Physical Kinetics

Marian Apostol

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1 Preface

Bodies with many degrees of freedom, in particular with many particles, exhibit certain patterns of their physical quantities, which can be viewed as a motion in space and time. The breakthrough into the nature of this motion was made by Maxwell in 1859, who showed, for gases, that this motion is a statistical motion which implies probabilities. This is a distinct type of motion, different from mechanical motion, or from other forms of motion like the elastic, fluid, electromagnetic or quantum-mechanical motions. Nevertheless, there was, and still is, a continuous attempt to derive the statistical motion from mechanical motion, or to reduce it to mechanical motion, such that Statistical Physics is often called Mechanical Statistics. In spite of Maxwell, founders of Statistical Physics like Boltzmann, Gibbs or Einstein persisted in connecting the statistical motion with the mechanical motion. The confusion is fuelled by the presence of the mechanical motion in statistical motion. The problem would rather be to see the compatibility of the statistical motion with the mechanical motion. This is the problem of Kinetics, to be developed in the present book.

This rather misleading line of thought arose from the evolution equation for the distribution function F, which, instead of being written as

$$\frac{dF}{dt} = \frac{\Delta F}{\Delta t} = -\gamma[F - F(t = \infty)] \quad , \tag{1.1}$$

is usually written as

$$\frac{dF}{dt} = C(\Delta F) \quad , \tag{1.2}$$

where $C(\Delta F)$ is the so-called collision integral ($\Delta F = F - F(t = \infty)$).[1] Equation (1.1) is an evolution equation, from the moment $t = 0$, when $F = F(t = 0)$ to $t = \infty$. The approximation used in the first equality in equation (1.1) is valid for a sudden decrease of the function F. Indeed, the time $\tau = 1/\gamma$ is the collision time of the particles (in the general sense of interaction), which is much shorter than any relevant time at our scale. It is related to the particle mean freepath Λ and the particle (thermal) velocity v. The solution of equation (1.1) is

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[1] Equation (1.1) has been used by Debye for molecular relaxation (P. Debye, *Polar Molecules*, Chem. Catalog Co., Inc., NY (1929)).

$$F = F(t=0)e^{-\gamma t} + F(t=\infty)(1-e^{-\gamma t}) \quad , \tag{1.3}$$

which shows that we may view $F(t=0)$ as the initial non-equilibrium distribution and $F(t=\infty)$ as the final equilibrium distribution. Therefore, equation (1.1) embodies the principle of statistical (thermal) equilibrium, which is the basic principle of Statistical Physics. In fact, since τ is very short in comparison with t (large γ), the equilibrium is established much faster (than $t \to \infty$).

The collision integral $C(\Delta F)$ does not include necessarily (*i.e.* without additional ingredients) the principle of equilibrium, although it includes collisions, vanishes at equilibrium and in spite that the collisions are represented by probabilities (which remain undefined; Stosszahlansatz). The usual arguments that equation (1.2) would imply an increase of entropy (Boltzmann's H-theorem) in the evolution towards equilibrium are valid only at equilibrium, when the entropy is stationary.

Equation (1.1) can also be written as $dF/dt = -\gamma f$, where $f = \Delta F = F - F(t=\infty)$ is the deviation of the distribution from its equilibrium value. If we keep $\gamma f \neq 0$ in equation (1.1) (or $C(\Delta F) \neq 0$ in equation (1.2)), we admit that we are not at equilibrium. Equation (1.1) shows how the ensemble tends to equilibrium. (As long as $C(\Delta F)$ is not determined in a form similar with $-\gamma f$, equation (1.2) does not show the approach to equilibrium). Inasmuch as we write $\gamma = 1/\tau$ and $\tau = \Lambda/v$, we admit that the approach to equilibrium is governed by collisions. But these collisions are not determined in the mechanical sense, they are determined in a statistical sense, through Λ and τ which are purely statistical concepts, such that the statistical motion remains a distinct motion, not derivable from the mechanical motion. If we attribute to the molecular collisions a mechanical sense, we have not anymore, for instance, an ideal gas, but a gas with interaction. We should realize that the equilibrium is achieved, locally, much faster than our time scale. Therefore, we need to use in Kinetics (local) equilibrium evolution equations. This approach was recognized by Landau in connection with the collisionless plasma, where $\gamma = 0^+$ and $\gamma \to 0^+$; it led to the Landau damping.[2] We emphasize that γ is not small as a consequence that $\tau = 1/\gamma$ is large; on the contrary, τ is short. We take the parameter γ zero because we are at local equilibrium.

Two types of problems are usually solved in Kinetics. In one type, we are interested in the slight perturbations produced in the equilibrium distribution by an external force. In these problems the kinetic equation (1.1) is solved by neglecting the small term $\gamma\Delta F$ and treating γ as $\gamma \to 0$. This approach means that the ensemble is at local equilibrium (but not at global equilibrium). Mechanical motion produced by external forces coexists with the statistical motion. The macroscopic phenomena imply much longer times than the relaxation time τ, such that, practically, they take place at equilibrium. The other type of problems is the transport. The standard approach is to use various ansatzen for the collision term $C(\Delta F)$ and solve equation (1.2) for F, as if the ensemble were not at equilibrium; then, fluxes (flows) are computed with the solution F, which depends on the spatial derivatives of the thermodynamic parameters, to get the transport laws. However, the transport time is of the order l/v, where l is the dimension of the macroscopic sample. Therefore, the transport time is much longer than the relaxation time, and the transport takes place at local (but not global) equilibrium. Consequently, the appropriate approach is to leave aside the term $\gamma\Delta F$ in equation (1.1) and to use the fact that the transport is made at local equilibrium. The statistical equilibrium is governed by probabilistic collisions (interactions) and the macroscopic phenomena are governed by local statistical equilibrium.

In transport equations time and spatial partial derivatives of the distribution may appear, or derivatives of the parameters of the distribution, or derivatives of quantities connected with the distribution. In the time partial derivatives of the type $\partial F/\partial t$ we may replace ΔF by F and Δt by τ, since these variations are sudden variations produced by particle collisions; likewise, in spatial derivatives we may use Λ. Usually, the variations ΔF are small (as τ is), but even for larger variations we may use such a procedure, as long as the contributions of the time and spatial derivatives compensate each other (as in the continuity equation), or are compensated by external forces, such that the equation of local equilibrium $dF/dt = 0$ is preserved. The approximations $\tau\partial/\partial t = 1$ and $\Lambda\partial/\partial x = 1$ are not always useful; first-order differential equations, or equations which imply second-order spatial derivatives at most, are useful for the evolution of the physical quantities.

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[2] L. Landau, "On the vibrations of the electronic plasma", ZhETF **16** 574 (1946) (J. Phys. USSR **10** 25 (1946)).

This book exhibits several original points. First, it derives the Boltzmann equation from atomic motion, making use extensively of Landau's concept of elementary excitations. Second, it includes external forces, besides the statistical motion, wherever relevant. The transport is treated at local equilibrium, according to the quasi-general evidence. In Kinetics we are at the limits of the Theoretical Physics, because we have to be content only with estimations of partially defined concepts like lifetime and mean freepath of elementary excitations; this makes Kinetics a particularly difficult (and intriguing) subject in the realm of Theoretical Physics, probably the most interesting one. This book presents the kinetic theory of the classical gas and the transport in classical gas. Special attention is devoted to the classical plasma, which raises a problem. The problem in classical plasma is the relation between the thermal equilibrium of the electrons, on one hand, and the ions, on the other. The Coulomb forces, and the correlations they produce, make the classical plasma a classical gas of interacting ions dressed with electrons, via the Debye-Huckel screening. This way, once correlated with the ions, the electrons acquire a special dynamics. The thermodynamics of a classical plasma is that of a gas of interacting dressed ions, which may exhibit condensed phases, like a liquid phase or a solid phase. The phonons in solids are a particularly interesting subject. Besides describing the thermoconductivity of a perfect lattice, this book emphasizes the role played by the anharmonic interactions in the phonon lifetime. Landau's fruitful concept of elementary excitations, quasiparticles and collective modes, is introduced especially in (normal) Fermi liquid, where the interaction is discussed in detail. The electron liquid is presented in connection with the cohesion of metals, and the transport in the magnetic field and in semiconductors is described. Special attention is devoted to the electron-phonon interaction, where an interesting particular case of non-equilibrium transport appears (the drag effect).[3] Except for such particular cases, the non-equilibrium transport, besides being irrelevant to a large extent, requires additional, particular hypotheses which are not related to a general, consistent method. Basic features of the superconductivity and superfluidity are presented, emphasizing the relation of the transport with the condensed phases. A special kind of thermoelectricity, consisting of flying pulses of charge and heat, is described. A consistent model of classical liquids is also presented, together with its transport properties. Finally, the sound anomaly in water is clarified and the role played by the kinetic modes (densitons) is discussed.

There exist subjects which have been omitted in the treatment presented in this book, or described succintly. Among them there are the magnetic resonance phenomena, the neutron transport, the ballistic transport, the electrodynamics of metals, plasmas in magnetic field, the electrolytes, chemical reactions, hydrodynamics, low-dimensional statistical ensembles. Most of these subjects do not exhibit new transport concepts or circumstances, having the general aspect of applications of the transport theory (in many cases routine applications).

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[3] T. Holstein, "Theory of ultrasonic absorption in metals: the collisions-drag effect", Phys. Rev. **113** 479 (1959).

2 Introduction

If Physics would be viewed as a set of provinces (disciplines), Statistical Physics would be the Queen: the Queen of Physics. It distinguishes itself not only by its power, richness and elegance, but especially by raising a deep problem. And Physical Kinetics, to be dealt with in this book, should be called the Crown Jewel, because it incorporates this very deep statistical problem. The fundamental problem raised by Statistical Physics originates in the fact that it identifies a distinct type of motion (statistical motion), probably the most general form of motion; the characteristic note of this motion, as compared with other types of motion, is the problem.

Let us consider a motion, *i.e.* a change in time from a physical (*i.e.* measurable) state to other physical states (a state is the set of values of measurable quantities). We may imagine that in a long duration of time T the motion spends some time ΔT in a state; or we may imagine that ΔN out of many identical motions N take up the same state at any moment; or, also, we may imagine that we have many times (N) the same motion and ΔN times this motion takes up the same state. Obviously, $\Delta T/T$ or $\Delta N/N$ is a probability, so we have a distribution of probability. Then, we can compute the mean values of any physical quantity (depending on states); and the deviations from these mean values. Thus, we are able to have some knowledge about that motion, providing, of course, we know the probability distribution. Such a motion would be a statistical motion, its realization a statistical ensemble and the determination of the probability distribution (statistical probability) would be the main task (problem) of Statistical Physics. The temporal ensemble defined above was employed by Einstein; the state ensembles originate with Boltzmann and, especially, Gibbs.

At this point the fundamental problem of the Statistical Physics appears: does such a statistical probability exist? Because, we note that the probability defined above is independent of time, while the motion depends on time. It is not obvious that statistical distributions exist. Statistical distributions, *i.e.* probability distributions which are independent of time, are specific for motions at statistical (thermal) equilibrium. The problem is cast now in the question whether statistical (thermal) equilibrium exists. Various plausible, reasonable arguments were brought in favour of the existence of the thermal equilibrium, for various physical ensembles, especially for gases. None is a proof of its existence. Thermal equilibrium is a postulate of Statistical Physics, one of the greatest principle of Physics. We may imagine probability distributions which depend on time, and we may devise evolution equations which, possibly, may bring these distributions to statistical distributions. This is a very popular misconception related to Physical Kinetics, perpetuated not as much by laymen, as by experts. In many instances the Physical Kinetics seems to prove the evolution towards equilibrium; in all these cases the arguments are misleading circular arguments, which presuppose the existence of the thermal equilibrium, or mistake the mechanical motion for statistical motion. The evolution equations of the Physical Kinetics show only that various other motions (like mechanical, quantum-mechanical, elastic, fluid, electromagnetic motion) are compatible with statistical motion.

It is worth noting that the statistical motion is not a deterministic motion, in the sense that the states in terms of which the statistical distribution is defined do not change in time. In the context of a deterministic motion the existence of the thermal equilibrium is sometimes called the "ergodic hypothesis" (or "quasi-ergodic hypothesis").[1]

Statistical distributions should depend only on the statistical motion and some external parameters; in the absence of other conditions, there is no reason to differentiate between the states; we note that the states are statistical coordinates. Consequently, we may admit that each available state has the same probability $w = 1/\Gamma$, where Γ is the total number of states. This is sometimes called the "hypothesis of molecular chaos". We may imagine a partition of any two sub-sets Γ_1 and Γ_2 of the Γ states; this is called a partition in two "sub-systems", or two "sub-ensembles", or a motion partition (the sub-systems were introduced by Gibbs). Since the motion is the same and if the relevant external parameters are the same, the probabilities of the partition states are $w_1 = 1/\Gamma_1$ and $w_2 = 1/\Gamma_2$ and the equality $w = w_1 w_2$ is valid. This is called the statistical independence. It follows that the function $\ln w$ is an additive function of "sub-systems". For an infinitesimal number of states the probability is $dw = \rho d\Gamma$, where ρ is the probability density; its ln is additive. Being constant in time, ρ may be related to other constants of motion, like, for instance, energy, momentum or angular momentum; the latter are additive, so $\ln \rho$ may be a linear combination of these additive integrals of motion, with coefficients which are to be viewed as external parameters. In particular, we should have $\ln \rho = \alpha - \beta \mathcal{E}$, where $\mathcal{E}$ is the energy of the motion associated with the states which define the probability density and α and β are (constant) coefficients; it follows $\rho \sim e^{-\beta \mathcal{E}}$. This is Gibbs's statistical distribution; of course, it should be normalized, such that $\int d\Gamma \rho = 1$; for quantum-mechanical states $d\Gamma$ is the multiplicity of the state, and $w \sim \rho$; the integration over Γ is replaced by summation over states. It is reasonable to assume $\beta > 0$, for stability. This connection indicates that the statistical motion may coexist with the mechanical motion. If the ensemble is a number $\mathcal{N}$ of identical particles, then we may set $\alpha = const + \beta \mu \mathcal{N}$, where μ is another coefficient; and the normalization should include integration (summation) with respect to $\mathcal{N}$. The existence of the parameters α (μ) and β may show that the motion is not isolated in fact, it is not closed. The existence of the energy $\mathcal{E}$ and the number of particles $\mathcal{N}$ show, to some extent, that the motion is closed. This is a very interesting particularity of the statistical motion. Motion with distribution $\sim e^{-\beta \mathcal{E}}$ is called canonical motion, that with distribution $\sim e^{\beta(\mu \mathcal{N} - \mathcal{E})}$ is called macrocanonical (or grand-canonical) motion. Of course, such distributions are for motions which possess energy and particle numbers.

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[1] See, for instance, E. Fermi, "Beweis, dass ein mechanishes Normalsystem im allgemeinen quasi-ergodisch ist", Z. Phys. **24** 261 (1923); E. Fermi, J. Pasta and S. Ulam, "Studies of non linear problems", Los Alamos Report No. 266, LA-1940, Los Alamos (1955).

If the statistical motion is associated with classical mechanical motion, *i.e.* if the classical mechanical motion is present, the definition of the states includes the dynamical variables p and q, where p denotes momenta and q denotes the coordinates; then, $\rho \sim e^{-\beta \mathcal{E}(p,q)}$ and the mean value of any physical quantity $f(p,q)$ is given by $\overline{f} = \int dpdq \rho(p,q) f(p,q)$; the dynamical variables are coordinates of the phase space (Γ includes points (p, q)) and the state ensemble is called phase ensemble. If the quantum-mechanical motion is present, then $\rho = \rho_n \sim e^{-\beta \mathcal{E}_n}$, where n denotes the quantum-mechanical state (in the energy representation); and the probability is $w_n = \rho_n$. The quantities ρ_n may be viewed as the diagonal elements of a matrix ρ, which is called the statistical matrix; what we measure in quantum-mechanical motion is the quantum-mechanical mean value $(\rho f)_{nn}$, which, in the energy representation is $\rho_n f_{nn}$; the statistical mean value is given by $\overline{f} = \sum_n (\rho f)_{nn} = tr(\rho f)$. Summation (integration) over other statistical variables, if present, should be included (*e.g.*, the particle number). Since ρ is diagonal in the energy representation we may see that the quantum-mechanical motion is statistically independent in this representation; we may infer that the statistical character of the statistical motion and the statistical character of the quantum-mechanical motion coincide in the energy representation. In other representations this is not true. In general, the statistical character of the quantum-mechanical motion is distinct from the statistical character of the statistical motion. The energy plays a special role in this context.

Also, we note that the existence of the conserved energy (and other integrals of motion) does not mean necessarily that the mechanical motion is integrable in terms of any dynamical variables (p, q), or any type of states n. However, $\ln \rho$ remains proportional to the energy, because the coordinates $p\,, q$ are not treated as dynamical variables, but as statistical variables (coordinates); this amounts to say again that the statistical motion is distinct from the mechanical motion.

We can see that by admitting the existence of the statistical equilibrium we are able to derive the statistical distributions. In the course of derivation we characterized the statistical motion by molecular chaos ("molecular-disorder", Boltzmann) and statistical independence. We note that the states, the energy, the particle number are statistical variables.

Let us assume that the statistical motion consists of a number N of identical statistical motions; a physical quantity f may be written as the sum $f = \sum_{i=1}^{N} f_i$ of all these "sub-motions"; then the mean value $\overline{f}$ is proportional to N and the root mean square deviation $\delta f = \sqrt{\overline{(\Delta f)^2}} = \sqrt{\sum_{ij} \overline{\Delta f_i \Delta f_j}}$ is proportional to $\sqrt{N}$, because of the statistical independence; it follows $\delta f/\overline{f} \sim 1/\sqrt{N}$ and, for large N, this ratio is zero. δf is called fluctuation. Therefore, statistical knowledge is useful for statistical motions with a large (macroscopic) number of degrees of freedom (states), when the fluctuations are small (vanishing); *i.e.*, the statistical variables are sharply distributed about their mean values. The extension of the statistical motion to one particle in an ensemble is a limiting case (we note that ρ and Γ may fluctuate).

Let us introduce the quantity $\mathcal{S} = -\ln\rho$ and require, in accordance with the molecular chaos, its maximum mean value in certain conditions; for instance, for a given mean energy and a mean particle number; *i.e.*, let us require the maximum of

$$-\int d\Gamma\rho\ln\rho + \alpha\int d\Gamma\rho\mathcal{N} - \beta\int d\Gamma\rho\mathcal{E} \ ; \tag{2.1}$$

we get immediately the statistical distribution $\rho = e^{\alpha\mathcal{N}-\beta\mathcal{E}}$. The quantity $\mathcal{S} = -\ln\rho$ is called entropy, its mean value

$$S = \overline{\mathcal{S}} = -\int d\Gamma\rho\ln\rho \tag{2.2}$$

is also called entropy; at equilibrium $\mathcal{S} = S = \ln\Gamma$ and $\partial S/\partial E = \beta$. Therefore, at equilibrium the entropy is stationary, as a reflection of the molecular chaos. Since the molecular chaos is absolute, any deviation from equilibrium would mean a regular, ordered pattern, which would decrease the entropy; therefore, the evolution (long time in the temporal ensemble) is towards an increase of the entropy, towards equilibrium; out of equilibrium (in non-equilibrium) the entropy is smaller than at equilibrium. This is the law of increase of entropy. It is equivalent with the principle of thermal equilibrium. Statistical Physics may equally well be constructed starting from the principle of increase of entropy. $-S$ is called Boltzmann's H function.[2] Processes where the entropy is constant (equilibrium processes) are reversible processes, those where the entropy increases are irreversible processes.

---

[2] L. Boltzmann, *Lectures on Gas Theory*, Dover, NY (1964) (translated from L. Boltzmann, *Vorlesungen uber Gastheorie*, Barth, Leipzig, Part I (1896) and Part II (1898)).

Among the reversible processes those which are adiabatic are special; an adiabatic process is characterized by a parameter λ which varies slowly in time, *i.e.* its time derivative $d\lambda/dt$ is small; we may expand the small derivative dS/dt of the entropy with respect to time in powers of $d\lambda/dt$; this expansion should start with the second power of $d\lambda/dt$, because $dS/dt > 0$; *i.e.*, $dS/dt = A(d\lambda/dt)^2$ $(A > 0)$. It follows that dS/dt is much smaller than $d\lambda/dt$, *i.e.* the adiabatic processes may take place and the entropy remains practically constant. The adiabatic processes are reversible to a good approximation. Of course, a reversible process is not necessarily adiabatic.

Let us write the statistical distribution as

$$\rho = e^{c+\beta\mu\mathcal{N}-\beta\mathcal{E}} \quad , \tag{2.3}$$

where c is a normalization constant,

$$e^{-c} = \int d\Gamma e^{\beta\mu\mathcal{N}-\beta\mathcal{E}} = Z = 1 \ ; \tag{2.4}$$

e^{-c} is denoted by Z; it is called partition function. Let us differentiate the normalization condition $\int d\Gamma\rho = 1$, with ρ given by equation (2.3), with respect to β and other external parameters λ which may enter the expression of the energy; we note that in such variations we assume the existence of the equilibrium, *i.e.* we consider equilibrium processes; we get

$$d(c - \beta E + \beta\mu N) = -\beta dE + \beta\frac{\partial E}{\partial\lambda}d\lambda + \beta\mu dN \quad , \tag{2.5}$$

where $E = \overline{\mathcal{E}}$ and $N = \overline{\mathcal{N}}$ are mean values; on the left in equation (2.5) we have an exact (total) differential; let us introduce the notation

$$d(c - \beta E + \beta\mu N) = -\beta dQ \ ; \tag{2.6}$$

then, equation (2.5) becomes

$$dE = \frac{\partial E}{\partial\lambda}d\lambda + dQ + \mu dN \ ; \tag{2.7}$$

here, we may view λ as volume V, $-\partial E/\partial\lambda$ as pressure p and dQ as heat. Statistical Physics identifies the heat as a form of energy.

μ is an energy associated with the presence of a particle; it is called chemical potential.

From $S=-\overline{\ln\rho}$ we get $S=-c+\beta E-\beta\mu N$ and

$$-dS=d(c-\beta E+\beta\mu N)=-\beta dQ \ ; \tag{2.8}$$

therefore, the entropy is a function of state (its differential is an exact differential) and $T=1/\beta$ is the temperature (hence the denomination "thermal" equilibrium). For $T\rightarrow 0$, when there exists only one state, $\rho\rightarrow 1$ and $S=-\overline{\ln\rho}\rightarrow 0$; this is called the "third principle of Thermodynamics" (the energy conservation would be the first, the law of increase of entropy the second). The entropy may increase, in an irreversible process, independently on the heat gained, so we have $TdS\geq dQ$. As regards the time τ of measuring the temperature, we should have $T\tau\gg\hbar$, where $\hbar$ is Planck's constant; otherwise, the quantum effects destroy the statistical equilibrium (*e.g.*, at very low temperatures or in very short times).

Equations (2.7) and $dQ=TdS$ define the thermodynamic potentials; in addition,

$$cT=-T\ln Z=E-TS-\mu N \ ; \tag{2.9}$$

$\Omega=E-TS-\mu N$ is called the grand-canonical potential, $F(V,T,N)=E-TS$ is the free energy ($E=E(V,S,N)$); $W(p,S,N)=E+pV$ is the enthalpy. We note the useful relation $\partial(\beta F)/\partial\beta=E$. From

$$d(E+pV-TS)=Vdp-SdT+\mu dN=d\Phi \ \ , \tag{2.10}$$

where $\Phi(p,T,N)=E+pV-TS$ is the Gibbs free energy (F is also called the Helmholtz free energy), it follows $\Phi=\mu N$ (since V and S are proportional to N); and $E+pV-TS=\mu N$ implies $\Omega(V,T,\mu)=E-TS-\mu N=-pV$. We note that $E+pV-TS-\mu N=0$ at equilibrium and, in general, since the entropy increases and is stationary at equilibrium, $E+pV-TS-\mu N\geq 0$; *i.e.*, the thermodynamic potentials have a minimum at equilibrium. Since the fluctuations are deviations from equilibrium mean values, we can use this expression for deriving their distribution; in order to do this, we should leave aside one contribution to this expression, say, μN, and take $\Delta E+p\Delta V-T\Delta S>0$ as defining the distribution $\rho\sim e^{-\beta(\Delta E+p\Delta V-T\Delta S)}$ for the fluctuations ΔE, ΔV and ΔS; note that the fluctuations are deviations of equilibrium type. If we take the derivative of

$$\int d\Gamma(\mathcal{E} - E)e^{-\beta\mathcal{E}} = 0 \tag{2.11}$$

with respect to the temperature we get the energy fluctuation $\delta E = T(\partial E/\partial T)^{1/2}$.

It is of the greatest importance to note the following circumstance. In canonical distribution $\rho \sim e^{-\beta\mathcal{E}}$ the variable $\mathcal{E}$ is the mechanical energy; this may induce the idea that the statistical motion would be a mechanical motion. In fact, ρ includes also the factor e^c ($\rho = e^{c-\beta\mathcal{E}}$), which leads to $d(c - \beta E) = -\beta dQ = -dS$ and

$$dE = -pdV + dQ \quad , \tag{2.12}$$

i.e. to the existence of another form of energy, distinct from the mechanical energy, which is heat. The occurrence of this new form of energy originates in the fact that ρ is a probability distribution, which should be normalized; *i.e.*, from the hypothesis of the molecular chaos and the principle of thermal equilibrium. It is this latter characteristic which is the distinctive feature of the statistical motion; and the existence of $\mathcal{E}$ in the definition of the statistical distribution shows only that the statistical motion is compatible with the mechanical motion, that both motions may coexist. The existence of $\mathcal{N}$ in the macrocanonical distribution also indicates the non-mechanical character of the statistical motion. The statistical character is embodied in the amount of heat which is $dQ = TdS = Td\ln\Gamma$ (for a variation between infinitesimally-separated equilibrium states); we can see that it is the variation of the number of states which gives the heat. This is not a mechanical motion, since in a mechanical motion a state is occupied (gained) only by leaving behind (losing) an empty state.

The statistical distributions are derived above from the assumption of thermal equilibrium, characterized by statistical independence and molecular chaos. We may think that an external agent, probably endowed with similar characteristics, generates such a special kind of motion (statistical motion). Let us consider a motion with fixed energy E_0 and fixed particle number N_0. Let us assume that it is possible to divide this motion into two parts, one larger, with various energies $\mathcal{E}^{'}$ and various particle numbers $\mathcal{N}^{'}$, called "bath", and another, smaller, with various energies $\mathcal{E}$ and various particle numbers $\mathcal{N}$. The probability distribution of the "0" motion will be proportional to δ-functions,

$$\rho_0 \sim \delta(E_0 - \mathcal{E}^{'} - \mathcal{E})\delta(N_0 - \mathcal{N}^{'} - \mathcal{N}) \tag{2.13}$$

and the probability distribution of the smaller motion is of the form

$$\begin{gathered}\rho = \int d\Gamma^{'} d\mathcal{N}^{'} \rho_0 \sim \\ \sim \int d\Gamma^{'} d\mathcal{N}^{'} \delta(E_0 - \mathcal{E}^{'} - \mathcal{E})\delta(N_0 - \mathcal{N}^{'} - \mathcal{N}) = \\ = \int d\Gamma^{'} \delta(E_0 - \mathcal{E}^{'} - \mathcal{E}) \mid_{\mathcal{N}^{'} = N_0 - \mathcal{N}} \quad .\end{gathered} \tag{2.14}$$

In this expression we use $d\Gamma^{'} = (d\Gamma^{'}/d\mathcal{E}^{'})d\mathcal{E}^{'} = (d\mathcal{S}^{'}/d\mathcal{E}^{'})e^{\mathcal{S}^{'}}d\mathcal{E}^{'}$, where $\mathcal{S}^{'} = \mathcal{S}^{'}(\mathcal{E}^{'}, \mathcal{N}^{'})$; the main contribution to equation (2.14) comes from $e^{\mathcal{S}^{'}(E_0 - \mathcal{E}, N_0 - \mathcal{N})}$; the series expansion of $\mathcal{S}^{'}$ for $\mathcal{E} \ll E_0$, $\mathcal{N} \ll N_0$ gives the statistical distribution $\rho \sim e^{\beta\mu\mathcal{N} - \beta\mathcal{E}}$; the assumption of thermal equilibrium is implicit, in the form of molecular chaos (and statistical independence), in the integration over the variables $\Gamma^{'}$ and $\mathcal{N}^{'}$ of the bath. The distribution given by equation (2.13) is called micro-canonical distribution.[3]

We include here another remark. Let a statistical motion of $\mathcal{N}_0$ identical particles have Γ_0 states for each particle; let us consider a partition $\mathcal{N}_0 = \mathcal{N}^{'} + \mathcal{N}$, $\Gamma = \Gamma^{'} + \Gamma$; the entropy is

$$\mathcal{S}_0 = \ln(N_0\Gamma_0) = \ln(\mathcal{N}^{'} + \mathcal{N}) + \ln(\Gamma^{'} + \Gamma) \ ; \tag{2.15}$$

for $\mathcal{N} \ll \mathcal{N}^{'}$, $\Gamma \ll \Gamma^{'}$ a series expansion in equation (2.15) gives $\mathcal{S}_0 = \mathcal{S}^{'} + \mathcal{S}$,

$$\mathcal{S} = const \cdot \mathcal{N} + const \cdot \Gamma \ ; \tag{2.16}$$

for independent particles with energy $\mathcal{E}$ the number of states Γ is proportional to $\mathcal{E}$ (the surface of the momenta sphere), so we get

$$\mathcal{S} = const \cdot \mathcal{N} + const \cdot \mathcal{E} \quad , \tag{2.17}$$

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[3] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (*The Rational Foundation of Thermodynamics*), Ch. Scribner's Sons, NY (1902) (Dover, NY (1960).

which leads to the statistical distribution. The assumption of thermal equilibrium, through statistical independence and molecular chaos, is implicit in this derivation.

During statistical motion, which passes from one state to another, other motions may be present, as, for instance, mechanical motion. In classical mechanics, the density ρ of the trajectories, which depends on coordinates and momenta (*i.e.* on the states), is left unchanged by the mechanical motion (so is the volume of the phase space defined by the trajectories); this is Liouville's theorem (the conservation of probabilities). Consequently, the statistical motion is not destroyed by the (classical) mechanical motion, and the two motions may coexist (are compatible). In quantum-mechanical motion, if the density matrix were diagonal in the energy representation, *i.e.* if it commutes with the hamiltonian, it is conserved. However, in general, this is not true. The quantum statistical distribution is unperturbed by the quantum-mechanical motion, because the mean statistical values need only mean quantum-mechanical values.

Arguments of the type given above are often used in the attempt to define the statistical motion. Actually, they are invalid. Indeed, it is claimed that, if ρ is a constant, then it obeys the equation of motion

$$\frac{d\rho}{dt}=\frac{\partial\rho}{\partial t}+\{H,\rho\}=0 \quad , \tag{2.18}$$

or

$$\frac{d\rho}{dt}=\frac{\partial\rho}{\partial t}+\frac{i}{\hbar}[H,\rho]=0 \quad , \tag{2.19}$$

where $\partial\rho/\partial t=0$, $\{\}$ is the Poisson bracket, $[\,]$ is the commutator, H is the hamiltonian and $\hbar$ is Planck's constant; from these equations we would derive that $\{H,\rho\}$ or $[H,\rho]$ are zero, *i.e.* the distribution would be conserved. These equations are invalid, since the statistical distribution ρ does not obey the laws of the mechanical motion given above; ρ in the above equations is the trajectory (Liouville) distribution or the density matrix. The mechanical motion of the states (*i.e.* the motion of the dynamical variables p, q, or quantum-mechanical states n) is disrupted by the statistical, chaotical motion. In the statistical motion the states (in particular the coordinates p, q) are viewed as statistical variables (coordinates). We note again that this particular circumstance does not prevent the constant $\ln \rho$ from being proportional to the constant energy $\mathcal{E}$, as shown above.

Finally, it is worth noting another feature of the statistical motion. This motion proceeds in time. The mean values tend to equilibrium mean values in a relaxation time. The deviations from mean values, *i.e.* the fluctuations, occur in longer times in non-equilibrium and in shorter times at equilibrium.

The main object of Statistical Physics is related to ensembles of many particles; these particles may be of various types, like fermions, bosons, radiation quanta, various elementary excitations; their mechanical motion may be classical or quantum-mechanical. Their Statistical Physics has many particularities; we limit ourselves here to give a general frame related to the statistical motion of the many-particle ensembles. If the particles do not interact (are free), their measurable physical quantities do not move; consequently, the ensemble does not have a statistical motion (except for the case where the ensemble has not been prepared in such a state by external agents; in which case an interaction is present). Therefore, in order to achieve a statistical motion and the statistical equilibrium the particles must interact. If a particle has at some instant an energy ε_{eq}, then, by interaction, it shares this energy with many other particles; after some time, when the statistical equilibrium is reached, the particles have a mean energy of the order of the temperature T; therefore, we must have the inequality $\varepsilon_{eq} > T$. Since the existence of the energy scale ε_{eq} is a necessary condition for statistical equilibrium, we may call this energy equilibrium energy and endow it with the suffix *eq* from "equilibrium". At equilibrium, there exist fluctuations, and the fluctuation energy $\delta\varepsilon_f$ should be lower than the temperature T, in order for the mean values to make sense; therefore, we have the inequalities $\varepsilon_{eq} > T > \delta\varepsilon_f$; in addition, the uncertainty $\delta\varepsilon_{ex}$ in the energy of the elementary excitations should be smaller than the fluctuation energy, in order for these excitations to be well defined. Of course, the mean spacing between the quantum states $\delta\varepsilon_q$ should be very small, and finally, the energy $\delta\varepsilon_{obs}$ involved in the measurement (observation) process should be the smallest. Therefore, we have the series of inequalities $\varepsilon_{eq} > T > \delta\varepsilon_f > \delta\varepsilon_{ex} \gg \delta\varepsilon_q > \delta\varepsilon_{obs}$. In the limit of a large number of particles the quantum-mechanical energies (and states) are not defined, and $\delta\varepsilon_q$ may be left aside in these inequalities. By the general uncertainty relation $\delta\varepsilon \simeq \hbar/\tau$, these inequalities transform themselves in a succession of time inequalities $\tau_{eq} < \tau_{th} < \tau_f < \tau_{lf} \ll \tau_q < \tau_{obs}$, where τ_{eq} may be viewed as the time of destroying the equilibrium by interaction, τ_{th} is the "thermal" time of establishing the equilibrium (determining the equilibrium), τ_f is the fluctuation time, τ_{lf} is the lifetime of the elementary excitations, τ_q is the time needed to establish the quantum levels and τ_{obs} is the time of observation of all these phenomena. τ_{eq} may be viewed also as the mean time of collisions between the particles. The mean freepath and the associated mean freetime in gases correspond to one-particle elementary excitations. All these estimations are made at equilibrium. We can see that the thermal equilibrium deviates fastest from equilibrium and comes back fastest, such that various observational processes are possible at equilibrium. The relaxation time is related to the observation time, and we can see that it is the longest.

Historical note. In *Hydrodynamica*, published between 1734-1738,[4] Daniel Bernoulli claimed explicitly that gases are composed of moving atoms and molecules, whose collisions with container's walls give pressure and their mean kinetic energy is proportional to the temperature and heat; this was the birth of the kinetic theory of gases. The merit of this book consists in the atomistic conception; its drawback is the association of the statistical motion with the mechanical motion. The atomistic conception introduces the notion of complex assemblies composed of many (identical) particles. Leaving aside that their mechanical motion may not be integrable (both classically and quantum-mechanically),[5] the probability distribution over the phase space of the coordinates q and momenta p is

$$\rho = \sum_i \delta(q - q_i(t))\delta(p - p_i(t)) \tag{2.20}$$

in classical motion, where the summation extends over the number of particles and $q_i(t)$, $p_i(t)$ describe the classical trajectory (trajectory distribution). The conservation of the particle number gives the equation of continuity

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[4] D. Bernoulli, *Hydrodynamics*, Dover (1968).

[5] See, for instance, H. Poincare, *Les Méthodes Nouvelles de la Mécanique Celeste*, Gauthier-Villars, Paris (1892, 1893, 1899); M. Apostol, "The many-body theory: its logic along the years", J. Theor. Phys. **152** (2007); see also, F. Diacu, "The solution of the n-body problem", Math. Intell. **18** 66 (1996).

$$\frac{\partial\rho}{\partial t}+div(\rho\mathbf{v})=0\quad , \tag{2.21}$$

where $\mathbf{v}=(\dot{q},\dot{p})$; if we assign the mechanical dynamics to the coordinates, we get

$$\frac{\partial\rho}{\partial t}+\mathbf{v}grad\rho=\frac{\partial\rho}{\partial t}+\dot{q}\frac{\partial\rho}{\partial q}+\dot{p}\frac{\partial\rho}{\partial p}=\frac{\partial\rho}{\partial t}+\{H,\rho\}=0\quad , \tag{2.22}$$

where H is the hamiltonian; this equation is in fact $d\rho/dt=0$. This is Liouville's theorem; with the Poisson bracket replaced by commutator, it is the equation of motion of the density matrix (which is not equal to zero, in general). The above equations are usually employed to show that the statistical distribution is an integral of motion (in the absence of the explicit time dependence); this would be the conservation of the probabilities (the conservation of the volume in the phase space is the conservation of the number of particles, or the number of states). In fact, equation (2.20) leads immediately to $d\rho/dt=0$. We should note, however, that as long as p and q are dynamical variables, the definition of a probability in reference to them is meaningless, since for statistical distributions p and q are statistical coordinates. Similarly, for a quantum-mechanical motion the microcanonical distribution (in the energy representation) may be taken as an equivalent of equation (2.20), which does not lead to statistical distribution without the additional assumption of molecular chaos (principle of statistical equilibrium). The statistical distribution is not given by equations like equation (2.20), but by $\rho=1/\Gamma$, where Γ is the number of states ($d\Gamma=1$ for quantum-mechanical motion). This was the merit of Boltzmann, who, implicitly, identified thereby the statistical motion as a distinct kind of motion.

The notion of probability made its way into Statistical Physics with Maxwell, who, in 1859, derived the velocity distribution of the particles in a gas, by assuming a random motion (which amounts to a uniform distribution $\rho=1/\Gamma$) .[6] He coined the term statistical motion. Maxwell showed also that the viscosity does not depend on density, a result which enforced the atomistic theory.[7] "The path of each molecule must be so irregular that it will defy all calculations. However, according to the laws of probability theory, one can assume a completely regular motion instead of this completely irregular one".[8]

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[6] J. C. Maxwell, "Illustrations of the dynamical theory of gases. Part I. On the motions and collisions of perfectly elastic spheres", Phil. Mag. **19** 19 (1860) (4-th series).

Since 1870, starting from Maxwell, in a long series of papers, Boltzmann enunciated the notion of statistical ensemble in terms of states (phase statistical ensemble) and claimed that $H = -\ln\Gamma$ or $H = \int d\Gamma\rho\ln\rho$ should decrease in time or be stationary (note that the function $x\ln x$ is negative for $0 < x < 1$); he related H to the entropy, $H \sim -S$.[9] If we accept that the change in time of the function H is caused by collisions, then, at equilibrium, the time reversal, or the combined time reversal and spatial inversion, leads to the principle of detailed balancing; more general, the unitarity of the scattering matrix leads to a similar conclusion;[10] making use of these results one can prove indeed that $dH/dt \leq 0$ (and $dS/dt \geq 0$).[11] This is the famous Boltzmann's "H -theorem".[12] However, these arguments are valid at equilibrium, which restricts the result to $dH/dt = 0$. The law of increase of entropy follows from the principle of statistical equilibrium.

Indeed, serious objections have been raised to the proof of Boltzmann's H-theorem. For instance, the invariance under time reversal or, equivalently, the unitarity of the scattering matrix, used in deriving the decrease in time of the function H, are incompatible with the decrease in time of the function H; in other terms, the reversible mechanical motion would be incompatible with the irreversible statistical motion. This is called Loschmidt's paradox, or reversibility (Umkehreinwand) paradox.[13] Similarly, a finite mechanical motion would recur through the same states (or very close to them), which would rather make H an oscillating function, not a decreasing one; this is Zermelo's paradox, or recurrence (Wiederkehreinwand) paradox (formulated on the basis of Poincare's recurrence theorem).[14] In fact, the proofs of the H-theorem are invalid, since in the time evolution of the statistical motion the number of states changes, while both the principle of detailed balancing and the unitarity of the scattering matrix used in the proofs assume a constant number of states, which amounts, in fact, to assuming the statistical equilibrium; by such a line of derivation we may only get $dH/dt = 0$ at equilibrium, which proves that the statistical motion at equilibrium is compatible with the mechanical motion; but they are distinct motions. The answer to the popular question: "How may the reversible mechanical motion lead to an irreversible statistical motion?" is provided by the fact that the two motions are distinct.

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[7] J. C. Maxwell, "Illustrations of the dynamical theory of gases. Part II. On the process of diffusion of two or more kinds of moving particles among one another", Phil. Mag. **20** 21 (1860) (4-th series).

[8] A. Kronig, "Grundzuge einer Theorie der Gase", Ann. Phys. **175** 315 (1856).

[9] L. Boltzmann, "Weitere Studien uber das Warmegleichgewicht unter Gasmolekulen", Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe **66** 275 (1872); "Uber die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Warmetheorie und der Wahrscheinlichkeitsrechnung respektive den Satzen uber das Warmegleichgewicht", Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe **76** 373 (1877).

[10] E. C. G. Stueckelberg, "Théorème H et unitarité de S", Helv. Phys. Acta **25** 577 (1952).

[11] See, for instance, L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 10, *Physical Kinetics* (E. Lifshitz and L. Pitaevskii), Elsevier, Oxford (1981).

[12] L. Boltzmann, *Lectures on Gas Theory*, Dover, NY (1964) (translated from L. Boltzmann, *Vorlesungen uber Gastheorie*, Barth, Leipzig, Part I (1896) and Part II (1898)).

