.
- [271] T. Ohta and K. Kawasaki, *Equilibrium Morphology of Copolymer Melts*, Macromolecules **19**, 2621 (1986).
- [272] G. H. Fredrickson and E. Helfand, *Fluctuation effects in the theory of microphase separation in block copolymers*, J. Chem. Phys. **87**, 697 (1987).
- [273] E. L. Thomas, D. M. Anderson, C. S. Henkee and D. Hoffman, *Periodic area-minimizing surfaces in bloc copolymers*, Nature **334**, 598 (1988).
- [274] A. de Candia, E. Del Gado, A. Fierro, N. Sator, M. Tarzia and A. Coniglio, *Columnar and lamellar phases in attractive colloidal systems*, Phys. Rev. E **74**, 010403(R) (2006).

- [275] A. Ciach, *Universal sequence of ordered structures obtained from mesoscopic description of self-assembly*, Phys. Rev. E **78**, 061505 (2008).
- [276] N. Asherie, A. Lomakin and G. B. Benedek, *Phase Diagram of Colloidal Solutions*, Phys. Rev. Lett. **77**, 4832 (1996).
- [277] A. Stradner, H. Sedgwick, F. Cardinaux, W. C. K. Poon, S. U. Egelhaaf and P. Schurtenberger, *Equilibrium cluster formation in concentrated protein solutions and colloids*, Nature **432**, 492 (2004).
- [278] J. Groenewold and W. K. Kegel, *Colloidal cluster phases, gelation and nuclear matter*, J. Phys.: Condens. Matter **16**, S4877 (2004).
- [279] T. Jiang and J. Wu, *Cluster formation and bulk phase behavior of colloidal dispersions*, Phys. Rev. E **80**, 021401 (2009).
- [280] Y. Gao and M. L. Kilfoil, *Direct Imaging of Dynamical Heterogeneities near the Colloid-Gel Transition*, Phys. Rev. Lett. **99**, 078301 (2007).
- [281] C. L. Klix, C. P. Royall and H. Tanaka, *Structural and Dynamical Features of Multiple Metastable Glassy States in a Colloidal System with Competing Interactions*, Phys. Rev. Lett. **104**, 165702 (2010).
- [282] E. Zaccarelli, S. Andreev, F. Sciortino and D. R. Reichman, *Numerical Investigation of Glassy Dynamics in Low-Density Systems*, Phys. Rev. Lett. **100**, 195701 (2008).
- [283] E. Wigner, *Effects of the electron interaction on the energy levels of electrons in metals*, Trans. Farad. Soc. **34**, 678 (1938).
- [284] A. I. Campbell, V. J. Anderson, J. S. van Duijneveldt and P. Barlett, *Dynamical Arrest in Attractive Colloids: The Effect of Long-Range Repulsion*, Phys. Rev. Lett. **94**, 208301 (2005).
- [285] L. Porcar, P. Falus, W. R. Chen, A. Faraone, E. Fratini, K. Hong, P. Baglioni and Y. Liu, *Formation of the Dynamic Clusters in Concentrated Lysozyme Protein Solutions*, J. Phys. Chem. Lett. **1**, 126 (2010).

- [286] Y. Liu, L. Porcar, J. Chen, W. R. Chen, P. Falus, A. Faraone, E. Fratini, K. Hong and P. Baglioni, *Lysozyme protein solution with an intermediate range order structure*, J. Phys. Chem. B **115**, 7238 (2011).
- [287] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press, Oxford (1971).
- [288] L. D. Landau and V. L. Ginzburg, Zh. Eksp. Teor. Fiz. **20**, 1064 (1950). The translation is given in *Men of Physics: L. D. Landau I*, by D. ter Haar, Pergamon, London (1965).
- [289] M. E. Fisher, *Correlation Functions and the Critical Region of Simple Fluids*, J. Math. Phys. **5**, 944 (1964).
- [290] G. Gompper and M. Schick, *Correlation between structural and interfacial properties of amphiphilic systems*, Phys. Rev. Lett. **65**, 1116 (1990).
- [291] G. H. Fredrickson and S. T. Milner, *Thermodynamics of Random Copolymer Melts*, Phys. Rev. Lett. **67**, 835 (1991).
- [292] R. Holyst and M. Schick, *Copolymers as amphiphiles in ternary mixtures: An analysis employing disorder, equimaxima, and Lifshitz lines*, J. Chem. Phys. **96**, 7728 (1992).
- [293] R. M. Hornreich, M. Luban and S. Shtrikman, *Critical Behavior at the Onset of k -Space Instability on the λ Line*, Phys. Rev. Lett. **35**, 1678 (1975).
- [294] J. H. Chen and T. C. Lubensky, *Landau-Ginzburg mean-field theory for the nematic to smectic-C and nematic to smectic-A phase transitions*, Phys. Rev. A **14**, 1202 (1976).
- [295] F. S. Bates, W. Maurer, T. P. Lodge, M. F. Schulz, M. W. Matsen, K. Almdal and K. Mortensen, *Isotropic Lifshitz Behavior in Block Copolymer-Homopolymer Blends*, Phys. Rev. Lett. **75**, 4429 (1995).
- [296] D. Schwahn, K. Mortensen, H. Frielinghaus and K. Almdal, *Crossover from 3D Ising to Isotropic Lifshitz Critical Behavior in a Mixture of a Homopolymer Blend and Diblock Copolymer*, Phys. Rev. Lett. **82**, 5056 (1999).