Suppose that we have a small amount of gas which diffuses in a large volume. The diffusion proceeds by collisions, by interactions between the particles of the gas and by the initial conditions, to the extent to which the latter are known; all these may be viewed, at first sight, as ingredients of the mechanical motion. However, the result of diffusion is not in mechanical terms of trajectories but in statistical terms of probabilities. This means that the motion is not mechanical, at least not in the terms of what we call mechanics, *i.e.* classical mechanics or quantum-mechanical terms, as given by Newton's law and the laws of the Quantum Mechanics. This mechanical motion, defined in these terms, is present, but there exists an additional motion, with probabilistic laws, which is statistical motion and is not mechanical motion, so defined.

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[13] J. Loschmidt, "Uber den Zustand des Warmegleichgewichtes eines Systems von Korpern mit Rucksicht auf die Schwerkraft. 1. Teil", Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe **73** 128 (1876).

[14] E. Zermelo, "Uber einen Satz der Dynamik und die mechanische Warmetheorie", Ann. Phys. **57** 485 (1896); "Uber mechanische Erklarungen irreversibler Vorgange. Eine Antwort auf Hrn. Boltzmann's "Entgegnung"", Ann. Phys. **59** 793 (1896).

While Boltzmann limited himself to the general frame of the kinetic theory of gases, Gibbs extended the statistical motion to its general definition, continuing to mix up the statistical motion with the mechanical motion.[15] Both derived the thermodynamics laws from statistical physics. About 1847 Joule recognized the heat as a form of energy, which participates in the energy conservation together with the mechanical energy; this became the first law of thermodynamics.[16] In 1865 Clausius introduced the notion of entropy (Verwandlungsinhalt) and formulated the law of increase of entropy from the analysis of the empirical observations related to the heat engine of Carnot[17] ("The energy of the universe is constant. The entropy of the universe tends to a maximum", Clausius).[18] Clausius, following Carnot, realized that the heat engine absorbs energy (heat) $Q+W$ at the hot temperature T_h, performs the mechanical work W and releases the heat Q at the cold temperature T_c. Then, he noticed, that in these circumstances, any amount of heat Q should be proportional to temperature T, and write $Q=ST$; if the process is stationary, S should be a constant ("the content of transformation"); then we have $(Q+W)/T_h = Q/T_c$; hence W and the Carnot efficiency quotient $\eta = W/(Q+W) = 1 - T_c/T_h$. In a cyclic process the conservation of S can be written as $\int dQ/T = 0$. If $(Q+W)/T_h > Q/T_c$, then $\eta < 1 - T_c/T_h$; hence, he derived the law of increase of entropy $\int dQ/T \geq 0$ or $\int dS \geq 0$.

In a series of papers published between 1902 and 1904 Einstein worked out, apparently independently of Gibbs, the formalism of the Statistical Physics, including the derivation of the laws of thermodynamics.[19] His views on the relation of the statistical motion to the mechanical motion are mixed. The merit of these papers is the introduction of the temporal statistical ensembles. In 1905-1906 Einstein emphasized fluctuations in the brownian motion;[20] the same subject was studied by Smoluchowski.[21] These papers and Perrin's experimental observations of the brownian motion[22] enforced the atomistic conception.

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[15] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (*The Rational Foundation of Thermodynamics*), Ch. Scribner's Sons, NY (1902) (Dover, NY (1960).

[16] J. P. Joule, "Expériences sur l'identité entre le calorique et la force mécanique. Determination de l'équivalent par la chaleur dégagée pendant la friction du mercure", Compt. Rend. August 23 (1847); "On the mechanical equivalent of heat", Phil. Trans. Roy. Soc. London **140** 61 (1850).

[17] S. Carnot, *Réflexions sur la Puissance Motrice du Feu*, Bachelier, Paris (1824).

[18] R. Clausius, "Uber verschiedene fur die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Warmetheorie", Ann. Phys. **125** 353 (1865); *The Mechanical Theory of Heat - with its Applications to the Steam Engine and to Physical Properties of Bodies*, van Voorst, London (1867).

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[19] A. Einstein, "Kinetische Theorie der Warmegleichgewichtes und des zweiten Hauptsatzes der Thermodynamik", Ann. Phys. **9** 417 (1902); "Eine Theorie der Grundlagen der Thermodynamik", Ann. Phys. **11** 170 (1903); "Zur allgemeinen molekularen Theorie der Warme", Ann. Phys. **14** 354 (1904).

[20] A. Einstein, "Uber die von der molekularkinetischen Theorie der Warme gefordete Bewegung von in ruhenden Flussigkeiten suspendierten Teilchen", Ann. Phys. **17** 549 (1905); "Zur Theorie der Brownschen Bewegung", Ann. Phys. **19** 371 (1906).

[21] M. Smoluchowski, "Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen", Ann. Phys. **21** 756 (1906).

[22] J. Perrin, *Les Atom*es, Alcan, Paris (1913).

3 Kinetics of Gases

3.1 Boltzmann's kinetic equation

Let us consider an ideal classical gas at thermal (statistical) equilibrium, consisting of $N \gg 1$ classical identical point particles (molecules) with mass m confined to a volume V; the gas has the density (concentration) $n = N/V$ and the temperature T; its equation of state is $p = nT$, where p is the pressure. The particles in the gas are distributed statistically with respect to their positions $\mathbf{r}$ and velocities $\mathbf{v}$; the distribution function is the Maxwell distribution $F(v) = n(\beta m/2\pi)^{3/2}e^{-\beta mv^2/2}$, $\int d\mathbf{v}F(v) = n$, where $\beta = 1/T$. The condition for a classical gas is $\hbar^2/ma^2 \ll T$, where $\hbar$ is Planck's constant and $a = 1/n^{1/3}$ is the mean inter-particle separation; since $v_{th} = \sqrt{3T/m}$ is the thermal velocity (root mean square velocity), this relation can also be written as $\hbar/mv_{th} \ll a$ (quantum-mechanical energy of localization much smaller than the temperature, quantum-mechanical wavelength much smaller than the mean inter-particle separation).

Let us assume that an external force $\mathbf{K}$ acts upon the particles in the gas; it produces a displacement $\mathbf{u}$ for each particle; we may think to solve the equation of motion $m(d\dot{\mathbf{u}}/dt) = \mathbf{K}$; the solution depends on the time t and the initial conditions $\mathbf{r}$ and $\mathbf{v}$ of the particles; this approach is called the Lagrange approach. Unfortunately, it is not practical, since the trajectories of the particles are disrupted by the molecular collisions. The molecular collisions are present in the gas at thermal equilibrium. The compatibility of the mechanical motion (or other forms of motion) with the thermal motion is the problem of Kinetics.

We may view the displacement $\mathbf{u}$ as a local displacement field $\mathbf{u}(t, \mathbf{r}, \mathbf{v})$ depending on time, position and velocity, and write the equation of motion as $\partial\dot{\mathbf{u}}/\partial t + (\mathbf{v} + \dot{\mathbf{u}})\partial\dot{\mathbf{u}}/\partial\mathbf{r} = \mathbf{K}$, where the effect of the collisions remains to be included. This is the Euler approach. We note the occurrence of the transport term $(\mathbf{v}+\dot{\mathbf{u}})\partial\mathbf{u}/\partial\mathbf{r}$. In solids and fluids the motion is ascribed to small, but macroscopic, regions of matter at equilibrium, such that the velocity $\mathbf{v}$ is absent; moreover, in solids the velocity $\dot{\mathbf{u}}$ is much smaller than the velocity of propagation of the disturbance, such that the term $\dot{\mathbf{u}}\partial\dot{\mathbf{u}}/\partial\mathbf{r}$ is absent too; however, both in solids and fluids there exists an interaction with the neighbouring "particles", similar to the molecular collisions (friction).

In thermal motion we still consider sufficiently large regions of matter, in order to be able to define the concentration, for instance; however, such regions are small enough to allow for fluctuations and molecular collisions; positions and velocities (in general phase-space variables) are continuously and statistically distributed up to the uncertainty of defining these regions; the thermal dynamics is defined in terms of probabilities. It follows that we must consider small displacements $\mathbf{u}$, with small variations in space and time, as well as small effects of the molecular collisions, in order to preserve the basic assumptions of concentration, probability, deviations, uncertainties, fluctuations and, ultimately, the Euler approach. This limitation is in accordance with the external perturbations, which, usually, are small and vary slowly in space and time, in the sense that their effects are small at our space and time scales. In particular, it follows that we may limit ourselves to $\mathbf{v}\partial\dot{\mathbf{u}}/\partial\mathbf{r}$ for the transport term.

The displacement velocity may suffer small changes due to collisions; therefore, an additional term $m\ddot{\mathbf{u}} \simeq m\dot{\mathbf{u}}/\tau$ must be added to the equation of motion, where τ is a large relaxation time; being large, it may be considered constant; therefore, the equation of motion reads

$$\frac{\partial\dot{\mathbf{u}}}{\partial t}+\mathbf{v}\frac{\partial\dot{\mathbf{u}}}{\partial\mathbf{r}}+\gamma\dot{\mathbf{u}}=\frac{\mathbf{K}}{m}\ , \tag{3.1}$$

where $\gamma = 1/\tau$ is the collision frequency.[1] We note that the collision term gives a force which opposes the mechanical motion; this force tends to establish the thermal equilibrium. Under the conditions presented here, equation (3.1) describes the accomodation of the mechanical motion ("mechanical equilibrium") with the thermal equilibrium;

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[1] The dissipation term $\gamma\dot{\mathbf{u}}$ has been introduced by Rayleigh, J. W. Strutt (Lord Rayleigh), "Some general theorems relating to vibrations", Proc. Math. Soc. London **s1-4** 357 (1871).

it describes mechanical motion compatible with thermal equilibrium. The relaxation time τ defines a molecular freepath $l = v\tau$ and a mean freepath $\Lambda = v_{th}\tau$. Close to equilibrium we may neglect the parameter γ, as if, formally, we put $\tau = \infty$. Therefore, we must have $\omega\tau \gg 1$, where ω is the frequency of variation of the displacement u. The limit $\tau \rightarrow \infty$ $(\gamma \rightarrow 0)$ is called the collisionless limit. In addition, we must have $\omega u \ll v$.

Equation (3.1) can be recast in an interesting form. Mechanical motion generates a variation $f = \delta F$ of the equilibrium distribution; it is given by

$$f = \delta F = -\dot{\mathbf{u}}\frac{\partial F}{\partial \mathbf{v}} \ ; \tag{3.2}$$

the minus sign implies a motion with velocity $-\dot{\mathbf{u}}$ ("observer's motion"); we note that $\dot{\mathbf{u}}$ is a local velocity and equation (3.2) is at local equilibrium. We may view $F(v)$ as a velocity density of particles; when $\mathbf{v} \rightarrow \mathbf{v} + \dot{\mathbf{u}}$ this density becomes $F(\mathbf{v} + \dot{\mathbf{u}})$ and the change in density is $\delta F = -[F(\mathbf{v} + \dot{\mathbf{u}}) - F(v)] = -\dot{\mathbf{u}}\partial F/\partial \mathbf{v}$; the minus sign accounts for the fact that this amount of particles is lost. In fact, the process is $F(v) \rightarrow F(\mathbf{v} - \dot{\mathbf{u}})$. Multiplying equation (3.1) by $\partial F/\partial \mathbf{v}$ we get

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{K}}{m}\frac{\partial F}{\partial \mathbf{v}} = -\gamma f \ ; \tag{3.3}$$

this is Boltzmann's kinetic equation.[2] It can also be written as

$$\frac{df}{dt} + \gamma f = 0 \ , \tag{3.4}$$

which shows that the total change brought by the mechanical motion plus the change due to collisions is zero; *i.e.*, the thermal equilibrium is consistent with the mechanical motion, in the terms discussed here. This is the general meaning of the Kinetics. Equation (3.4) may be viewed as the general relaxation equation for any physical quantity.

We note that the equilibrium is local in the Boltzmann kinetic equation; leaving aside the collisions (and the force term), we get the transport equation; the compatibility of this equation with the statistical distribution is assured locally by equation (3.2); but not globally. In this context, we note also that we may use equally well equation (3.1) for kinetic phenomena, or its transport part for transport, each time in the context of local thermal equilibrium.

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[2] L. Boltzmann, *Lectures on Gas Theory*, Dover, NY (1964) (translated from L. Boltzmann, *Vorlesungen uber Gastheorie*, Barth, Leipzig, Part I (1896) and Part II (1898)).

We note also that the collision term γf is relevant for the change f of the distribution function; though present, the collisions do not appear in the equation of motion of the equilibrium function F, which is stationary, *i.e.* $dF/dt = 0$ (this is related, formally, to Liouville's theorem). The dependence on the thermal velocities $\mathbf{v}$ and the occurrence of $\partial F/\partial \mathbf{v}$ in equation (3.3) ensure the thermal equilibrium in the presence of the mechanical motion.

In view of the small contributions in equation (3.1), we should limit ourselves to first-order (small) variations f, as in equation (3.3). The attempt of including higher-order variations in equation (3.3), or non-linearities, is not warranted. The entropy is maximal at equilibrium, such that it is affected only by higher-order variations of the distribution function, not by first-order variations. Therefore, we must consider the change f in the distribution function as an equilibrium transformation.

In general, achieving the thermal (statistical) equilibrium may be viewed as an open problem in Statistical Physics. The existence of the thermal equilibrium and the increase of entropy towards equilibrium, as well as its stationarity at equilibrium, are, in fact, the principles of statistical motion. The existence of γ (and $\gamma > 0$) in equation (3.1) indicates a dissipation of motion, which does not mean, necessarily, equilibrium. The evolution of the statistical distribution towards equilibrium implied by equation (3.4) is generated by the assumption in equation (3.2), which means, in fact, this evolution. A more general analysis of the collisions, made in the next section, strenghtens the hypothetical nature of the thermal equilibrium. Transport phenomena, plasmas or chemical reactions may offer instances of, at least limited, special thermal equilibrium.

3.2 Collision integral

The change in the number of particles with velocity $\mathbf{v}$ per unit time and unit volume due to collisions is given by the collision integral[3]

$$C(\widetilde{F}) = \int (w^{'}\widetilde{F}^{'}\widetilde{F}_1^{'} - w\widetilde{F}\widetilde{F}_1)d\mathbf{v}_1 d\mathbf{v}^{'}d\mathbf{v}_1^{'} \ , \tag{3.5}$$

where two particles with velocities $\mathbf{v}$ and $\mathbf{v}_1$ collide and get velocities $\mathbf{v}^{'}$and $\mathbf{v}_1^{'}$, respectively, the coefficient $w(\mathbf{v}^{'},\mathbf{v}_1^{'};\mathbf{v},\mathbf{v}_1)$ being a probability coefficient; $\widetilde{F}(t,\mathbf{r},\mathbf{v})$ is the distribution function and the notation of the type $\widetilde{F}^{'}$ means $\widetilde{F}^{'} = \widetilde{F}(t,\mathbf{r},\mathbf{v}^{'})$. At equilibrium, the principle of detailed balancing is valid, as a consequence of the time reversal, or the time reversal and space inversion; it provides the equality $w(\mathbf{v}^{'},\mathbf{v}_1^{'};\mathbf{v},\mathbf{v}_1) = w(\mathbf{v},\mathbf{v}_1;\mathbf{v}^{'},\mathbf{v}_1^{'}) = w^{'}(\mathbf{v}^{'},\mathbf{v}_1^{'};\mathbf{v},\mathbf{v}_1)$ (in general, with the corresponding transformed velocities). The total number of collisions is zero, $\int d\mathbf{v}C(\widetilde{F}) = 0$. At equilibrium $F^{'}F_1^{'} = FF_1$, due to the energy conservation at rest; in motion with uniform velocity, the energy and the momentum conservation ensure this equality (in uniform motion with velocity $\mathbf{V}$ the distribution function is proportional to $e^{-\frac{1}{2}\beta mv^2+\beta m\mathbf{V}\mathbf{v}}$). The differential cross-section of a particle is $d\sigma = (w/v_r)d\mathbf{v}^{'}d\mathbf{v}_1^{'}$, where $v_r =\mid \mathbf{v}-\mathbf{v}_1 \mid$ is the relative velocity of the particle in the collision $\mathbf{v}+\mathbf{v}_1 \rightarrow \mathbf{v}^{'}+\mathbf{v}_1^{'}$. The collision integral is non-linear and non-local (in velocities) with respect to the distribution function $\widetilde{F}$; if we attempt to linearize the collision integral by $\widetilde{F} = F + f$, where F is the equilibrium distribution, we get a general expression of the form

$$C(\widetilde{F}) = A(f) - Bf \ , \tag{3.6}$$

where $A(f)$ is a functional of f and B is a (positive) coefficient which may depend on $\mathbf{v}$; we recognize here the collision frequency B. The term $A(f)$, which arises from $w^{'} \neq w$, in general (at non-equilibrium), may take the gas out of equilibrium, while the term $-Bf$ carries the gas towards equilibrium.

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[3] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 10, *Physical Kinetics* (E. Lifshitz and L. Pitaevskii), Elsevier, Oxford (1981).

Obviously, the collision integral changes the distribution function according to $d\widetilde{F}/dt = C(\widetilde{F})$; at equilibrium $C(\widetilde{F}) = 0$, and we recover "Liouville's theorem"

$$\frac{dF}{dt} = \mathbf{v}\frac{\partial F}{\partial \mathbf{r}} + \dot{\mathbf{v}}\frac{\partial F}{d\mathbf{v}} = 0 \ , \tag{3.7}$$

which is an identity, since F does not depend on $\mathbf{r}$ and $\mathbf{v}$ and it does not depend on time. The equation $d\widetilde{F}/dt = C(\widetilde{F})$ and the collision integral given by equation (3.5) are compatible with the increase of the entropy due to collisions (the so-called Boltzmann's H-theorem), which means that in the form given by equation (3.6) the negative terms in $C(\widetilde{F})$, like $-Bf$, prevail over the positive terms; but, of course, it does not provide a "proof" for the second law of Statistical Physics.[4] In fact, the principle of detailed balancing, or the conservation of the quantum-mechanical properties are valid at equilibrium, where $F^{'}F_1^{'} = FF_1$ is valid and the collision integral is vanishing; by such type of reasoning we can only prove the stationarity of the entropy (and Boltzmann's H function) at equilibrium.

In the presence of an external force $\mathbf{K}$ equation $d\widetilde{F}/dt = C(\widetilde{F})$ reads

$$\frac{d\widetilde{F}}{dt} = \frac{\partial \widetilde{F}}{\partial t} + (\mathbf{v} + \dot{\mathbf{u}})\frac{\partial \widetilde{F}}{\partial \mathbf{r}} + \frac{\mathbf{K}}{m}\frac{\partial \widetilde{F}}{\partial \mathbf{v}} = C(\widetilde{F}) \ , \tag{3.8}$$

where $\widetilde{F}(t, \mathbf{r}, \mathbf{v})$ becomes a function $\widetilde{F}(t, \mathbf{r}, \mathbf{v}+\dot{\mathbf{u}})$; in addition, we have

$$\frac{\partial \dot{\mathbf{u}}}{\partial t} + (\mathbf{v} + \dot{\mathbf{u}})\frac{\partial \dot{\mathbf{u}}}{\partial \mathbf{r}} + c = \frac{\mathbf{K}}{m} \ , \tag{3.9}$$

where c is an undetermined collision term (corresponding to $\gamma\dot{\mathbf{u}}$ in equation (3.1)). The two coupled equations (3.8) and (3.9) describe the evolution of a gas at non-equilibrium in the presence of an external force. We leave aside here this very complicate (and, probably, not very relevant) problem.

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[4] The entropy of the classical gas of point particles is $S = -\int d\tau \rho \ln(\rho/e)$, where $d\tau = d\mathbf{r}d\mathbf{v}/(2\pi\hbar)^3$ and $\int d\tau\rho = N$ (L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier, Oxford (1980)); we can see that the phase-space distribution function ρ is proportional to $\widetilde{F}$. The technical points used in the H-theorem presuppose statistical equilibrium or relate it to other types of motion; in particular the Stueckelberg property of the collision probabilities (E. C. G. Stueckelberg, "Théorème H et unitarité de S", Helv. Phys. Acta **25** 577 (1952); L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 10, *Physical Kinetics* (E. Lifshitz and L. Pitaevskii), Elsevier, Oxford (1981)) assumes the quantum-mechanical motion.

If the $\dot{\mathbf{u}}$-term in equation (3.8) is sufficiently small to be neglected, then the $\mathbf{K}$-term is also sufficiently small to be neglected (and viceversa), such that, we are left with the equation

$$\frac{\partial \widetilde{F}}{\partial t} + \mathbf{v}\frac{\partial \widetilde{F}}{\partial \mathbf{r}} = C(\widetilde{F}) \ ; \tag{3.10}$$

this equation describes the evolution of the gas at non-equilibrium; for local equilibrium the collision term is zero and the remaining equation $\partial f/\partial t + \mathbf{v}\partial f/\partial \mathbf{r} = 0$ for $f = \widetilde{F} - F$ describes transport phenomena. We may be tempted to absorb the velocity $\dot{\mathbf{u}}$ in the velocities $\mathbf{v}$ in equation (3.8); not only the $\mathbf{K}$-term becomes then irrelevant, and it should be dropped, but the function $\widetilde{F}$ becomes the equilibrium function, the collision term is zero and we are left with a trivial identity. Equation

$$\frac{\partial \widetilde{F}}{\partial t} + \mathbf{v}\frac{\partial \widetilde{F}}{\partial \mathbf{r}} + \frac{\mathbf{K}}{m}\frac{\partial \widetilde{F}}{\partial \mathbf{v}} = C(\widetilde{F}) \tag{3.11}$$

is inconsistent. Indeed, making use of $\widetilde{F} = F + f$, where F is the equilibrium distribution, and using also equation (3.6), we may write it as

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{K}}{m}\frac{\partial F}{\partial \mathbf{v}} + \frac{\mathbf{K}}{m}\frac{\partial f}{\partial \mathbf{v}} = A(f) - Bf \ , \tag{3.12}$$

or

$$\frac{\mathbf{K}}{m}\frac{\partial f}{\partial \mathbf{v}} = A(f) - Bf + \gamma f \ ; \tag{3.13}$$

since both terms Bf and γf have a common nature, we may take them equal; but, even leaving aside this circumstance, we are left with an equation which shows that the external force would be determined by equilibrium, which is a non-sense.

3.3 Solution of the Boltzmann equation

Let us assume a sufficiently general force of the form

$$\mathbf{K} = \mathbf{K}_0 e^{-i\omega t + i\mathbf{k}\mathbf{r}} \ , \tag{3.14}$$

where ω is a frequency, $\mathbf{k}$ is a wavevector and $\mathbf{K}_0$ is a constant; we consider the real part of this force. We give here the solution of the Boltzmann equation (3.3)

$$\frac{\partial f}{\partial t}+\mathbf{v}\frac{\partial f}{\partial \mathbf{r}}+\gamma f=-\frac{\mathbf{K}_0}{m}\frac{\partial F}{\partial \mathbf{v}}e^{-i\omega t+i\mathbf{kr}} \ ; \tag{3.15}$$

the boundary condition for $v\rightarrow\infty$ is $f\rightarrow 0$ (or the usual plane wave); the initial condition is $f(t=0,\mathbf{r},\mathbf{v})=0$. The solution is the sum $f=f_1+f_2$ of the solution f_1 of the homogeneous equation

$$\frac{\partial f_1}{\partial t}+\mathbf{v}\frac{\partial f_1}{\partial \mathbf{r}}+\gamma f_1=0 \tag{3.16}$$

and a particular solution f_2 of the inhomogeneous equation

$$\frac{\partial f_2}{\partial t}+\mathbf{v}\frac{\partial f_2}{\partial \mathbf{r}}+\gamma f_2=-\frac{\mathbf{K}_0}{m}\frac{\partial F}{\partial \mathbf{v}}e^{-i\omega t+i\mathbf{kr}} \ . \tag{3.17}$$

The solution f_1 is

$$f_1=Ce^{-i\mathbf{vq}t+i\mathbf{qr}-\gamma t} \ , \tag{3.18}$$

where C and $\mathbf{q}$ are undetermined constants; the solution f_2 is

$$f_2=-\frac{i}{\omega-\mathbf{vk}+i\gamma}\cdot\frac{\mathbf{K}_0}{m}\frac{\partial F}{\partial \mathbf{v}}e^{-i\omega t+i\mathbf{kr}} \ ; \tag{3.19}$$

the condition $f(t=0)=f_1(t=0)+f_2(t=0)=0$ gives $\mathbf{q}=\mathbf{k}$ and

$$C=\frac{i}{\omega-\mathbf{vk}+i\gamma}\cdot\frac{\mathbf{K}_0}{m}\frac{\partial F}{\partial \mathbf{v}} \ , \tag{3.20}$$

such that the full solution is

$$f=-\frac{i}{\omega-\mathbf{vk}+i\gamma}\cdot\frac{\mathbf{K}_0}{m}\frac{\partial F}{\partial \mathbf{v}}\left(e^{-i\omega t}-e^{-i\mathbf{vk}t-\gamma t}\right)e^{i\mathbf{kr}} \ . \tag{3.21}$$

We can see that the solution consists of two parts: an eigenmode of the transport equation $\partial f_1/\partial t+\mathbf{v}\partial f_1/\partial\mathbf{r}=-\gamma f_1$ (homogeneous equation) for $\mathbf{q}=\mathbf{k}$, which is damped; and a stationary part f_2. The force takes the gas out of equilibrium at the initial moment, excites the eigenmode, which relaxes in time, and finally the gas accomodates the stationary motion produced by the force; this mechanical motion included, the gas is at equilibrium. Therefore, at long times we may take

$$f = -\frac{i}{\omega - \mathbf{vk} + i\gamma} \cdot \frac{\mathbf{K}_0}{m}\frac{\partial F}{\partial \mathbf{v}} e^{-i\omega t + i\mathbf{kr}} \ , \tag{3.22}$$

or

$$f = -\frac{(\omega - \mathbf{vk})\sin(\omega t - \mathbf{kr}) + \gamma\cos(\omega t - \mathbf{kr})}{(\omega - \mathbf{vk})^2 + \gamma^2} \cdot \frac{\mathbf{K}_0}{m}\frac{\partial F}{\partial \mathbf{v}} \ , \tag{3.23}$$

where we have taken the real part. We note that f can be written as $f = -\dot{\mathbf{u}}\partial F/\partial \mathbf{v}$, where

$$\dot{\mathbf{u}} = \frac{i}{\omega - \mathbf{vk} + i\gamma} \cdot \frac{\mathbf{K}_0}{m} e^{-i\omega t + i\mathbf{kr}} \ , \tag{3.24}$$

from equation (3.1) and in accordance with equation (3.2); therefore, the full distribution function can be written as

$$\widetilde{F} = F + f = F - \dot{\mathbf{u}}\partial F/\partial \mathbf{v} \simeq F(\mathbf{v} - \dot{\mathbf{u}}) \ ; \tag{3.25}$$

we can see that the equilibrium form of the distribution function is preserved in the presence of the external field; $\dot{\mathbf{u}}$ depends on time, position and velocity ("Liouville's theorem" does not apply, since the gas is not isolated anymore). It should be emphasized that we limit ourselves to linear terms in $\dot{\mathbf{u}}$ in equation (3.25), *i.e.*

$$\widetilde{F} = F - \dot{\mathbf{u}}\partial F/\partial \mathbf{v} \sim e^{-\frac{1}{2}\beta m v^2 + \beta m \mathbf{v}\dot{\mathbf{u}}} \ , \tag{3.26}$$

in accordance with the general assumption given in equation (3.2).

We note that in writing $\mathbf{v} - \dot{\mathbf{u}}$ in the argument of the distribution function above we understand in fact $mv^2/2 - m\mathbf{v}\dot{\mathbf{u}}$, which can also be written as $m(\mathbf{v} - \dot{\mathbf{u}})^2/2 - m\dot{\mathbf{u}}^2/2$; if there exists a potential energy U of the external force, we have $m\dot{\mathbf{u}}^2/2 + U = const$ (leaving aside the spatial dependence), and our expression becomes $m(\mathbf{v} - \dot{\mathbf{u}})^2/2 + U$, up to an immaterial constant; with the redefinition of the velocities, this is the sum of the kinetic and potential energy, which is the correct exponential factor in the equilibrium distribution. Strictly speaking, the kinetic effects are limited to using $f = -\dot{\mathbf{u}}\partial F/\partial \mathbf{v}$, without using exponential form and discarding higher-order terms in $\dot{\mathbf{u}}$; consequently, full equilibrium contributions may not arise formally in the kinetic approach.

We note that equation (3.11) with a harmonic-like force $\sim e^{-i\omega t+i\mathbf{kr}}$ can be solved recursively with a series of higher-order harmonics; the solution includes terms both increasing and decreasing in time, according to the structure of the collision integral, which has the form $I_1(\widetilde{F})-I_2(\widetilde{F})\widetilde{F}$, where $I_{1,2}$ are the corresponding integrals in equation (3.5); leaving aside that the solution cannot satisfy a spatially-uniform initial condition for a non-uniform force, since the equation does not include a free term, the existence of a stationary regime cannot be achieved.

Also, we note a more general method of solving equation (3.15) by using Fourier transforms; to this end it is convenient to include the initial condition in equation. The procedure consists in multiplying the equation by the step function $\theta(t)$ ($\theta(t) = 1$ for $t > 0$, $\theta(t) = 0$ for $t < 0$), absorbing the factor θ into the time derivative and limiting ourselves to $t > 0$; this way an additional term $f(t = 0)\delta(t)$ appears on the right in equation (3.15) (which becomes an equation with generalized functions (distributions)) and the solution can be obtained by using time Fourier expansions.

There is another important point worthwhile discussing here. The motion of the particles exchanges energy with the external agent. Due to collisions, they dissipate this energy to the ensemble of particles, with a rate which is controlled by the collision frequency γ; in the long run, the transferred energy changes the temperature of the ensemble. From equation (3.25) we may be tempted to estimate the change in temperature as $\delta T \simeq m\overline{\dot{\mathbf{u}}^2}$, where the average should be taken over velocities, space and time; in addition, for instance, $\overline{\dot{\mathbf{u}}} = (1/n)\int d\mathbf{v}F\dot{\mathbf{u}}$. However, this estimation is not warranted by the kinetic approach. The change in temperature may be estimated from $mv^2/2 - m\mathbf{v}\dot{\mathbf{u}}$ in the exponent of the distribution function; we get $\delta T = m\overline{\mathbf{v}\dot{\mathbf{u}}} = T\overline{f/F}$, where the average means $N^{-1}\int(f/F)Fd\mathbf{v}d\mathbf{r}$. Making use of f given by equation (3.22), we get $\delta T = 0$. The Fourier components of the forces do not change the temperature.

3.4 Thermalization

Let us assume that the gas is taken out of equilibrium by a localized force $\mathbf{K} = \mathbf{K}_0\delta(\mathbf{r})\delta(t)$; equation (3.15) reads

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} + \gamma f = -f_0\delta(\mathbf{r})\delta(t) \ , \tag{3.27}$$

where $f_0 = (\mathbf{K}_0/m)(\partial F/\partial \mathbf{v})$. This is the homogeneous equation for the distribution with the initial condition $f(t = 0) = -f_0\delta(\mathbf{r})$. The solution is a superposition of damped plane waves given by equation (3.18) which leads to

$$f = -f_0\delta(\mathbf{r} - \mathbf{v}t)e^{-\gamma t} \ . \tag{3.28}$$

We can see that the perturbation propagates as a succession of damped spherical shells moving with distinct velocities. An estimate of the relaxation (thermalization) time is provided by $\tau = 1/\gamma \simeq \Delta l/v_{th}$, where Δl is the spatial extension of the original perturbation and $v_{th} = \sqrt{T/m}$ is the thermal velocity.

It is worth discussing in this context the thermalization of quantum-mechanical ensembles. Macroscopic bodies (consisting of $N \gg 1$ particles) have not (definite) energy levels, in the sense that the number of energy levels in a finite range of energy is enormous; the energy levels of a macroscopic body are very densely distributed. The degenerate energy level of two interacting particles are split by interaction; a third particle causes another splitting, and so on, such that the number of energy levels of N particles is of the order 2^N. The statistical matrix moves according to $\dot{w}_{nm} = \frac{i}{\hbar}(E_m - E_n)w_{nm}$, while at equilibrium it is $w_n = e^{-\beta E_n}/\sum_n e^{-\beta E_n}$. The energy $E_n = E$ in these formulae are distributed continuously. The deviation f of $w_n = F$ from equilibrium obeys the equation

$$\frac{\partial f}{\partial t} + \frac{\partial F}{\partial E}\frac{\partial E}{\partial t} = -\gamma f \ , \tag{3.29}$$

where $P = \partial E/\partial t$ $(= dE/dt)$ is the external power introduced in the body or absorbed from the body. We note that the variable is the energy, while a spatial variation pertains only to classical (or quasi-classical) ensembles. Let us assume $P = TP_0\delta(t)$, *i.e.* a power pulse of a short duration T; the solution is $f = \beta F T P_0 e^{-\gamma t}$ ($\partial F/\partial E = -\beta F$). The product TP_0 is the amount of energy ΔE exchanged in time T. The energy ΔE does not change the distribution of energy levels; it follows that we have an estimate $\tau = 1/\gamma \simeq T \simeq \hbar/\Delta E$ for the relaxation (thermalization) rate.

Small samples of condensed matter thermalize quickly, while the thermalization may become problematic in the nanoscopic range ($10 - 10^3$Å); in the mesoscopic range ($10^3 - 10^5$Å) the fluctuations are large.

3.5 A particular case: constant and uniform force

Let us assume a constant uniform force $\mathbf{K}$ directed along the $-z$ axis, like the gravitational force at the Earth's surface; therefore, we take $K_z = -mg$, where g is the gravitational constant. Equation (3.15) reads

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial z} + \gamma f = g\frac{\partial F}{\partial v} \ , \tag{3.30}$$

where $v = v_z$. We may leave aside the transient part of the solution (damped in time) and neglect γ in the stationary (particular solution); with the initial condition $f(t=0) = 0$ we get

$$f = gt\frac{\partial F}{\partial v} \ ; \tag{3.31}$$

making use of $F \sim e^{-\frac{1}{2}\beta m v^2}$, the modified distribution function is

$$\widetilde{F} = Ce^{-\frac{1}{2}\beta m v^2 - \beta m v g t} \ , \tag{3.32}$$

where we leave aside the components $\sim e^{-\frac{1}{2}\beta m(v_x^2+v_y^2)}$ and the constant C remains to be determined; we note the limitation to the linear term in gt in the exponent. The expression in equation (3.32) can also be written as

$$\widetilde{F} = Ce^{-\frac{1}{2}\beta m(v+gt)^2 + \frac{1}{2}\beta m g^2 t^2} \ ; \tag{3.33}$$

now, we note that gt is the velocity $-\dot{u}$ acquired by the particle and $z = -gt^2/2$ is the displacement of the particle along the z-axis; therefore, the term $\frac{1}{2}\beta m g^2 t^2$ in the exponent in equation (3.33) can be written as $\frac{1}{2}\beta m g^2 t^2 = -\beta m g z$; we recognize here the potential energy $U = mgz$, such that this term becomes

$$\frac{1}{2}\beta m g^2 t^2 = -\beta m g z = -\beta U \ ; \tag{3.34}$$

the distribution function acquires the form

$$\widetilde{F} = C e^{-\frac{1}{2}\beta m (v+gt)^2 - \beta m g z} = C e^{-\frac{1}{2}\beta m (v+gt)^2 - \beta U} \ , \tag{3.35}$$

which, with the redefinition $v \rightarrow v^{'} + gt$ of the velocity, acquires the standard form of the equilibrium (Gibbs) distribution. The constant C can be computed easily; we get the (full) distribution function

$$\widetilde{F} = n_s (\beta m / 2\pi)^{3/2} \beta m g \cdot e^{-\frac{1}{2}\beta m v^2 - \beta m g z} \ , \tag{3.36}$$

where n_s is the surface density of particles (number of particles per unit cross section in the z-direction); the number of particles per unit volume is given by

$$n = \int \widetilde{F} d\mathbf{v} = n_s \beta m g \cdot e^{-\beta m g z} \ , \tag{3.37}$$

which is the well known barometric formula; usually, $n_s \beta m g$ is replaced by the density n_0 at the level $z = 0$.

We note that, strictly speaking, the derivation given above of the barometric formula by using the kinetic approach, is not rigorous, since it implies the quadratic term$\sim g^2 t^2 = \dot{u}^2$, which is not valid in the kinetic approach.

3.6 Other particular cases

Let us assume a uniform oscillating force $K_1 e^{-i\omega t}$ directed along the x-axis; we denote the axes by x, y, z or 1, 2, 3. Equation (3.15) reads

$$\frac{\partial f}{\partial t} + \gamma f = -\frac{K_1}{m} \frac{\partial F}{\partial v_1} e^{-i\omega t} \ ; \tag{3.38}$$

the solution is

$$f = -\frac{i}{\omega + i\gamma} \frac{K_1}{m} \frac{\partial F}{\partial v_1} e^{-i\omega t} \ ; \tag{3.39}$$

its real part is

$$Ref = \frac{\omega \sin \omega t + \gamma \cos \omega t}{\omega^2 + \gamma^2} K_1 \beta v_1 F \ ; \tag{3.40}$$

the full distribution function is

$$\widetilde{F} = C \left(1 + \frac{\omega \sin \omega t + \gamma \cos \omega t}{\omega^2 + \gamma^2} K_1 \beta v_1 \right) e^{-\frac{1}{2}\beta m v^2} \ ; \tag{3.41}$$

the v_1-term does not contribute to the integral of $\widetilde{F}$, since it is an odd function of v_1; therefore, the normalization constant is $C = n(\beta m/2\pi)^{3/2}$; the distribution function is

$$\widetilde{F} = n(\beta m/2\pi)^{3/2} \left(1 + \frac{\omega \sin \omega t + \gamma \cos \omega t}{\omega^2 + \gamma^2} K_1 \beta v_1 \right) e^{-\frac{1}{2}\beta m v^2} \ ; \tag{3.42}$$

for finite ω we may take $\gamma \to 0$, in accordance with our general assumptions. We may see that mean values of some physical quantities are affected by the force; for instance $\overline{v}_1$ is not zero anymore; it is

$$\overline{v}_1 = \frac{K_1}{m\omega} \sin \omega t \ . \tag{3.43}$$

Let us consider a longitudinal constant non-uniform force $K_1 e^{ikx}$; equation (3.15) reads

$$v_1 \frac{\partial f}{\partial x} + \gamma f = -\frac{K_1}{m} \frac{\partial F}{\partial v_1} e^{ikx} \tag{3.44}$$

with the solution (real part)

$$Ref = \frac{sinkx}{k} K_1 \beta F \ ; \tag{3.45}$$

the distribution function is

$$\widetilde{F} = C \left(1 + \frac{sinkx}{k} K_1 \beta \right) e^{-\frac{1}{2}\beta m v^2} \ ; \tag{3.46}$$

for determining the normalization constant we need to integrate over the volume too; the $\sin kx$-term does not contribute to this integral; therefore, the distribution function reads

$$\widetilde{F} = n(\beta m/2\pi)^{3/2} \left(1 + \frac{sinkx}{k} K_1 \beta \right) e^{-\frac{1}{2}\beta m v^2} \ ; \tag{3.47}$$

we can see that functions which depend on x may have a non-zero contribution to their mean values arising from the force.

Let us consider a transverse constant non-uniform force $K_1 e^{ikx}$; equation (3.15) is

$$v_1 \frac{\partial f}{\partial x} + \gamma f = -\frac{K_2}{m}\frac{\partial F}{\partial v_2} e^{ikx} \ , \tag{3.48}$$

with solution

$$f = -\frac{i}{v_1 k - i\gamma} K_2 \beta v_2 F e^{ikx} \ ; \tag{3.49}$$

the renormalization constant C is determined from

$$\begin{gathered} C(V \int d\mathbf{v} e^{-\frac{1}{2}\beta m v^2} + K_2 \beta Im \int dx dv_1 \tfrac{1}{v_1 k - i\gamma} e^{-\frac{1}{2}\beta m v_1^2} \times \\ \times \int dy dv_2 \cdot v_2 e^{-\frac{1}{2}\beta m v_2^2} \int dz dv_3 e^{-\frac{1}{2}\beta m v_3^2}) = N \ ; \end{gathered} \tag{3.50}$$

the contribution of f to C is zero, due to the integration over x (or v_2); we write the distribution function as

$$\widetilde{F} = n(\beta m/2\pi)^{3/2} \left(1 - Re \frac{i}{v_1 k - i\gamma} K_2 \beta v_2 e^{ikx}\right) e^{-\frac{1}{2}\beta m v^2} \ ; \tag{3.51}$$

it is important to maintain the coefficient γ in the denominator, because it shows the way to avoid the singularity $v_1 = 0$; in fact, we may take $\gamma \to 0^+$, and write the distribution function as

$$\widetilde{F} = n(\beta m/2\pi)^{3/2} \left(1 - Re \frac{i}{v_1 k - i0^+} K_2 \beta v_2 e^{ikx}\right) e^{-\frac{1}{2}\beta m v^2} \ , \tag{3.52}$$

where

$$\frac{1}{v_1 k - i0^+} = \frac{1}{k} P \frac{1}{v_1} + \frac{i\pi}{k}\delta(v_1) \ ; \tag{3.53}$$

P in equation (3.53) denotes the (Cauchy) principal value.

3.7 General case. Landau damping

Let us consider the general case where ω and $\mathbf{k}$ are non-zero; making use of equation (3.22) the distribution function can be written as

$$\widetilde{F} = C\left(1 - Im \frac{1}{\omega - \mathbf{vk} + i\gamma} \cdot \beta \mathbf{K}_0 \mathbf{v} e^{-i\omega t + i\mathbf{kr}}\right) e^{-\frac{1}{2}\beta m v^2} \ , \tag{3.54}$$

where the constant C is determined from

$$C[V(2\pi/\beta m)^{3/2}- \\ -Im\int d\mathbf{r}d\mathbf{v}\frac{e^{-\frac{1}{2}\beta mv^2}}{\omega-\mathbf{vk}+i\gamma}\cdot\beta\mathbf{K}_0\mathbf{v}e^{-i\omega t+i\mathbf{kr}}]=N\ ; \tag{3.55}$$

the integral in equation (3.55) is zero, due to the $\mathbf{r}$-integration. It follows

$$\widetilde{F}=n(\beta m/2\pi)^{3/2}\cdot \\ \cdot\left(1-Im\frac{1}{\omega-\mathbf{vk}+i\gamma}\cdot\beta\mathbf{K}_0\mathbf{v}e^{-i\omega t+i\mathbf{kr}}\right)e^{-\frac{1}{2}\beta mv^2}\ . \tag{3.56}$$

The evaluation of the integral

$$I=\int d\mathbf{v}\frac{G}{\omega-\mathbf{vk}+i\gamma}\ , \tag{3.57}$$

where G is a function of $\mathbf{v}$, is particularly important.

When we try to get functions of time, by integrating over ω in Fourier transforms, we must observe the causality principle, which tells us that a perturbation occurring at $t=0$ must not propagate in the past ($t<0$), but it must have effects only in the future ($t>0$). We can see that for $t<0$ we should integrate over the upper ω-half-plane, while for $t>0$ we should integrate over the lower ω-half-plane (due to the factor $e^{-i\omega t}$); therefore, the integrand should have ω-poles only in the lower ω-half-plane; indeed, this is the case with our function in the integral in equation (3.57), where the pole is $\omega=\mathbf{vk}-i\gamma$, $\gamma>0$. The result of the integration is then $\sim e^{-\gamma t}$, which shows that the perturbation not only acts in the future, but it is also damped in time; any perturbation should take us to equilibrium after a shorter or longer time. Thus, the causality principle is in accordance with the second law of Statistical Physics. Therefore, in these cases, we should maintain the coefficient γ in our equations; however, according to our general conditions γ is a small parameter, such that we may take it to zero in the final results, which refer to equilibrium. An illustration of this circumstance is given below, for the "dissipated" energy.

On the other hand, in many cases of computing physical quantities we need integrals like the integral in equation (3.57) over velocity. In such cases we may take $\gamma \to 0^+$, according to our general conditions, as for finite physical quantities; this means to use the identity

$$\frac{1}{\omega - \mathbf{vk} + i\gamma} \to \frac{1}{\omega - \mathbf{vk} + i0^+} = P\frac{1}{\omega - \mathbf{vk}} - i\pi\delta(\omega - \mathbf{vk}) \ , \quad (3.58)$$

where P denotes the principal value. The procedure ensures a finite lifetime (a damping) for the resonance $\omega = \mathbf{vk}$, which otherwise would have a zero integration measure. We can see that the principle of causality and the principle of establishing the thermal equilibrium give a sense to the resonant modes of individual particles ($\omega = \mathbf{vk}$), which are responsible for the lifetime of the collective modes (the modes $\omega = \mathbf{vk}$ are collective since the resonance $\omega = \mathbf{vk}$ implies all the $\mathbf{k}$ located on a plane perpendicular to $\mathbf{v}$; such sort of zero-measure contributions (in this case a plane, *i.e.* a surface-like contribution) are important in collective modes); the profound technical reason for such a circumstance resides in the linear dependence on v of the denominator in equation (3.58). The damping brought about by the $i\pi\delta$-term in equation (3.58) is called Landau damping; the collective resonance $\omega - \mathbf{vk} = 0$ is called Landau (or Vlasov) resonance.[5] It is true indeed that a collective mode has only one frequency, in comparison with the multitude of frequencies of the individual particles, but to it contribute all the particles, which makes its strength comparable with the strength of all the individual modes. The macroscopic relevance of the marginal character of the collective modes follows from their resonant behaviour. This is another illustration of the concept of emergent dynamics.[6] The collective mode has only one frequency, but to it participate many particles, so it has macroscopic relevance: indeed "more is different"; this is the principle of emergent dynamics. On the other hand, the number of particles which participate to the lifetime of the collective mode is of zero-measure, but their singular (resonant) behaviour makes their contribution macroscopically relevant; therefore, the "infinite" is different too; which may be seen also as "more is different".

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[5] L. Landau, "On the vibrations of the electronic plasma", ZhETF **16** 574 (1946) (J. Phys. USSR **10** 25 (1946)) (in Russian); A. A. Vlasov, "On the kinetic theory of an assembly of particles with collective interaction", J. Phys. (USSR) **9** 25 (1945) (in Russian).

[6] P. W. Anderson, "More is different: broken symmetry and the nature of the hierarchical structure of science", Science **177** 393 (1972).

The distribution function established above is an equilibrium distribution function; the kinetic approach accommodates mechanical motion with thermal equilibrium. One may wonder how does a dissipation occur, like the one of the damped collective modes, at equilibrium. Actually, the kinetic approach indicates the (slow) evolution to equilibrium, as expressed by the small coefficient γ (and seen also in the damped transient solution which was discarded in the above treatment); in other words, the calculations are done by taking the limit $\gamma \rightarrow 0$ in the final results. In this respect we recall that the kinetic equation is established from the equation of mechanical motion (3.1) with friction,

$$\frac{d\dot{\mathbf{u}}}{dt} + \gamma\dot{\mathbf{u}} = \frac{\mathbf{K}}{m} \ , \tag{3.59}$$

which implies the energy conservation

$$\frac{d}{dt}\left(\frac{1}{2}m\dot{\mathbf{u}}^2\right) + m\gamma\dot{\mathbf{u}}^2 = \dot{\mathbf{u}}\mathbf{K} \ ; \tag{3.60}$$

this equation shows that the mechanical work per unit time $\dot{\mathbf{u}}\mathbf{K}$ of the external force $\mathbf{K}$ is equal to the rate of change in time of the kinetic energy $d(m\dot{\mathbf{u}}^2/2)/dt$ plus the rate of dissipated energy $m\gamma\dot{\mathbf{u}}^2$; since the dissipated energy $m\dot{\mathbf{u}}^2$ is quadratic in $\dot{\mathbf{u}}$ we may neglect it according to our general assumptions; moreover, in the final results we may take $\gamma \rightarrow 0$, which again amounts to neglecting the dissipation; under these conditions the kinetic evolution is, indeed, one of equilibrium.

3.8 Calculation of the principal value

In equation (3.57) we limit to the velocity component denoted by v along the wavevector $\mathbf{k}$; we show here how to compute the principal value

$$I_1 = P\int dv\frac{G(v)}{\omega - vk} \ . \tag{3.61}$$

Since the function is integrable (goes to zero at infinity) and the principal value vanishes in the neighbourhood of the singularity, we may restrict to $\mid vk/\omega \mid < 1$) and use a series expansion; we get

$$I_1 = \frac{1}{\omega}\int dvG(v)\left(1 + \frac{vk}{\omega} + \frac{v^2k^2}{\omega^2} + ...\right) \ ; \tag{3.62}$$

this method gives a sufficiently accurate estimation of the principal value for $\omega \neq 0$.

3.9 Non-equilibrium entropy

Let us assume groups of N_i particles, each with G_i states; the total number of microscopic states of the i-th group is $G_i^{N_i}/N_i!$; the entropy is

$$S = \sum_i \ln\left(G_i^{N_i}/N_i!\right) = \sum_i N_i \ln(eG_i/N_i) \;; \tag{3.63}$$

or, with the mean number of particles $n_i = N_i/G_i$,

$$S = \sum G_i n_i \ln(e/n_i) \;; \tag{3.64}$$

the weight G_i can be written as

$$G_i = \Delta p^{(i)} \Delta q^{(i)}/(2\pi\hbar)^s = \Delta\tau^{(i)} \;, \tag{3.65}$$

where p are momenta, w are coordinates, $\hbar$ is Planck's constant and τ denotes the number of states in the phase space; we get

$$S = -\int d\tau n \ln(n/e) \;. \tag{3.66}$$

Let us maximize it, with the constraints of a fixed number of particles and a fixed energy; we need the minimum of

$$-\int d\tau n \ln(n/e) + \beta\mu \int d\tau n - \beta \int d\tau \varepsilon n \;; \tag{3.67}$$

we get

$$dE = TdS + \mu dN \;, \tag{3.68}$$

where N is the total number of particles, E is the total energy (and ε is the energy of a particle); also, we get

$$n = const \cdot e^{\beta\mu} e^{-\beta\varepsilon} \;, \tag{3.69}$$

which is the Gibbs distribution with μ the chemical potential and $\beta = 1/T$ is the reciprocal of the temperature T; this is the equilibrium distribution; the constant is determined by $N = \int d\tau n$; the volume is constant; if an external energy (per particle) Φ is present, then $\varepsilon \to \varepsilon + \Phi$.

3.10 Approach to equilibrium

Let us assume that an ideal classical gas of identical particles is at equilibrium, with a distribution function F which depends on the velocities $\mathbf{v}$ of the particles; actually, it is easy to see that F is a function of v^2; if $\mathbf{v}$ is changed by $\mathbf{v} \longrightarrow \mathbf{v} + \dot{\mathbf{u}}$, where $\dot{\mathbf{u}}$ is an external velocity, then the change in the square of the velocity is $\delta(v^2) = 2\dot{\mathbf{u}}\mathbf{v}$ and we have the change

$$\delta F = -\delta(v^2)\frac{\partial F}{\partial(v^2)} = -2\dot{\mathbf{u}}\mathbf{v}\frac{\partial F}{\partial(v^2)} = -\dot{\mathbf{u}}\frac{\partial F}{\partial \mathbf{v}} \tag{3.70}$$

in the distribution, as in equation (3.2); the minus sign is chosen for physical reasons, which will become obvious shortly. In equation (3.70) $2\dot{\mathbf{u}}\mathbf{v}$ may also be viewed as the change in $\dot{u}^2$, when the velocity is brought from infinity to value $\mathbf{v}$; *i.e.*, we may write also

$$\delta F = -\delta(\dot{u}^2)\frac{\partial F}{\partial(v^2)} \quad ; \tag{3.71}$$

in this equation $\delta(\dot{u}^2)$ is an external parameter, such that δF should be proportional to it; moreover, while going from $\mathbf{v} = \infty$ to $\mathbf{v}$, the equilibrium distribution function changes from zero to a value which is proportional to F; it follows that we can write

$$\frac{\delta F}{\delta(\dot{u}^2)} = \frac{\lambda\delta(\dot{u}^2)F}{\delta(\dot{u}^2)} = \lambda F \quad , \tag{3.72}$$

where λ is a constant. By comparing equations (3.71) and (3.72), we get

$$\frac{\partial F}{\partial(v^2)} = -\lambda F \tag{3.73}$$

and the Maxwell distribution $F \sim e^{-\lambda v^2}$. Therefore, if equilibrium exists, the equilibrium distribution function is well determined (which, in fact, amounts to the existence of the equilibrium), and it is the Maxwell distribution. Making use of the entropy S and the normalization condition of the distribution F, we can identify the amount of heat TdS in energy, where $T = 1/\beta$ is the temperature.

Let us assume that a static, non-uniform external field with potential energy $U(\mathbf{r})$ is applied to an ideal classical gas of identical particles with mass m. The change produced in gas is described by the change f in the distribution function which satisfies the Boltzmann equation (3.3)

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} + \gamma f = -\frac{\mathbf{K}}{m}\frac{\partial F}{\partial \mathbf{v}} \quad , \tag{3.74}$$

where the force is given by $\mathbf{K} = -\partial U/\partial \mathbf{r}$. The solutions of the homogeneous part of this equation go to zero after a long time, while the stationary, equilibrium solution is given by

$$\mathbf{v}\frac{\partial f}{\partial \mathbf{r}} = -\frac{\mathbf{K}}{m}\frac{\partial F}{\partial \mathbf{v}} = -\beta \mathbf{v}\frac{\partial U}{\partial \mathbf{r}}F \ ; \tag{3.75}$$

hence, $f = -\beta UF$ and the modified distribution is given by

$$\widetilde{F} = F - \beta UF = Fe^{-\beta U} \sim e^{-\frac{1}{2}\beta mv^2 - \beta U} \tag{3.76}$$

(for $\beta \mid U \mid \ll 1$). We can see that the gas, in the presence of a static external field, tends to equilibrium, where its statistical distribution is the Gibbs distribution. The particle density becomes non-uniform,

$$n(\mathbf{r}) = \int d\mathbf{v}Fe^{-\beta U(\mathbf{r})} = ne^{-\beta U(\mathbf{r})} \ . \tag{3.77}$$

During the process of establishing the equilibrium the forces acting upon the particles do a mechanical work, which, other parameters being unchanged, results in an increase in temperature. This temperature change can be estimated from the variation of the free energy (for constant volume and number of particles). For $\beta \mid U \mid \ll 1$ we can estimate this change by writing

$$\frac{mv^2}{2T} + \frac{U}{T} = \frac{mv^2}{2T}\left(1 + \frac{U}{mv^2/2}\right) \quad , \tag{3.78}$$

whence we get $\delta T \simeq -U$, with the mean value for $m\overline{v^2}/2 \simeq T$. Such an estimation is in agreement with the virial coefficients of a non-ideal gas, where the field U is an interaction field between particles. We can see that the temperature variation is non-uniform; in those points where $U > 0$, the temperature decreases, and it increases where $U < 0$.

A global estimation would require a spatial mean value $\overline{U}$. The spatial average eliminates the effect of the Fourier components, except for the uniform one; we can see again that forces derived from potentials which have Fourier transforms do not change the temperature (the gravitational potential has not a Fourier transform).

The solution $f = -\beta UF$ given above implies, according to equation (3.2),

$$f = -\beta UF = -\dot{\mathbf{u}}\frac{\partial F}{\partial \mathbf{v}} = \beta m\dot{\mathbf{u}}\mathbf{v}F \quad , \tag{3.79}$$

whence $m\dot{\mathbf{u}}\mathbf{v} = -U$, or

$$\delta E_{kin} + U = 0 \quad , \tag{3.80}$$

where E_{kin} is the kinetic energy of a particle; it is worth noting that we limit ourselves to the first-order terms in $\dot{\mathbf{u}}$, such that the estimation of the change in temperature by using $m\dot{u}^2$ is not warranted by the kinetic approach in the presence of an external potential; the correct estimation is $\delta T \simeq -\overline{U}$ $(\ll T)$.

It is worth discussing the effect of $m\dot{u}^2$ in this context. Equation (3.80) leads to

$$2v\dot{u}\cos\theta + u^2 + 2U/m = 0 \quad , \tag{3.81}$$

where θ is the angle made by $\mathbf{v}$ with $\dot{\mathbf{u}}$. For $U < 0$ the solution of this equation is

$$\dot{u} = \begin{cases} -v\cos\theta + \sqrt{v^2\cos^2\theta + 2\mid U\mid/m} \ , & 0 < \theta < \pi/2 \ , \\ -v\cos\theta - \sqrt{v^2\cos^2\theta + 2\mid U\mid/m} \ , & \pi/2 < \theta < \pi \ ; \end{cases} \tag{3.82}$$

for $U > 0$ we assume $2U/mv^2 < 1$; this inequality may not be valid for small velocities, but, for sufficiently small U $(\ll T)$, the range of these velocities brings a negligible contribution to the thermal mean values. In these conditions, the solution of equation (3.80) is

$$\dot{u} = \begin{cases} -v\cos\theta + \sqrt{v^2\cos^2\theta - 2U/m} \ , & 0 < \theta < \theta_0 \ , \\ -v\cos\theta - \sqrt{v^2\cos^2\theta - 2U/m} \ , & \pi - \theta_0 < \theta < \pi \ , \end{cases} \tag{3.83}$$

where $\cos\theta_0 = \sqrt{2U/mv^2}$. The integration of $m\dot{u}^2$ over the angle θ gives $(2\alpha mv^2/3)(2\mid U\mid/mv^2)^{3/2}$, where $\alpha = 1$ for $U > 0$ and $\alpha = 2$

for $U < 0$ and we have retained only the leading terms in powers of $2 \mid U \mid /mv^2 \ll 1$. The integration over v gives

$$\overline{m\dot{u}^2} = \frac{2\alpha}{3}\sqrt{2/\pi} \mid U \mid (\mid U \mid /T)^{1/2} \ ; \tag{3.84}$$

we can see that this result is different from $-U$.

The variation of the atmospheric temperature with the altitude is given by $\Delta T = -\Delta\mathcal{F}/S$, where $\mathcal{F}$ is the free energy and S is the entropy. The potential energy mgz of the gravitational field, where m is the mass of a gas particle, g is the gravitational acceleration and z is the altitude, brings a correction factor $(T/mgz)(1 - e^{-mgz/T})$ in the partition function; the variation of the density with the altitude affects the entropy only to a small extent, such that we get

$$\Delta T \simeq T \ln \frac{T(1 - e^{-mgz/T})}{mgz} \simeq -\frac{1}{2}mgz \ \ , \tag{3.85}$$

which agrees with the estimation of the type $-U = -mgz$ given above (we note that $\overline{z} = z/2$). Also, it is worth noting the inequality $mg/T \ll 1$.

3.11 Corrections to the thermodynamic potentials

The free energy of a gas consisting of N pointlike identical particles with mass m is given by

$$\mathcal{F} = -NT \ln\left(\frac{e}{N}\frac{1}{(2\pi\hbar)^3}\int e^{-\frac{1}{2}\beta mv^2} d\mathbf{p}d\mathbf{r}\right) \ \ , \tag{3.86}$$

where T is the temperature ($\beta = 1/T$), $\mathbf{p} = m\mathbf{v}$ is the momentum and $\hbar$ is Planck's constant ($e \simeq 2.73$). The energy is $E = \frac{3}{2}NT$. Making use of the distribution function $F = n(\beta m/2\pi)^{3/2}e^{-\beta mv^2/2}$, where $n = N/V$ and V is the volume, we can write the free energy as

$$\mathcal{F} = -NT \ln\left[e\left(\frac{ma^2}{2\pi\beta\hbar^2}\right)^{3/2}\frac{1}{N}\int F d\mathbf{v}d\mathbf{r}\right] \ \ , \tag{3.87}$$

where $a=(V/N)^{1/3}$ is the mean separation distance between the particles; for a change in F of the form $F\longrightarrow F+f$, we get a change in the free energy

$$\Delta\mathcal{F}=-T\int fd\mathbf{v}d\mathbf{r}\quad , \tag{3.88}$$

or, making use of $\delta T=(T/N)\int fd\mathbf{v}d\mathbf{r}$ given before, $\Delta\mathcal{F}=-N\delta T$ (the rigorous change in temperature is $\Delta T=-\Delta\mathcal{F}/S$, where S is the entropy). In an external potential U the change in the distribution function is $f=-\beta UF$, such that we get the change in the free energy $\Delta\mathcal{F}=n\int Ud\mathbf{r}$. Indeed, in an external field the partition function acquires a factor

$$\left(\frac{1}{V}\int d\mathbf{r}e^{-\beta U}\right)^{N}\quad , \tag{3.89}$$

which gives a change

$$\begin{gathered}\Delta\mathcal{F}=-NT\ln\left(\tfrac{1}{V}\int d\mathbf{r}e^{-\beta U}\right)\simeq\\ \simeq-NT\ln\left(1-\tfrac{\beta}{V}\int d\mathbf{r}U\right)\simeq n\int d\mathbf{r}U\end{gathered} \tag{3.90}$$

in the free energy. We can see that, in this approximation, the entropy

$$S=N\ln\left[e^{5/2}\left(\frac{ma^2}{2\pi\beta\hbar^2}\right)^{3/2}\right] \tag{3.91}$$

is not changed. (In normal conditions the ln in equation (3.91) is a numerical factor of the order $\simeq 10$; this numerical factor has been put equal to unity in deriving equation (3.85) above). Since $\Delta F=n\int Ud\mathbf{r}$ does not depend on the temperature (the entropy is constant), we may say that the temperature change ΔT is absorbed as heat in the internal energy $\Delta E=-T\Delta S$.

Making use of the change in the free energy we can get the changes in pressure and chemical potential; in particular, leaving aside the surface effects the change in pressure

$$\Delta p=\frac{N}{V^2}\int d\mathbf{r}U \tag{3.92}$$

agrees with the van der Waals contribution to non-ideal gases. The change in the free energy is the change in all the thermodynamic potentials. We note that all these thermodynamic estimations are also valid for an external potential which varies slowly in time.

For a change in the distribution function generated by a force, the change in the free energy can be estimated by replacing formally U by $-m\mathbf{v}\dot{\mathbf{u}}$ (and including the average over velocities); we get

$$\Delta\mathcal{F} = -m\int d\mathbf{v}d\mathbf{r}(\mathbf{v}\dot{\mathbf{u}})F(v) \quad , \tag{3.93}$$

where, in general, $\dot{\mathbf{u}}$ is a function of $\mathbf{r}$, $\mathbf{v}$ and t (and $F(v) = n(\beta m/2\pi)^{3/2}\cdot$ $\cdot e^{-\beta mv^2/2}$).

3.12 Interaction. Collective excitations

Under the action of an external force a particle acquires the energy

$$\delta\varepsilon(t, \mathbf{r}, \mathbf{v}) = m\mathbf{v}\dot{\mathbf{u}} = f/\beta F \ ; \tag{3.94}$$

this energy generates a force $-\partial\delta\varepsilon/\partial\mathbf{r}$ and a momentum $\mathbf{p} = \partial\delta\varepsilon/\partial\mathbf{v}$; we are in the presence of one-particle elementary excitations (quasi-particles) of the ideal classical gas. In principle, the force generated by the quasi-particles acts upon the other particles, and we may be in the presence of a dynamics of the quasi-particles. However, the mean energy

$$\delta\varepsilon(t, \mathbf{r}) = \frac{T}{n}\int d\mathbf{v}f \tag{3.95}$$

is zero (equation (3.55)), and we have, in fact, no effect.

Apart from the motion of the individual particles, a gas may exhibit a correlated motion, which implies collective degrees of freedom; in an ideal gas do not exist mechanical forces between the particles, but the existence of the thermal equilibrium may generate forces. Indeed, a displacement $\mathbf{u}$ generates a local change $\delta n = -n div\mathbf{u}$ in density; the expansion of the energy density in powers of δn, when integrated over the volume, gives the first contribution in the second power of δn, such that we can write the lagrangian of this motion as

$$\mathcal{L} = \int d\mathbf{r}mn\left[\frac{1}{2}\dot{u}^2 - \frac{1}{2}c^2(div\mathbf{u})^2\right] \ ; \tag{3.96}$$

the equation of motion is

$$\ddot{\mathbf{u}} - c^2 grad(div\mathbf{u}) = 0 \quad , \tag{3.97}$$

which is the Cauchy-Navier equation for an elastic body with $c^2 = \lambda/\rho$, λ being the compressibility modulus (one of the Lame coefficients) and $\rho = mn$ being the mass density. For gases $\lambda = \rho(\partial p/\partial\rho)_S$, where p is the pressure and S is the entropy; it is $\rho(c_pT/c_v)$, where $c_{p,v}$ are the specific heats at constant pressure and volume, respectively. The solutions of equation (3.97) are waves of the form $\mathbf{u_k}e^{-i\omega t+i\mathbf{kr}}$, where $\omega^2 = c^2k^2$; from $\delta n = -ndiv\mathbf{u}$ we can see that these waves are longitudinal ($\mathbf{u_k} \sim \mathbf{k}$); they are sound (elastic) waves, which propagate with the sound velocity c.

In principle, we cannot say a priori how the degrees of freedom are shared among the individual particles and the sound waves; however, the magnitude k of the wavevector has a natural cutoff k_0, given by the $k_0 \simeq 1/a$, where a is the mean separation distance between the particles (this is called the Debye cutoff[7]); then, the number of states $4\pi k_0^3/3$ is of the order of the number N of particles. Such a conclusion is expected from the fact that the waves are extended in the whole space. The sound waves are eigenmodes of oscillation of the gas, and they are determined from the initial condition, which in principle, determines both the extension of the wavevectors $\mathbf{k}$ and the magnitude of the amplitudes $\mathbf{u_k}$. For instance, a localized initial disturbance of the gas (δ-function) will generate all the $\mathbf{k}$'s with equal magnitudes $\mathbf{u_k}$. It is worth noting that the existence of the sound waves in an ideal gas is conditioned, on one hand, by the thermal equilibrium of the motion of the particles as individual entities and, on the other hand, by an initial disturbance. Therefore, the sound waves will appear in an ideal gas as a change f in the distribution function of the particles, caused by an initial disturbance, *i.e.* in the framework of the kinetic approach to the thermal motion of the individual particles. They are collective elementary excitations.

Due to their delocalization the sound waves have a quantum-mechanical nature. The quantization of their equation of motion is the quantization of a harmonic oscillator, with the matrix elements of the displacement u (along any fixed $\mathbf{k}$) given by $u_{n,n-1} = u_{n-1,n} = \sqrt{\hbar n/2m\omega}$, where n (not to be mistaken for density) is any positive integer and $\omega = ck$. Subject to the condition $uk \ll 1$ (from $\delta n \ll n$), the quantum number n may go to infinity for long wavelengths. It defines quantum-mechanical particles (actually, collective elementary excitations) called phonons, with an energy $\varepsilon = \hbar ck$ and a wavevector $\mathbf{k}$ (momentum $\mathbf{p} = \hbar\mathbf{k}$); the infinitesimal number of states is $Vd\mathbf{k}/(2\pi)^3$; they are bosons, and their (thermal) occupation number $n(\mathbf{k})$ is given by the Bose statistics. An interaction may renormalize their energy (velocity included), in the limit of long wavelengths. In the opposite limit of short wavelengths (comparable with a) the phonons are in the quasi-classical limit. The occupation number $n(\mathbf{k})$ plays the role of the distribution function F for individual particles, and an external force $\mathbf{K}$ may bring about a change $\delta n(t, \mathbf{r}, \mathbf{k})$ in the occupation number, which should satisfy Boltzmann's kinetic equation

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[7] P. Debye, "Zur Theorie der spezifischen Waermen", Ann. Phys. **39** 789 (1912).

$$\frac{\partial \delta n}{\partial t} + \frac{c\mathbf{k}}{k}\frac{\partial \delta n}{\partial \mathbf{r}} + \frac{\mathbf{K}}{\hbar}\frac{\partial n}{\partial \mathbf{k}} = -\gamma \delta n \quad , \tag{3.98}$$

exactly in the same way as for particles (this equation should be solved in the limit $\hbar \to 0$); noteworthy, the velocity $c\mathbf{k}/k$ is, in fact, the group velocity $\partial\varepsilon/\partial\mathbf{p}$.

The kinetic approach has been described above for an external force $\mathbf{K}$, including the case when this force derives from a potential. The question related to the presence of an interaction may appear. First, we note that the existence of an interaction between the particles cancels out their statistical independence and, consequently, makes the change produced by this interaction in the equilibrium distribution meaningless. Actually, the particles accommodate the interaction and get thermal equilibrium; this amounts to say that we need first to solve the problem of interaction and thereafter ask for statistical properties. A gas with interaction is a non-ideal gas; the thermal behaviour of a non-ideal classical gas is described by the van der Waals equation. In general, the dynamics of non-ideal (interacting) ensembles of particles is governed by the elementary excitations introduced by Landau.[8]

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[8] L. Landau, "The theory of a Fermi liquid", Sov. Phys.-JETP **3** 920 (1957) (ZhETF **30** 1058 (1956)); "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1057) (ZhETF **32** 59 (1957)); "On the theory of the Fermi liquid", Sov. Phys.-JETP **8** 70 (1959) (ZhETF **35** 97 (1958)).

3.13 van der Waals equation

Let us consider a classical gas of N identical pointlike particles enclosed in a volume V with the interaction energy

$$E=\frac{1}{2}\sum_{i\neq j}U(\mathbf{r}_i-\mathbf{r}_j)\ \ , \tag{3.99}$$

where $U(\mathbf{r}_i-\mathbf{r}_j)$ is the two-particle interaction and i, $j=1,2,...N$ denote the particles. For pointlike particles $U(\mathbf{r}_i-\mathbf{r}_j)$ is a function only of $\mid \mathbf{r}_i-\mathbf{r}_j \mid$. The correction to the free energy can be written as

$$\Delta\mathcal{F}=-T\ln\left(\frac{1}{V^N}\int e^{-\beta E}d\mathbf{r}_1...d\mathbf{r}_N\right)\ \ , \tag{3.100}$$

where $T=1/\beta$ is the temperature. We assume a short-range (integrable) interaction $U(\mathbf{r}_i-\mathbf{r}_j)$. From equation (3.99) we see that each particle i is acted by the rest of the particles by a potential

$$\Phi(\mathbf{r}_i)=\sum_j{}^{'}U(\mathbf{r}_i-\mathbf{r}_j)\ \ , \tag{3.101}$$

where the prime means $j\neq i$; the total energy can be written as

$$E=\frac{1}{2}\sum_i\Phi(\mathbf{r}_i)\ \ . \tag{3.102}$$

The integration over $\mathbf{r}_i$ in equation (3.100) must take into account the requirement $j\neq i$, *i.e.* $\mathbf{r}_j\neq\mathbf{r}_i$ for any pairs (i,j).[9] It follows that the correction to the free energy is given by

$$\Delta\mathcal{F}=-T\ln\left(\frac{1}{V^N}\int{}^{'}e^{-\beta E}d\mathbf{r}_1...d\mathbf{r}_N\right)\ \ , \tag{3.103}$$

where the prime means $\mathbf{r}_j\neq\mathbf{r}_i$. We perform this integration over a volume $V-Nb$, where b is an excluded volume for each particle. A convenient approximation to the potential $\Phi(\mathbf{r}_i)$ is the mean-field approximation.[10] In the mean-field approximation the potential $\Phi(\mathbf{r}_i)$ does not depend on $\mathbf{r}_i$ and the summation in equation (3.101) is computed by

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[9] M. Apostol, "On the van der Waals equation", J. Theor. Phys. **290** (2018).

$$\Phi = \sum_j{}' U(r_j) = \frac{N}{V}\int_{2r_0} d\mathbf{r}U(r) = \frac{2Na}{V} \ \ , \tag{3.104}$$

where $b \simeq \frac{1}{2}\cdot 32\pi r_0^3/3$; the factor 1/2 in estimating the volume b arises from the fact that the independent integration with respect to any pair $\mathbf{r}_i$,$\mathbf{r}_j$ counts twice the excluded volume. This excluded volume views the particles as rigid spheres of radius r_0. The change in the free energy becomes (equation (3.103))

$$\begin{aligned} \Delta\mathcal{F} = -T\ln\left(\tfrac{(V-Nb)^N}{V^N}e^{-\frac{1}{2}\beta N\Phi}\right) = \\ = N\Phi - NT\ln\left(1-\tfrac{Nb}{V}\right) = \tfrac{N^2a}{V} - NT\ln\left(1-\tfrac{Nb}{V}\right) \ \ . \end{aligned} \tag{3.105}$$

We get the pressure

$$\begin{aligned} p = \tfrac{NT}{V} + \tfrac{N^2a}{V^2} + NT\tfrac{Nb/V^2}{1-Nb/V} = \\ = \tfrac{NT}{V}\left(1+\tfrac{Nb/V}{1-Nb/V}\right) + \tfrac{N^2a}{V^2} = \tfrac{NT}{V-Nb} + \tfrac{N^2a}{V^2} \ \ ; \end{aligned} \tag{3.106}$$

hence, it follows immediately the van der Waals equation[11]

$$\left(p - \frac{N^2a}{V^2}\right)(V-Nb) = NT \ \ . \tag{3.107}$$

We note that we use the same cutoff $2r_0$ both in the integration in equation (3.103) and in the potential given by equation (3.104); this is due to the abrupt, repulsive hard core of the potential; in general, the two cutoffs are distinct. Also, we note that the mean-field approximation is equivalent with restricting ourselves only to one-particle elementary excitations (quasiparticles). We have assumed that a and b do not depend on V, and $b > 0$ (by its definition). Usually, the interaction is attractive at long distances, such that a is negative.

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[10] The mean-field approximation was introduced for atoms by N. Bohr, "On the constitution of atoms and molecules", Phil. Mag. **26** 1, 476, 857 (1913) and extended to the atomic nucleus.

[11] J. D. van der Waals, *Over de Continuiteit van den Gas- en Vloeistoftoestand*, Doctoral Thesis, Leiden (1873) (*On the Continuity of the Gas and Liquid State*); "The equation of state for gases and liquids", Nobel Lecture, 1910 (Elsevier, Amsterdam (1967)).

It may happen that an external potential $\varphi(\mathbf{r})$ is present and we wish to estimate its effects in the presence of the internal interaction. Then, the total energy is written as

$$E = \sum_i \varphi(\mathbf{r}_i) + \frac{1}{2}N\Phi \quad , \tag{3.108}$$

where Φ is a mean-field potential (also, the external potential may derive from a mean-field approximation). The ensemble has not translational symmetry anymore, since $\varphi(\mathbf{r})$ depends on position. The change in the free energy is

$$\begin{aligned} \Delta\mathcal{F} = -T\ln\left(\tfrac{1}{V^N}\int' e^{-\beta\sum_i\varphi(\mathbf{r}_i)-\frac{1}{2}N\Phi}d\mathbf{r}_1...d\mathbf{r}_N\right) = \\ = -T\ln\left[\left(\tfrac{1}{V}\int' e^{-\beta\varphi(\mathbf{r})}d\mathbf{r}\right)^N e^{-\frac{1}{2}\beta N\Phi}\right] = \\ = -NT\ln\left(\tfrac{1}{V}\int' e^{-\beta\varphi(\mathbf{r})}d\mathbf{r}\right) + \tfrac{1}{2}N\Phi \ ; \end{aligned} \tag{3.109}$$

the integral in equation (3.109) can be written as

$$\begin{aligned} \int' e^{-\beta\varphi(\mathbf{r})}d\mathbf{r} = \int e^{-\beta\varphi(\mathbf{r})}d\mathbf{r} - b\sum_i e^{-\beta\varphi(\mathbf{r}_i)} = \\ = \int e^{-\beta\varphi(\mathbf{r})}d\mathbf{r} - \tfrac{Nb}{V}\int e^{-\beta\varphi(\mathbf{r})}d\mathbf{r} = \left(1-\tfrac{Nb}{V}\right)\int e^{-\beta\varphi(\mathbf{r})}d\mathbf{r} \quad , \end{aligned} \tag{3.110}$$

such that we get

$$\begin{aligned} \Delta\mathcal{F} = -NT\ln\left(1-\tfrac{Nb}{V}\right) - \\ -NT\ln\left(\tfrac{1}{V}\int e^{-\beta\varphi(\mathbf{r})}d\mathbf{r}\right) + \tfrac{1}{2}N\Phi \ ; \end{aligned} \tag{3.111}$$

we can see that we recover the van der Waals equation and get also the effects of the external field; for a finite ensemble, such effects may include surface contributions.

The general way of deriving the van der Waals equation consists in estimating the effects of the interaction in the mean-field equation (3.104) and taking account of the excluded volume, according to the definition of the interaction energy.

3.14 Kinetic approach for the non-ideal gas

The equilibrium distribution function $F(v)$ is identified by

$$V\int d\mathbf{v}F(v)=N\ \ , \tag{3.112}$$

or

$$\int d\mathbf{r}d\mathbf{v}F(v)=N \tag{3.113}$$

(equation (3.87)). According to the above discussion, the distribution function is modified by $F\longrightarrow Fe^{-\beta\Phi}$ for a non-ideal classical gas, where Φ does not depend on t, $\mathbf{r}$, $\mathbf{v}$ (in the mean-field approximation). Consequently, for the kinetic approach in the presence of the interaction we may use the equilibrium function F of an ideal gas; however, when computing the equilibrium properties generated by the change in this equilibrium distribution we should include the factor $e^{-\beta\Phi}$ and integrate over the restrained volume.

In principle, the thermodynamics of a phase is solved after solving the interaction problem for that phase. This would imply, at first sight, that we need zero temperature to solve the interaction problem. However, the zero temperature is unphysical and we need to solve the interaction problem at finite temperatures. The van der Waals equation is an example of this situation for a non-ideal gas. Another example is the superconductivity, another is provided by the elementary excitations, which is an instance of interaction solved with the limitations of a finite temperature. We can see that in each case the interaction is solved at finite temperatures with additional assumptions, which, basically, pertain to thermodynamics. Instances are provided by the introduction of the excluded volume and the derivation of the virial coefficients for the van der Waals equation, the mean-field and the order parameter for phase transitions,[12] the lifetime and the mean freepath for elementary excitations. Systematic techniques are developed for estimating the interaction effects at finite temperatures, like Matsubara,[13] or Zubarev[14] Green functions (and the corresponding diagrammatic techniques).[15] Also, the idea occurred that the approach to equilibrium is driven by interaction, although the mechanical framework (Liouville equation) such theoretical procedures are embedded in is always mixed up with statistical hypotheses.[16]

3.15 Sound

Let us imagine a continuous body consisting of identical particles, *e.g.* molecules in a gas. A molecule with mass m, placed at position $\mathbf{r}$ at time t, has velocity $\mathbf{v}$. Let us assume that an additional velocity $\dot{\mathbf{u}}$ is superimposed upon this molecule. The equation of motion is

$$m\frac{\partial(\dot{\mathbf{u}}+\mathbf{v})}{\partial t}+m(\dot{\mathbf{u}}+\mathbf{v})\frac{\partial(\dot{\mathbf{u}}+\mathbf{v})}{\partial\mathbf{r}}=\mathbf{F}\ , \qquad (3.114)$$

where $\mathbf{F}$ is the force acting upon the molecule. Let us assume now that the molecules are in thermal equilibrium and the additonal velocity $\dot{\mathbf{u}}$ is a small perturbation; then $\mathbf{v}$ does not depend on $\mathbf{r}$ and t and the quadratic term $\dot{\mathbf{u}}(\partial\dot{\mathbf{u}}/\partial\mathbf{r})$ may be neglected. Equation (3.114) becomes the kinetic equation (3.1)

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[12] P. Weiss, "La variation du ferromagnetisme avec la temperature", Comp. Rend. **143** 1136 (1906); "L'hypothese du champ moleculaire et la propriete ferromagnetique, J. Physique **6** 661 (1907); J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, NY (1940);

[13] T. Matsubara, "A new approach to quantum-statistical mechanics", Progr. Theor. Phys. **14** 351 (1955).

[14] D. N. Zubarev, "Double time Green's functions in statistical physics", Sov. Phys. Usp. **3** 320 (1960) (Usp. Fiz. Nauk **71** 71 (1960)).

[15] See, for instance, A. A. Abrikosov, L. P. Gorkov and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics*, Dover, NY (1963).

[16] I. Prigogine, *Non-equilibrium Statistical Mechanics*, Interscience Publishers, Groningen (1962); R. Balescu, *Equilibrium and Non-equilibrium Statistical Mechanics*, Wiley, NY (1975); L. V. Keldysh, "Diagram technique for Nonequilibrium Processes", Sov. Phys.-JETP **20** 1018 (1965) (ZhETF **47** 1515 (1965)); D. Zubarev, V. Morozov and G. Ropke, *Statistical Mechanics of Nonequilibrium Processes*, Akademie Verlag, Berlin (1996)

$$m\frac{\partial \dot{\mathbf{u}}}{\partial t}+m\mathbf{v}\frac{\partial \dot{\mathbf{u}}}{\partial \mathbf{r}}=\mathbf{F} \tag{3.115}$$

which leads to Boltzmann equation. A dissipation term $\gamma\dot{\mathbf{u}}$ may be included, which accounts for the molecular collisions. Indeed, a disruption produced by a collision implies an additional contribution $\partial\dot{\mathbf{u}}/\partial t \simeq \dot{\mathbf{u}}/\tau$, where time $\tau = 1/\gamma$ is much longer than any characteristic time of velocity variation; we note that we are at local equilibrium, but not at global equilibrium.

Let us attribute the velocity $\dot{\mathbf{u}}$ to a small, but sufficiently large, particle, consisting of $N \gg 1$ molecules, such that each of these particles is at thermal equilibrium. We may neglect, for the moment, the fluctuations, such that the velocity $\mathbf{v}$ in equation (3.114) may be viewed as a mean velocity, which is zero. Then we multiply equation (3.114) by the density n, such that $\rho = mn$ is the mass density. The force acting upon such a particle is

$$n\mathbf{F}=\frac{N}{V}\mathbf{F}=-\frac{1}{V}\oint pd\mathbf{S}=-\frac{1}{V}\int d\mathbf{r}\frac{\partial p}{\partial \mathbf{r}}=-\frac{\partial p}{\partial \mathbf{r}}\ , \tag{3.116}$$

where p the pressure acting (outwards) upon the surface S of the particle with the volume V. Equation (3.114) becomes Euler's equation

$$\rho\frac{\partial \dot{\mathbf{u}}}{\partial t}+\rho\dot{\mathbf{u}}\frac{\partial \dot{\mathbf{u}}}{\partial \mathbf{r}}=-\frac{\partial p}{\partial \mathbf{r}} \tag{3.117}$$

of the motion of an ideal fluid.[17] An external force may be included. The equation of continuity (mass conservation) and the equation of the entropy conservation may be added (in the absence of viscosity and thermoconduction); if the fluid is compressible the density may be included in the derivatives. If the viscosity is included, we get the Navier-Stokes equations of motion of fluids.[18] They read

$$\rho\frac{\partial \dot{\mathbf{u}}}{\partial t}+\rho\dot{\mathbf{u}}\frac{\partial \dot{\mathbf{u}}}{\partial \mathbf{r}}=-\frac{\partial p}{\partial \mathbf{r}}+\eta\Delta\dot{\mathbf{u}}+\left(\zeta+\frac{1}{3}\eta\right)grad\,div\dot{\mathbf{u}}\ , \tag{3.118}$$

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[17] L. Euler, "Principes generaux du mouvement des fluides", Hist. de l'Acad. de Berlin (1755).

[18] C. L. Navier, "Sur les lois du mouvement des fluides", Mem. Acad. R. Sci. Inst. France **6** 389 (1823); G. G. Stokes, "On the theories of the internal friction of fluids in motion and of equilibrium and motion of elastic solids", Trans. Phil. Soc. Cambridge **8** 287 (1845).

where η, ζ are viscosity coefficients. We note that viscosity is a friction, arising from molecular collisions at the surface of the particles. Again we are at local equilibrium, but not at a global equilibrium.

If the fluctuating contributions (of the type of the velocity $\mathbf{v}$) are retained in equation (3.114), the quadratic term brings averages of products of two fluctuating velocities.[19] The corresponding equations are the Reynolds equations.[20] Such contributions generate (statistical) turbulence. Turbulent instabilities are generated by high values of the Reynolds number $R = \rho\dot{u}l/\eta$, obtained by comparing the viscosity terms with the quadratic terms, where l is a characteristic length of velocity variation.