- [297] L. Kielhorn and M. Muthukumar, *Fluctuation theory of diblock copolymer/homopolymer blends and its effects on the Lifshitz point*, J. Chem. Phys. **107**, 5588 (1997).
- [298] V. Pipich, D. Schwahn and L. Willner, *Ginzburg Number of a Homopolymer–Diblock Copolymer Mixture Covering the 3D-Ising, Isotropic Lifshitz, and Brasovski Classes of Critical Universality*, Phys. Rev. Lett. **94**, 117801 (2005).
- [299] S. Høye and L. Blum, *Solution of the Yukawa Closure of the Ornstein-Zernike Equation*, J. Stat. Phys. **16**, 399 (1977).
- [300] R. P. Sear and W. M. Gelbart, *Microphase separation versus the vapor-liquid transition in systems of spherical particles*, J. Chem. Phys. **110**, 4582 (1999).
- [301] A. J. Archer, C. Ionescu, D. Pini and L. Reatto, *Theory for the phase behaviour of a colloidal fluid with competing interactions*, J. Phys.: Condens. Matter **20**, 415106 (2008).
- [302] J. L. Bretonnet and C. Regnaut, *Determination of the structure factor of simple liquid metals from the pseudopotential theory and optimized random-phase approximation: Application to Al and Ga*, Phys. Rev. B **31**, 5071 (1985).
- [303] J. M. Bomont, J. L. Bretonnet and D. Costa, *Temperature study of cluster formation in two-Yukawa fluids*, J. Chem. Phys. **132**, 184508 (2010).
- [304] J. M. Bomont, D. Costa and J. L. Bretonnet, *Tiny changes in local order trigger the cluster formation in model fluids with competing interactions*, Phys. Chem. Chem. Phys. **19**, 1527 (2017).
- [305] J. L. Bretonnet, J. M. Bomont and D. Costa, *A semianalytical “reverse” approach to link structure and microscopic interactions in two-Yukawa competing fluids*, J. Chem. Phys. **149**, 234907 (2018).
- [306] P. D. Godfrin, R. Castaneda-Priego, Y. Liu and N. J. Wagner, *Intermediate range order and structure in colloidal dispersions with competing interactions*, J. Chem. Phys. **139**, 154904 (2013).
- [307] R. B. Jadrich, J. A. Bollinger, K. P. Johnson and T. M. Truskett, *Origin and detection of microstructural clustering in fluids with*

- spatial-range competitive interactions*, Phys. Rev. E **91**, 042312 (2015).
- [308] A. de Candia, E. Del Gado, A. Fierro, N. Sator, M. Tarzia and A. Coniglio, *Columnar and lamellar phases in attractive colloidal systems*, Phys. Rev. E **74**, 010403(R) (2006).
- [309] J. C. F. Toledano, F. Sciortino, E. Zaccarelli, *Colloidal systems with competing interactions: from an arrested repulsive cluster phase to a gel*, Soft Matter **5**, 2390 (2009).
- [310] C. B. Muratov, *Theory of domain patterns in systems with long-range interactions of Coulomb type*, Phys. Rev. E **66**, 066108 (2002).
- [311] G. H. Fredrickson, *Nonequilibrium structure of the homogeneous phase of block copolymers under steady flow*, J. Chem. Phys. **85**, 5306 (1986).

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