Apart from viscosity, thermoconduction is another mechanism of dissipation in fluids, due to molecular collisions; in fluids, thermoconduction is not only local, it may arise by convection too. Except for special cases, fluid motion implies more viscosity than thermoconduction, due to the large extension of fluid particles.

Let us assume now that the velocity $\dot{\mathbf{u}}$ varies slightly over long distances or in short times, $i.e.\dot{u} \ll \Delta r/\Delta t$; then, in equation (3.117) we may neglect the term quadratic in velocity. In this case, equation (3.117) can also be applied to solids, and the variations of the pressure are adiabatic; we may reduce the dimension of the particles and the transfer of heat is zero in first approximation (for instance, in a gas, the molecules are slightly displaced, but they do not collide with one another). We can write the variations of pressure and density as

$$\delta p = \frac{1}{(\partial\rho/\partial p)_s}\delta\rho \ , \ \delta\rho = -\rho div\mathbf{u} \ , \tag{3.119}$$

where $(\partial\rho/\partial p)_s$ is related to the coefficient of compressibility $-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_s$ at constant entropy (s). Equation (3.117) becomes

$$\frac{\partial^2\mathbf{u}}{\partial t^2} - \frac{1}{(\partial\rho/\partial p)_s} grad\, div\mathbf{u} = \mathbf{F}/\rho \ , \tag{3.120}$$

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[19] G. K. Batchelor, *The Theory of Homogeneous Turbulence*, Cambridge Science Classics Series, Cambridge University Press (1953).

[20] O. Reynolds, "On the dynamical theory of incompressible viscous fluids and the determination of the criterion", Phil. Trans. Roy. Soc. Lond. **A186** 123 (1895).

where we introduced an external force $\mathbf{F}$. Taking the *div*, it is easy to see that equation (3.120) describes longitudinal waves propagating with velocity $c^2 = 1/(\partial\rho/\partial p)_s$; obviously, $\dot{\mathbf{u}}$ should be much smaller than c and $\mathbf{u}$ should be much smaller than the mean separation distance a between particles ($n = 1/a^3$). The motion described by equation (3.120) is sound. The compressibilty coefficients are related through

$$\left(\frac{\partial p}{\partial\rho}\right)_s = \frac{c_p}{c_v}\left(\frac{\partial p}{\partial\rho}\right)_T \ , \tag{3.121}$$

where $c_{p,v}$ are the specific heats at constant pressure and constant volume, respectively. For instance, for an ideal classical gas $c^2 = c_pT/mc_v$.

Equation (3.120) includes only longitudinal motion; it can be generalized to

$$\begin{gathered}\rho\ddot{u}_i = \partial_j\sigma_{ij} + F_i \ , \ \sigma_{ij} = 2\mu u_{ij} + \lambda div\mathbf{u}\delta_{ij} \ , \\ u_{ij} = \tfrac{1}{2}\left(\partial_i u_j + \partial_j u_i\right) \ ,\end{gathered} \tag{3.122}$$

i.e.

$$\rho\ddot{\mathbf{u}} = \mu\Delta\mathbf{u} + (\lambda+\mu)\, grad\, div\mathbf{u} + \mathbf{F} \ , \tag{3.123}$$

where σ_{ij} is the stress tensor, u_{ij} is the strain tensor and λ, μ are the Lame elastic coefficients (Hooke law[21]). Equation (3.123) is the Navier-Cauchy equation for elastic motion.[22] The coefficient μ is the shear coefficient, while λ is the compressibility coefficient. The velocity of the longitudinal wave (sound wave) is $c_l = \sqrt{(\lambda+2\mu)/\rho}$ and the velocity of the transverse wave is $c_t = \sqrt{\mu/\rho}$. Since $curl\, curl = -\Delta + grad\, div$, it is easy to see, by comparing equations (3.120) and (3.123), that $\lambda + 2\mu = \rho/(\partial\rho/\partial p)_s$.

In solids, the moving particles are smaller than in fluids, corresponding to smaller elastic motion; dissipation takes place first by thermoconduction and then by viscosity, the motion implies elastic deformations and elastic waves (convection is absent), the equilibrium is local, but not global.

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[21] R. Hooke, *Lectures of Spring*, Roy. Soc. London, London (1678) ("ut tensio, sic vis").

[22] C. L. Navier, Mem. Acad. Sci. t. 7 (1827) (read in the Paris Academy in 1821); A. L. Cauchy, in "Sur les equations qui expriment les conditions d'equilibre ou les lois du mouvement interieur d'un corps solide, elastique ou nonelastique", *Exercices de Mathematique* (1828) (communicated to the Paris Academy in 1822).

All these equations of motion imply a transport of energy, momentum, velocity. For instance, if we multiply by $\dot{u}_i$ equation (3.115) we get the continuity equation

$$\frac{\partial E}{\partial t} + div\mathbf{S} = \dot{\mathbf{u}}\mathbf{F} \ , \tag{3.124}$$

where $E = \frac{1}{2}m\dot{\mathbf{u}}^2$ is energy, $\mathbf{S} = \mathbf{v}E$ is the energy flux and $\dot{\mathbf{u}}\mathbf{F}$ is the mechanical work done by force per unit time.

4 Transport in Gases

4.1 Molecular kinetic theory. Transport

Let us consider a gas of identical molecules with mass m at equilibrium, limited by a surface $x = 0$; the number of collisions of the molecules with velocity $\mathbf{v}$ with the surface per unit time and unit area of the surface is $nv_x(\beta m/2\pi)^{3/2}e^{-\frac{1}{2}\beta mv^2}d\mathbf{v}$, where $v_x > 0$ and $\beta = 1/T$ is the inverse of the temperature T; integrating, we get the total number of collisions $n/(2\pi\beta m)^{1/2}$, where n is the concentration. The colliding molecules exchange with the surface the energy (per unit time and unit area) $(mv_x^2/2)nv_x(\beta m/2\pi)^{3/2}e^{-\frac{1}{2}\beta mv^2}d\mathbf{v}$, or, integrating, $n/(2\pi m\beta^3)^{1/2}$. A colliding molecule exchanges the momentum $2mv_x$ with the surface; per unit time and unit area these molecules generate a pressure $p = \frac{1}{2}(2nm\overline{v_x^2}) = \frac{1}{3}nm\overline{v^2}$; since $\frac{1}{2}m\overline{v^2} = \frac{3}{2}T$ (for a monoatomic gas), we get the law of ideal gases $p = nT$.

Let us consider a particle in a gas; its cross-section σ is defined as the number of collisions sufferred by this particle per unit time $dN^{'}/dt$ divided by the particle flow (flux) Φ incident on that particle; the particles are in relative motion with respect to that particle, *i.e.* they move with the relative velocity $v^{'}$, with the reduced mass $m^{'} = m/2$ and have the energy $mv^{'2}/4$; the differential number of colliding particles is therefore $dN = n(\beta m/4\pi)^{3/2} \cdot 4\pi e^{-\frac{1}{2}\beta mv^{'2}/4}v^{'2}dv^{'}$; it follows that the number of collisions per unit time is

$$\frac{dN^{'}}{dt} = n(\beta m/4\pi)^{3/2} \cdot 4\pi \int_0 e^{-\frac{1}{4}\beta mv^{'2}}\sigma v^{'3}dv^{'} = \frac{4n\sigma}{(\pi\beta m)^{1/2}} \tag{4.1}$$

$(\Phi = v^{'})$; the total number of collisions per unit time is $(dN^{'}/dt)N/2$.

Let us assume a gas in local equilibrium; the flux (flow) of a quantity A per unit time and unit area of the surface perpendicular to a direction, say x, is given by

$$\frac{\partial^2 A}{\partial t \partial S} = \Delta(nv_x A) \ , \tag{4.2}$$

where Δ denotes the local variation; it may be replaced by $-\Lambda \frac{\partial}{\partial x}(nv_x A)$, where Λ is the mean freepath;[1] n denotes the concentration, v_x is the x-component of the velocity, S denotes the surface and t is the time. The time and the spatial derivatives are much smaller than $1/\Lambda$, the changes in A proceed in long times and over large distances. Equation (4.2) must be averaged over the local thermal equilibrium, where $v_x > 0$. We may see that the gas is not in global non-equilibrium (since the quantity A flows). Equation (4.2) is a transport equation. Let us compute the flow of heat through a gas with a small gradient of temperature; the heat is $Q = CT$, where C is the heat capacity; we denote by q the heat flux ($q = \partial Q/\partial S$) and get

$$\frac{\partial q}{\partial t} = -n\overline{v}_x \Lambda C \frac{\partial T}{\partial x} \ ; \tag{4.3}$$

the coefficient $K = n\overline{v}_x \Lambda C$ is the thermoconductivity. Let $A = p = m\dot{u}$ be the macroscopic momentum of a molecule with mass m along the x-direction; its time derivative is a force; it follows that there appears a pressure in the gas given by

$$\frac{\partial^2 p}{\partial t \partial S} = -\rho\overline{v}_x \Lambda \frac{\partial \dot{u}}{\partial x} \ , \tag{4.4}$$

due to the spatial variation of the macroscopic velocity; $\rho = nm$ is the mass density. The coefficient $\rho\overline{v}_x\Lambda$ is the viscosity $\eta = \rho\overline{v}_x\Lambda$, which is responsible of the internal friction in fluids. Let $c = n_1/n$ be the concentration of a gas with density n_1 in a mixture with density n; we endow all the quantities pertaining to this gas component with the suffix 1; the flow of concentration is given by

$$\frac{\partial^2 c}{\partial t \partial S} = -\Lambda_1 \frac{\partial}{\partial x}(\overline{v}_{1x} n_1) \ ; \tag{4.5}$$

here the density n_1 may vary in space, as for diffusion, but there may exist a variation in space of the temperature too (incorporated in v_{1x}), which is a thermodiffusion; of course, the component with density $n - n_1$ diffuses in the opposite direction. The change of density n_1 in time can be obtained by integrating over a closed surface; we get

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[1] The mean freepath was introduced by R. Clausius, "Uber die Art der Bewegung, welche wir Warme nennen", Ann. Phys. **176** 353 (1857).

$$\frac{\partial n_1}{\partial t} = \Lambda_1 \frac{\partial}{\partial x}[n\Lambda_1 \frac{\partial}{\partial x}(\overline{v}_{1x} n_1)]\Delta S \ , \tag{4.6}$$

where $\Delta S \simeq \Lambda_1^2$; the coefficient D in $\partial n_1/\partial t = D(\partial^2 n_1/\partial x^2)$ (or $\partial n_1/\partial t = D\Delta n_1$ with the laplacian in two or three dimensions) is the diffusion coefficient.

Let us assume that we have a gas of point charges q; $\partial q/\partial t$ is the current and $\partial^2 q/\partial t \partial S = I$ is the current "intensity", *i.e.* the charge per unit time and unit area; it is also the current density j; it follows

$$j = \overline{v}_x \Lambda \frac{\partial F}{\partial \varepsilon} \cdot q \frac{\partial U}{\partial x} \cdot q = n\beta \overline{v}_x \Lambda q^2 F E \ , \tag{4.7}$$

where $\varepsilon = mv^2/2$ is the energy, F denotes the Boltzmann distribution $(\beta m/2\pi)^{3/2} e^{-\beta\varepsilon}$, U is the electric potential and E is the electric field; we get the electrical conductivity

$$\sigma = \frac{nq^2\Lambda}{(2\pi m T)^{1/2}} \ , \tag{4.8}$$

or $\sigma = nq^2\tau/m$, where τ is a relaxation (transport, diffusion) time (of the order $\Lambda/\overline{v}_x$); it justifies the equation of motion $d\dot{u}/dt \simeq \dot{u}/\tau = qE/m$, which gives the current density $j = nq\dot{u} = (nq^2\tau/m)E$. It is easy to see that the ratio $K/\sigma T$ is of the order of $1/q^2$; this is known as the Wiedemann-Franz law and the ratio is called the Lorenz number.[2]

We note that all the above transport equations reflect laws which can be viewed as semi-phenomenological, due to the uncertainties in the parameters τ and Λ.

4.2 Transport equation

Let us assume that the equilibrium distribution F is slightly perturbed, such that the local equilibrium is still preserved, but not the global one. We can write

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[2] G. Wiedemann and R. Franz, "Uber die Warme Leitungsfahigkeit der Metalle", Ann. Phys. **89** 497 (1853); L. Lorenz, "Bestimmung der Warmegrade in absolutem Maasse", Ann. Phys. **223** 429 (1872); "Uber das Leitungsvermogen der Metalle fur Warme und Elektricitat", Ann. Phys. **249** 422 (1881).

$$\frac{dF}{dt}=\frac{\Delta F}{\Delta t}=-\frac{f}{\tau}=-\gamma f \quad , \tag{4.9}$$

where f is the change (ΔF) in the distribution, τ is the relaxation time, $\gamma = 1/\tau$ is the collision frequency and the minus sign accounts for relaxation. The time τ is much shorter than the observable time scale, such that equation (4.9) gives immediately the local equilibrium. Therefore, we are left with

$$\frac{dF}{dt}=\frac{\partial F}{\partial t}+\mathbf{v} gradF=0 \tag{4.10}$$

(in the absence of external forces); this equation may be viewed with **v** replaced by its mean value along the direction of *grad*. This is known as the transport equation.

Let us consider a change in temperature T along the x-direction. Equation (4.10) gives

$$\frac{\partial T}{\partial t}+\overline{v}_x\frac{\partial T}{\partial x}=0 \quad , \tag{4.11}$$

or, multiplying by the heat capacity C,

$$\frac{\partial Q}{\partial t}=-C\overline{v}_x\frac{\partial T}{\partial x} \quad ; \tag{4.12}$$

here we divide by the area σ of the cross-section associated to a particle, and write $\sigma = v/\Lambda$, where v is the volume associated with a particle and Λ is the mean freepath. We note that the mean freepath is $\Lambda = (a^2/\sigma)a$, where a is the mean separation distance between the particles; so, $v = \sigma\Lambda = a^3 = 1/n$, where n is the concentration. Equation (4.12) gives the law of thermoconduction

$$\frac{\partial q}{\partial t}=-Cn\Lambda\overline{v}_x\frac{\partial T}{\partial x} \quad , \tag{4.13}$$

where $q = Q/\sigma$ is the flux of heat and $K = Cn\Lambda\overline{v}_x$ is the thermoconductivity.

Let us assume that the particles have a charge q and a voltage drop U is applied along the x-direction, such that $F \sim e^{-\frac{1}{2}\beta mv^2-\beta qU}$; equation (4.10) gives

$$m\frac{\partial v_x}{\partial t}=-q\frac{\partial U}{\partial x}=qE \quad , \tag{4.14}$$

where E is the electric field; this is the law of motion of a particle in the electric field; the average requires to replace $\partial v_x/\partial t$ by $\overline{v}_x/\tau$; we get

$$j=nqv_x=\frac{nq^2\tau}{m}E \quad , \tag{4.15}$$

which is Ohm's law (Joule-Lenz law) with conductivity $\sigma=nq^2\tau/m$ (not to be mistaken for the cross-section).

Let us assume a macroscopic velocity V along the x-direction; we have $\partial F/\partial t\sim -\beta mv_x(\partial V/\partial t)$ and $\partial F/\partial x\sim -\beta mv_x(\partial V/\partial x)$; hence (equation (4.10))

$$\frac{\partial P}{\partial t}=-m\overline{v}_x\frac{\partial V}{\partial x} \quad , \tag{4.16}$$

where $P=m\overline{v}_x$ is the momentum; we divide by $\sigma=v/\Lambda=1/n\Lambda$ and get

$$\frac{\partial p}{\partial t}=-\rho\Lambda\overline{v}_x\frac{\partial V}{\partial x} \quad , \tag{4.17}$$

where $p=P/\sigma$ is the momentum flux and $\rho=mn$ is the mass density; this is Maxwell's law of momentum transport with viscosity $\eta=\rho\Lambda\overline{v}_x$; $\nu=\eta/\rho$ is the kinematic viscosity; $\partial p/\partial t$ is a pressure.

Let us assume now the diffusion of a gaseous component with concentration n_1 into a gas with concentration $n\gg n_1$ along the x-direction. Since $F\sim n$, we have $\partial F_1/\partial t=(\partial n_1/\partial t)(F_1/n_1)$. On the other hand, when n_1 increases the velocity v_{1x} decreases, such that we have

$$v_{1x}\frac{\partial F_1}{\partial x}=v_{1x}\frac{\partial n_1}{\partial x}\frac{F_1}{n_1}+\beta mv_{1x}^2\frac{\partial v_{1x}}{\partial x}n_1\frac{F_1}{n_1}\simeq\frac{\partial}{\partial x}(n_1v_{1x})\frac{F_1}{n_1} \quad , \tag{4.18}$$

where we have approximated $\beta m\overline{v_{1x}^2}$ by 1; therefore, we get

$$\frac{\partial n_1}{\partial t}=-\frac{\partial}{\partial x}(n_1\overline{v}_{1x}) \tag{4.19}$$

(the velocity is viewed here as its mean value). In equation (4.19) we take the flux of concentration n_1/σ_1 and use $\sigma_1 = v_1/\Lambda_1$, $v_1 = \Lambda_1\sigma_1 = \frac{a^2}{\sigma_1}a\sigma_1 = a^3$; therefore, we have

$$\frac{\partial^2 n_1}{\partial t \partial S} = -n\Lambda_1 \frac{\partial}{\partial x}(n_1 v_{1x}) \quad , \tag{4.20}$$

or

$$\frac{\partial^2 c}{\partial t \partial S} = -\Lambda_1 \frac{\partial}{\partial x}(n_1 \overline{v}_{1x}) \tag{4.21}$$

for the concentration $c = n_1/n$. The velocity $\overline{v}_{1x}$ is kept under the spatial derivative for the case of thermodiffusion, when $\overline{v}_{1x}$ varies with the temperature; the macroscopic change in time of the concentration is given by equation (4.6).

4.3 Thermopower

Sometimes, it is convenient to define the distribution function as $F = Ce^{-\frac{1}{2}\beta mv^2 - \beta U}$, where U is the potential energy, and

$$\frac{1}{(2\pi\hbar^2)^3} \int d\mathbf{p} d\mathbf{r} F = N \quad , \tag{4.22}$$

where $\mathbf{p} = m\mathbf{v}$ is the momentum; for $U = 0$ we get

$$F = \left(\frac{2\pi\beta\hbar^2}{ma^2}\right)^{3/2} e^{-\frac{1}{2}\beta mv^2} = e^{\beta\mu - \frac{1}{2}\beta mv^2} \quad , \tag{4.23}$$

where

$$\mu = \frac{3}{2} T \ln\left(\frac{2\pi\beta\hbar^2}{ma^2}\right) \tag{4.24}$$

is the chemical potential; for an ideal classical gas $\hbar^2/ma^2 \ll T$ and μ has large negative values.

The stability of the distribution function at equilibrium implies the occurrence of an electromotive force $\mathcal{E} = \Delta U$ (a voltage drop ΔU) as a consequence of a difference of temperature; indeed, from equation (4.23) we have

$$\mu\delta\beta - \frac{1}{2} m\overline{v^2}\delta\beta + \beta\delta\mu = 0 \quad , \tag{4.25}$$

or

$$\delta\mu = \left(-\frac{3}{2} + \frac{\mu}{T}\right)\delta T \tag{4.26}$$

(with $\frac{1}{2}m\overline{v^2} = \frac{3}{2}T$); the change $\delta\mu$ in the chemical potential is $-q\mathcal{E}$, where q is the charge of the particle; therefore,

$$\mathcal{E} = \frac{1}{q}\left(\frac{3}{2} - \frac{\mu}{T}\right)\delta T = Q\delta T \quad , \tag{4.27}$$

where

$$Q = \frac{1}{q}\left(\frac{3}{2} - \frac{\mu}{T}\right) \tag{4.28}$$

is called thermopower.

4.4 General transport

The distribution function (particle density)

$$F = e^{\beta\mu - \beta p^2/2m} \tag{4.29}$$

derived above (equation (4.23)), with the general normalization condition

$$\frac{1}{(2\pi\hbar^2)^3}\int d\mathbf{p}d\mathbf{r}F = \sum F = N \tag{4.30}$$

(equation (4.22)) depends on the parameter T and on the parameter $\mu(T, p)$, where p is the pressure. We can introduce another parameter, a macroscopic velocity $\mathbf{V}$, through

$$F = e^{\beta\mu - \beta p^2/2m} = e^{\beta\mu - \frac{1}{2}\beta m(\mathbf{v}-\mathbf{V})^2} \tag{4.31}$$

(without changing the normalization condition); of course, we may include an energy ε in this distribution. In computations we understand $(\mathbf{v} - \mathbf{V})^2 = v^2 - 2\mathbf{v}\mathbf{V}$. The parameters T, p and $\mathbf{V}$ may depend on the time t and position $\mathbf{r}$, such that we have a local equilibrium, but not a global one. The transport equation for the density F will give an equation which reflects the time and position variations of these parameters; these are general transport equations.[3] In particular, the statistical averaging of the transport equation leads to the equations of the conservation of the density, momentum and energy of a fluid, *i.e.* the Navier-Stokes equation.

Let us assume that the entropy S depends on some variables x_α, $S(x_\alpha)$; its time derivative can be written as

$$\frac{dS}{dt} = \frac{\partial S}{\partial x_\alpha}\dot{x}_\alpha = -X_\alpha \dot{x}_\alpha \quad , \tag{4.32}$$

where $X_\alpha = -\partial S/\partial x_\alpha$ may be viewed as generalized forces for the generalized coordinates x_α; since the entropy must increase in time, we should have, in first approximation,

$$\dot{x}_\alpha = -\gamma_{\alpha\beta} X_\beta \ ; \tag{4.33}$$

then, the quadratic form

$$\frac{dS}{dt} = \gamma_{\alpha\beta} X_\alpha X_\beta \tag{4.34}$$

where the symmetric matrix $\gamma_{\alpha\beta}$ should be positive. These are Onsager's reciprocity relations,[4] and equations (4.33) give the general transport laws. The coefficients $\gamma_{\alpha\beta}$ are called kinetic coefficients.

If an external force is present, then we should first solve the Boltzmann equation for the distribution function and thereafter compute the transport laws with this distribution; external fields affect the kinetic coefficients. However, approximate methods can be used to estimate directly the effect of the force upon the kinetic coefficients.

There exist two limiting regimes of flow in fluids, one characterized by the Mach number $M = V/v_s \gtrsim 1$ and another characterized by the Reynolds number $R = Vl/\nu > 1$, where V is the flow velocity, v_s is the sound velocity, l is the dimension of the container and $\nu = \eta/\rho$ is the kinematic viscosity; the first condition gives a supersonic flow, while the second condition gives a turbulent flow. In gases v_s is of the order of the thermal velocity v and ν is of the order $\rho v \Lambda$, where Λ is the mean freepath; it follows $M/R \simeq \Lambda/l$; this is called the Knudsen number K. The transport equations assume $K \ll 1$. Higher-order contributions in powers of K would imply higher-order variations of the distribution function, which are not warranted by the kinetic approach. Moreover, higher K would imply taking into account the boundary conditions. If K is of the order unity the spatial derivatives become meaningless, and they may be replaced by finite differences.

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[3] D. Enskog, *Kinetische Theorie der Vorgange in massig verdunnten Gasen*, PhD Thesis, Uppsala, 1917; S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, Cambridge University Press, Cambridge (1970).

[4] L. Onsager, "Reciprocal relations in irreversible processes. I.", Phys. Rev. **37** 405 (1931); "Reciprocal relations in irreversible processes. II.", **38** 2265 (1931); H. B. Callen, "The application of Onsager's reciprocal relations to thermoelectric, thermomagnetic, and galvanomagnetic effects", Phys. Rev. **73** 1349 (1948).

4.5 Brownian motion

Small particles, with dimensions in the range from tens to of thousands nanometers (nm, $1nm = 10^{-7}cm$), move chaotically when suspended in a liquid, as a consequence of the atomic (molecular) collisions. This motion is known as the Brownian motion.[5] The Brownian particles may be viewed as a statistical ensemble, which reflects the statistical motion in liquids, with one amendment: each particle suffers many collisions, such that the velocity imparted to each particle is the fluctuation of the statistical velocity of the molecules; therefore, it may be viewed as a single velocity $\mathbf{v}$; the Brownian particles are a statistical ensemble only with respect to the spatial distribution of their concentration.[6]

A large ensemble of a dilute solute consisting of N atoms or molecules confined to a volume V and dissolved into a solvent has an osmotic (van't Hoff's) pressure p given by

$$pV = NT \quad , \tag{4.35}$$

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[5] R. Brown, "A brief account of microscopical observations made in the months of June, July and August 1827 on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies", Phil. Mag. **4** 161 (1828).

[6] A. Einstein, "Uber die von der molekularkinetischen Theorie der Warme geforderte Bewegung von in ruhenden Flussigkeiten suspendierten Teilchen", Ann. Phys. **17** 549 (1905).

where T denotes the temperature, according to the equation of state of a classical ideal gas. The osmotic pressure is exerted, for instance, on the wall of a partition separating the solute from the rest of the solvent, the partition being impermeable for the solute but permeable for the solvent. A similar osmotic pressure is expected if the solute atoms or molecules are replaced by small particles suspended into the solvent, because the theory of heat does not differentiate between particles with small dimensions. Consequently, small particles suspended into a solvent perform a chaotic motion, which is the Brownian motion. A surface tension appears in this case too, on the partition wall.

Between two successive collisions we may consider a uniform motion of the Brownian particles. Small particles moving uniformly in a viscous liquid (fluid) experience a force of resistance. Indeed, the force term in the Navier-Stokes equations for incompressible fluids is $-gradp+\eta\Delta\mathbf{v}$, where p is the pressure, η is the (first) viscosity coefficient and $\mathbf{v}$ is the fluid velocity;[7] we can see that the viscosity generates a pressure, which, for motion along one direction, say, the x-direction, can be written approximately $p = \eta\partial v/\partial x$ for small particles; v being the x-component of the fluid velocity. The force exerted by the pressure p on the particle along the direction of motion is given by

$$F = \oint dSp = \eta\oint dS\frac{\partial v}{\partial x} \quad , \tag{4.36}$$

where the integration is performed over the surface S of the body. The integral in equation (4.36) can be approximated by $4\pi rv$ for small velocities, where r is the "radius" of the body and v is the velocity of the body; we use the same letter v for the velocity of the particle and the velocity of the fluid. Therefore, we can write the force as

$$F = 2\pi\alpha r\eta v \quad , \tag{4.37}$$

where α is a numerical coefficient of the order of unity, which accounts for the shape of the particle. For a sphere $\alpha = 3$. This is known as Stokes' law. Along a distance δx this force does a mechanical work $F\delta x$, such that the mechanical work done per unit area perpendicular to the direction of motion is

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[7] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 6, *Fluid Mechanics*, Elsevier (2004).

$$\int dxnF\delta x \ \ , \tag{4.38}$$

where n is the concentration of the particles.

The free energy of an ideal classical gas of pointlike particles with mass m is[8]

$$\mathcal{F} = -NT\ln\left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right] \tag{4.39}$$

(the entropy is

$$\mathcal{S} = -\partial F/\partial T = N\ln\left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right] + \frac{3}{2}N \ \ . \tag{4.40}$$

Along a distance δx the (local) free energy given by equation (4.40) acquires a change $\delta\mathcal{F} = -nT\delta x$ per unit area; consequently, a force $nT\frac{\partial(\delta x)}{\partial x}$ occurs per unit area and a mechanical work

$$T\int dxn\frac{\partial(\delta x)}{\partial x} = -T\int dx\frac{\partial n}{\partial x}\delta x \tag{4.41}$$

(at constant temperature). At equilibrium the total energy must be constant, so we have

$$\int dxnF\delta x + T\int dxn\frac{\partial(\delta x)}{\partial x} = 0 \ \ , \tag{4.42}$$

or

$$nF = T\frac{\partial n}{\partial x} \tag{4.43}$$

(in absolute value). Since the (osmotic) pressure is $p = nT$, we can also write

$$nF = \frac{\partial p}{\partial x} \ \ . \tag{4.44}$$

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[8] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier (1980).

The variation of the concentration in time during the motion along the x-direction is

$$\frac{\partial n}{\partial t} = v\frac{\partial n}{\partial x} = \frac{vT}{F}\frac{\partial^2 n}{\partial x^2} = \frac{T}{2\pi\alpha r\eta}\frac{\partial^2 n}{\partial x^2} \quad , \tag{4.45}$$

which is the diffusion equation with the diffusion coefficient $D = T/2\pi\alpha r\eta$. If we multiply this equation by v we get $nv = D\frac{\partial n}{\partial x}$ (in absolute value), an equation known as Fick's law.

It is worth noting that if a force field $\Phi(x)$ acts upon the particles, then their concentration $n(x) \sim e^{-\Phi(x)/T}$ has the derivative $\partial n/\partial x = -\frac{1}{T}(\partial\Phi/\partial x)n$, or $\partial n/\partial x = (F/T)n$, where F is the force; then we get Fick's law $nv = (Tv/F)(\partial n/\partial x)$ with $D = Tv/F$; v/F is called mobility. Fick's law can be applied to generalized coordinates; for instance, if the coordinate is the electric charge q, then the velocity is $v = dq/dt = I$ (the intensity of the electric current) and the force is $F = U$ (since $\partial(qU)/\partial q = U$); it follows $D = TI/U = T/R$, where R is the electric resistance.

4.6 Diffusion equation

First we note that, since $\delta\mathcal{S} = -(NT/n)\delta n$, the diffusion equation

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} \tag{4.46}$$

is also the equation of heat diffusion. Of course, in two or three dimensions it looks like $\partial n/\partial t = D\Delta n$. For an infinite space the solution of equation (4.46) can be written as a Fourier integral

$$n(t,x) = \frac{1}{2\pi}\int dkn(t,k)e^{ikx} \tag{4.47}$$

with $n(t,k) = n(0,k)e^{-Dk^2t}$; hence,

$$n(t,x) = \frac{1}{2\pi}\int dkn(0,k)e^{-Dk^2t+ikx} \quad . \tag{4.48}$$

If we assume that at the initial time the concentration n_0 is distributed over a small distance d, *i.e.* if $n(0,x) = n_0 d\delta(x)$, then $n(0,k) = n_o d$

and

$$n(t,x)=\frac{n_0d}{2\pi}\int dke^{-Dk^2t+ikx}=\frac{n_0d}{\sqrt{4\pi Dt}}e^{-\frac{x^2}{4Dt}}\ . \tag{4.49}$$

The obvious generalization to two or three dimensions is

$$n(t,r)=\frac{n_0d^3}{(4\pi Dt)^{3/2}}e^{-\frac{r^2}{4Dt}}\ . \tag{4.50}$$

We can see that the concentration is distributed according to a gaussian law, with a front surface which propagates as $r\simeq 2\sqrt{Dt}$; the deviation of the distance is $\delta x=\sqrt{\overline{x^2}}=\sqrt{2Dt}$; the number of particles is conserved, $\int d\mathbf{r}n(t,r)=n_0d^3$.

The mean square deviation $\left[\overline{\delta r^2}(t)\right]^{1/2}=\sqrt{2Dt}$ implies fluctuations. Indeed, let us assume that the displacement proceeds in steps, from 1 to N, and write

$$\mathbf{r}_N=\mathbf{r}_N-\mathbf{r}_{N-1}+\mathbf{r}_{N-1}-\mathbf{r}_{N-2}+...=\sum_{i=1}^{N}\delta\mathbf{r}_i\ ; \tag{4.51}$$

then,

$$\overline{\delta r^2}(t)=\overline{r_N^2}=\sum_{i,j}\overline{\delta\mathbf{r}_i\delta\mathbf{r}_j}=N\delta r^2\ \ , \tag{4.52}$$

where $\delta r^2=\overline{\delta r_i^2}$; each step needs a duration τ, which is a fluctuation time, such that $N=t/\tau$. It follows $2Dt=t\delta r^2/\tau$ and $\delta r^2=2D\tau$, $D=\delta r^2/2\tau$. This is called the random walk process.

For $2r=10^{-4}cm$ ($1\mu m$) at room temperature ($T=300K$) and water with viscosity $\eta=1.35\times10^{-2}g/s\cdot cm$ we get a mean displacement $\delta x\simeq 0.8\times10^{-4}cm$ per second (for spherical particles, $\alpha=3$).[9] We can see that the diffusion is much slower than the thermal motion. Making use of the Boltzmann constant $k_B=R/N$, where R is the universal constant of gases and N is Avogadro's number, we can get $N=6\times10^{23}mol^{-1}$ from measurements of δx (R is known from the law of the ideal gases). For molar volumes of the order $1cm^3$ we get the atomic dimensions of the order $10^{-8}cm$. Einstein's theory of brownian motion enforced the atomistic conception of matter.

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[9] J. Perrin, *Les Atomes*, Alcan, Paris (1913).

The Brownian motion occurs also for the rotation of the particles, with the mean square displacement given by $r^2\delta\varphi^2 = 2Dt$, where φ is the rotation angle and $D = T/2\pi\alpha r\eta$.

The electric charge in a mol of singly ionized molecules is Faraday's number $F = 96000C/mol$, given by $F = qN$, where $-q = 1.6 \times 10^{-19}C$ is the electron charge and $N = 6 \times 10^{23}mol^{-1}$ is Avogadro's number. The force acting upon the charges in a mol in electrolysis is $qE = qU/l = qRI/l = q^2RNv/l^2$, where E is the electric field, U is the voltage drop, I is the intensity of the electric current, R is the electric resistance and l is the length of the sample; hence we get $D = vT/qE = l^2T/Rq^2N$ and the mean square displacement given by $\delta x^2 = 2Dt$.

The flow of electric charges through a conductor is a diffusion. The equation of motion $mv/\tau = qE$ for an electric charge q with mass m in the electric field E, where τ is the collision (relaxation) time, gives the current density $j = nqv = nq^2\tau E/m$ and the conductivity $\sigma = nq^2\tau/m$ ($\omega_p^2 = 4\pi nq^2/m$ is the plasma frequency). On the other hand, from the equilibrium concentration $n \sim e^{-qU/T}$, where U is the voltage drop, we have $\partial n/\partial x = qnE/T = nmv/\tau T$; hence, we get Fick's law $nv = D\partial n/\partial x$, where $D = \tau T/m$; or, taking the derivative, $v\partial n/\partial x = D\partial^2 n/\partial x^2$, or the diffusion equation $\partial n/\partial t = D\partial^2 n/\partial x^2$. The equation is valid also for oscillating fields, providing their frequency ω is smaller than $1/\tau$ ($\omega\tau \ll 1$). The stationary equation $\partial^2 n/\partial x^2 = 0$ gives the stationary electric flow $n = Ax + B$, where the constants A and B are determined from the boundary conditions (the charge density at the boundary determines the voltage drop).

4.7 Thermodiffusion

In equation (4.41) the temperature is constant; the change in the free energy at constant temperature is the same as the change in the energy at constant entropy (this is the so-called law of small increments of the thermodynamic potentials); therefore, we may allow the temperature to vary in space, and get

$$nF = T\frac{\partial n}{\partial x} + n\frac{\partial T}{\partial x} \tag{4.53}$$

instead of equation (4.43); Fick's law becomes

$$nv = D\left(\frac{\partial n}{\partial x} + \frac{n}{T}\frac{\partial T}{\partial x}\right) \quad ; \tag{4.54}$$

the additional term $\sim \partial T/\partial x$ is responsible for thermodiffusion.[10] In general, from $nv = D(\partial n/\partial x)$ we can see that D is of the order $v\Lambda$. This result is valid for the Brownian motion.

For the diffusion of a gas into another gas the stationarity of the distribution $F \sim ne^{-\frac{1}{2}\beta mv^2}$ (where v is along the direction x of the diffusion) implies the derivatives

$$\frac{\partial F}{\partial x} = \frac{\partial n}{\partial x}\frac{F}{n} - \frac{1}{2}mv^2\frac{\partial \beta}{\partial x}F \tag{4.55}$$

and $\partial F/\partial t = (\partial n/\partial t)(F/n)$; making use of $\overline{mv^2}/2 = T/2$ and $\partial n/\partial t = n/\tau$, and taking the correct sign, we get Fick's law

$$nv = D\left(\frac{\partial n}{\partial x} + \frac{n}{2T}\frac{\partial T}{\partial x}\right) \quad , \tag{4.56}$$

where $D = v\Lambda$. We note the difference in the numerical coefficients in equations (4.54) and (4.56).

4.8 Particle density

The partition function of an ideal classical gas with N (pointlike) particles is

$$Z = \frac{1}{N!}\left[\frac{1}{(2\pi\hbar)^3}\int d\mathbf{p}d\mathbf{r}e^{-\beta\varepsilon}\right]^N = e^{-\beta\mathcal{F}} \quad , \tag{4.57}$$

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[10] D. Enskog, "Bemerkungen zu einer Fundamentalgleichung in der kinetischen Gastheorie", Phys. Z. **12** 538 (1911).

where ε is the energy of the particle and $\mathcal{F}$ is the free energy; this equation can also be written as

$$Z = \frac{1}{N!}\left[\sum e^{-\beta\varepsilon}\right]^N = e^{-\beta\mathcal{F}} \quad , \tag{4.58}$$

where the summation is extended to all the states of a particle. The pre-factor $1/N!$ is Gibbs's pre-factor, which accounts for the identity of the particles. Since $N! = (N/e)^N$, we can also write

$$\left[\frac{e \cdot e^{\beta\mathcal{F}/N}}{N}\sum e^{-\beta\varepsilon}\right]^N = 1 \ ; \tag{4.59}$$

obviously,

$$\rho = \frac{e \cdot e^{\beta\mathcal{F}/N}}{N} e^{-\beta\varepsilon} \tag{4.60}$$

is a probability density and

$$f(\mathbf{p}, \mathbf{r}) = e \cdot e^{\beta\mathcal{F}/N} e^{-\beta\varepsilon} \tag{4.61}$$

with the normalization

$$\sum f(\mathbf{p}, \mathbf{r}) = N \tag{4.62}$$

is the particle density (particle distribution; the same distribution is derived above, with the chemical potential μ included explicitly); we may write also $f(\mathbf{p}, \mathbf{r}) = Ce^{-\beta\varepsilon}$ with the constant C given by the normalization condition (4.62); and $\rho = f/N$.

From equation (4.61) we have

$$\ln(f/e) = \beta\mathcal{F}/N - \beta\varepsilon \quad , \tag{4.63}$$

or

$$\varepsilon = \mathcal{F}/N - T\ln(f/e) \ ; \tag{4.64}$$

it follows that

$$\mathcal{S} = -\sum f \ln(f/e) = -\frac{1}{(2\pi\hbar)^3}\int d\mathbf{p}d\mathbf{r} f \ln(f/e) \tag{4.65}$$

is the entropy.

4.9 Fluctuations. Einstein's kinetic equation

In contrast with the mechanical motion, the statistical motion goes by independent changes of states $\mathbf{p}$, $\mathbf{r}$. A corresponding change appears in the particle density f introduced above. Let us assume that $\mathbf{r}$ is changed by $\mathbf{a}$ in time τ, and leave aside for the moment the $\mathbf{p}$-dependence. The conservation of the number of particles requires

$$\begin{gathered} f(t+\tau,\mathbf{r})-f(t,\mathbf{r})=f(t,\mathbf{r}-\mathbf{a})-f(t,\mathbf{r})+ \\ f(t,\mathbf{r}+\mathbf{a})-f(t,\mathbf{r}) \ \ , \end{gathered} \tag{4.66}$$

or

$$\frac{\partial f}{\partial t}=\frac{a_i a_j}{2\tau}\partial_i\partial_j f \ \ . \tag{4.67}$$

The changes a_i are fluctuations in position; consequently, their mean values are zero and $\overline{a_i a_j}=a^2\delta_{ij}$; we get

$$\frac{\partial f}{\partial t}=\frac{a^2}{2\tau}\Delta f \ \ . \tag{4.68}$$

Including similar changes b in momentum, we have

$$\frac{\partial f}{\partial t}=(a^2/2\tau)\Delta_{\mathbf{r}}f+(b^2/2\tau)\Delta_{\mathbf{p}}f \ \ . \tag{4.69}$$

This is a diffusion equation for states. It is Einstein's kinetic equation.[11] The change in time of the entropy given by equation (4.65) is

$$\begin{gathered} \tfrac{\partial S}{\partial t}=-\sum\tfrac{\partial f}{\partial t}\ln f= \\ =-\sum\left[(a^2/2\tau)\Delta_{\mathbf{r}}f+(b^2/2\tau)\Delta_{\mathbf{p}}f\right]\ln f \ \ ; \end{gathered} \tag{4.70}$$

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[11] A. Einstein, "Zur Theorie der Brownschen Bewegung", Ann. Phys. **19** 371 (1906). Equation (4.69) with only the $\mathbf{p}$-term is known as the Fokker-Planck equation (A. D. Fokker, "Die mittlere Energie rotierender elektrischer Dipole im Strahlungsfeld", Ann. Phys. **348** 810 (1914); M. Planck, "Uber einen Satz der statistischen Dynamik und seine Erweiterung in der Quantentheorie", Sitzungsber. Preuss. Akad. Wiss. Berlin **24** 324 (1917)). The Brownian motion also suggested an equation of motion with a stochastic force, called Langevin equation (P. Langevin, "Sur la theorie du mouvement brownien", C. R. Acad. Sci. Paris **146** 530 (1908)).

an integration by parts here leads to

$$\frac{\partial S}{\partial t} = \sum \frac{1}{f}\left[(a^2/2\tau)(grad_{\mathbf{r}} f)^2 + (b^2/2\tau)(grad_{\mathbf{p}} f)^2\right] \geq 0 \ ; \qquad (4.71)$$

this inequality shows the increase of entropy in time. At equilibrium $a = b = 0$. It is worth noting that, although Einstein's kinetic equation has the form of a diffusion equation, the coefficients a and τ have a different meaning than in the diffusion equation; these coefficients are fluctuations in position and time, while those in the diffusion (transport) equation are governed by the mean freepath and the thermal velocity. In Einstein's kinetic equation a is of the order of the mean separation between the particles.

It is worth noting the meaning of Einstein's kinetic equation. It is thought that the collisions may bring about these fluctuations; this is not correct, because in (pointlike) collisions the position is not changed, and the momentum changes according to the mechanical laws, not by fluctuations. This is more visible in cases where the equilibrium is not achieved by collisions, but by interactions. At equilibrium the fluctuations a and b vanish, and the statistical motion ceases (fluctuations become stationary). The fluctuations drive the ensemble to equilibrium. Einstein's fluctuations capture the nature of the statistical motion and are equivalent with the principle of equilibrium and the law of increase of entropy.

The above considerations apply to the Brownian motion and to the particle concentration $n(t, r) \sim f$ given by equation (4.50), inasmuch as we view the Brownian motion as an approach to equilibrium. Indeed, if we write

$$n(r, t) = \frac{C}{(\pi\alpha)^{3/2}} e^{-r^2/\alpha} \qquad (4.72)$$

with $C = n_0 d^3$ and $\alpha = 4Dt$ in equation (4.50), then $f = a^3 n$, where a is the mean inter-particle separation; we assume that initially N particles are distributed in the small volume d^3. Then, the entropy given by equation (4.65) can be computed; we get

$$\mathcal{S} = -N \ln \frac{a^3 N}{e(e\pi\alpha)^{3/2}} = -N \ln \frac{a^3 N}{e(4e\pi D t)^{3/2}} \ ; \qquad (4.73)$$

we can see that the entropy in the Brownian motion increases in time. We note that this is the global entropy of the Brownian motion, which is different from the local entropy given by equation (4.40); in particular, it does not depend on the volume, as expected (the Brownian particles move in the whole space). In order to deal conveniently with the initial time, we introduce the cutoff $t_0 = d^2/4\pi eD$ and write the entropy as

$$\mathcal{S} = -N \ln \left[\frac{a^3 N}{ed^3} (t_0/t)^{3/2} \right] \ ; \tag{4.74}$$

indeed, the entropy of the initial particle distribution (with concentration $n_0 d^3 \delta(x)$) is $S_0 = -N \ln(a^3 N/ed^3)$. From $S = -\partial \mathcal{F}/\partial T$ we can compute the free energy $\mathcal{F}$ of the Brownian particles; the constant of integration being determined from the initial free energy $\mathcal{F}_0 = E_0 - T\mathcal{S}_0$, where we take the initial energy $E_0 = 3NT/2$ (which is conserved); we get

$$F = NT \ln \left[\frac{a^3 N \sqrt{e}}{d^3} (t_0/t)^{3/2} \right] = \frac{3}{2} NT - T\mathcal{S} \ . \tag{4.75}$$

The Brownian particles absorb the heat

$$\frac{dQ}{dt} = T \frac{d\mathcal{S}}{dt} = \frac{3NT}{2t} \tag{4.76}$$

per unit time from the background, which gets colder; the two ensembles (Brownian particles and the background), initially in thermal equilibrium, suffer a thermal decoupling. We note that the Brownian motion is at local equilibrium (the derivation of the diffusion law in equations (4.39)-(4.41) make use of this circumstance), while it is not at global equilibrium. This is a typical situation for the transport phenomena.

Similar considerations can be applied to the diffusion of a gas into another gas; in that case, in general, we should use the diffusion equation given by equation (4.69), where a is the mean freepath, b is the momentum change in collisions and τ is the collision time. The two gases should not be in mutual thermal equilibrium at the initial moment.

4.10 Molecular fluctuations

The statistical motion still deserves a further discussion. Let us assume a classical gas of identical, interacting, pointlike particles; even if the gas is an ideal gas, there exist collisions, which imply an interaction. According to the Classical Mechanics we may try to solve Newton's equations of motion for each particle in the gas; and hope to get trajectories, *i.e.* time-dependent coordinates q (and time-dependent momenta p) which would depend on the initial conditions q_0 and p_0. In general, for $N > 2$ particles this task is impossible. Indeed, first, the equations of motion for each particle are not integrable.[12] Second, it is believed that there exist integrals of the motion, *i.e.* functions of q and p constant in time, as many as the number of unknown coordinates and momenta (which would correspond to the initial conditions), which would give the solution; unfortunately, only a few may be algebraic (and, therefore, useful); even if such integrals existed, their use would imply either infinite Taylor expansions or approximate numerical calculations;[13] approximate solutions depend chaotically on the initial conditions.[14] All these show that the classical motion of many particles is not integrable. A similar conclusion is more than evident for the quantum-mechanical motion.

In these conditions what is left for us to say about the classical motion? We can only say that there exists a function $S(t, q)$ of classical action, with an energy $E = -\partial S/\partial t$ and momenta $p = \partial S/\partial q$, and a Hamilton function written as

$$H(t, p, q) = \sum \frac{1}{2m} p^2 + U(t, q) \quad , \tag{4.77}$$

where m is the particle mass and U is the interaction, such that $E = H$; if the problem were soluble, we would have the Hamilton-Jacobi equation

$$\frac{\partial S}{\partial t} + H(t, \partial S/\partial q, q) = 0 \tag{4.78}$$

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[12] M. Apostol, "The many-body theory: its logic along the years", J. Theor. Phys. **152** (2007).

[13] See, for instance, F. Diacu, "The solution of the n-body problem", Math. Intell. **18** 66 (1996) and references therein.

[14] H. Poincare, *Les Méthodes Nouvelles de la Mécanique Celeste*, Gauthier-Villars, Paris (1892, 1893, 1899).

for the function S; but the problem is not soluble, so we have not such an equation. However, the symmetries under time translations, spatial translations and rotations imply the conservation of the energy E, total momentum and total angular momentum.

We may attempt to get a way out from this problem by resorting to the quantum-mechanical motion; after all, the quantum-mechanical motion is the basic form of mechanical motion. Indeed, the most general form of motion is

$$-Edt + pdq = dS \quad , \tag{4.79}$$

and, if there exists a quantum of action h, then $\Delta S = h\Delta n$, where Δn is an integer; and we may write $E = h\Delta n/T$, $p = h\Delta n/\lambda$; *i.e.* there should exist a period T and a wavelength λ of a wave which can be written as $\psi = e^{i2\pi S/h}$. If this motion were soluble, the wavefunction would obey the Schrodinger equation $i\hbar\partial\psi/\partial t = H\psi$, with $p = -i\hbar\partial/\partial q$ (and $\hbar = h/2\pi$), which becomes the Hamilton-Jacobi equation for $h \rightarrow 0$. But it is not, and we are left with the (quasi-classical) quantization rules given above and the conservation of the energy, momentum and angular momentum; and, of course, with the uncertainty relations associated with the wavefunction.

We can see from the above discussion that we cannot describe the many-body assemblies by their mechanical motion. But we may admit that the initial conditions are distributed chaotically, with a probability, especially that such a suggestion seems to be supported by the experimental observations; then, at the next infinitesimal moment this description is valid, with the same probability. It follows that a probability distribution which is uniform and constant in time for states defined by p, q (or for the quantum-mechanical states) is a consistent assumption, and, therefore, it may correspond to natural phenomena. The motion that obeys a constant probability distribution of states is the (equilibrium) statistical motion; its time-independence is the statistical equilibrium. Making use of the conservation laws we get immediately the Gibbs statistical distribution, temperature and heat; this is why the statistical equilibrium is called also thermal equilibrium. Subjected to external perturbations the statistical distribution may change globally in time, but locally its constant character is preserved (such changes include the transport phenomena). A chaotical distribution with conservation of energy, momentum or angular momentum implies the maximum of the entropy; any deviation from equilibrium would mean a decrease in entropy. In given conditions the entropy is the (mean) logarithm of the number of states.

Making use of statistical distributions we can only have access to mean values and deviations from mean values, which are the fluctuations. From the definition of the entropy S, it follows that any deviation from equilibrum, driven by a variable x, will have a probability $\sim e^{\frac{1}{2}(\partial^2 S/\partial x^2)x^2}$, where the derivative is taken at equilibrium ($x = 0$; the first-order derivative of the entropy at equilibrium vanishes; $\partial^2 S/\partial x^2 < 0$). It follows $\overline{x} = 0$ and $\overline{x^2} = 1/(\partial^2 S/\partial x^2)$; we denote by δx the root mean square $\delta x = \sqrt{\overline{x^2}}$; this is the fluctuation of x. For instance, the fluctuations of the molecular volume of an ideal classical gas is $\delta v = v$ ($S/N \sim \ln v$) and $\delta a = v^{1/3}/3$, where a is the mean separation distance between the particles. Similarly, since $S \sim \frac{3}{2} \ln T$, the energy fluctuation per particle is $\delta e = \frac{3}{2}\delta T = \sqrt{3/2}T$ (3/2 is the heat capacity per particle); since $\delta S = nh = \delta(e\tau) = \delta e \delta\tau$, where $\delta\tau$ is the fluctuating time, we get $\delta\tau = \sqrt{2/3}nh/T$ (we note that the statistical fluctuating time is much longer than the quantum-mechanical fluctuating time h/T) . We may extend the equation of diffusion to these molecular fluctuations, with $D = \delta a^2/2\delta\tau = a^2 Tnh/6^{2/3}$; we may also extend the formula $D = T/2\pi\alpha\eta a$ to a "viscosity" produced by interaction, such that we get $\eta = (3\sqrt{6}/\pi\alpha)(nh/a^3)$, which indicates a quantum of viscosity of the order h/a^3 (or h/m).[15]

It is worth comparing the fluctuating time with the collision time in a classical gas. The number of particles with velocity v and moving along the z-direction per unit time across the unit area of the cross section is

$$d\nu = \frac{N}{V}(m/2\pi T)^{3/2} e^{-mv^2/2T} v_z d\mathbf{v} \;\; ; \tag{4.80}$$

the reduced mass $m \to m/2$ must be introduced here for the motion with respect to one particle, and, with σ denoting the cross-section of a collision process, one obtains the number of collisions per unit time

$$\nu = \frac{\pi N}{2V}(m/\pi T)^{3/2} \int e^{-mv^2/4T} \sigma v^3 dv \tag{4.81}$$

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[15] M. Apostol, "Quanta of viscosity", Roum. J. Phys. **46** 339 (2001).

for one particle, or $\nu = (4\sigma/a^3)\sqrt{T/\pi m}$. Therefore, the collision time is $\tau_{coll} = 1/\nu \sim (a^2/\sigma)a\sqrt{m/T}$; the mean freepath is $l = v_{th}\tau_{coll} \sim (a^2/\sigma)a$, where $v_{th} = \sqrt{T/m}$. The gas is classical providing $n\lambda^3 \ll 1$, where $\lambda \sim h/\sqrt{mT}$ is the thermal wavelength, or $a\sqrt{mT} \gg h$, *i.e.* the classical action is much larger than the quantum of action. It follows that $\tau_{coll} \sim (a^2/\sigma)(1/T)a\sqrt{mT} \sim (a^2/\sigma)\delta\tau(a\sqrt{mT}/nh)$, where $\delta\tau$ is the fluctuating time. The classical action $a\sqrt{mT}$ is, however, much larger than the fluctuating action nh, so that $\tau_{coll} \gg \tau$ ($a^2/\sigma \gg 1$ also), *i.e.* the collision time is much longer than the fluctuating time, as expected. This is to be completed with $\delta\tau \gg h/T$, *i.e.* the statistical fluctuating time is much longer than the quantum-mechanical fluctuating time. Similarly, the quantum-mechanical elementary excitations have a much longer lifetime than $\delta\tau$, and τ_{coll} above may be viewed as the lifetime of a classical particle.

4.11 Quantum-mechanical "diffusion"

The statistical motion of quantum-mechanical particles deserves a special discussion. The quantum-mechanical nature is usually revealed for individual particles moving in restricted spaces, where the statistical motion is meaningless to a large extent. There exists a quantum-mechanical behaviour for macroscopic bodies, like superfluidity, or superconductivity, but there exists one purely quantum-mechanical state in such cases, such that a statistical motion is again pointless, to a large extent. The particles in condensed matter have a quantum-mechanical character, since they move in small spatial regions, but their localization energy is usually much larger than the temperature, such that the statistical motion affects only the quasi-particle elementary excitations, like in fermion matter; we have then a special thermodynamics of Fermi gases, like in He^3, or electrons in metals; usually, these quasi-particles have a quasi-classical behaviour. An exception is provided by the black-body radiation, or the long-wavelength phonons (sound waves), or collective elementary excitations, which may form purely quantum-mechanical Bose gases; these gases may also be viewed as gases of elementary excitations, but they are special, because they have practically infinite mean freepaths and lifetimes. It follows that transport properties, or the approach to equilibrium, do not imply usually a quantum-mechanical character.

However, we may consider formally the evolution of the quantum-mechanical distribution of probability ρ_n (diagonal elements of the density matrix) given by the master equation

$$\partial\rho_n/\partial t = \sum_m (T_{nm}\rho_m - T_{mn}\rho_n) \quad , \tag{4.82}$$

where T_{nm} is the transition probability per unit time from state n to state m; the quantum-mechanical counterpart of Einstein's kinetic equation is recognizable here. The transition probability T_{nm} is symmetric and positive. The entropy $S = -\sum \rho_n \ln \rho_n$ evolves in time according to

$$\partial S/\partial t = (1/2) \sum T_{nm}(\rho_m - \rho_n)(\ln\rho_m - \ln\rho_n) \geq 0 \quad , \tag{4.83}$$

i.e. it increases with time. In the quasi-classical description the states m in equation (4.82) are close to n, and the transition probability may be written as $T_{nm} \sim 1/n_c\tau$, where τ is the fluctuating time and n_c is the range of m-states in the neighbourhood of n; in addition, the distribution of probability can be expanded as $\rho_m = \rho_n + (m-n)(\partial\rho_n/\partial n) + (1/2)(m-n)^2(\partial^2\rho_n/\partial n^2) + ...$, so that equation (4.82) becomes

$$\begin{gathered}\partial\rho/\partial t \simeq \tfrac{1}{n_c\tau}\int dn \cdot (1/2)n^2(\partial^2\rho/\partial n^2) \simeq \\ \simeq (n_c^2/2\tau)(\partial^2\rho/\partial n^2) \quad .\end{gathered} \tag{4.84}$$

For the states n corresponding to position for instance, one recovers the classical equation of diffusion $\partial n/\partial t = (a^2/2\tau)(\partial^2 n/\partial x^2)$, since the distribution ρ is proportional to the particle density in the classical limit (the matrix elements nm are the $(n-m)$-Fourier transforms, and the states are described by position, momentum, and the rest of classical variables). It is worth noting here that approaching equilibrium by fluctuations is meaningful for statistical ensembles only, as expected, *i.e.* for ensembles with a large number of degrees of freedom (including wavevectors, as for fields), where the quasiclassical description works.

It is also worth noting that the usual kinetics, *i.e.* transport, either classical or quantum-mechanical, proceeds over long times and large distances, being limited, first, by carriers' lifetime (and the corresponding mean freepath), and, second, by fluctuations, both statistical and quantum-mechanical, in principle. In such circumstances, it is described by the continuity equation (which is the starting point of Einstein's kinetic equation too), where, however, a represents the mean freepath and τ represents the lifetime, or collision time.

4.12 A general form of diffusion equation

Let us assume an ideal classical gas which diffuses into a medium. First, we have a driving force $-Tgradn$ (per unit volume) which derives from the change in the free energy (osmotic pressure), as in equation (4.42); also, we may have an external force nF_e per unit volume. The equation of motion is

$$nm\frac{d\mathbf{v}}{dt} = n\mathbf{F}_e - Tgradn \ . \tag{4.85}$$

We are interested in slowly varying quantities, such that we may replace dt in this equation by the collision time τ and write $\Delta\mathbf{v} = \mathbf{v}$ instead of $d\mathbf{v}$, as an average velocity change in collision. We get

$$n\mathbf{v} = \frac{\tau}{m}n\mathbf{F}_e - \frac{\tau T}{m}gradn \ . \tag{4.86}$$

We recognize here the diffusion coefficient $D = \tau T/m$ and the mobility $B = \tau/m$ $(v/F = v/(mv/\tau))$; this is a general Fick's law. The transport equation

$$\frac{\partial n}{\partial t} + (\mathbf{v}grad)n = 0 \tag{4.87}$$

can be written

$$\frac{\partial n}{\partial t} + div\mathbf{i} = 0 \ \ , \tag{4.88}$$

where

$$\mathbf{i} = n\mathbf{v} = Bn\mathbf{F}_e - Dgradn \tag{4.89}$$

is the particle current density (flow); equation (4.88) is the continuity equation, which ensures the conservation of the number of particles.

The external-force term may be viewed as a correction to the diffusion coefficient (the collision time τ). Equation (4.88) can be written as

$$\frac{\partial n}{\partial t} = -B div(n\mathbf{F}_e) + D\Delta n \ . \tag{4.90}$$

We can see that the molecular nature of the gas is included in the collision time τ, which is of the order Λ/v, where $v \simeq \sqrt{T/m}$ is the mean thermal velocity.

4.13 Ionized gases

4.13.1 Plasma

Electric discharge or heating may ionize a gas, producing an electron density n and an ion density n_i; the gas remains electrically neutral, but multiple ionizations make n different from n_i. We get a plasma, whose place is in one of the next chapters. However, if plasma is sufficiently rarefied, *e.g.* if n, n_i are much smaller than the density of the atoms which remain neutral, the long range Coulomb forces are almost mutually compensated, such that we may view the electrons and the ions as ideal classical gases. The electrons get rapidly thermalized, due to their high mobility and Coulomb forces; usually, the ions are initially at thermal equilibrium and the ionization leaves them in thermal equilibrium. But the exchange of energy between ions and electrons is unbalanced, due to the great difference between the electron mass and the ion mass, such that the plasma is non-thermal, *i.e.* the electron temperature is much higher than the ion (and neutral atoms) temperature. The motion of the much heavier ions and neutral atoms is not of much interest, such that we may focus on the electron gas, which, in these conditions may be viewed as an ideal classical gas. The stability of the plasma is a problem which is approached in one of the next chapters.

We may admit that there is a rate of ionization, either a photoionization, or an ionization through collisions; and there is a rate of recombination, proportional to the product nn_i. The latter, due to radiative recombination or collisions mediated by a neutral atom, is very small.

For a slow recombination process wherein the electron energy ε is lost gradually a diffusion equation of the type $\partial n/\partial t = D(\partial^2 n/\partial\varepsilon^2)$ can be written, where D is given by $D = \delta\varepsilon^2/2\tau$.

4.13.2 Electrical conduction

Let us assume a collection of electrons with mass m ($m = 10^{-27}g$) and charge q ($q = -4.8 \times 10^{-10} esu$), with a sufficiently high temperature T ($1K = 1.38\times10^{-16} erg$), such that they behave as classical particles, *i.e.* $\hbar^2/ma^2 \ll T$, where $\hbar = 10^{-27} erg\cdot s$ is Planck's constant and $a = 1/n^{1/3}$ is the mean separation distance between them, n being their density. A background of positive ions with the same density n ensures the electrical neutrality. The electron distribution is the Maxwell distribution. The electrons and the ions interact with Coulomb forces; their interaction with neutral atoms may be neglected. A measure of the Coulomb interaction is the charge self-energy q^2/a. If the ensemble of charges is sufficiently rarefied and at a sufficiently high temperature, such that $q^2/a \ll T$, we may leave aside the Coulomb interaction and view the electrons as an ideal classical gas, each electron having a "radius" of the order $a_0 = q^2/T \ll a$. It follows that the electrons have a mean freepath $\Lambda = (a^2/a_0^2)a$ ($\Lambda \sim T^2$), a collision time $\tau = \Lambda/v$, where $v \simeq \sqrt{T/m}$ is the mean thermal velocity ($\tau \sim T^{3/2}$) and a collision frequency $\gamma = 1/\tau \sim T^{-3/2}$. A similar "radius" can be defined for ions, which are usually at a much lower temperature, such that their cross-section is much larger and dominate the collisions.

Let us assume that a uniform and constant electric field $\mathbf{E}$ acts upon the ensemble. We can start with the Boltzmann equation for the change in the distribution function; the collisions realize the local equilibrium very soon, much faster than the time scale we are interested in. We prefer to start with the equation of motion for the displacement $\mathbf{u}$ suffered by electrons (this is the Drude-Lorentz approach[16]). If the gas is very rarefied, the equation of motion reads

$$m\frac{d\dot{\mathbf{u}}}{dt} = q\mathbf{E} \ . \tag{4.91}$$

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[16] P. Drude, "Zur Elektronentheorie der Metalle", Ann. Phys. **306** 566 (1900); "Zur Elektronentheorie der Metalle, 2. Teile. Galvanomagnetische und thermomagnetische Effecte", Ann. Phys. **308** 369 (1900); H. A. Lorentz, *The Theory of Electrons*, Teubner, Leipzig (1916).

Since we are interested in long times, we may approximate this equation by

$$m\frac{\dot{\mathbf{u}}}{\tau} = q\mathbf{E} \ , \ \ \dot{\mathbf{u}} = \frac{q\tau}{m}\mathbf{E} \ . \tag{4.92}$$

Obviously, this is a transport equation, if we write $\mathbf{E} = -\partial U/d\mathbf{r}$, where U is the voltage drop. From equation (4.92) we get the current density

$$\mathbf{j} = nq\dot{\mathbf{u}} = \frac{nq^2\tau}{m}\mathbf{E} \tag{4.93}$$

and the conductivity

$$\sigma = \frac{nq^2\tau}{m} \ ; \tag{4.94}$$

it is called drift conductivity, because it proceeds by collisions; it is a diffusion conductivity ($\sigma \sim T^{3/2}$). We recognize here the mobility τ/m. If we include the electron-ion collisions, then τ in equation (4.94) is dominated by the much shorter electron-ion collision time. If we multiply equation (4.93) by a^2 we get the intensity of current $I = ja^2$ and

$$I = \frac{nq^2\tau a^2}{m}E \ \ , \tag{4.95}$$

or

$$U = \frac{Rq^2\tau}{ma}\frac{\partial U}{\partial x} \ \ , \tag{4.96}$$

where R is the electric resistance and the field is directed along the x-axis. Since $R = \rho(l/a^2)$, where $\rho = 1/\sigma$ is the resistivity, this equation reads also

$$U = l\frac{\partial U}{\partial x} \ \ , \tag{4.97}$$

which is a Fick's equation, or, more general,

$$\frac{\partial U}{\partial t} = vl\frac{\partial^2 U}{\partial x^2} \ \ , \tag{4.98}$$

when there exists a time dependence, which is the diffusion equation with $D = vl$; the length fluctuations are given by $\delta x^2 = 2\tau vl$. Since, from equations (4.95) and (4.96) we have $\delta I/I = \delta x/a$, we get the current fluctuation $\delta I/I = \sqrt{2al}/a_0 \sim T$.

Obviously, in equation (4.92) $m\gamma\dot{\mathbf{u}}$, where $\gamma = 1/\tau$, is a force which opposes the motion, such that the equation of motion reads

$$m\frac{d\dot{\mathbf{u}}}{dt} + m\gamma\dot{\mathbf{u}} = q\mathbf{E} \ ; \tag{4.99}$$

we can see that there exists a transient regime of damped motion $\dot{\mathbf{u}} \sim e^{-\gamma t}$.

If the gas is not too rarefied, we cannot neglect any longer the internal field of polarization; indeed, the displacement $\mathbf{u}$ generates a disturbance $\delta n = -n div\mathbf{u}$ in density (for a uniform displacement, this disturbance appears at the boundaries); consequently, we have a polarization charge density $-nq div\mathbf{u}$ (and a polarization current density $nq\dot{\mathbf{u}}$ which satisfies the charge conservation), an internal field $\mathbf{E}_i = -4\pi nq\mathbf{u}$ (and a polarization $\mathbf{P} = nq\mathbf{u}$), such that the equation of motion reads

$$m\ddot{\mathbf{u}} + m\gamma\dot{\mathbf{u}} = q\mathbf{E} - 4\pi nq^2\mathbf{u} \ \ , \tag{4.100}$$

or

$$\ddot{\mathbf{u}} + \omega_0^2\mathbf{u} + \gamma\dot{\mathbf{u}} = \frac{q\mathbf{E}}{m} \ \ , \tag{4.101}$$

where $\omega_0 = (4\pi nq^2/m)^{1/2}$ is the plasma frequency. For an oscillating field $\mathbf{E} = \mathbf{E}_0 e^{i\omega t}$ with the frequency ω the stationary solution of equation (4.101) is

$$\mathbf{u} = -\tfrac{q\mathbf{E}}{m}\tfrac{1}{\omega^2-\omega_0^2-i\gamma\omega} \ \ ; \tag{4.102}$$

equation (4.101) and its solution are valid for $\omega \ll \gamma$. The total electric field is

$$\mathbf{E}_t = \mathbf{E} + \mathbf{E}_i = \tfrac{\omega^2-i\gamma\omega}{\omega^2-\omega_0^2-i\gamma\omega}\mathbf{E} \tag{4.103}$$

and the conductivity in $\mathbf{j} = \sigma\mathbf{E}_t$ is

$$\sigma = -\frac{1}{4\pi}\frac{i\omega_0^2}{\omega - i\gamma} \ \ . \tag{4.104}$$

Similarly, we can get the polarization and the electric susceptibility. The rate of energy dissipation $dQ/dt = mn\gamma\dot{\mathbf{u}}^2$ per unit volume (equation (4.101)), averaged over time, is

$$\overline{\frac{dQ}{dt}} = \frac{E_0^2}{8\pi}\frac{\gamma\omega_0^2\omega^2}{(\omega^2-\omega_0^2)^2 + \omega^2\gamma^2} \ \ . \tag{4.105}$$

An electron displaced by $\mathbf{u}$ can be viewed as a single-particle excitation, with the lifetime τ and mean freepath Λ. It is worth noting that such a disturbance is associated with the collective excitation of the plasmons with frequency ω_0.[17] For a non-uniform field it is more convenient to use the Boltzmann equation (with partial derivatives for the distribution) and to impose the internal field (Vlasov equation[18]).

4.13.3 Ambipolar diffusion

Charge carriers in semiconductors (electrons and holes) behave to a large extent as ideal classical gases, the cohesion being ensured by a mean field (potential well). At semiconducting junctions the two types of carriers may diffuse into one another.[19] Let $n_{1,2}$ be the densities of the two types of carriers, denoted by 1 and 2, with charges $-q$ and q. The diffusion is governed by the law given by equation (4.90), where the external force is $\pm q\mathbf{E}$, the electric field being $\mathbf{E} = -grad\varphi$, where the potential φ satisfies the Poisson equation

$$\Delta\varphi = -4\pi(n_2 - n_1)q \ . \tag{4.106}$$

We get

$$\begin{aligned} \frac{\partial n_1}{\partial t} &= D_1 div\left[gradn_1 - \frac{qn_1}{T}grad\varphi)\right] \ , \\ \frac{\partial n_2}{\partial t} &= D_2 div\left[gradn_2 + \frac{qn_2}{T}grad\varphi)\right] \ . \end{aligned} \tag{4.107}$$

We may assume that $n_{1,2}$ vary slowly, such that

$$\begin{aligned} \frac{\partial n_1}{\partial t} &= D_1\left[\Delta n_1 - \kappa^2(n_1 - n_2)\right] \ , \\ \frac{\partial n_2}{\partial t} &= D_2\left[\Delta n_2 + \kappa^2(n_1 - n_2)\right] \ , \end{aligned} \tag{4.108}$$

where $\kappa = (4\pi nq^2/T)^{1/2}$, n being the mean density; $\lambda = 1/\kappa = a\sqrt{aT/4\pi q^2}$ is the Debye-Huckel screening length;[20] we recognize here the length $a_0 = q^2/T$. For slowly varying densities we may neglect the derivatives in equations (4.108), which leads to

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[17] D. Bohm and D. Pines, "A collective description of electron interaction. III. Coulomb interactions in a degenerate electron gas", Phys. Rev. **92** 609 (1953).

[18] A. A. Vlasov, "On the kinetic theory of an assembly of particles with collective interaction", J. Phys. (USSR) **9** 25 (1945).

[19] W. Schottky, "Wandstrome und Theorie der positiven Saule", Phys. Z. **25** 342 (1924); "Diffusions-Theorie der positiven Saule", Phys. Z. **25** 635 (1924).

[20] P. Debye and E. Huckel, "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen", Phys. Z. **24** 185 (1923); “Zur Theorie

$$\frac{\partial}{\partial t}(n_1 - n_2) = -2D\kappa^2(n_1 - n_2) \quad , \tag{4.109}$$

where $D \simeq D_1 \simeq D_2$. This equation shows that the two concentrations equalize themselves in time, as expected.

4.13.4 Electrolytes

The ions in (dilute) electrolytes diffuse as an ideal classical gas; however, we need to include the internal electric field generated by ions. Equation (4.90) becomes

$$\frac{\partial n}{\partial t} = -Bdiv(nq\mathbf{E}_0 - nqgrad\varphi) + D\Delta n \quad , \tag{4.110}$$

where $\mathbf{E}_0$ is the external field, q is the ion charge and φ is the potential generated by ions. We may consider a uniform and constant external field, such that we may write

$$\frac{\partial n}{\partial t} = -Bq\mathbf{E}_0 gradn + Bqdiv(ngrad\varphi) + D\Delta n \ . \tag{4.111}$$

First, it is worth noting the effect of the external field; leaving aside the internal potential and the Fourier transforming of the above equation, we get

$$n(t, \mathbf{r}) = \frac{1}{(2\pi)^3}\int d\mathbf{k}n(\mathbf{k})e^{i\mathbf{k}(\mathbf{r}-Bq\mathbf{E}_0 t)}e^{-Dk^2 t} \quad , \tag{4.112}$$

whence we can see that the effect of the external field is to change $\mathbf{r}$ into $\mathbf{r} - Bq\mathbf{E}_0 t$, as expected; the external field transports the charges with velocity $Bq\mathbf{E}_0$.

Let us assume that the diffusion proceeds in a (large) volume; we may define the ion concentration n_0; n given by equation (4.111) is the disturbance caused by diffusion in this uniform concentration. Also, n_0

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der Elektrolyte. II. Das Grenzgesetz fur die elektrische Leitfahigkeit", Phys. Z. **24** 305 (1923).

may be viewed as a local mean concentration. The potential generated by n_0 is zero (we assume a uniform neutralizing background); therefore, the potential φ is generated by the charge density n, according to the Poisson equation

$$\Delta\varphi = -4\pi qn \ ; \tag{4.113}$$

this equation must be solved with boundary conditions $\varphi = q/r$ in the vicinity of each ion. On the other hand, we have local equilibrium at temperature T, such that

$$n = n_0\delta\left(e^{-q\varphi/T}\right) = -n_0 q\varphi/T \tag{4.114}$$

and

$$\varphi = q\frac{e^{-\kappa r}}{r} \tag{4.115}$$

from equation (4.113), for each ion, where $\kappa = (4\pi n_0 q^2/T)^{1/2}$ is the Debye-Huckel screening parameter. Now we introduce φ given by equation (4.114) in equation (4.111), which becomes

$$\frac{\partial n}{\partial t} = -Bq\left(\mathbf{E}_0 + \frac{T}{qn_0} gradn\right) grad\, n + D\left(1 - \frac{n}{n_0}\right)\Delta n \ . \tag{4.116}$$

We can see that the internal field transforms the diffusion equation into a non-linear equation (which can be solved by means of a perturbation theory; the corrections to the regular diffusion are sometimes called relaxational corrections).[21] The effect of the internal field is to reduce the mobility, as expected. This effect is diminished in the presence of both positive and negative ions (with a vanishing mean charge).

4.13.5 Electrophoresis

Let us consider the motion of an ion in the electrolyte; the external force $qn\mathbf{E}_0$ acts upon the ion, where $\mathbf{E}_0$ is the (uniform and constant) external field, n is the ion diffusion density and q is the ion charge. Let us consider the motion of the (fluid) electrolyte with velocity $\mathbf{v}$. In a stationary motion the forces are in equilibrium, *i.e.*

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[21] P. Debye and E. Huckel, "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen", Phys. Z. **24** 185 (1923); “Zur Theorie der Elektrolyte. II. Das Grenzgesetz fur die elektrische Leitfahigkeit”, Phys. Z. **24** 305 (1923); L. Onsager, "Zur Theorie der Elektrolyte. I.", Phys. Z. **27** 388 (1926); II., **28** 277 (1927).

$$\eta\Delta\mathbf{v} - gradP + qn\mathbf{E}_0 = 0 \quad , \tag{4.117}$$

where η is a coefficient of viscosity and P is the pressure. The Fourier transform of the above equation leads to

$$-\eta k^2\mathbf{v}(\mathbf{k}) - iP\mathbf{k} + qn(\mathbf{k})\mathbf{E}_0 = 0 \ ; \tag{4.118}$$

we may consider the flow incompressible, *i.e.* $div\mathbf{v} = 0$ ($\mathbf{kv}(\mathbf{k}) = 0$); we get

$$P = -iqn(\mathbf{k})\frac{\mathbf{kE}_0}{k^2} \tag{4.119}$$

and

$$\mathbf{v}(\mathbf{k}) = \frac{qn(\mathbf{k})}{\eta}\frac{k^2\mathbf{E}_0 - \mathbf{k}(\mathbf{kE}_0)}{k^4} \quad . \tag{4.120}$$

From equations (4.114) and (4.115) the density is

$$n(r) = -\frac{n_0q^2}{T}\frac{e^{-\kappa r}}{r} \tag{4.121}$$

and

$$n(\mathbf{k}) = -\frac{n_0q^2}{T}\int d\mathbf{r}\frac{e^{-\kappa r}}{r}e^{-i\mathbf{kr}} = -\frac{\kappa^2}{k^2+\kappa^2} \quad . \tag{4.122}$$

The velocity of the fluid at the position of the ion is

$$\mathbf{v}(0) = \frac{1}{(2\pi)^3}\int d\mathbf{k}v(\mathbf{k}) \ ; \tag{4.123}$$

introducing here equations (4.120) and (4.122) we get

$$\mathbf{v}(0) = -\frac{q\kappa}{6\pi\eta}\mathbf{E}_0 \quad . \tag{4.124}$$

This velocity is added to the ion velocity $qB\mathbf{E}_0$, which leads to a decrease in the mobility, which becomes $B - \kappa/6\pi\eta$. The mobility B may depend on the particle size and shape, such that charged particles may be separated in an electric field; this is the phenomenon of electrophoresis. Equation (4.124) is an electrophoretic correction.

5 Kinetics of Plasma

5.1 Gaseous plasma

Let us assume a classical gas of identical atoms (molecules) in normal conditions. Normal conditions mean a temperature $T = 300K$ (room temperature) and a pressure $p = 10^6 dyn/cm^2$ (atmospheric pressure) ($1K = 1.38 \times 10^{-16} erg$). From the equation of state $p = nT$ of an ideal gas we can derive the density $n = 1/a^3$ and the mean separation distance a between the atoms; in normal conditions it is $a \simeq 35\text{Å}$ ($n \simeq 10^{19} cm^{-3}$); it is much larger than the atomic scale length given by $\hbar^2/Ma^2 = T$, where M is the atomic mass ($\hbar = 10^{-27} erg \cdot s$ is Planck's constant and $1erg = 1.38 \times 10^{-16} K$ (Boltzmann constant); $m = 10^{-27} g$ is the electron mass and $e = -4.8 \times 10^{-10} esu$ is the electron charge).

The ionization potential of the atoms is of the order of a few eV ($1eV = 1.6 \times 10^{-12} erg$). If a potential difference U of a few V's is applied across an atom, the atom may get ionized. $1V$ is $1/300 esu$; the corresponding electric field is $E = U/a_H \simeq 10^6 esu \simeq 3 \times 10^{10} V/m$, where $a_H = \hbar^2/me^2 \simeq 0.53\text{Å}$ is the Bohr radius (atomic dimension); this is a very high electric field, which produces an electric discharge in gas. If the field is increased, the atoms may get multiply ionized, and the released electrons may acquire a high energy ($1eV = 1.16 \times 10^4 K$). The electrons interact with the long-range Coulomb forces and have a great mobility; consequently, they may get rapidly thermalized. The ions were initially in thermal equilibrium and they preserve the equilibrium in the ionization process. The recombination processes are rare; thereby, we get a plasma. We can see that the electrons are at a temperature T, which is much higher than the ionic temperature T_i. A similar result is obtained by collisions in a gas heated at high temperature. During collisions, the ions get colder, and transfer their energy to the released electrons; the electron temperature is again much higher than the ion temperature. These plasmas are called non-thermal.

The ionization process is a statistical one; not all the atoms are ionized; some remain neutral (sometimes most of them). The cross-section of neutral atoms with electrons and ions is small (in comparison with the Coulomb forces). It follows that the electrons and the ions may have their own, separate, statistical equilibrium, and the neutral atoms may have their own, distinct, statistical equilibrium. We may neglect the neutral atoms in a plasma.

The equilibrium between ions and electrons and the stability of a plasma raise important problems.

In general, the problem of achieving the thermal equilibrium is an open problem in Statistical Physics. Since the electrons are identical and uniformly generated from identical atoms, there is no obvious reason not to assume that the electrons are in thermal equilibrium and, similarly, that the ions are in thermal equilibrium. However, due to large disparity between the ion mass and the electron mass, the mutual equilibrium between the electrons and the ions is not obvious; we may view the electrons with their own temperature T_e, the ions with their own temperature T_i and the neutral fraction of atoms with their own temperature T_0. Since the electron mass is much smaller than the atom (and ion) mass, in high-energy ionization the electrons carry the largest fraction of energy, and their temperature is the highest. The electrons are highly mobile, so we may view them as a fluid. Due to the same reason, the elastic binary collisions preserve this unbalanced energy distribution among the electrons, on one side, and ions and atoms, on the other. However, the electrons and the ions are strongly coupled by Coulomb forces, and we may expect a special kind of equilibrium between electrons and ions. Moreover, the electron and ion motions are correlated, by the Debye length to be introduced shortly below, so it seems more reasonably to view the plasma as a collection of ions surrounded by the electron fluid. It is worth noting that the equilibrium between electrons, or the equilibrium between ions, is established not by collisions but rather by the long-range repulsive Coulomb interaction. The Coulomb interaction generates a correlation between electrons and ions, as we shall show below, which leads us to view the plasma as a non-ideal gas of ions dressed with electrons, at equilibrium.

Let us assume for the moment a thermal plasma, *i.e.* let us assume $T_e = T_i = T_0 = T$. Let n_i be the density of the ionized atoms; the (classical) number of states available to these ions is $\mathcal{N}_i = n_i V e^{\beta\varepsilon_i}/g_i$, where V is the volume, ε_i is the energy of the ion, $\beta = 1/T$ is the reciprocal of the temperature T and g_i is the multiplicity (degeneracy) of the state. Similarly, the number of states of the electrons with (low) density n_e is $\mathcal{N}_e = n_e \lambda_q^3$, where $\lambda_q = (\hbar^2/mT)^{1/2}$ is the de Broglie quantum (thermal) length, and $n_e = n_i$. The equation of equilibrium reads $\mathcal{N}_i \mathcal{N}_e = \mathcal{N}_0$, where $\mathcal{N}_0 = n_0 V e^{\beta\varepsilon_0}/g_0$ is the number of states of the neutral atoms (with density n_0, energy ε_0 and multiplicity g_0). It follows

$$\frac{n_i n_e}{n_0} = \frac{n_i^2}{n_0} = \frac{n_e^2}{n_0} = \frac{g_i}{g_0}\frac{1}{\lambda_q^3} e^{-\beta\Delta\varepsilon_i} \ , \tag{5.1}$$

where $\Delta\varepsilon_i = \varepsilon_i - \varepsilon_0$ is the ionization energy. Equation (5.1) is known as the Saha equation.[1] We can see that only at very high temperatures the degree of ionization of a gaseous plasma is high ($\lambda_q \simeq 10$Å at $T = 300K$); the gas is almost fully ionized for temperatures $T = 10^3 - 10^4 K$; for lower temperatures ($10^2 - 10^3 K$) the electron density decreases appreciably ($n_e \simeq 10^{10} cm^{-3}$). The Saha equation gives a quantitative estimate of the degree of ionization of a plasma at equilibrium; noteworthy, this equation does not take into account the Coulomb correlations. Its applicability is very limited.

Plasma is a collection of both types of electric charges, usually with any macroscopical region electrically neutral; each type of charge may have its own motion. Plasma is a special state of matter; due to the long range character of the Coulomb interaction, the motion in plasma is a collective, correlated motion. The typical plasma is the gaseous plasma of ionized gases. We need ionizing agents to create a gaseous plasma, like high temperature or high electric fields. In normal conditions a gas is poorly ionized, but at high temperatures the ionization degree increases, due to collisions; similarly, for a high electric field.

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[1] M. N. Saha, "Ionization in the solar chromosphere", Phil. Mag. (6) **40** 472 (1920); "On a physical theory of stellar spectra", Proc. Roy. Soc. **A99** 135 (1921); K. Kingdon and I. Langmuir, "The removal of Thorium from the surface of a Thoriated tungsten filament by positive ion bombardment", Phys. Rev. **22** 148 (1923).

For simplicity, in the following we shall consider mainly a singly-ionized species of identical atoms, though, in principle, the considerations may be extended to N_a ions, $a = 1, 2, ...$, with charge $z_a q$ and $N = \sum_a z_a N_a$ electrons (where z_a is a positive integer) and $-q$ $(= e)$ is the electron charge. This would be a multi-component plasma; the former, is a two-component plasma. We leave aside the neutral part of the gas. In the jellium model all the ions form a uniform background of neutralizing positive charges, the electrons moving in this background (for example, electrons on the surface of liquid helium is an experimental realization of the (two-dimensional) jellium model); or, conversely, we may view the electrons as a uniform background, with moving ions; also, trapped ions may be viewed as a realization of the jellium model. We have, in this case, a one-component plasma.

We should note that in a plasma the mean inter-ionic separation a is much larger than the atomic scale length $(\hbar^2/MT)^{1/2}$, where M is the ion mass; this is the condition for a classical ionic gas. Moreover, a is also the mean separation distance between the electrons, and it is much larger than the atomic dimension given by Bohr $a_H = \hbar^2/me^2$. Also, we note that there exist three types of relevant energies in a plasma: the quantum localization energy $\hbar^2/ma^2$ of the electrons, the mean Coulomb interaction q^2/a and the temperature T of the electrons. Since $a \gg a_H$, we have always $\hbar^2/ma^2 \ll q^2/a$ $(a_H = \hbar^2/mq^2)$, *i.e.* the Coulomb energy dominates over the quantum energy. The quantum energy $\hbar^2/Ma^2$ of the ions is much smaller than the quantum energy of the electrons. The temperature T may be placed everywhere in these inequalities. If $T < \hbar^2/ma^2$, the quantum effects dominate, and we have a cold, degenerate plasma, where the electrons are delocalized, as in a Fermi gas; an example is the degenerate plasma of electrons in solids (metals).[2] If $\hbar^2/ma^2 < T$, we may neglect the quantum effects, and the electrons behave as a classical gas (though correlated); we note that this condition is $\lambda_q = (\hbar^2/mT)^{1/2} < a$, which indeed is the condition of quasi-classical behaviour of the electrons. We assume that T is always higher than the quantum energy of the ions, *i.e.* the ions behave classically. It remains to compare T with the mean Coulomb energy q^2/a. At equilibrium, the classical plasma is governed by Maxwell distribution. The mean thermal velocity of the electrons is of the order $v_{th} = \sqrt{T/m}$; we assume that the temperature is sufficiently low to treat the plasma non-relativistically ($T \ll mc^2 \simeq 0.5MeV$, where c is the speed of light in vacuum).

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[2] We shall see below that the correlations may relax this condition of quantum-classical border.

It is important to know that it was argumented that a classical plasma is unstable,[3] in the sense that classical charges tend to recombine in neutral "point atoms", which, classically, have an infinite negative energy. Quantum-mechanical arguments have been used to make the plasma stable. In one of the next sections we show the thermodynamic stability of the classical plasma.

In a fluorescent tube the electron density is about $10^9 cm^{-3}$ and the temperature is about $10^4 K$ (since the density is very low, the heating of the walls is extremely low); in fusion reactors the electron density is $10^{15} cm^{-3}$ and the temperature is $10^8 K$; in the planetary space the electron density is $1 cm^{-3}$ and the temperature is $100K$.[4] A typical fully ionized plasma at very low pressure has the density $n = 10^{12} cm^{-3}$, the temperature $T = 10^4 K$ and the mean interparticle separation (electrons) $a = 1/n^{1/3} = 10^{-4} cm$ $(= 10^4 \text{Å})$.

There exists an important feature of plasmas, arising from the Coulomb interaction between charges. The electrons repel each other, while they are attracted by ions; the ions repel each other as well. The electrons being more mobile, they may be redistributed in space, as a consequence of this interaction. Let q be the charge of an ion localized at the origin, with density $q\delta(\mathbf{r})$. It produces a change $\delta n \sim ne^{\beta q\varphi} - n$ in the electron density n, where φ is the potential generated by charge q and charge density is $-q\delta n$, $-q$ being the electron charge; for an interaction $q\varphi$ much smaller than the temperature T we may approximate the change δn as $\delta n \simeq nq\beta\varphi$ (we set the normalization constant equal to unity). The potential φ is determined by the Gauss equation

$$\Delta\varphi = -4\pi q\delta(\mathbf{r}) + 4\pi nq^2\beta\varphi \ ; \tag{5.2}$$

we can see that at small distances the potential is dominated by the singular δ-term; therefore, the approximation made for δn may be viewed as satisfactory for any finite distance. The solution of equation (5.2) is the screened potential

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[3] F. J. Dyson and A. Lenard, "Stability of matter." I., J. Math. Phys. **8** 423 (1967); A. Lenard and F. J. Dyson, "Stability of matter." II. J. Math. Phys. **9** 698 (1968); E. Teller, "On the stability of molecules in the Thomas-Fermi theory", Revs. Mod. Phys. **34** 627 (1962); E. H. Lieb, "The stability of matter", Revs. Mod. Phys. **48** 553 (1976).

[4] F. F. Chen, *Introduction to Plasma Physics*, Plenum, NY (1974).

$$\varphi = \frac{q}{r} e^{-r/\lambda} \ , \ \lambda = \sqrt{\frac{T}{4\pi n q^2}} \ , \tag{5.3}$$

this is known as the Debye screened potential (derived originally for electrolytes); λ is the Debye screening length.[5] It is worth noting that, while we treat the ions as pointlike particles, the electrons are viewed as a fluid, due to their high mobility. Making use of the mean inter-particle distance (electrons) a, given by $n = 1/a^3$, the screening length can be written as $\lambda = a\sqrt{T/4\pi(q^2/a)}$, which implies the ratio of the thermal energy T to the Coulomb energy q^2/a per particle. The parameter aT/q^2 defines the coupling regime in plasma. For $aT/q^2 < 1$ the Debye length is smaller than the mean inter-particle distance; this is the strong-coupling regime.

In this case we might view the ions dressed by electrons as rigid particles with diameter of the order $d = 2\lambda$; it is easy to see that their mean freepath is of the order $\Lambda = a(a/d)^2$, or $\Lambda = \pi q^2/T$ $(> a)$; it is worth noting that this mean freepath is independent of the gas density; it generates a collision frequency $\gamma = v_{th}/\Lambda$, where the thermal velocity is $v_{th} = \sqrt{T/M}$, M being the ion mass. We note that the Maxwell distribution can be written as $e^{-\frac{1}{2}\beta M v^2} = e^{-v^2/2v_{th}^2}$; consequently, there exist few particles with velocity greater than v_{th} and with a higher collision frequency than γ; most particles have a collision frequency less than $\gamma = v_{th}/\Lambda$. We shall show below that this picture is in fact invalid, the strongly-coupled plasma being unstable.

The opposite case $aT/q^2 > 1$ is the weak-coupling regime. In this case the electrons interact practically by Coulomb interaction with the ions and with the other electrons (and ions do the same). The critical condition of strong-weak coupling is $(aT)_{cr} \simeq 10^{-18} erg \cdot cm$ (for the electron charge $-q = 4.8 \times 10^{-10} esu = 1.6 \times 10^{19} C$). In the weak-coupling regime the mean freepath of the electrons is of the order $\Lambda \simeq a$ (mean inter-particle distance); a collision frequency may be estimated in this case as $\gamma = v_{th}/a$.

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[5] P. Debye and E. Huckel, "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen", Phys. Z. **24** 185 (1923); “Zur Theorie der Elektrolyte. II. Das Grenzgesetz fur die elektrische Leitfahigkeit”, Phys. Z. **24** 305 (1923).

It is worth noting that we may include the ion mobility in the screened interaction, by

$$\Delta\varphi = -4\pi q\delta(\mathbf{r}) + 4\pi nq^2\beta_e\varphi + 4\pi nq^2\beta_i\varphi \ , \tag{5.4}$$

where β_i is the inverse of the ionic temperature T_i, distinct from the electron temperature $T_e = 1/\beta_e$ (the change in the ion density is $\delta n_i \simeq -nq\beta_i\varphi$); the Debye length is controlled in this case by the lower ionic temperature, and it is much shorter than the purely electronic Debye length. The electrons are attracted by ions, and screen the ionic Coulomb potential; the ions are repelled by ions, and diminish the strength of the ionic Coulomb potential; we can see that both charges have a screening effect; since the ions are less mobile, they dominate the screening. However, treating the ions as a fluid, as in equation (5.4), is not a realistic approximation.

As a consequence of the long range of the Coulomb interaction the motion in plasma is a collective, correlated motion, *i.e.* it proceeds by small displacements extended over large distances; there exists a special, exceptional, case, discussed below. Let us assume that the mobile electron charges move entirely, as a compact body, in a rectangular box, by a small distance u along a certain direction perpendicular to the surface; the surface charge $-q/a^2$ suffers a change $(q/a^3)u$ (along one direction) and generates an electric field $2\pi(q/a^3)u$ and a force $-2\pi(q^2/a^3)u$ acting upon each particle; the two surfaces generate a force $-4\pi(q^2/a^3)u$; the equation of motion $m\ddot{u} = -4\pi(q^2/a^3)u$ leads to an eigenfrequency $\omega_0 = \sqrt{4\pi nq^2/m}$, which is the plasma frequency; for $n = 10^{12}cm^{-3}$, $q = 4.8 \times 10^{-10}esu$ and $m = 10^{-27}g$ (electrons) it is of the order $\omega_0 = 5 \times 10^{10}s^{-1}$ ($\nu \simeq 10^{10}s^{-1}$). The plasma frequency, generated by the internal field, is associated with any disturbance occurring in plasma. It is due to the long-range character of the Coulomb force (and the related pointlike character of the mobile charges). It is worth noting that the surfaces bounding the plasma may be extended to infinity, and the plasma frequency thus estimated here is a bulk property. The displacement u (along one direction) changes the density $n = 1/a^3$ into $1/a^2(a+u) \simeq -u/a^4 = -n(u/a)$;

it is easy to see that the change can be viewed as $\delta n = -n div\mathbf{u}$; the Gauss equation becomes $div\mathbf{E} = -4\pi nq div\mathbf{u} = -4\pi div\mathbf{P}$ for a charge q, where $\mathbf{P} = nq\mathbf{u} = -\mathbf{E}/4\pi$ is the polarization; and $\mathbf{E}_0 + \mathbf{E} + 4\pi\mathbf{P} = \mathbf{E}_t + 4\pi\mathbf{P} = \mathbf{D} = \mathbf{E}_0$ is the electric displacement (induction), where $\mathbf{E}_0$ is the external field, $\mathbf{E}$ is the internal field and $\mathbf{E}_t = \mathbf{E}_0 + \mathbf{E}$ is the total field; χ in $\mathbf{P} = \chi\mathbf{E}_t$ is the electric susceptibility and $\varepsilon = 1 + 4\pi\chi$ in $\mathbf{D} = \varepsilon\mathbf{E}_t$ is the dielectric function. We may include the motion of the positive ions; it is easy to see that the relevant motion is the relative ion-electron motion, which leads to a plasma frequency $\omega_0 = \sqrt{4\pi nq^2/\mu}$, where μ is the reduced mass given by $1/\mu = 1/m + 1/M$, M being the ion mass; since $M \gg m$, we may leave aside the ionic motion; in this respect, the ions may be viewed as a continuous, uniform, rigid background of positive, neutralizing charges.

Under these conditions, the equation of motion of the displacement $\mathbf{u}$ can be written as

$$\ddot{\mathbf{u}} + \gamma\dot{\mathbf{u}} = \frac{q}{m}\mathbf{E}_0 + \frac{q}{m}\mathbf{E} \ , \tag{5.5}$$

where $\mathbf{E} = -4\pi nq\mathbf{u}$ is the internal field, γ is the collision frequency and $\dot{\mathbf{u}} = d\mathbf{u}/dt$ (in this case, it is convenient to use q for the electron charge). This equation will serve as the starting point for the Boltzmann equation of plasma; it is also known as the Drude-Lorentz equation of motion of charges in matter.[6] We note that the velocity of the electrons, of the order of v_{th}, is small, such that we may leave aside the magnetic effects (similarly, the magnetic moments may be left aside); in this case, we say that plasma is unmagnetized. For our typical plasma with temperature 10^4K, the thermal velocity is $v_{th} = \sqrt{T/m} = 3.7 \times 10^7 cm/s$.

The physics of classical plasmas is confronted with the interaction problem arising from the long-range Coulomb forces between ions and electrons. As long as the interaction persists, especially when it implies multi-particle correlations due to the long-range character of the Coulomb forces, the statistical theory cannot be used, since the particles are not statistically independent. In order to be able to use statistical approaches for plasmas we need first to solve, in a convenient way, the interaction problem in plasmas.

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[6] P. Drude, "Zur Elektronentheorie der Metalle", Ann. Phys. **306** 566 (1900); P. Drude, "Zur Elektronentheorie der Metalle, 2. Teile. Galvanomagnetische und thermomagnetische Effecte", **308** 369 (1900); H. A. Lorentz, *The Theory of Electrons*, Teubner, Leipzig (1916).

5.2 Energy distribution in ionization

Let us consider a (classical) gas of identical molecules (atoms), each with mass M at thermal equilibrium. As long as the thermal energy per molecule is smaller than the ionization (dissociation) energy of a molecule, the thermal energy is taken up in translation, rotation, vibration, etc, motion. The corresponding thermal energy E per molecule for translation generates a molecular momentum $\mathbf{P}$, such that $E = P^2/2M$. If the thermal energy exceeds the ionization (dissociation) energy the momentum and the energy conservation laws are

$$\begin{gathered} \mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 \ , \\ E = p_1^2/2m_1 + p_2^2/2m_2 \ , \end{gathered} \tag{5.6}$$

where $\mathbf{P}$ is the momentum of the molecule (atom) and E is the excess energy which generates the momenta $\mathbf{p}_{1,2}$ of the two molecular fragments (*e.g.*, an ion and an electron) with masses $m_{1,2}$. Equations (5.6) lead to

$$p_1^2 - 2\frac{\mu}{m_2}P\cos\theta \cdot p_1 - \left(2\mu E - \mu P^2/m_2\right) = 0 \ , \tag{5.7}$$

where $\mu = m_1 m_2/M$ is the reduced mass ($M = m_1 + m_2$) and θ is the angle made by $\mathbf{P}$ with $\mathbf{p}_1$; the solutions of equation (5.7) are .

$$p_1 = \frac{\mu}{m_2}P\cos\theta \pm \sqrt{2\mu E - \frac{\mu}{m_2}P^2\left(1 - \frac{\mu}{m_2}\cos^2\theta\right)} \ . \tag{5.8}$$

Let us assume $m_2 \ll m_1$ and $E \gg P^2/2m_2$; then, we get from equation (5.8) $p_1 \simeq \sqrt{2m_2E}$ and the energies

$$E_1 = p_1^2/2m_1 \simeq \frac{m_2}{m_1}E \ , \ E_2 \simeq E \ ; \tag{5.9}$$

we can see that the high amount of excess energy is taken by the lighter fragments, in the proportion of the mass ratio, as expected

($E_1/E_2 \simeq m_2/m_1$); the magnitudes of the momenta are close to each other (since $\mathbf{P}$ is small).[7] In the opposite limit, when $E \ll P^2/2m_2$, the ionization (dissociation) takes place in the forward direction ($\theta \simeq 0$) and the energy is retained, practically, by the heavier fragment. The same energy distribution is valid for the ionization produced by high electric fields.

In elastic binary collisions the two fragments preserve their energy distribution and the scattering angles, only the relative momentum changes direction; this follows from the conservation laws

$$\begin{gathered}\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_1^{'} + \mathbf{p}_2^{'} \ , \\ p_1^2/2m_1 + p_2^2/2m_2 = p_1^{'2}/2m_1 + p_2^{'2}/2m_2 \ \ ,\end{gathered} \tag{5.10}$$

where $\mathbf{p}_{1,2}^{'}$ are momenta after collision; indeed, from the second equation (5.10) we get $E_2 = E_2^{'}$ and $E_1 = E_1^{'}$ and, from the first equation (5.10), we get $\varphi \simeq \varphi^{'}$, where φ is the angle made by $\mathbf{p}_1$ with $\mathbf{p}_2$ and $\varphi^{'}$ is the angle made by $\mathbf{p}_1^{'}$ with $\mathbf{p}_2^{'}$.

The energy $P^2/2M + E$ is a measure of the mean energy; it leads to $(2N + N_0)T$, where N is the original number of atoms which are ionized and N_0 is the number of atoms which remain neutral. Since $E \gg P^2/2M$ we may write $T \simeq E$. On the other hand, we have from the above calculations $E_1 \simeq \frac{m_2}{m_1} \cdot 2NT = NT_1$ and $E_2 \simeq 2NT = NT_2$, where the temperatures $T_{1,2}$ are given by $T_1 \simeq 2\frac{m_2}{m_1}T$ and $T_2 \simeq 2T$. We can see that the ratio of the two temperatures is $T_1/T_2 \simeq m_2/m_1$. We are in the presence of two distinct gases (*e.g.*, ions and electrons), or three distinct gases if we include the neutral atoms, all at their own equilibrium.

Let us consider two fragments with masses $m_{1,2}$, $m_2 \ll m_1$; making use of the energy E_c of their center of mass and the energy E_r of their relative motion we can express the (kinetic) energies of the two fragments as

$$\begin{gathered}E_1 = \tfrac{m_1}{M}E_c + \tfrac{m_2}{M}E_r + 2\sqrt{\tfrac{\mu}{M}E_cE_r}\cos\alpha \simeq E_c \ \ , \\ E_2 = \tfrac{m_2}{M}E_c + \tfrac{m_1}{M}E_r - 2\sqrt{\tfrac{\mu}{M}E_cE_r}\cos\alpha \simeq E_r \ \ ,\end{gathered} \tag{5.11}$$

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[7] M. Apostol, "Energy distribution in ionization and dissociation", J. Theor. Phys. **287** (2018).

where $M = m_1 + m_2$ is the total mass, $\mu = m_1 m_2 / M$ is the reduced mass and α is the angle made by the relative momentum with the center-of-mass momentum. Since $E_{c,r}$ are conserved in elastic collisions, we can see, that, in general, only the angle α (which is a free parameter) may change in collisions; since the center-of-mass momentum is conserved, this implies a rotation of the relative momentum. This change induces an energy re-distribution between the two particles. However, for $m_2 \ll m_1$, the energies of the two particles remain, practically, unchanged, as derived above from equation (5.10); for high-energy, the lighter fragment carries the (higher) relative energy, while the heavier fragment carries the (lower) center-of-mass energy. However, for electrical charges the equilibrium is reached by Coulomb interaction, not by collisions.

Let us assume that a force acts between the two fragments, which may lead to a bound state. The energy of the center of mass is conserved, such that the kinetic energy of the heavier fragment is conserved, $E_1 = E_c$. The relative energy E_r is changed, such that the kinetic energy E_2 of the lighter fragment is changed. It becomes

$$E_2^{'} = \frac{m_2}{M} E_c + E_{kin} = \frac{m_2}{M} E_c + W - Q \simeq W - Q \quad , \tag{5.12}$$

where the first term arises from the motion of the lighter particle together with the heavier fragment (common velocity), E_{kin} is the kinetic energy of the lighter particle in the potential well with depth W and $-Q$ is the binding energy. The total energy of the lighter particle is $\mathcal{E}_1^{'} = E_1^{'} - W \simeq -Q$. The high kinetic energy of the lighter particle is transferred, approximately, to the high kinetic energy of the lighter particle in the bound state; the potential well ensures the binding energy of this particle. The kinetic energy of the bound state remains the low kinetic energy of the heavier particle.

5.3 Thermodynamic stability of the classical plasma

There is a long-standing issue regarding the relation between the neutral state of a classical atomic ensemble (a gas) and its ionized (plasma) state. This problem may be termed the thermodynamic stability (instability) of a classical plasma, in the sense of the existence of a finite lower bound to the energy. Interesting arguments have been advanced in the past to show that the classical plasma would be thermodinamically unstable.[8] The stability is usually ensured by resorting to the quantum-mechanical behaviour of the electrons in atoms. The problem is still debated at present.[9] We show here, by means of a linearized self-consistent variational approach, that the classical plasma, which is a collection of ions dressed by electrons, has a well-defined thermodynamics.[10] In the strong-coupling regime[11] the plasma is a solid, while, on passing to the weak-coupling regime, it becomes gradually a liquid, a non-ideal gas, and, finally, an ideal classical gas. Probably the first authors who suggested the existence of an ionic lattice as the "ground-state" of a plasma at (very) high densities were Kirzhnits[12] and Abrikosov.[13] Long-range ordered phases have been reported recently in cold, strongly-coupled plasmas by computer simulations.[14] Coulomb crystals of jellium and one-component plasmas are known since long.[15]

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[8] F. J. Dyson and A. Lenard, "Stability of matter." I., J. Math. Phys. **8** 423 (1967); A. Lenard and F. J. Dyson, "Stability of matter." II., J. Math. Phys. **9** 698 (1968); E. Teller, "On the stability of molecules in the Thomas-Fermi theory", Revs. Mod. Phys. **34** 627 (1962); E. H. Lieb, "The stability of matter", Revs. Mod, Phys. **48** 553 (1976).

[9] E.H. Lieb, "Thomas-Fermi theory", arXiv; 0003040v1 (math-ph) (2000); "The stability of matter and Quantum Electrodynamics", Jahresbericht of the German Mathematical Society, JB **106** 93, Teubner, (2004) (arXiv: 0401004v1 (math-ph) (2004)); J. P. Solovej, "A new look at the Thomas-Fermi theory", arXiv: 160100497v1 (math-ph) (2016).

[10] M. Apostol and L. C. Cune, "On the stability of a classical plasma", Phys. Lett. **A383** 1831 (2019).

[11] M. S. Murillo, "Strongly-coupled plasma physics and high energy-density matter", Phys. Plasmas **11** 2964 (2004) and references therein.

[12] D. A. Kirzhnits, "Internal structure of super-dense stars", Sov. Phys.-JETP **11** 365 (1960) (ZhETF **38** 503 (1960)).

[13] A. A. Abrikosov, "Nekotorye svoistva sil'no szhatogo veschestva. I.", ZhETF **39** 1797 (1960) (in Russian; Sov. Phys.-JETP **12** 1254 (1961)); "Contribution to the theory of highly-compressed matter. II.", Sov. Phys.-JETP **14** 408 (1962) (ZhETF **41** 569 (1961)).

[14] T. Pohl, T. Pattard and J. M. Rost, "Coulomb crystalization in expanding laser-cooled neutral plasmas", Phys Rev. Lett. **92** 155003 (2004) and references therein; M. Bonitz, P. Ludwig, H. Baumgartner, C. Henning, A. Filinov, D. Block, O. Arp, A. Piel, S. Kaeding, Y. Ivanov, A. Melzer, H. Fehske and V. Filinov, "Classical and quantum Coulomb crystals", Phys. Plasmas **15** 055704

We consider a classical plasma consisting of a large (macroscopic) number N of identical ions with electric charge q and an equal number N of electrons with charge $-q$, confined to a large (macroscopic) volume V and interacting by Coulomb forces. For simplicity we consider one type of singly-ionized atoms, though the procedure described below is valid for N_a ions, $a = 1, 2, ...$, with charge $z_a q$ and $N = \sum_a z_a N_a$ electrons (where z_a is a positive integer). The ions are viewed as point particles, while the electrons, due to their high mobility, are viewed as a fluid with density $n(\mathbf{r})$, where $\mathbf{r}$ is the position vector. We leave aside for the moment the thermal motion of the ions and give the ions parametric positions $\mathbf{R}_i$, $i = 1, 2, ...N$. We may expect such an ensemble to be unstable, as will be shown below, in the sense that the ions get dressed with electrons. We shall show here that the dressed ions exhibit thermodynamically stable phases.

We denote by a the mean separation between ions (electrons) and write the concentration as $n = N/V = 1/a^3$. We assume $T \gg \hbar^2/ma^2$, where T is the electron temperature, which is the condition of classical thermodynamics of the electrons with mass m; also, we assume $a \gg a_H = \hbar^2/mq^2$, where a_H is the Bohr radius and $\hbar$ is Planck's constant.

The potential $\Phi(\mathbf{r})$ generated by the electric charges in plasma satisfies the Poisson equation

$$\Delta\Phi = -4\pi q \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi q n(\mathbf{r}) \ . \tag{5.13}$$

The solution of this equation can be written as

$$\Phi(\mathbf{r}) = q \sum_i \frac{1}{\mid \mathbf{r} - \mathbf{R}_i \mid} - q \int d\mathbf{r}' \frac{n(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} + f(\mathbf{r}) \ \ , \tag{5.14}$$

where the function $f(\mathbf{r})$ is a solution of the Laplace equation $\Delta f = 0$. If we identify the interaction Coulomb potential Ψ through $\Phi = \Psi + f$,

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(2008).

[15] E. Wigner, "On the interaction of electrons in metals", Phys. Rev. **46** 1002 (1934); D. H. E. Dubin and T. M. O'Neill, "Trapped non-neutral plasmas liquids, and crystals (the thermal equilibrium states)", Revs. Mod. Phys. **71** 87 (1999).

the potential energy of the plasma is given by

$$\begin{aligned} E_p = \tfrac{1}{2}q^2 \textstyle\sum_{i\neq j} \frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} - \tfrac{1}{2}q\int d\mathbf{r}n(\mathbf{r})\Psi(\mathbf{r}) - \\ -\tfrac{1}{2}q^2\textstyle\sum_i \int d\mathbf{r}\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|} + q\sum_i f(\mathbf{R}_i) - q\int d\mathbf{r}n(\mathbf{r})f(\mathbf{r}) \quad , \end{aligned} \tag{5.15}$$

or

$$\begin{aligned} E_p = \tfrac{1}{2}q^2 \textstyle\sum_{i\neq j} \frac{1}{|\mathbf{R}_i-\mathbf{R}_j|} - q^2\sum_i \int d\mathbf{r}\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|} + \\ +\tfrac{1}{2}q^2\int d\mathbf{r}d\mathbf{r}^{'}\frac{n(\mathbf{r})n(\mathbf{r}^{'})}{|\mathbf{r}-\mathbf{r}^{'}|} + q\textstyle\sum_i f(\mathbf{R}_i) - q\int d\mathbf{r}n(\mathbf{r})f(\mathbf{r}) \quad , \end{aligned} \tag{5.16}$$

where we recognize the ion-ion and electron-electron Coulomb repulsion and the ion-electron Coulomb attraction. The function $f(\mathbf{r})$ plays the role of an external potential, whose effect in energy disappears for $f = const$, as expected. For a uniform density of ions and electrons the potential given by equation (5.13) and the potential energy given by equation (5.16) are vanishing. For pointlike electrons placed at $\mathbf{r}_j$ an infinite attraction may arise for $\mathbf{r}_j = \mathbf{R}_i$ (we assume that all $\mathbf{R}_i$ are distinct and, separately, all $\mathbf{r}_j$ are distinct), with an infinite negative energy, which would mean the collapse of the plasma. This "catastrophic" situation is avoided by the quantum-mechanical behaviour of the electrons inside the atoms.

At thermal equilibrium the electron density is given by Gibbs distribution

$$n(\mathbf{r}) = Cne^{\beta q\Phi(\mathbf{r})} \quad , \tag{5.17}$$

where C is a normalization constant and $\beta = 1/T$ is the reciprocal of the temperature T. The normalization constant C is given by

$$Cn\int d\mathbf{r}e^{\beta q\Phi(\mathbf{r})} = N \quad . \tag{5.18}$$

For a quasi-uniform potential Φ we may use the representation

$$\begin{aligned} e^{\beta q\Phi} = 1 + \beta q\Phi + \tfrac{1}{2!}\beta^2q^2\Phi^2 + \tfrac{1}{3!}\beta^3q^3\Phi^3 + ... \simeq \\ \simeq 1 + \beta q\Phi\left(1 + \tfrac{1}{2!}\beta q\overline{\Phi} + \tfrac{1}{3!}\beta^2q^2\overline{\Phi^2} + ...\right) \quad , \end{aligned} \tag{5.19}$$

or

$$e^{\beta q\Phi} \simeq 1 + \lambda\beta q\Phi \ , \tag{5.20}$$

where

$$\lambda = 1 + \frac{1}{2!}\beta q\overline{\Phi} + \frac{1}{3!}\beta^2 q^2 \overline{\Phi^2} + ... \tag{5.21}$$

and

$$\overline{\Phi^n} = \frac{1}{V}\int d\mathbf{r}\Phi^n(\mathbf{r}) \ , \ \ n = 1, 2, 3... \ . \tag{5.22}$$

Moreover, for a quasi-uniform potential Φ the correlations involved in $\overline{\Phi^n}$, for any integer n in equation (5.22), can be left aside; we may replace $\overline{\Phi^n}$ by $\overline{\Phi}^n$ and write

$$\lambda = \frac{e^{\beta q\overline{\Phi}} - 1}{\beta q\overline{\Phi}} \ . \tag{5.23}$$

The mean potential $\overline{\Phi}$ plays the role of the chemical potential; it is viewed here as a variational parameter for minimizing the energy.

Making use of this variational approach, we get from equations (5.17) and (5.18) the electron density

$$n(\mathbf{r}) = Cn(1 + \lambda\beta q\Phi) \ , \ \ C = \frac{1}{1 + \lambda\beta q\overline{\Phi}} = e^{-\beta q\overline{\Phi}} \ \ , \tag{5.24}$$

where $n(\mathbf{r})$ is a linear functional of the potential Φ (hence the denomination "linearized variational approach").

Inserting the density $n(\mathbf{r})$ given by equation (5.24) in equation (5.13), we get

$$\Delta\Phi = -4\pi q\sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi Cnq + 4\pi C\lambda n\beta q^2\Phi \ . \tag{5.25}$$

We note that the neutrality of the plasma implies $C = 1$ and $\overline{\Phi} = 0$, $\lambda = 1$, a result which will be obtained below. Also, from equation (5.14) we expect $\overline{\Phi} \geq 0$, due to the contributions of the regions where $\mathbf{r}$ is close to $\mathbf{R}_i$. We write the potential Φ in equation (5.25) as $\Phi = \Psi - 1/\lambda\beta q$ and identify the function $f(\mathbf{r})$ in equation (5.14) by the constant $f(\mathbf{r}) = -1/\lambda\beta q$; being a constant, $f(\mathbf{r})$ does not contribute to the potential energy. Equation (5.25) becomes

$$\Delta\Psi = -4\pi q \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi C\lambda n\beta q^2 \Psi \ , \tag{5.26}$$

whose solution is the well-known Debye-Huckel screened potential[16]

$$\Psi(\mathbf{r}) = q \sum_i \frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_i|}}{\mid \mathbf{r} - \mathbf{R}_i \mid} \ , \tag{5.27}$$

with the screening parameter $\kappa = (4\pi C\lambda n\beta q^2)^{1/2}$. Making use of the potential Ψ in equation (5.24), we can express the electron density as

$$n(\mathbf{r}) = C\lambda n\beta q\Psi(\mathbf{r}) \ ; \tag{5.28}$$

the potential energy given by equation (5.15) becomes

$$E_p = \frac{1}{2}q^2 \sum_{i\neq j} \frac{1}{R_{ij}} - \frac{\kappa^2}{8\pi} \int d\mathbf{r}\Psi^2(\mathbf{r}) - \frac{\kappa^2 q}{8\pi} \sum_i \int d\mathbf{r} \frac{\Psi(\mathbf{r})}{\mid \mathbf{r} - \mathbf{R}_i \mid} \ , \tag{5.29}$$

where $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. The integrals in equation (5.29) can be effected immediately (they are two-centre integrals[17]); we get the potential energy

$$E_p = -\frac{1}{4}q^2\kappa \left[3N + \sum_{i\neq j} \left(1 - \frac{2}{\kappa R_{ij}} \right) e^{-\kappa R_{ij}} \right] \ . \tag{5.30}$$

From equations (5.27) and (5.28) we can see that each ion is surrounded by an electron cloud extending, approximately, over distances of the order κ^{-1}. Also, from equation (5.30) we can see that these dressed ions have a self-energy $-(3q^2\kappa N/4)$ (the first term on the right in equation (5.30)) and interact by the screened effective (pseudo-) potential $\sim -(1-2/\kappa R_{ij})e^{-\kappa R_{ij}}$, which has a zero at $\kappa R_{ij}=2$ and a minimum for $\kappa R_{ij}=\sqrt{3}+1$. As it is well-known, the electrons dress the ions and screen the original Coulomb interaction. The same form of the ion-ion interaction potential has been derived for a solid-state (quantum) plasma.[18]

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[16] P. Debye and E. Huckel, "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen", Phys. Z. **24** 185 (1923); “Zur Theorie der Elektrolyte. II. Das Grenzgesetz fur die elektrische Leitfahigkeit”, Phys. Z. **24** 305 (1923).

[17] J. C. Slater, *Quantum Theory of Molecules and Solids*, vol. 1, *Electronic Structure of Molecules*, Mc-Graw-Hill, NY (1963).

The equilibrium is achieved for well-defined values of the parameters κR_{ij}, which ensure the minimum of the potential energy (interacting part) given by equation (5.30). The global minimum of the potential energy requires also the maximum value of the parameter $\kappa=(4\pi C\lambda n\beta q^2)^{1/2}$, *i.e.* the maximum value of the product

$$C\lambda=\frac{\lambda}{1+\lambda\beta q\overline{\overline{\Phi}}}=\frac{1-e^{-\beta q\overline{\Phi}}}{\beta q\overline{\Phi}} \tag{5.31}$$

(according to equations (5.23) and (5.24)). It is easy to see that the maximum value of this parameter is reached for $\overline{\Phi}=0$, $C=\lambda=1$ (as expected from neutrality). For $C=\lambda=1$ the screening parameter κ becomes $\kappa_D=1/\lambda_D=(4\pi n\beta q^2)^{1/2}$, where $\lambda_D=a(aT/4\pi q^2)^{1/2}$ is the well-known Debye length. Henceforth, we use κ_D for κ and λ_D for $\lambda=1/\kappa$ (not to be mistaken for the variational parameter $\lambda=1$) and remove the suffix D.

The equilibrium mean value of the parameters κR_{ij} is given approximately by $\kappa\overline{R}_{ij}\simeq\sqrt{3}+1$; making use of this value, the potential energy given by equation (5.30) can be written as

$$\begin{aligned}E_p &\simeq -\tfrac{1}{4}q^2(4\pi n\beta q^2)^{1/2}\left[3+\tfrac{\sqrt{3}-1}{\sqrt{3}+1}e^{-(\sqrt{3}+1)}z\right]N\simeq\\ &\simeq -\tfrac{3q^2}{4\lambda}N\ ,\end{aligned} \tag{5.32}$$

where z is the mean number of nearest-neighbours; we can see that the interaction energy brings a small contribution in comparison with the self-energy of the dressed ions. The equilibrium configuration of $N=23$ ions, resulting from numerical calculation (gradient method), is shown in Fig. 5.1. In quantum-mechanical terms this solid phase

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[18] L. C. Cune and M. Apostol, "Ground-state energy and geometric magic numbers for homo-atomic metallic clusters", Phys. Lett **A273** 117 (2000).

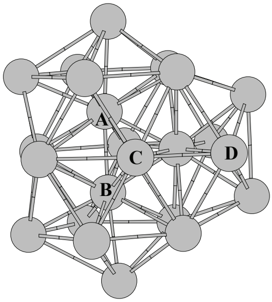

Figure 5.1: Equilibrium configuration (solid state) of $N = 23$ ions, according to equation (5.30); configuration parameters $x_{ij} = \kappa R_{ij}$ are of the order $x_{AB} = 2.04$, $x_{BC} = 2.4$, $x_{CD} = 2.27$, and bond angles are of the order $(ABC) = 64.83$, $(ACD) = (BCD) = 103.57$ (degrees); the interaction energy is $-1.2(q^2/\lambda)$.

of the "plasma" may be viewed as its "ground-state" (though it is at a finite temperature). The frequency of oscillation ω_0 of an ion in the potential well generated by its nearest-neighbours can be estimated from the potential given by equation (5.30); it is of the order $\omega_0 \simeq (zq^2/M\lambda^3)^{1/2}$, where M is the ion mass. For a highly-compressed plasma the existence of an ionic lattice ground-state was suggested long ago.[19]

The solid phase of the "plasma" exists for $\overline{R}_{ij} \simeq (\sqrt{3}+1)\lambda < a$, *i.e.* for $aT < 1.68q^2$ (strongly-coupled plasma).[20] It is convenient to introduce the length $a_0 = q^2/T$ and the notation $a_s = 1.68a_0$; the ratio a/a_0 is the coupling parameter of the plasma. We can see that in the strong-coupling limit $(a \ll a_0)$ the "plasma" is a solid. For $a \simeq a_s$ the vibration energy of an ion is comparable with the depth of the potential well and its vibration amplitude is comparable with the mean inter-ionic distance. If we compare the electron localization energy $\hbar^2/m\lambda^2$ with the temperature T, we find that the quantum-mechanical solid appears for $T < \sqrt{4\pi(\hbar^2/ma^2)(q^2/a)}$ (which is, usually, smaller than the Coulomb energy q^2/a). For $a = a_s$ this condition becomes $a_H > 0.38a_0$. We can see that for $T < 0.38(q^2/a_H)$ the "plasma" solid is a classical solid. This classical solid-phase of a plasma is a distinct type of a classical solid, which may be termed a "plasmonic" solid, produced by inter-ionic (pseudo-) potentials which depend on the density (equation (5.27)).[21] On passing to the weak-coupling regime, the "plasma" behaves gradually as a liquid, a non-ideal gas, and, finally, in the weak-coupling limit, the plasma becomes an ideal gas (genuine plasma). This is the well-known condition of the existence of a (genuine) plasma.[22] A numerical example of the parameter a_0 is $a_0 \simeq 10^{-7}cm$ for $T = 10^4K$ (electron charge $-q = 4.8 \times 10^{-10}esu$). The parameter a_0^2 may be taken as the electron-electron collision cross-section in the weak-coupling limit of the plasma gas. (A similar, usually much larger, parameter exists for ions. It is worth noting that we can compute the mean freepath, and the lifetime, associated with electron-electron, electron-ion and ion-ion collision processes, in the weak-coupling regime, as for a neutral classical gas. Since the electron temperature is much higher than the ion temperature, the electron-ion dominates the electron behaviour, which is another indication of the electron-ion correlations).

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[19] D. A. Kirzhnits, "Internal structure of super-dense stars", Sov. Phys.-JETP **11** 365 (1960) (ZhETF **38** 503 (1960)); A. A. Abrikosov, "Nekotorye svoistva sil'no szhatogo veschestva. I.", ZhETF **39** 1797 (1960) (in Russian; Sov. Phys.-JETP **12** 1254 (1961)); "Contribution to the theory of highly-compressed matter. II.", Sov. Phys.-JETP **14** 408 (1962) (ZhETF **41** 569 (1961)).

[20] M. Apostol and L. C. Cune, "On the stability of a classical plasma", Phys. Lett. **A383** 1831 (2019).

The above estimations are valid as long as the potential Ψ is quasi-uniform, *i.e.* it differs little from its mean value $\overline{\psi} = 1/\beta q$ ($\overline{\Phi} = 0$). This condition is not fulfilled in small regions surrounding the ion position, so we may estimate the error by comparing

$$\frac{1}{v}\int_v d\mathbf{r}\frac{qe^{-\kappa r}}{r} \tag{5.33}$$

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[21] We can see that the quantum-classical border is relaxed, since $\hbar^2/ma^2 < \sqrt{(\hbar^2/ma^2)(q^2/a)} < q^2/a$; this is an effect of the correlations brought about by the Debye-Huckel dressing of the ions.

[22] D. G. Swanson, *Plasma Kinetic Theory*, Taylor Francis, NY (2008); P. A. Sturrock, *Plasma Physics*, Cambridge University Press, Cambridge (1994); R. J. Goldston and P. H. Rutheford, *Introduction to Plasma Physics*, IOP Publishing, London (1985); F. E. Chen, *Introduction to Plasma Physics*, Plenum Press, NY (1974).

with $\overline{\Psi} = 1/\beta q$, where v is a volume of the order λ^3; we get the relative error $\simeq (a/\lambda)^3$, which is very small for $\lambda \gg a$. In the solid phase, when $a \simeq \lambda$, we can get a more accurate estimation of the error by computing the self-energy

$$E_s = -\frac{1}{2}q\int_v d\mathbf{r}n(\mathbf{r})\Psi(\mathbf{r}) - \frac{1}{2}q^2\int_v d\mathbf{r}\frac{n(\mathbf{r})}{r} \tag{5.34}$$

associated with the volume v per ion (equation (5.15)); we get $E_s = -(q^2/4\lambda)[3-(1+2e)/e^2]$, which should be compared with $-(3q^2/4\lambda)$ given in equation (5.32). We get a relative error $\simeq 0.28$ and we can see that equation (5.32) provides a lower bound to the binding energy.

In conclusion, we may say that the model of classical plasma investigated here by means of a linearized self-consistent variational approach consists of ions dressed by electrons, which interact by a screened Coulomb potential. In the strong-coupling regime the ensemble is in a solid-state phase, while, on passing to the weak-coupling regime, the ensemble becomes a liquid, a non-ideal gas, and finally an ideal gas. Therefore, the Coulomb interacting classical ions and electrons have a consistent thermodynamics.

5.4 The stability of matter

It is worth taking a digression on the stability of matter. This problem appeared, probably, for the first time in connection with the non-integrability of the three-body mechanical motion and its chaotic behaviour.[23] Then, it occurred that the classical motion of an electron about the nucleus would lead to the collapse of the atom. This problem led to the apparition of the Quantum Mechanics. The quantum-mechanical motion and Pauli's exclusion principle ensure the atomic stability. The reason is that the kinetic energy of a quantum-mechanical particle may exceed the Coulomb attraction. This was shown explicitly by the Thomas-Fermi model for many-electron atoms (heavy atoms).[24] Latter it was shown that the Thomas-Fermi model does not bind atoms in molecules.[25] This is due to an overestimation of the kinetic energy. A linearized form of the Thomas-Fermi theory leads to the cohesion of matter.[26] The stability of the mechanical motion of the (neutral) ensemble of many Coulomb interacting charges has been proved by assuming quantum-mechanical motion of the charges and Pauli's exclusion principle; in particular, by making use of the Thomas-Fermi theory in the limit of an infinite number of charges.[27]

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[23] See, for instance, H. Poincare, *Les Méthodes Nouvelles de la Mécanique Celeste*, Gauthier-Villars, Paris (1892, 1893, 1899).

[24] L. H. Thomas, "The calculation of atomic fields", Proc. Cambr. Phil. Soc. **23** 542 (1927); E. Fermi, "Un metodo statistico per la determinazione di al-

All these show that (neutral) Coulomb interacting matter, both at the atomic level and in bulk, does not collapse, as a consequence of its quantum-mechanical behaviour. But this does not prevent the bulk matter to crumble into molecules and atoms, which amounts to say that (bulk) matter would be thermodynamically unstable. It is believed, reasonably, that on lowering the temperature a classical gas becomes condensed in a liquid and, further, a solid; the condensed phases have a distinct thermodynamics, in comparison with the gas, because interaction comes into play in condensed phases, and the condensation needs to be proved; it was proved above. Moreover, a compression may leave the ensemble with sufficiently high temperature, such that its particles still behave classically; but the interaction is important in the compressed state, and a liquid, or a solid may appear; this may not be a quantum-mechanical condensed phase, in the sense that the electrons may still behave classically, and we are then in the

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cune proprieta dell'atomo", Rend. Accad. Naz. Lincei **6** 602 (1927); "Eine statistiche Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente", Z. Phys. **48** 73 (1928).

[25] E. Teller, "On the stability of molecules in the Thomas-Fermi theory", Revs. Mod. Phys. **34** 627 (1962); see also L. Spruch, "Pedagogic notes on Thomas-Fermi theory (and on some improvements): atoms, stars, and the stability of bulk matter", Revs. Mod. Phys. **63** 151 (1991).

[26] L. C. Cune and M. Apostol, "Ground-state energy and geometric magic numbers for homo-atomic metallic clusters", Phys. Lett. **A273** 117 (2000); M. Apostol, "Giant dipole oscillations and ionization of heavy atoms by intense electromagnetic fields", Roum. Reps. Phys. **67** 837 (2015).

[27] F. J. Dyson, "Ground-state energy of a finite system of charged particles", J. Math. Phys. **8** 1538 (1967); F. J. Dyson and A. Lenard, "Stability of matter. I", J. Math. Phys. **8** 423 (1967); A. Lenard and F. J. Dyson, "Stability of matter. II", J. Math. Phys. **9** 698 (1968); E. H. Lieb and W. E. Thirring, "A bound for the kinetic energy of fermions which proves the stability of matter, Phys. Rev. Lett. **35** 687 (1975) (errata 1116); E. H. Lieb, "The stability of matter", Revs. Mod. Phys. **48** 533 (1976).

situation of not being able to make use of the quantum-mechanical motion as an argument for stability. The stability in this case, which has also been proved above, arises from classical statistical motion, which leaves a sufficiently high kinetic energy to exceed the attraction.

Classically speaking, any plasma is unstable because the attraction energy between ions and electrons is infinite when their positions coincide. The quantum-mechanical motion prevents these positions to coincide, so we may expect a quantum-mechanical stability. But the classical statistical motion does the same, so we also may expect a statistical stability of a classical plasma. It is this statistical stability, due to classical statistical motion of classical charges which is proved above. In statistical motion the electrons have not definite positions (or they have with a probability); instead, they are statistically distributed with a density.

Also, there is another sense of viewing the thermodynamic stability, which does not refer to a collapse, but to an explosion, which would be brought about by the long-range character of the Coulomb interaction; however, the screening may prevent such a situation in a neutral ensemble.

The stability of a plasma raises an important problem. Let us assume that we have created a gaseous plasma by electric discharge, or by heating; or it was created by other agencies as in stars, white dwarfs, neutron stars, etc. Let us assume that the external agency (discharge, heating) ceased. Obviously, the conditions of classical motion are satisfied for all particles. Though we may admit that the neutral atoms, the ions and the electrons are each in separate, distinct thermal equilibrium, it is difficult to admit that the equilibrium is mutual, because of the disparity in sharing the energy between the light electrons and the heavy ions (atoms). Very likely, we are in the presence of a non-thermal plasma. If we view this plasma as pointlike classical electrons and ions, we are led to admit that this plasma is unstable, since the Coulomb attraction energy is infinite when the positions of the ions and the electrons coincide. But the electrons (at least) are not pointlike classical particles, they are classical statistical particles distributed with a density; this may ensure the stability, as was proven, in fact, above. It was also proven above that the electrons become correlated with the ions, their density being higher around the ions. In the weak-coupling regime these correlations are weak, but in the strong-coupling regime they are strong. It is difficult to see the correlated electrons as a statistical ensemble; in fact, they are in quasi-bound states, where the statistical motion is meaningless. Their thermal energy is taken up now in their mechanical energy, and their original temperature is now only a parameter for their characteristics. We may imagine that the correlated electrons move classically around the ions, in a collective classical motion (for higher densities their motion becomes quantum-mechanical). The correlations originate in the Coulomb ion-electron attraction and the Coulomb electron-electron repulsion. Do the electrons lose energy through radiation in this case? Because we know that in the weak coupling regime an important cause of energy loss is the radiation of electromagnetic energy. It is difficult to view the correlated electrons in plasma as a black body, as long as their statistical motion is not present anymore. In the presence of the correlations it is unlikely that a collective classical motion lose much energy. In an isolated atom an electron moving classically do lose energy through radiation, but in a collective classical motion an electron radiates and at the same time absorbs radiation emitted by the other electrons. In quantum-mechanical motion radiation exceeds absorption due to the Einstein uneven emission and absorption coefficients, but classically, this unevenness disappears. Along those portions of their trajectory where the electrons are accelerated they emit radiation, along those portions where they are slowed down, they absorb radiation. In the strong-coupling regime plasma is a collection of interacting ions dressed by electrons.

5.5 The effect of the Debye screening length

The existence of the Debye screening length λ has important consequences; it illustrates the fact that we have solved the problem of the long-range Coulomb interaction. The Coulomb repulsive interaction between the electrons has been taken into account in this solution. What happens with the original thermal equilibrium of the electrons, as they were initially generated? The attractive Coulomb interaction between the ions and the electrons has been partially included in this solution, so what about the equilibrium between the ions and the electrons? Also, the repulsive Coulomb interaction between the ions has been included partially in solution, so how is their original equilibrium affected? The answer to these questions resides in the fact that we should realize that immediately after its creation the gaseous classical plasma is unstable, and an electronic cloud appears around each ion. Under these circumstances it becomes meaningless to talk about the ion-electron equilibrium, because the main part of the corresponding interaction does not exist anymore, and the remaining part acts between the dressed ions. The ion-ion equilibrium is preserved, though it is affected by the screened ion-ion interaction. The thermal equilibrium between the electrons is spoiled, in principle, because their motion becomes highly correlated around the ions. What about their temperature T and their thermal energy?

Let us write the normalization condition for the distribution function of an ideal classical gas of N electrons:

$$\frac{1}{N!}\left[V\left(\frac{m}{2\pi\hbar^2}\right)^3\int d\mathbf{v}e^{-\frac{1}{2}\beta mv^2}\right]^N=e^{-\beta\mathcal{F}}\quad , \tag{5.35}$$

where $\mathcal{F}$ is its free energy. We can insert in this equation the distribution function $F=n(\beta m/2\pi)^{3/2}e^{-\beta mv^2/2}$ and get

$$\frac{1}{N!}\left[V\left(\frac{ma^2T}{2\pi\hbar^2}\right)^{3/2}\int d\mathbf{v}F\right]^N=e^{-\beta\mathcal{F}}\quad , \tag{5.36}$$

where $n=N/V=1/a^3$ is the concentration; making use here of $\int d\mathbf{v}F=n$ we get immediately the well-known free energy of an ideal classical gas. Let us suppose now that the electrons acquire a velocity $\mathbf{V}$, generated by the interaction with the ions. For simplicity we assume a constant $\mathbf{V}$. Equation (5.35) becomes

$$\frac{1}{N!}\left[V\left(\frac{m}{2\pi\hbar^2}\right)^3\int d\mathbf{v}e^{-\frac{1}{2}\beta mv^2+\beta m\mathbf{v}\mathbf{V}}\right]^N=e^{-\beta\mathcal{F}'}\quad , \tag{5.37}$$

or

$$\frac{1}{N!}\left[V\left(\frac{m}{2\pi\hbar^2}\right)^3\int d\mathbf{v}e^{-\frac{1}{2}\beta mv^2}\cdot e^{\frac{1}{2}\beta mV^2}\right]^N=e^{-\beta\mathcal{F}'}\quad ; \tag{5.38}$$

we can see that the free energy becomes

$$\mathcal{F}^{'} = \mathcal{F} - \frac{1}{2}NmV^2 \ . \tag{5.39}$$

Since an interaction cannot modify the total energy, it follows that the electrons lose from their thermal energy exactly the mechanical energy corresponding to the velocity $\mathbf{V}$. A similar process is suffered by the ions, though to a lesser extent. Of course, this loss may be viewed as a released heat, and a reduction in the entropy; it is an irreversible transformation, so it is allowed by the second law of thermodynamics. If this change is small, *i.e.* if the Debye length is very large, we may still view the electrons in thermal equilibrium at their temperature T. But in the strong-coupling regime, when the Debye length is short, we cannot speak of thermal equilibrium for the electrons; they preserve their temperature T as a parameter in the Debye length, but their thermal energy is taken now in their mechanical motion. If the electrons are in the quantum-mechanical regime, we recover this energy in their kinetic energy, corresponding to their Fermi levels, which is indeed a mechanical energy. Their motion is now a mechanical motion, not a statistical one.

In conclusion, we may say that as a consequence of the long-range Coulomb interaction in plasma we are left with a set of dressed ions interacting by the screened potential. In the weak-coupling regime (*e.g.*, low densities), where the screening is very weak, we may still view the plasma as a classical gas of electrons at thermal equilibrium at temperature T and a classical gas of ions in thermal equilibrium at temperature T_i ($T_i \ll T$); the negative tails of the long-range Coulomb potentials cancel out the positive part of the interaction, such that we may view these gases as ideal gases. This is the regime of a genuine plasma. On the contrary, in the strong-coupling regime, we cannot speak anymore of a thermal equilibrium of the electrons, or thermal equilibrium between the electrons and the ions; the electron temperature is preserved as a parameter in the Debye length; the thermal energy of the electrons is transformed into mechanical energy corresponding to their motion around the ions. We are left with a collection of dressed ions which interact with the screened potential, and may become a liquid or a solid.

It is worth noting that the Saha equation is not valid anymore for a correlated, strongly-coupled plasma. The preparation of any plasma implies, in fact, $T_i \ll T_e$, *i.e.* a non-thermal plasma. However, let us consider the ideal case of a thermal plasma. The electrons and the ions may be originally in thermal equilibrium, at a common temperature $T_e = T_i$, and their (common) density may be given by the Saha equation. Immediately after its creation this plasma becomes correlated, more or less, and the Debye length occurs; if the correlations are weak (in the weak-coupling regime), the Saha equation may keep its validity, approximately. The plasma may suffer transformations; if these transformations imply a dilatation, in the weak-coupling regime, the Saha equation is valid and the plasma temperature decreases as a result of the decrease in the density; if we keep the temperature constant, more ionization processes appear in order to keep the density constant (which means to give energy from the outside). If we compress the plasma at constant temperature, recombination processes occur, in order to satisfy the Saha equation. Only in these conditions we may compress the thermal plasma, preserving its temperature. We can see that equilibrium transformations are allowed for a thermal plasma, for a limited range of parameters. Indeed, on compression, the correlations begin to become important, and the Saha equation does not hold anymore; the ions get decoupled from electrons. Of course, transformations at constant temperatures (both for ions and electrons) are possible for a non-thermal plasma.

5.6 Plasma isotherms. Phase diagram

According to the standard theory of the non-ideal gases and the standard van der Waals equation, before reaching the solid state a non-ideal gas may have a liquid phase. It is controlled by the condensation phenomenon, which may occur at a transition temperature related to the depth of the potential well of the two-particle interaction potential.[28] This is valid for short-range potentials, *i.e.* for potentials which have a sharp, abrupt (hard-core) repulsive part and an integrable (usually attractive) tail. The presence of the (pseudo-) potential U_{ij} (given by equation (5.30)) brings some specific features in plasmas.

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[28] M. Apostol, "The condensation of matter - a model of phase transition of the first kind", Mod. Phys. Lett. **B21** 893 (2007).

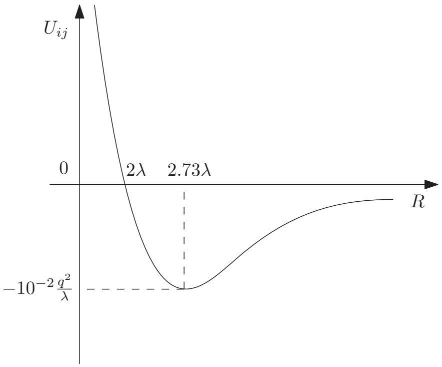

Figure 5.2: Schematic representation of the screened two-body potential U_{ij} given by equation (5.41) *vs* the inter-ionic distance R; $\lambda = 1/\kappa$ denotes the Debye length.

Let us assume a classical plasma with the electron temperature T and the ion temperature T_i; we assume the usual situation $T_i \ll T$. In order to take into account the interaction (correlations), we view the electrons as moving around the ions, with their temperature T as a parameter, and consider the statistical properties only for dressed ions interacting by the screened potential. The potential energy of the ions is given by equation (5.30); it can be written as

$$E_p = N\Phi_0 + \frac{1}{2}\sum_i \Phi_i \ \ , \tag{5.40}$$

where $\Phi_0 = -3q^2\kappa/4$ is the ionic self-energy (equation (5.30)) and

$$\begin{gathered} \Phi_i = \sum\nolimits_j^{\prime} U_{ij} \ \ , \\ U_{ij} = -\tfrac{1}{2}q^2\kappa\left(1 - \tfrac{2}{\kappa R_{ij}}\right)e^{-\kappa R_{ij}} \ \ ; \end{gathered} \tag{5.41}$$

the prime on the summation sign in equation (5.41) means $j \neq i$. The screened two-particle potential U_{ij} given by equation (5.41) is shown in Fig. 5.2. It is worth noting that this potential has a zero at $R_{ij} = 2\lambda$, where $\lambda = 1/\kappa = a\sqrt{aT/4\pi q^2}$ is the Debye length (and a

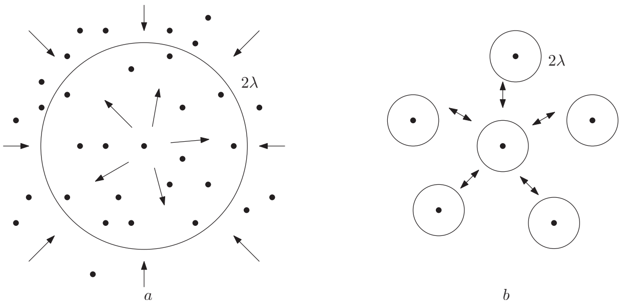

Figure 5.3: Two regimes of interaction in plasma, depending on the relation between the Debye length λ and the mean separation distance a between ions. For $2\lambda \gg a$ (figure a) the positive part of the interaction inside the sphere with radius 2λ is cancelled out by the negative part of the interaction generated by the ions outside the Debye sphere. For $2\lambda \gtrsim a$ the Coulomb repulsion dominates, and we have an excluded volume; for $2\lambda < a$ (figure b) the solid may appear.

is the mean separation distance between ions). The change brought about by the interaction in the free energy is given by

$$\begin{aligned}\Delta\mathcal{F} = -T_i \ln\left(\tfrac{1}{V^N}\int' e^{-\beta_i E_p} d\mathbf{r}_1 ... d\mathbf{r}_N\right) = \\ = -T_i \ln\left(\tfrac{e^{-\beta_i N\Phi_0}}{V^N}\int' e^{-\frac{1}{2}\beta_i \sum_i \Phi_i} d\mathbf{r}_1 ... d\mathbf{r}_N\right) \quad .\end{aligned} \tag{5.42}$$

For the potential Φ_i we adopt a mean-field approximation

$$\begin{aligned}\Phi_i = \tfrac{N}{V}\int_{r_1} d\mathbf{r} U(r) = \\ = -2\pi q^2 \kappa \tfrac{N}{V}\int_{r_1} dr \cdot r^2 (1 - 2/\kappa r) e^{-\kappa r} = -2A\tfrac{N}{V} \quad ,\end{aligned} \tag{5.43}$$

where r_1 is the parameter which accounts for the prime in the summation in equation (5.41); we get

$$A = \pi q^2 r_1^2 e^{-\kappa r_1} \quad . \tag{5.44}$$

Similarly, the prime in the integration in equation (5.42) is accounted by an excluded-volume parameter r_2, such that each integration is performed over the volume $V - NB$, where $B = \frac{1}{2} \cdot 4\pi r_2^3/3$.[29] The change in the free energy (equation (5.42)) is

$$\Delta\mathcal{F} = -NT_i \ln\left(1 - \frac{NB}{V}\right) + N\Phi_0 - \frac{N^2 A}{V} \quad . \tag{5.45}$$

The potential Φ_0 can be written as

$$\Phi_0 = -\frac{3}{4}q^2\kappa = -\frac{3}{4}\frac{q^2}{\lambda} = -\frac{3}{4}\frac{q^2}{a}\sqrt{\frac{4\pi q^2}{aT}} = -\frac{3}{2}\frac{q^2}{a}\sqrt{\pi a_0/a} \quad , \tag{5.46}$$

where we have introduced the parameter $a_0 = q^2/T$ (a/a_0 is the coupling parameter of the plasma); as long as the ensemble is gaseous we have the inequalities $a_0 \ll a \ll \lambda$ (weak-coupling regime; for $T = 10^4$ this parameter is $a_0 \simeq 16\text{Å}$). The self-energy term in equation (5.45) becomes

$$N\Phi_0 = -\frac{3}{2}q^2\sqrt{\pi a_0}N\left(\frac{N}{V}\right)^{1/2} \quad . \tag{5.47}$$

For short-range potentials with a sharp, abrupt, repulsive hard core the two parameters $r_{1,2}$ coincide, but for a plasma they are distinct. Indeed, in plasma each ion is surrounded by an electronic cloud extended over a distance of the order of the Debye length λ, such that, usually, $a_0 \ll a \ll \lambda$. We can see that inside the screening sphere of radius 2λ (Debye sphere) there are many ions ($2\lambda \gg a$), interacting by the positive part of the potential. This positive interaction is cancelled out by the negative part of the potential of the ions lying outside the screening sphere; indeed, $\int d\mathbf{r}U_{ij}(r) = 0$, such that, in this situation, we may view the ions as quasi-free particles. A special situation appears when 2λ is comparable with a. In this case the electrons inside the Debye sphere are shared by a few ions, and the ionic self-energy may increase appreciably in magnitude, such that it may become greater than the thermal energy T_i; a negative pressure may be expected in this situation. For $2\lambda \gtrsim a$ the repulsive Coulomb interaction dominates; the integration in equation (5.42) should be viewed

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[29] M. Apostol, "On the van der Waals equation", J. Math. Theor. Phys. **1** 215 (2018).

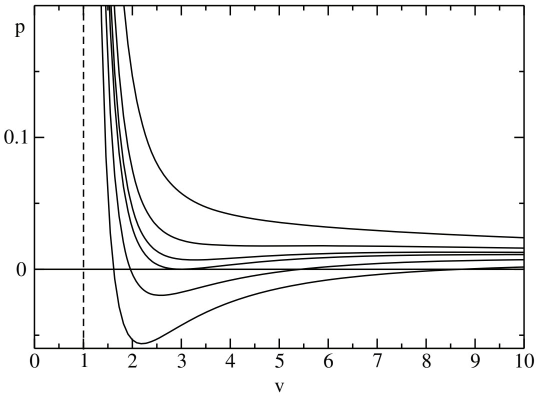

Figure 5.4: van der Waals isotherms $p(v) = T_i/(v-1) - 1/v^{3/2}$ (equation (5.48)) for reduced pressure p and volume $v = V/N$; from top to bottom the temperatures are $T_i = 0.5, 0.429, 0.4, 0.385, 0.35, 0.3$.

as a summation over the ion positions; the approximation of this summation by an integral should be corrected by an Euler-Maclaurin formula; the most convenient way of including these corrections is to introduce an excluded volume. It follows that this excluded volume is given by the condition $2\lambda = a$ ($a = \pi a_0$). We may have a liquid in these regions. Further on, when $2\lambda < a$, *i.e.* $a < \pi a_0$, the minima of the interaction potential U_{ij} may lie between ions, so we may get the solid phase. All these regions, corresponding to 2λ comparable with a or smaller are strong-coupling regions. This picture is shown schematically in Fig. 5.3. According to this picture, it is natural to assume that the parameter r_1 is practically zero and the parameter r_2 is of the order πa_0. We get $A = 0$ and $B = 2\pi^4 a_0^3/3$. If we compare the electron localization energy $\hbar^2/m\lambda^2$ with the temperature T for $a = \pi a_0$, we get that the liquid phase may be viewed as a classical liquid for $T < 2.46(q^2/a_H)$. Making use of these estimations in equation

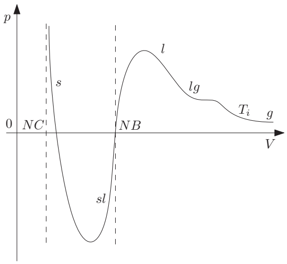

Figure 5.5: The phase diagram (pressure *vs* volume, equation (5.54)) of a classical plasma; in the vicinity of the asymptote NB the plasma is a liquid, near the asymptote NC the plasma is a solid ("plasmonic" solid); N is the number of ions (and electrons), T_i is the ionic temperature and the excluded-volume parameters B and C are defined in text. The gaseous (g), liquid (l) and solid (s) phases are indicated, as well as the liquid-gas (lg) and solid-liquid (sl) mixed phases.

(5.45), we get the pressure

$$\begin{aligned} p = \tfrac{NT_i}{V} + \tfrac{NT_i}{V}\tfrac{NB/V}{1-NB/V} - \tfrac{3}{4}q^2\sqrt{\pi a_0}\left(\tfrac{N}{V}\right)^{3/2} = \\ = \tfrac{NT_i}{V-NB} - \alpha\left(\tfrac{N}{V}\right)^{3/2} \end{aligned} \tag{5.48}$$

and the van der Waals equation

$$\left(p + \alpha\frac{N^{3/2}}{V^{3/2}}\right)(V - NB) = NT_i \quad , \tag{5.49}$$

where we have introduced the notation $\alpha = \frac{3}{4}q^2\sqrt{\pi a_0}$ ($B = 2\pi^4 a_0^3/3$). Equation (5.49) can be viewed as the equation of state of a classical plasma. It differs from the equation of state of a classical plasma with continuously-distributed ions.[30]

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[30] A. A. Vedenov and A. I. Larkin, "Equation of state of a plasma", Sov. Phys.-JETP **9** 806 (1959) (ZhETF **36** 1133 (1959)).

The $(N/V)^{3/2}$-term in equation (5.49) was derived by Debye and Huckel (correlation-energy term);[31] its relation to a possible phase transition was discussed by Zeldovich and Landau.[32] The van de Waals equation for plasma (5.49) differs from the standard van de Waals equation (for gases with short-range interaction) by the power $(N/V)^{3/2}$ in the internal (self-energy) pressure instead of $(N/V)^2$. Formally, this may not look as a qualitative difference. However, a qualitative difference appears from the relation between the parameters α and $T_i B$. While in the standard van der Waals equation this relation prevents the pressure to acquire negative values, in plasmas such a circumstance may appear; this is due to the long-range character of the Coulomb forces. The pressure given by equation (5.49) has an asymptote at the excluded volume $V = NB$, two extrema and one inflexion point (the pressure is positive for $T_i > 2\alpha/3\sqrt{3B} = T/(2\pi)^{3/2}$). The region near the asymptote corresponds to the dominating Coulomb repulsion, while the region with negative pressure is caused by an excess of ionic self-energy. A family of curves $p(v = V/N)$ given by equation (5.49) are shown in Fig. 5.4. The inflexion point occurs at the critical values $V_c = 5NB$, $T_{ic} = 24\alpha/25\sqrt{5}B^{1/2}$ and $p_c = \alpha/25\sqrt{5}B^{3/2}$. It is worth noting that

$$T_{ic} = \frac{18}{25\pi}\sqrt{\frac{3}{10\pi}}\frac{q^2}{a_0} = \frac{18}{25\pi}\sqrt{\frac{3}{10\pi}}T \tag{5.50}$$

($T_{ic} \simeq 7 \times 10^{-2}T$). The latent heat can be computed at T_{ic} from the change in energy $\Delta E = \Delta\mathcal{F} - T_{ic}\partial(\Delta\mathcal{F})/\partial T_i$; it is of the order NT_{ic}. The region defined by the extrema points of the curve $p(V)$ corresponds to liquid-gas mixed states; for V in the vicinity of NB the "plasma" is a liquid, for $V \longrightarrow \infty$ the plasma is an ideal gas. We can see that a thermal plasma ($T_i = T$) does not exhibit these features, neither a critical point.

We have seen in one of the preceding sections that the plasma becomes a solid for $\overline{R}_{ij} \simeq (\sqrt{3}+1)\lambda < a$, *i.e.* for $a < 4\pi a_0/(2.73)^2 \simeq 0.5\pi a_0$

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[31] P. Debye and E. Huckel, "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen", Phys. Z. **24** 185 (1923); “Zur Theorie der Elektrolyte. II. Das Grenzgesetz fur die elektrische Leitfahigkeit”, Phys. Z. **24** 305 (1923).

[32] Y. Zeldovich and L. Landau, "On the relation between the liquid and the gaseous states of metals", ZhETF **14** 32 (1944).

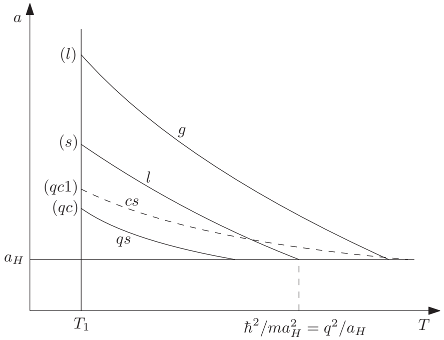

Figure 5.6: The phases of a plasma (gas-g, liquid-l, classical (plasmonic) solid-cs, quantum solid-qs) in coordinates a (mean interparticle separation distance) and T (temperature of the electrons); the curves are (l): $a = \pi(q^2/T)$, (s): $a = 1.68(q^2/T)$, $(qc1)$: $T = [4\pi(\hbar^2/ma^2)(q^2/a)]^{1/2}$ and (qc): $T = \hbar^2/ma^2$; T_1 is the ionization temperature.

(strong-coupling regime); we may take the parameter $r_3 = 0.5\pi a_0 = 0.5r_2$ as the parameter of the excluded volume $C = \frac{1}{2} \cdot 4\pi r_3^3/3$ of the solid. The two excluded volumes can be accommodated by noticing that in pressure we have the quantity

$$1 + \frac{NB/V}{1 - NB/V} \simeq 1 + NB/V \quad , \tag{5.51}$$

which now may be replaced by

$$1 + N(B + C)/2V \simeq \frac{1}{2}\frac{1}{1 - NB/V} + \frac{1}{2}\frac{1}{1 - NC/V} \quad ; \tag{5.52}$$

thus, we get the pressure

$$p = \frac{NT_i/2}{V - NC} + \frac{NT_i/2}{V - NB} - \alpha\left(\frac{N}{V}\right)^{3/2} \tag{5.53}$$

(and a generalized van der Waals equation). On approaching the excluded volume $NC < NB$ we see that we pass over the asymptote

$V = NB$; actually, this passing is a smooth one, which can be obtained formally by replacing $V - NB$ by $V - N(B + i\gamma)$, where γ is a small parameter ($\gamma \longrightarrow 0$), and taking the real part; the parameter γ accounts for the solid-liquid mixed phase, which has a very narrow extension in volume. We can write the pressure as

$$p = \frac{NT_i/2}{V - NC} + \frac{(NT_i/2)(V - NB)}{(V - NB)^2 + \gamma^2} - \alpha\left(\frac{N}{V}\right)^{3/2} \quad . \tag{5.54}$$

The curve $p(V)$ given by equation (5.54) is sketched in Fig. 5.5. It exhibits the gaseous, liquid-vapours, liquid, liquid-solid and solid phases of a plasma. We note that the ideal-gas free energy (equation (5.42)) is not appropriate for condensed phases like liquids or solids (*i.e.*, for V too close of the excluded volumes NB or NC).

According to the above discussion, the plasma is defined for mean inter-electron (ion) distance $a > a_H$ (where a_h is the Bohr radius) and temperature $T > T_1$, where T_1 is the ionization temperature. The classical regime of the electrons is separated from the quantum-mechanical regime by the curves $T = \hbar^2/ma^2$ or $T = [4\pi(\hbar^2/ma^2)\cdot \cdot(q^2/a)]^{1/2}$. The separation gas-liquid and liquid-solid appears at $a = \pi q^2/T$ and $a = 1.68q^2/T$, respectively. These phases of a plasma are shown in Fig. 5.6.

In the following we understand by "plasma" a genuine plasma, *i.e.* a plasma in the weak-coupling limit (if not specified otherwise); it is practically in the collisionless regime.

5.7 Equation of motion

For a periodic external electric field $\mathbf{E}_0 e^{-i\omega t}$ the equation of motion (5.5) reads

$$\ddot{\mathbf{u}} + \omega_0^2\mathbf{u} + \gamma\dot{\mathbf{u}} = \frac{q}{m}\mathbf{E}_0 e^{-i\omega t} \quad , \tag{5.55}$$

where $\omega_0 = (4\pi nq^2/m)^{1/2}$ is the plasma frequency. The homogeneous equation (5.55) has a transient, damped solution $\mathbf{u} \sim e^{\pm\sqrt{\omega_0^2+\gamma^2/4}t}e^{-\gamma t/2}$, which disappears in time, and a particular, stationary solution

$$\mathbf{u} = -\frac{q\mathbf{E}_0}{m}\frac{1}{\omega^2 - \omega_0^2 + i\gamma\omega}e^{-i\omega t} \quad ; \tag{5.56}$$

since the equation is linear, we can take the real part of the expression in equation (5.56). The internal field is

$$\mathbf{E} = -4\pi nq\mathbf{u} = \frac{\omega_0^2}{\omega^2 - \omega_0^2 + i\gamma\omega}\mathbf{E}_0 e^{-i\omega t} \ , \tag{5.57}$$

the polarization is

$$\mathbf{P} = nq\mathbf{u} = -\frac{1}{4\pi}\frac{\omega_0^2}{\omega^2 - \omega_0^2 + i\gamma\omega}\mathbf{E}_0 e^{-i\omega t} \ , \tag{5.58}$$

the total field is

$$\mathbf{E}_t = \mathbf{E}_0 + \mathbf{E} = \frac{\omega^2 + i\gamma\omega}{\omega^2 - \omega_0^2 + i\gamma\omega}\mathbf{E}_0 e^{-i\omega t} \ , \tag{5.59}$$

the dielectric function in $\mathbf{E}_0 = \mathbf{D} = \varepsilon\mathbf{E}_t$, where $\mathbf{D}$ is the electric displacement (induction), is

$$\varepsilon = 1 - \frac{\omega_0^2}{\omega^2 + i\gamma\omega} \tag{5.60}$$

and the electric susceptibility in $\mathbf{P} = \chi\mathbf{E}_t$ is

$$\chi = -\frac{1}{4\pi}\frac{\omega_0^2}{\omega^2 + i\gamma\omega} \tag{5.61}$$

($\varepsilon = 1 + 4\pi\chi$). The polarization current density $\mathbf{j} = nq\dot{\mathbf{u}}$ is

$$\mathbf{j} = \frac{1}{4\pi}\frac{i\omega\omega_0^2}{\omega^2 - \omega_0^2 + i\gamma\omega}\mathbf{E}_0 e^{-i\omega t} \tag{5.62}$$

and the conductivity in $\mathbf{j} = \sigma\mathbf{E}_t$ is

$$\sigma = \frac{1}{4\pi}\frac{i\omega_0^2}{\omega + i\gamma} \tag{5.63}$$

($\varepsilon = 1 + 4\pi i\sigma/\omega$). We can see that in the limit of constant fields $\omega \to 0$, the conductivity becomes the drift conductivity $\sigma = nq^2/m\gamma = nq^2\tau/m$, where $\tau = 1/\gamma$ is the relaxation time, a result which follows from $\ddot{\mathbf{u}} \simeq \dot{\mathbf{u}}/\tau$ in the equation of motion $\ddot{\mathbf{u}} = q\mathbf{E}_0 e^{-i\omega t}/m$. From equation (5.55) we get the rate of energy dissipation $dQ/dt = mn\gamma\dot{\mathbf{u}}^2$ per unit volume; its time average is

$$\overline{\frac{dQ}{dt}} = \gamma\frac{E_0^2}{8\pi}\frac{\omega_0^2\omega^2}{(\omega^2-\omega_0^2)^2+\omega^2\gamma^2} \ . \tag{5.64}$$

It is worth noting that for a uniform field the displacement $\mathbf{u}$ is uniform and the density change $\delta n = -n div\mathbf{u}$ is zero; it comes from the change on the surfaces at infinity. Equally well, we can derive it from the Maxwell-Ampere equation $curl\mathbf{H} = -(1/c)\dot{\mathbf{E}} + (4\pi/c)\mathbf{j}$ for $\mathbf{H} = 0$, *i.e.* $i\omega\mathbf{E} + 4\pi nq\dot{\mathbf{u}} = 0$, which is, in fact, the charge conservation $q\partial(\delta n)/\partial t + div\mathbf{j} = 0$.

Equation (5.56) provides a very interesting insight into the behaviour of a plasma; we can see from this equation that the maximum displacement $u_0 = qE_0/m\gamma\omega_0$ occurs in plasma for $\omega = \omega_0$, *i.e.* at resonance. In $\gamma = v_{th}/\Lambda$, $\Lambda = (a/a_0)^2 a$ (with a_0 arising from ions), we may take $\Lambda = a$, for the sake of a simplified estimation. The displacement u_0 is much smaller than the mean inter-particle distance a for most of the plasmas, due, especially to the low intensity of the common electric fields; indeed, for our typical plasma with $\omega_0 = 5\times10^{10}s^{-1}$, $\gamma = v_{th}/a$, $v_{th} = 3.7\times10^7 cm/s$, $a = 10^{-4}cm$, we get $u_0 \simeq 2.6\times10^{-5}E_0(cm)$; the usual highest electric fields in laboratory are of the order $E_0 = 10^3 V/m \simeq 3\times10^{-2}esu$ $(1esu = 3\times10^4 V/m)$; we can see that $u_0 \ll a$. It follows that the collisions are not effective in usual plasmas, and we may consider these plasmas as collisionless plasmas. Usually, we are far from resonance and may take $\gamma \to 0$ (in accordance with the general rule of the causality principle); in addition, the velocity $\dot{\mathbf{u}}$ is much smaller than thermal velocity. In plasma the thermal equilibrium is not achieved by collisions, but by the long-range Coulomb interaction; practically, the "collision frequency" in plasma is zero, since the range of the interaction is infinite.

The use of the displacement $\mathbf{u}$ and its equation of motion is equivalent with assuming elementary excitations in plasma; we can see that the individual motion of the electrons, *i.e.* single-particle elementary excitations, is connected with their collective motion, *i.e.* the collective elementary excitations (plasmons), through the occurrence of the internal field and the plasma frequency ω_0; the displacement $\mathbf{u}$ may be formally associated with single electrons, while $\delta n = -n div\mathbf{u}$ may be associated with the plasmons. The lifetime of all these elementary excitations is controlled by the parameter γ. The association of $\mathbf{u}$ (more precisely $\dot{\mathbf{u}}$) with the change f in the distribution function (through $f = -\dot{\mathbf{u}}\partial F/\partial\mathbf{v}$) and the corresponding Boltzmann equation account for the existence of the thermal equilibrium in the motion of the elementary excitations. A similar situation exists in quantum-mechanical ensembles.[33] The collective character of the elementary excitations in plasma has been emphasized by Bohm and Pines.[34]

5.8 Transverse field

A uniform (oscillating) electric field can be created between the plates of a capacitor (for wavelengths much longer than the distance between the plates; the magnetic field is practically zero in this case); this is called also a longitudinal field. Similarly, a uniform oscillating magnetic field can be generated inside a solenoid, practically without an electric field.

Let $\mathbf{E}_0(\mathbf{r}, t)$ be a transverse electric field, with the magnetic field $\mathbf{H}_0(\mathbf{r}, t)$ (radiation field); these fields are proportional to $e^{-i\omega t+i\mathbf{kr}}$, where $\omega = ck$ is the frequency and $\mathbf{k}$ is the wavevector ($\mathbf{kE}_0 = \mathbf{kH}_0 = 0$). They satisfy the Maxwell equations $div\mathbf{E}_0 = 0$, $div\mathbf{H}_0 = 0$, $curl\mathbf{E}_0 = -(1/c)\partial\mathbf{H}_0/\partial t$, $curl\mathbf{H}_0 = (1/c)\partial\mathbf{E}_0/\partial t$. In an infinite plasma, the electric field generates a transverse (bulk) displacement $\mathbf{u}$, $div\mathbf{u} = 0$ (the displacement determined by the magnetic field is too small and may be neglected); consequently, the (bulk) polarization charge is zero, but there exists a polarization current $\mathbf{j} = nq\dot{\mathbf{u}}$, $div\mathbf{j} = 0$; an internal magnetic field $\mathbf{H}$ and an internal electric field $\mathbf{E}$ appear, obeying the Maxwell equations

$$\begin{gathered} div\mathbf{E} = 0 \ , \ div\mathbf{H} = 0 \ , \\ curl\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t} \ , \ curl\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} + \frac{4\pi}{c}nq\dot{\mathbf{u}} \ ; \end{gathered} \tag{5.65}$$

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[33] L. Landau, "The theory of a Fermi liquid", Sov. Phys.-JETP **3** 920 (1957) (ZhETF **30** 1058 (1956)); "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1057) (ZhETF **32** 59 (1957)); "On the theory of the Fermi liquid", Sov. Phys.-JETP **8** 70 (1959) (ZhETF **35** 97 (1958)).

[34] D. Bohm and D. Pines, "A collective description of electron interaction. III. Coulomb interactions in a degenerate electron gas", Phys. Rev. **92** 609 (1953).

the equation of motion is

$$\ddot{\mathbf{u}} + \gamma\dot{\mathbf{u}} = \frac{q}{m}(\mathbf{E}_0 + \mathbf{E}) \ . \tag{5.66}$$

From these equations we get immediately

$$\mathbf{u} = -\frac{q\mathbf{E}_0}{m}\frac{\omega^2-c^2k^2}{\omega^2(\omega^2-\omega_0^2-c^2k^2)+i\omega\gamma(\omega^2-c^2k^2)} \ ,$$

$$\mathbf{E} = \frac{\omega_0^2\omega^2}{\omega^2(\omega^2-\omega_0^2-c^2k^2)+i\omega\gamma(\omega^2-c^2k^2)}\mathbf{E}_0 \ , \tag{5.67}$$

$$\mathbf{E}_t = \mathbf{E}_0 + \mathbf{E} = \frac{(\omega^2+i\omega\gamma)(\omega^2-c^2k^2)}{\omega^2(\omega^2-\omega_0^2-c^2k^2)+i\omega\gamma(\omega^2-c^2k^2)}\mathbf{E}_0 \ ,$$

where ω_0 is the plasma frequency; we can see that $\mathbf{u} = 0$, $\mathbf{E} = -\mathbf{E}_0$ and $\mathbf{E}_t = 0$ (since $\omega = ck$), *i.e.* the plasma (matter) reacts to the electromagnetic wave such that it annihilates it; in an infinite plasma (in infinite matter) the electromagnetic fields cannot be propagated. This is the Ewald-Oseen theorem of extinction.[35] For a finite sample of plasma the eigenmodes of these equations can be propagated, with frequencies given by $\Omega^2 = \omega_0^2 + c^2k^2$; these modes are the polaritonic modes; they are responsible for the refraction of the electromagnetic waves at surface. In this case, $\mathbf{j} = \sigma\mathbf{E}_t$, where the conductivity σ is given by equation (5.63), and the field generates the skin effect at the surface.

5.9 Surface plasmons

The displacement $\mathbf{u}$ of the electrons relative to the ion positions produces a density imbalance $\delta n = -ndiv\mathbf{u}$ in a uniform plasma, such that the internal field is given by

$$div\mathbf{E} = -4\pi nqdiv\mathbf{u} \ . \tag{5.68}$$

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[35] P. P. Ewald, "Zur Begrundung der Kristalloptik, I-III", Ann. Physik **49** 1, 117 (1916), **54** 519 (1917); C. W. Oseen, "Uber die Wechselwirkung zwischen zwei elektrischen Dipolen der Polarisationsebene in Kristallen und Flussigkeiten", Ann. Physik **48** 1 (1915); M. Born and E. Wolf, *Principles of Optics*, Pergamon (1959).

In order to account for the presence of a (plane) surface at $x=0$, we write $\mathbf{u}=\mathbf{v}\theta(x)$, where $\theta(x)$ is the step function (the plasma extends over the region $x>0$); equation (5.68) becomes

$$div\mathbf{E}=-4\pi nqdiv\mathbf{v}\cdot\theta(x)-4\pi nqv_{sx}\delta(x)\ \ , \tag{5.69}$$

where v_{sx} is v_x for $x=0$; for $x\geq 0$ this equation has the solution $\mathbf{E}=\mathbf{E}_b+\mathbf{E}_s$, where

$$div\mathbf{E}_b=-4\pi nqdiv\mathbf{v}\ ,\ \ x>0 \tag{5.70}$$

and

$$E_{sx}=-2\pi nqv_{sx}\ \ x=0\ . \tag{5.71}$$

The field $\mathbf{E}_b$ is the internal bulk field, while the field $\mathbf{E}_s$ is the surface field ($x=0$); the latter is reduced to its x-component; from equation (5.70) we get $\mathbf{E}_b=-4\pi nq\mathbf{v}$ (for $x>0$). The equation of motion leads to

$$\ddot{\mathbf{v}}+\omega_0^2\mathbf{v}=\frac{q}{m}\mathbf{E}_0\ ,\ \ x>0 \tag{5.72}$$

and

$$\ddot{v}_{sx}+\frac{1}{2}\omega_0^2 v_{sx}=\frac{q}{m}E_{0sx}\ ,\ \ x=0\ \ , \tag{5.73}$$

where $\omega_0=\sqrt{4\pi nq^2/m}$ is the (bulk) plasma frequency and $\omega_0/\sqrt{2}$ is the frequency of the surface plasmons; $\mathbf{E}_0$ is the external electric field. The solutions of equations (5.72) and (5.73) are obtained immediately as

$$\begin{aligned}\mathbf{v}&=-\tfrac{q\mathbf{E}_0}{m}\tfrac{1}{\omega^2-\omega_0^2}\ \ ,\ \ x>0\ \ ,\\ v_{sxz}&=-\tfrac{qE_{0sx}}{m}\tfrac{1}{\omega^2-\omega_0^2/2}\ \ ,\ \ x=0\ \ .\end{aligned} \tag{5.74}$$

The eigenmodes with the frequency $\omega_0/\sqrt{2}$ are the surface plasmons. Close to the plasmonic resonances (*i.e.* for ω close to ω_0 or $\omega_0/\sqrt{2}$) the displacement becomes large and the equation of motion in the Lagrange form used here is not appropriate, because of the disruptions caused by collisions. Euler's form of the equation of motion is more convenient, though non-linearities may appear.

A special feature occurs in the electromagnetic fields in finite plasmas, related to the surface motion. The magnetic field is given by the

Maxwell equation

$$curl\mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c}\mathbf{j} \ \ , \tag{5.75}$$

where $\mathbf{j} = nq\dot{\mathbf{u}}$ is the internal current density (we neglect intrinsic magnetization). For bulk charges and currents $\mathbf{j} = nq\dot{\mathbf{v}}$ and $\mathbf{E} = -4\pi nq\mathbf{v}$ (as derived above), such that the internal contribution $\partial\mathbf{E}/\partial t + 4\pi\mathbf{j}$ in equation (5.75) is vanishing; the magnetic field is not affected by the bulk internal polarization (in the preceding section we have considered an infinite plasma, with no internal electric field). This reflects the charge conservation inside the body. On the contrary, in the presence of a surface $j_{sx} = nq\dot{v}_{sx}$ and $E_{sx} = -2\pi nqv_{sx}$ and equation (5.75) becomes

$$(curl\mathbf{H})_{sx} = \frac{1}{c}\frac{\partial \mathbf{E}_{sx}}{\partial t} + \frac{4\pi}{c}nq\dot{v}_{sx} = \frac{4\pi}{c}\left(\frac{1}{2}j_{sx}\right) \ \ ; \tag{5.76}$$

this equation shows that surface currents and a related surface magnetic field appear, as a consequence of the fact that charges oscillating below the surface ($x < 0$) are not anymore in the body; and the surface charge is not conserved in the body. Since these currents arise from oscillating charges at the surface they are called uni-polar currents. They generate a radiation field.

5.10 Boltzmann equation for plasma

The equation of motion for the displacement $\mathbf{u}$ and the derivation of the Boltzmann equation for a plasma are complicated by the Debye correlations. The density of the plasma is non-uniform and the equilibrium distribution function depends also on the density, and, therefore, on position. We may view the plasma as a collection of ions dressed by electrons, which would move in a uniform mean-field potential; unfortunately, this picture deviates from the non-ideal character of the ion motion and complicates the matters by the internal polarization of the electrons in the presence of an external electric field. Also, we may view static ions and an electron fluid with a non-uniform density; the density change would then be $-div(n\mathbf{u})$ and the internal field $-4\pi nq\mathbf{u}$. We may solve the equation of motion for $\mathbf{u}$

with non-uniform coefficients (*e.g.*, plasma frequency) and compute thereafter the change in the distribution function brought about by both $\mathbf{u}$ and $\dot{\mathbf{u}}$; we lose in this case a Boltzmann equation for the distribution function. We adopt here the simplifying procedure of a weakly-coupled plasma, with a uniform distribution of electrons and static ions, *i.e.* we neglect the Debye correlations.

Then, the Boltzmann equation for plasma is derived from the equation of motion (5.5) according to the general rules described previously. First, we introduce the velocity-dependent displacement $\mathbf{u}(t, \mathbf{r}, \mathbf{v})$ and write $d\mathbf{u}/dt \dot{=} \partial\dot{\mathbf{u}}/\partial t + (\mathbf{v} + \dot{\mathbf{u}})grad\dot{\mathbf{u}}$ in the Euler representation; then, we neglect here the velocity $\dot{\mathbf{u}}$ which is too small in comparison with velocity $\mathbf{v}$. Thereafter, we note that the change f in the distribution function F (usually the equilibrium Boltzmann distribution) is given by $f = -\dot{\mathbf{u}}\partial F/\partial\mathbf{v}$, and multiply the equation of motion (5.5) by $\partial F/\partial\mathbf{v}$; we get the Boltzmann equation

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} + \frac{q}{m}(\mathbf{E}_0 + \mathbf{E})\frac{\partial F}{\partial \mathbf{v}} = -\gamma f \ , \tag{5.77}$$

where the internal electric field is given by

$$div\mathbf{E} = 4\pi q \int d\mathbf{v} f \tag{5.78}$$

($div\mathbf{E}_0 = 0$) or

$$\frac{\partial \mathbf{E}}{\partial t} = -4\pi q \int d\mathbf{v} \cdot \mathbf{v} f \ ; \tag{5.79}$$

equation (5.78) arises from the polarization charge, while equation (5.79) originates in the polarization current. It is worth noting that this latter equation may generate longitudinal electric fields which vary in space, as expected in a medium with electric charges. The contribution of the magnetic field to the force term is neglected here (as for an unmagnetized plasma). The internal field $\mathbf{E}$ was introduced in Boltzmann equation by Vlasov (equation (5.77) is known also as Vlasov equation).[36] Equation (5.77) is valid for small variations f of the distribution function, small variations of the particle displacement and velocity and a small collision term (practically, collisionless regime).

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[36] A. A. Vlasov, "On the kinetic theory of an assembly of particles with collective interaction", J. Phys. (USSR) **9** 25 (1945).

5.11 Eigenfrequencies. Plasma oscillations

First, we assume that the external field $\mathbf{E}_0$ is absent in equation (5.77); we are interested in the response of the plasma to an initial perturbation $f_i = f(t=0, \mathbf{r}, \mathbf{v})$. Since the plasma is homogeneous, we may restrict ourselves to a spatial dependence $\sim e^{i\mathbf{kr}}$ (F does not depend on $\mathbf{r}$, nor t); we take the coordinate, denoted by x, along the direction of the wavevector $\mathbf{k}$; since the field is directed along the x-direction we may integrate over the transverse velocities and use for the Maxwell distribution $F = n(\beta m/2\pi)^{1/2} e^{-\frac{1}{2}\beta m v^2}$, where v is the velocity along the x-direction and $\beta = 1/T$ is the reciprocal temperature; equations (5.77) and (5.78) become

$$\frac{\partial f}{\partial t} + ivkf + \frac{qE}{m}\frac{\partial F}{\partial v} = 0 \tag{5.80}$$

and

$$ikE = 4\pi q \int dvf \ ; \tag{5.81}$$

the collision term, is set equal to zero. In order to account for the initial condition ($t=0$) we multiply equation (5.80) by the step function $\theta(t)$ and restrict ourselves to $t > 0$; equation (5.80) becomes

$$\frac{\partial f}{\partial t} + ivkf + \frac{qE}{m}\frac{\partial F}{\partial v} = f_i \delta(t) \ ; \tag{5.82}$$

now we may perform the Fourier transform with respect to the time, and get

$$-i(\omega - vk)f + \frac{qE}{m}\frac{\partial F}{\partial v} = f_i \ , \tag{5.83}$$

or

$$f = i\frac{f_i - \frac{qE}{m}\frac{\partial F}{\partial v}}{\omega - vk} \ ; \tag{5.84}$$

and, from equation (5.81),

$$E = 4\pi q \frac{\int dv \frac{f_i}{\omega - vk}}{k + \frac{4\pi q^2}{m}\int dv \frac{\partial F/\partial v}{\omega - vk}} \ ; \tag{5.85}$$

the change in the distribution function is given by

$$f = \frac{i}{\omega - vk}\left(f_i - \frac{4\pi q^2}{m}\frac{\partial F}{\partial v}\frac{\int dv \frac{f_i}{\omega - vk}}{k + \frac{4\pi q^2}{m}\int dv \frac{\partial F/\partial v}{\omega - vk}}\right) \ . \tag{5.86}$$

This equation offers several interesting points. First, since we analyze the perturbation in terms of waves, the motion of the individual particles acquires a wave character too; such that an individual particle with velocity v exhibits a frequency vk. Then, we may see from equation (5.86) that there exist singularities in the distribution function for $v = \omega/k$ and divergent integrals arising from these singularities. At this point we should resort to the natural boundary condition which requires causality, *i.e.* $f = 0$ for $t < 0$. Therefore, the integration over ω shoud be performed in the lower half-plane, which requires the presence of a pole in that half-plane, *i.e.* ω in equation (5.86) should be replaced by $\omega + i\gamma$, $\gamma \rightarrow 0^+$. Had we retained the collision term in the Boltzmann equation, the γ-contributions to ω would have arisen. We perform first the integration over ω in such terms and thereafter take the limit $\gamma \rightarrow 0^+$. In integrals with respect to velocity v we may take the limit $\gamma \rightarrow 0^+$ before effecting the integrals, because these are well-defined physical quantities which exist in the absence of collisions, according to our assumption. These prescriptions of dealing with the singularities arising in Vlasov (Boltzmann) equation are due to Landau.[37]

Therefore, the above equations should be written as

$$E = 4\pi q \frac{\int dv \frac{f_i}{\omega - vk + i0^+}}{k + \frac{4\pi q^2}{m}\int dv \frac{\partial F/\partial v}{\omega - vk + i0^+}} \tag{5.87}$$

and

$$f = \frac{i}{\omega - vk + i\gamma}\left(f_i - \frac{4\pi q^2}{m}\frac{\partial F}{\partial v}\frac{\int dv \frac{f_i}{\omega - vk + i0^+}}{k + \frac{4\pi q^2}{m}\int dv \frac{\partial F/\partial v}{\omega - vk + i0^+}}\right) \ . \tag{5.88}$$

Terms like $1/(\omega - vk + i0^+)$ lead to

$$\frac{1}{\omega - vk + i0^+} = P\frac{1}{\omega - vk} - i\pi\delta(\omega - vk) \ ; \tag{5.89}$$

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[37] L. Landau, "On the vibrations of the electronic plasma", ZhETF **16** 574 (1946) (J. Phys. USSR **10** 25 (1946)).

such a circumstance makes the integrals over v in f finite; for instance,

$$\int dv \frac{f_i}{\omega - vk + i0^+} = P\int dv \frac{f_i}{\omega - vk} - \frac{i\pi}{v} f_i(v = \omega/k) \ , \qquad (5.90)$$

where the principal value in this equation can be approximated satisfactorily by

$$P\int dv \frac{f_i}{\omega - vk} \simeq \frac{1}{\omega}\int dv f_i \left(1 + \frac{vk}{\omega} + ...\right) \ . \qquad (5.91)$$

The situation is similar for the denominator involving $\partial F/\partial v$ in equation (5.86). Its zero provides an equation which gives the eigenfrequency of the distribution function. Due to the replacement $\omega \rightarrow \omega + i0^+$ this is a complex equation; it follows that the root ω of this equation (the eigenfrequency) acquires a damping factor, *i.e.*, we should solve this equation for $\omega \rightarrow \omega - i\Gamma$, where $\Gamma > 0$ is the damping coefficient. As we can see, we are led to admit that the causality implies a damped response. The causality, which acts at the level of the individual particles, leads to a damped behaviour of the collective mode, *i.e.* of the macroscopic behaviour. This is a profound consequence of the equations governing the condensed matter, and an instance of an emergent dynamics.[38] The damping of the collective mode is known as the Landau damping. We emphasize that the eigenfrequency discussed here is a collective mode since it appears from an integral over velocities of the individual particles. It is the plasmon mode.

According to the scheme delineated above, we write

$$\begin{gathered} k + \tfrac{4\pi q^2}{m}\int dv \tfrac{\partial F/\partial v}{\omega - vk + i0^+} = \\ = k + \tfrac{4\pi q^2}{m} P\int dv \tfrac{\partial F/\partial v}{\omega - vk} - i\tfrac{4\pi^2 q^2}{m}\int dv \tfrac{\partial F}{\partial v}\delta(\omega - vk) \ , \end{gathered} \qquad (5.92)$$

or

$$k + \frac{4\pi q^2}{m}\int dv \frac{\partial F/\partial v}{\omega - vk + i0^+} \simeq k - \frac{4\pi n q^2}{m\omega^2}k - i\frac{4\pi^2 q^2}{mk}\frac{\partial F}{\partial v}\,|_{v=\omega/k} \quad (5.93)$$

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[38] P. W. Anderson, "More is different: broken symmetry and the nature of the hierarchical structure of science", Science **177** 393 (1972).

(it is worth noting that the result of integration in equation (5.93) holds for any distribution function). It follows that the perturbation of the distribution function (equation (5.86)) should be written as

$$f = \tfrac{i}{\omega - vk + i\gamma} \cdot$$

$$\cdot \left[f_i - \frac{4\pi q^2}{m} \frac{\partial F}{\partial v} \frac{\int dv \frac{f_i}{\omega - vk + i0^+}}{k\left(1 - \frac{\omega_0^2}{\omega^2} - i\frac{4\pi^2 q^2}{mk^2} \frac{\partial F}{\partial v}\left|_{v=\omega/k}\right.\right)} \right] \ . \tag{5.94}$$

The initial condition

$$\frac{1}{2\pi} \int d\omega f = f_i \tag{5.95}$$

leads to

$$\int d\omega \frac{E(\omega)}{\omega - vk + i\gamma} = 0 \ , \tag{5.96}$$

where $E(\omega)$ is given by equation (5.85). Making use of the poles of the field $E(\omega)$ (equation (5.55)), we can see that the integral which includes $E(\omega)$ in equation (5.96) is indeed zero.

If we view ω as $\omega - i\Gamma$ we get

$$\begin{gathered} k + \tfrac{4\pi q^2}{m} \int dv \tfrac{\partial F/\partial v}{\omega - vk + i0^+} \simeq \\ \simeq k(1 - \omega_0^2/\omega^2) - i\left(\tfrac{2\gamma k}{\omega_0} + \tfrac{4\pi^2 q^2}{mk} \tfrac{\partial F}{\partial v}\left|_{v=\omega_0/k}\right.\right) \ , \end{gathered} \tag{5.97}$$

an equation which gives the damping coefficient

$$\Gamma = -\frac{2\pi^2 q^2 \omega_0}{mk^2} \frac{\partial F}{\partial v}\left|_{v=\omega_0/k}\right. \ . \tag{5.98}$$

The Landau damping generated a long-standing debate regarding its origin in a collisionless plasma (*i.e.*, a plasma without dissipation).[39] We note that the Landau damping pertains to the collective mode (not to the individual motion of the particles), it is produced by the thermal motion of the individual particles; this motion tends to destroy any organized, regular (collective) motion and takes the ensemble towards an equilibrium state, characterized by a fully chaotic (thermal) motion.

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[39] D. Bohm and E. P. Gross, "Theory of plasma oscillations. B. Excitation and damping of oscillations", Phys. Rev. **75** 1864 (1949); N. G. van Kampen, "On the theory of stationary waves in plasmas", Physica **21** 949 (1955); K. M. Case, "Plasma oscillations", Ann. Phys. **7** 349 (1959); J. Dawson, "On Landau damping", Phys. Fluids **4** 869 (1961); J. Ecker and J. Holling, "Limits of collective description and their consequences for Landau damping", Phys.

5.12 External field

Let us consider a longitudinal electric field $E_0e^{-i\omega t}$; the field is uniform and the position variable does not appear in Boltzmann equation (5.77), which reads

$$-i\omega f+\frac{q}{m}(E_0+E)\frac{\partial F}{\partial v}=0. \tag{5.99}$$

The Poisson equation

$$div\mathbf{E}=4\pi q\int d\mathbf{v}f \tag{5.100}$$

is identically zero (f is an odd function of v); however, if we take the time derivative and use the continuity equation, we get

$$div\frac{\partial\mathbf{E}}{\partial t}=4\pi q\int d\mathbf{v}\frac{\partial f}{\partial t}=-4\pi q\int d\mathbf{v}\cdot div\mathbf{v}f\ \ , \tag{5.101}$$

where $q\mathbf{v}f$ is the current density; therefore, we use $\partial\mathbf{E}/\partial t=-4\pi q\int d\mathbf{v}\cdot\mathbf{v}f$, or

$$i\omega E=4\pi q\int dv\cdot vf\ . \tag{5.102}$$

Fluids **6** 70 (1963); H. Weitzner, "Plasma oscillations and Landau damping", Phys. Fluids **6** 1123 (1963); J. H. Malmberg and C. B. Wharton, "Collisionless damping of electrostatic plasma waves", Phys. Rev. Lett. **13** 184 (1964); "Dispersion of electron plasma waves", Phys. Rev. Lett. **17** 175 (1966); F. G. R. Crownfield, Jr., "Plasma oscillations and Landau damping", Phys. Fluids **20** 1483 (1977); J. Weiland, "A derivation of Landau damping from the Vlasov equation without contour integration", Eur. J. Phys. **2** 171 (1981); Y. Elskens, "Irreversible behaviours in Vlasov equation and many-body Hamiltonian dynamics: Landau damping, chaos and granularity in the kinetic limit", in *Topics in Kinetic Theory*, eds. T. Passot, C. Sulem and P. L. Sulem, *Fields Institute Communications*, vol. 46, Amer. Math. Soc., Providence (2005), p. 89.

We get immediately the solution

$$f=-i\tfrac{qE_0}{m}\tfrac{\omega}{\omega^2-\omega_0^2}\tfrac{\partial F}{\partial v}\ ,\ E=E_0\tfrac{\omega_0^2}{\omega^2-\omega_0^2}\ ,$$
$$E_t=E_0+E=E_0\tfrac{\omega^2}{\omega^2-\omega_0^2}\ . \tag{5.103}$$

These are well-known relations for a uniform, oscillating electric field in plasma (without collisions). We can see that the total field E_t is vanishing in the static limit $\omega\rightarrow 0$, due to the reaction of the equal and opposite internal field E. The same result can be obtained from the equation of motion (5.55) (without dissipation), which gives the displacement

$$u=-\frac{qE_0}{m}\frac{1}{\omega^2-\omega_0^2}\ ; \tag{5.104}$$

from $div\mathbf{E}=-4\pi div\mathbf{P}$ and $div\mathbf{E}=4\pi q\delta n=-4\pi nq div\mathbf{u}$ (actually, from $\dot{\mathbf{P}}=\mathbf{j}$) we get the polarization

$$P=nqu=-\frac{nq^2E_0}{m}\frac{1}{\omega^2-\omega_0^2}=\chi E_t\ \ , \tag{5.105}$$

where $\chi=-nq^2/m\omega^2$ is the electric susceptibility and $\varepsilon=1+4\pi\chi=1-\omega_0^2/\omega^2$ is the dielectric function.

According to equation (5.103), the distribution function changes as

$$F\rightarrow F+f=F-\frac{qE_0}{m}\frac{\omega}{\omega^2-\omega_0^2}\frac{\partial F}{\partial v}\sin\omega t \tag{5.106}$$

under the action of a uniform longitudinal electric field; this equation reads

$$F(v)\rightarrow F(v+A)\ ,\ A=-\frac{qE_0}{m}\frac{\omega}{\omega^2-\omega_0^2}\sin\omega t\ . \tag{5.107}$$

The external forces are slow, such that the thermal equilibrium is achieved over their period. The thermal equilibrium is given by the maximum of the entropy, *i.e.* the maximum of $\int(F\ln F-\mathcal{E}F/T)$, where $\mathcal{E}$ is the energy and the integration is performed over the relevant phase-space variables. The preservation of the equilibrium under the action of the external forces implies a change in temperature $\delta T=-m\overline{vA}$ ($\dot{u}=A$), which is zero.

5.13 Surface field. Penetration length

It is well known that the Landau damping implies an attenuated electric field in a semi-infinite classical plasma, besides a uniform component, as a response to a uniform oscillating external electric field.[40] In the current calculations, including the original Landau calculation, the attenuated field is presented as being proportional to $x^{2/3}e^{-\frac{3}{4}(\omega x/v_{th})^{2/3}}$, where x is the distance from the wall of the plasma, ω is the frequency of the field and $v_{th}=\sqrt{T/m}$ is the thermal velocity, T being the temperature and m being the particle mass (electrons); sometimes, an exponential attenuation $\sim e^{-\omega_0 x/v_{th}}$ is included, where ω_0 is the plasma frequency. Such x-functional laws arise from various assumptions made upon boundary conditions and approximate manipulations of the Landau damping for the differential Boltzmann kinetic equation. We show here that, irrespective of the boundary conditions, the attenuated field obeys the standard exponential attenuation law e^{-x/λ_e} (apart from factors oscillating in space), where λ_e is an extinction length (penetration depth, attenuation length) which is computed here explicitly; up to immaterial numerical factors, it is of the order $\lambda_e \simeq [\mid \varepsilon \mid /(1-\varepsilon)]^{1/3} v_{th}/\omega$, where ε is the dielectric function. The calculations are performed by including explicitly surface terms in the Boltzmann equation. Although Landau damping enjoyed an extensive discussion along the years, regarding especially its origin and nature, and is still of current interest, the penetration depth received comparatively little attention.

We consider a classical plasma at thermal equilibrium consisting of mobile charges q with mass m and concentration n moving in a rigid neutralizing background. We confine this plasma to a semi-infinite space (half-space) $x>0$, bounded by a plane surface $x=0$. The plasma is subject to a uniform oscillating external electric field (longitudinal electric field) $E_0 e^{-i\omega t}$, where E_0 is directed along the x-direction. The plasma is governed by the Maxwell distribution. The mean thermal velocity is sufficiently small to consider plasma unmagnetized. Since the field is directed along the x-direction we may integrate over the transverse velocities and use for the Maxwell distribution $F = n(\beta m/2\pi)^{1/2}e^{-\frac{1}{2}\beta mv^2}$, where v is the velocity along the x-direction and $\beta = 1/T$ is the reciprocal temperature. In the collisionless regime the change $f(x,v)e^{-i\omega t}$ in the Maxwell distribution is governed by the Boltzmann (Vlasov) equation

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[40] L. Landau, "On the vibrations of the electronic plasma", ZhETF **16** 574 (1946) (J. Phys. USSR **10** 25 (1946)).

$$-i\omega f + v\frac{\partial f}{\partial x} + \frac{q}{m}(E_0 + E + E_1)\frac{\partial F}{\partial v} = 0 \ , \tag{5.108}$$

where E is a uniform internal electric field and E_1 is another internal electric field, which may vary in space; these fields are generated by internal charges and currents. The uniform reaction field E occurs in an "infinite" space too, *i.e.* a space bounded by surfaces at infinity (it is a bulk reaction field), while the non-uniform field E_1 is due to the presence of the surface (it is a "surface" field). We seek the solution of equation (5.108) as $f(x,v) = f_0(v) + f_1(x,v)$, where

$$-i\omega f_0 + \frac{q}{m}(E_0 + E)\frac{\partial F}{\partial v} = 0 \tag{5.109}$$

and

$$-i\omega f_1 + v\frac{\partial f_1}{\partial x} + \frac{q}{m}E_1\frac{\partial F}{\partial v} = 0 \ . \tag{5.110}$$

The uniform part f_0 of the solution does not generate charge density in plasma; it generates a current density; therefore, it should satisfy the equation

$$i\omega E = 4\pi q\int dv \cdot vf_0 \ ; \tag{5.111}$$

it is easy to see that this equation arises from the general equation $\partial\mathbf{E}/\partial t + 4\pi\mathbf{j} = 0$, where $\mathbf{j}$ is the current density; this equation ensures the vanishing of the (internal) magnetic field, as expected. The non-uniform part f_1 of the solution generates a charge density in plasma; it satisfies the equation

$$\frac{\partial E_1}{\partial x} = 4\pi q\int dvf_1 \ . \tag{5.112}$$

The solution of equations (5.109) and (5.111) is

$$f_0 = -\frac{iq\omega E_0}{m(\omega^2 - \omega_0^2)}\frac{\partial F}{\partial v} \tag{5.113}$$

and

$$E = \frac{\omega_0^2}{\omega^2 - \omega_0^2} E_0 \ , \ E_t = E_0 + E = \frac{\omega^2}{\omega^2 - \omega_0^2} E_0 \ \ , \tag{5.114}$$

where $\omega_0 = (4\pi n q^2/m)^{1/2}$ is the plasma frequency; we recognize here the response to an electric field, where $\varepsilon = 1 - \omega_0^2/\omega^2$ is the dielectric function and E_t is the total field in plasma ($P = \chi E_t$ is the polarization and $\chi = (\varepsilon - 1)/4\pi = -nq^2/m\omega^2$ is the electric susceptibility).

The coupled equations (5.110) and (5.112) raise, usually, difficulties which may affect the final result, as discussed above. The most convenient way to solve these equations is to use Fourier (or Laplace) transforms. In this situation, the functions f_1 and E_1 should be viewed as being defined over the whole space x. On the other hand, these functions should vanish for $x < 0$, so they are discontinuous at $x = 0$; therefore, care must be exercised in treating these equations. A similar situation occurs, of course, for the functions f_0 and E, but there the discontinuity is not problematic, because the equations for f_0 and E do not include the derivatives with respect to x; in this case we may solve the equations in the whole space and restrict ourselves to the domain $x > 0$. For f_1 and E_1 we must explicitly include the discontinuity in equations, *i.e.* to include the boundary condition in equations. In order to deal conveniently with the boundary condition at the surface we multiply equation (5.110) by the step function $\theta(x)$ ($\theta(x) = 1$ for $x > 0$, $\theta(x) = 0$ for $x < 0$) and restrict ourselves to the solution for $x > 0$; equation (5.110) becomes

$$-i\omega f_1 + v\frac{\partial f_1}{\partial x} + \frac{q}{m} E_1 \frac{\partial F}{\partial v} = v f_s \delta(x) \ \ , \tag{5.115}$$

where $f_s = f_1(x = 0, v)$ (in fact, $f_s = f_1(d, v)$, $d \to 0^+$); we can check directly this surface term by integrating equation (5.115) along a small distance perpendicular to the surface $x = 0$. Similarly, equation (5.112) becomes

$$\frac{\partial E_1}{\partial x} - E_{1s}\delta(x) = 4\pi q \int dv f_1 \ \ ,. \tag{5.116}$$

where $E_{1s} = E_1(x = 0)$.

In equations (5.115) and (5.116) we use the Fourier transform with respect to the coordinate x (and restrict ourselves to $x > 0$); we get

$$f_1(k,v) = \frac{i}{\omega - vk + i\gamma}\left[vf_s(v) - \frac{q}{m}\frac{\partial F}{\partial v}E_1(k)\right] \tag{5.117}$$

and

$$E_1(k) = \frac{4\pi q\int dv\frac{vf_s(v)}{\omega - vk + i0^+} - iE_{s1}}{k + \frac{4\pi q^2}{m}\int dv\frac{\partial F/\partial v}{\omega - vk + i0^+}}\ , \tag{5.118}$$

where $\gamma \to 0^+$. It is worth noting that in the Fourier transform we replace ω by $\omega + i\gamma$, $\gamma \to 0^+$, in order to ensure the causal behaviour (*i.e.*, zero response for time $t < 0$, which requires a pole in the lower ω-half-plane); this procedure gives a pole in the upper k-half-plane. At the same time, in the integrals with respect to v we may take the limit $\gamma \to 0^+$, which avoids the singularity $\omega = vk$; the insertion of the parameter γ produces the Landau damping. We denote by A the denominator in equation (5.118); it can be estimated as

$$\begin{aligned} A &= k + \tfrac{4\pi q^2}{m}\int dv\tfrac{\partial F/\partial v}{\omega - vk + i0^+} = \\ &= k + \tfrac{4\pi q^2}{m}P\int dv\tfrac{\partial F/\partial v}{\omega - vk} - i\tfrac{4\pi^2 q^2}{mk}\tfrac{\partial F}{\partial v}\mid_{v=\omega/k}\simeq \\ &\simeq k(1 - \omega_0^2/\omega^2) - i\tfrac{4\pi^2 q^2}{mk}\tfrac{\partial F}{\partial v}\mid_{v=\omega/k}\ ; \end{aligned} \tag{5.119}$$

we can see that the zeroes of A give the damped collective eigenmodes $\omega = \pm\omega_0 - i\Gamma$ (plasma frequency), where Γ is given by the imaginary part in equation (5.80) ($\Gamma \simeq -2\pi^2 q^2\omega_0/mk^2)(\partial F/\partial v)\mid_{v=\omega_0/k}$); this is the Landau damping.

In order to estimate the field $E_1(x)$ we need the zeroes of A with respect to k in equation (5.118). It is convenient to introduce the variable $\xi = \sqrt{\beta m/2}\omega/k$. We can see easily that the zeroes of A are given by $\xi^2 \mid \xi \mid e^{-\xi^2} = -i\alpha$, where $\alpha = \mid \varepsilon \mid /2\sqrt{\pi}(1-\varepsilon)$; we consider the case $\omega < \omega_0$ ($\varepsilon < 0$; the rather unrealistic case $\omega > \omega_0$ can be treated similarly, by using the equation $\xi^2 \mid \xi \mid e^{-\xi^2} = i\alpha$). For small values of α we get two roots of the equation $A = 0$, given by $k_{1,2} \simeq \pm\frac{1}{2\alpha^{1/3}}\sqrt{\beta m}\omega(1+i)$; only k_1 (placed in the upper half-plane) contributes to the k-integration for $x > 0$. In estimating the integral in the numerator of equation (5.118) we may leave aside the contribution of the principal value. For k near k_1 the field $E_1(k)$ has the form

$$E_1(k) \simeq \frac{B}{k-k_1+\frac{i}{5}(k-k_1)^*} \ ,$$
$$B = \frac{8\sqrt{2}\pi q\alpha^{2/3}v_{th}^2}{5\omega|\varepsilon|}(1+i)f_s\left(\alpha^{1/3}v_{th}(1-i)\right) + \frac{2i}{5|\varepsilon|}E_{1s} \ . \tag{5.120}$$

The reverse Fourier transformation leads to

$$E_1(x) = E_{1s}e^{(i-1)\omega x/2\alpha^{1/3}v_{th}} \tag{5.121}$$

with the relationship

$$E_{1s} = -\frac{8\sqrt{2}\pi q\alpha^{2/3}v_{th}^2}{(2+5\mid\varepsilon\mid)\omega}(1-i)f_s\left(\alpha^{1/3}v_{th}(1-i)\right) \tag{5.122}$$

(or $E_{1s} = iB$). The final result is given by $E_1(t,x) = Re\left[E_1(x)e^{-i\omega t}\right]$. We can see that an additional, non-uniform, electric field $E_1(x)$ appears as a result of the presence of the surface. This field oscillates in space and is attenuated with an attenuation length (penetration depth, extinction length) $\lambda_e \simeq (1/\pi)^{1/6}[\mid\varepsilon\mid/(1-\varepsilon)]^{1/3}v_{th}/\omega$. It is worth noting that the penetration depth and the wavelength of the spatial oscillations have the same order of magnitude.

Making use of $E_1(k)$ given by equations (5.118) and (5.120) we can calculate the change $f_1(x,v)$ in the distribution function (equation (5.117)); if we limit ourselves to slow spatial oscillations, we get

$$f_1(x,v) \simeq -\frac{iq}{m\omega}sgn(v)\frac{\partial F}{\partial v}E_1(x) \tag{5.123}$$

(compare with equations (5.113) and (5.114)). Within this approximation $f_s(v) = -(iq/m\omega)sgn(v)(\partial F/\partial v)E_{1s}$ and the polarization charge and current densities are zero (as expected for slow oscillations).

The amplitude of the field $E_1(x)$ depends on the parameter E_{1s}, which accounts for the boundary condition at $x = 0$. It is related to $f_s(v) = \frac{1}{2\pi}\int dkf_1(k,v)$ by equation (5.122), where $f_1(k,v)$ is given by equation (5.117); it is easy to see that the integration of the first term in equation (5.117) gives f_s, while, making use of equations (5.120), the integration with respect to k of the term which includes $E_1(k)$ is zero.

Within the kinetic approach we may estimate the local change in temperature by $\delta T = 2T\overline{f/F}$, where the overbar implies an integration over velocities (thermal average). We can see that only f_1 contributes to this integration. Making use of equation (5.123) we get $\delta T = 0$. However, if we keep the contribution of the fast oscillations, we get a surface change of temperature

$$\delta T \simeq \frac{2iT}{n\omega} \int dv \cdot v f_s(v) \cdot \delta(x) + ... \ . \tag{5.124}$$

$(i.e.,\ Re\left(\delta T e^{-i\omega t}\right))$. The δ-type contribution in equation (5.124) corresponds to the surface sheath in plasma heating models.

Similar calculations of the penetration depth can be made for a plasma confined between two plane-parallel walls (or other geometries); the result depends on the boundary conditions incorporated in parameters like f_s. The boundary parameter f_s is a model parameter; we may take $f_0+f_s = 0$ ($f(x=0,v) = 0$) as a natural assumption, an equation which provides the parameter f_s. For $f_s = -f_0$ the field E_1 at the surface (maximum value) is of the order $E_1 \simeq E/\mid \varepsilon \mid$, where E is the internal uniform field given by equation (5.114). The surface change in temperature (equation (5.124)) can be written in this case as

$$\delta T = \frac{1}{2\pi}\left(\frac{E_0}{q/a^2}\right) T \cdot a\delta(x) \tag{5.125}$$

(for $\omega \ll \omega_0$), where a is the mean separation distance between the particles ($a = n^{-1/3}$); $q/a^2 \gg E_0$ is an electric field of the order of the microscopic (inter-particle) field.

In conclusion, we may say that the penetration of an electric field in a semi-infinite classical plasma obeys the standard exponential penetration law e^{-x/λ_e} (besides a uniform component), which may exhibit spatial oscillations, the extinction length λ_e (penetration depth, attenuation length) being of the order $\lambda_e \simeq [\mid \varepsilon \mid /(1-\varepsilon)]^{1/3} v_{th}/\omega$; ($\varepsilon$ is the dielectric function, ω is the frequency of the field and $v_{th} = \sqrt{T/m}$ is the thermal velocity).

6 Phonons in Solids

6.1 Phonons

The atomic constituents of solids (atoms, ions, molecules) may move slightly about their equilibrium positions. For small displacements they move as coupled harmonic oscillators in the potential wells formed by the inter-atomic interaction. This is an elastic wave-like motion, which in the long wavelength limit is a sound wave and for shorter wavelengths is a vibration motion of independent atoms. In gases the sound waves are governed by adiabatic variations of the pressure (not by interactions), in liquids both types of waves may coexist, over rather separate ranges of wavevectors. In crystalline solids the motion extends over (and is limited to) the Brillouin zone, in amorphous solids the motion consists of sound waves for long wavelengths and local vibrations for shorter wavelengths.

Let us consider a Bravais lattice (one atom per unit cell) of atoms with mass M, placed at ordered positions $\mathbf{R}_i$ interacting through the potential $U(\mathbf{R}_i - \mathbf{R}_j)$; we may limit to the nearest-neighbours; for displacements $\mathbf{u}_i = \mathbf{u}(\mathbf{R}_i)$ we may expand the potential $U(\mathbf{R}_i + \mathbf{u}_i - \mathbf{R}_j - \mathbf{u}_j)$ in powers of the components of the difference $\mathbf{u}_i - \mathbf{u}_j$ up to the second-order derivatives (the first-order derivatives are zero at equilibrium); the second-order derivatives do not depend on $\mathbf{R}_i$ and we assume (for simplicity) that they do not depend on the direction either (as for an isotropic crystal); we denote these derivatives by U. The hamiltonian of the atomic motion reads

$$H = \sum_i \left[\frac{1}{2M} p_i^2 + \frac{1}{4} U \sum_j (\mathbf{u}_i - \mathbf{u}_j)^2 \right] \quad , \tag{6.1}$$

where the summation over j extends to the nearest-neighbours (and $\mathbf{p}_i$ is the momentum associated to the coordinate $\mathbf{u}_i$). If the lattice is not a Bravais lattice, *i.e.* if there are several atoms in the unit cell (in general with different masses), then we must introduce labels for all these atoms, and the coupling U will depend on these labels; but the summation over the unit cells (label i) and the nearest-neigbouring cells (label j) are preserved. The additional factor $1/2$ (in $1/4$, besides the other factor $1/2$ from the series expansion) in equation (6.1) arises from the double summation over the nearest-neighbours. Equation (6.1) gives the hamiltonian of the atomic motion in a perfect, infinite solid. We use Fourier transforms of the type

$$\mathbf{u}_i = \sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_i} \ , \ \mathbf{u}_k = \frac{1}{N} \sum_i \mathbf{u}_i e^{-i\mathbf{k}\mathbf{R}_i} \quad , \tag{6.2}$$

where N is the number of unit cells; the components of the wavevectors $\mathbf{k}$ are of the form $k_\alpha = (2\pi/L_\alpha)n_\alpha$, $\alpha = 1,\, 2,\, 3$, where L_α is the length of the crystal along the α-direction and n_α are integers. The position vectors $\mathbf{R}_i$ are of the form $n_\alpha \mathbf{a}_\alpha$, where the unit vectors $\mathbf{a}_\alpha$ are the vectors of the unit cell and n_α are integers. There exist reciprocal vectors of the form $\mathbf{G} = \mathbf{g}_\alpha n_\alpha$, where the unit reciprocal vectors are given by $\mathbf{g}_1 = (2\pi/v)\mathbf{a}_2 \times \mathbf{a}_3$, etc, where $v = \mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)$ is the volume of the unit cell. We can see that $\mathbf{G}\mathbf{R}_i = 2\pi \times \mathit{integer}$, such that we restrict the summation over $\mathbf{k}$ in equations (6.2) to the (first) Brillouin zone defined by the basic reciprocal vectors $\mathbf{g}_\alpha$. Making use of these Fourier transforms, the hamiltonian becomes

$$H = N \sum_{\mathbf{k}} \left[\frac{1}{2M} \mathbf{p}_k \mathbf{p}_{-k} + \frac{1}{2} M\omega^2(\mathbf{k}) \mathbf{u}_{\mathbf{k}} \mathbf{u}_{-\mathbf{k}} \right] \quad , \tag{6.3}$$

where the frequency $\omega(\mathbf{k})$ is given by

$$\omega^2(\mathbf{k}) = (U/M) \sum_\alpha (1 - \cos \mathbf{k}\mathbf{a}_\alpha) \quad . \tag{6.4}$$

We can see that we have three branches of frequencies, which in our particular case are identical; if U were dependent on direction, the three branches would be distinct, corresponding to the three polarizations labelled by α. In the long wavelength limit $\omega(\mathbf{k})$ goes like ck, where c (which depends on the direction of the wavevector $\mathbf{k}$) is the sound velocity (and the waves propagate with velocity c), while near the edges of the Brillouin zone (defined at half the basic reciprocal vectors) the frequency does not depend on $\mathbf{k}$ (and the waves do not propagate).

The sound velocity in solids is of the order $c = 10^5 - 10^6 cm/s$, and the inter-atomic distances a are of the order of a few Å. It follows that the elastic frequencies are of the order $\omega = c/a \simeq 10^{13} s^{-1}$ ($10meV$, $100K$), at most. We can estimate the mechanical action $M\omega u^2$ in the motion of one atom, where u is the displacement; we get $M\omega u^2 \simeq 10^{-11} Au^2$, for an atomic mass of the order $10^{-24} A(g)$, where A is the mass number of the atom; we can see that for $u \simeq 10^{-8} cm$ this amount of mechanical action is of the order $10^{-27} A(erg \cdot s)$, at most. Therefore, the atomic motion is quantum-mechanical, at least for low frequencies.

The quantization of the hamiltonian given by equation (6.3) is achieved as usually, by introducing the creation and destruction operators $a^+_{\mathbf{k}}$, $a_{\mathbf{k}}$ for each branch of frequencies (each component $u_{\mathbf{k}}$ of $\mathbf{u}_{\mathbf{k}}$), $[a_{\mathbf{k}}, a^+_{\mathbf{k}'}] = \delta_{\mathbf{k},\mathbf{k}'}$,

$$\begin{gathered} u_{\mathbf{k}} = \sqrt{\tfrac{\hbar}{2M\omega(\mathbf{k})}}(a^+_{\mathbf{k}} + a_{-\mathbf{k}}) \ , \\ p_{\mathbf{k}} = i\sqrt{\tfrac{\hbar M\omega(\mathbf{k})}{2}}(a^+_{\mathbf{k}} - a_{-\mathbf{k}}) \ ; \end{gathered} \tag{6.5}$$

the hamiltonian becomes

$$H = N\sum_{\mathbf{k}} \hbar\omega(\mathbf{k})(a^+_{\mathbf{k}} a_{\mathbf{k}} + 1/2) \tag{6.6}$$

and $a_{\mathbf{k}} \sim e^{-i\omega(\mathbf{k})t}$ ($a^+_{\mathbf{k}} \sim e^{i\omega(\mathbf{k})t}$); this time dependence is transferred to the displacement $\mathbf{u}_i$. $n_{\mathbf{k}} = a^+_{\mathbf{k}} a_{\mathbf{k}}$ is a bosonic occupation number ($n_{\mathbf{k}} = 0$, 1, 2...). In order to get the correct commutation relations we should introduce a factor $N^{-1/2}$ in the definition of the creation and destruction operators (equations (6.5)), or in the Fourier transform of $\mathbf{u}_i$ (equations (6.2)); we prefer to discard this N-factor. We can see that for each frequency branch and each wavevector $\mathbf{k}$ we have an infinite set of particles with energy $\hbar\omega(\mathbf{k})$ and momentum $\hbar\mathbf{k}$, which appear as waves in the displacement $\mathbf{u}_i \sim e^{\pm i\omega(\mathbf{k})t + i\mathbf{k}\mathbf{R}_i}$ (or $\mathbf{u}_i \sim e^{\frac{i}{\hbar}[\pm\hbar\omega(\mathbf{k})t + \hbar\mathbf{k}\mathbf{R}_i]}$). The particles (waves) are called phonons. For sound-like frequencies (3 branches) they are called acoustic phonons, for the frequency branches which are non-zero in the limit $\mathbf{k} \rightarrow 0$ they are called optical phonons; the number of optical branches is $3s-3$, where s is the number of atoms in the unit cell.[1] Sometimes, the frequencies lying near the edges of the Brillouin zone in the acoustic branches are also called optical frequencies.

The thermodynamics of the phonons is the thermodynamics of an ideal gas of bosons with an undefined number (zero chemical potential). The free energy (grand-canonical potential) is given by

$$F = T \sum \ln \left(1 - e^{-\hbar\omega/T}\right) \quad , \tag{6.7}$$

where T is the temperature and the summation is extended to all frequency branches and all wavevectors (leaving aside the zero-point energy). For simplification we limit ourselves to one branch of acoustic phonons, with a mean velocity denoted by c; we get

$$F = T \sum_{\mathbf{k}} \ln \left(1 - e^{-\hbar ck/T}\right) = \frac{VT}{2\pi^2} \int dk \cdot k^2 \ln \left(1 - e^{-\hbar ck/T}\right) \ , \tag{6.8}$$

or

$$F = \frac{VT}{2\pi^2 c^3} \int d\omega \cdot \omega^2 \ln \left(1 - e^{-\hbar\omega/T}\right) \quad , \tag{6.9}$$

where V is the volume. (The integral in equation (6.9) can be reduced to $\int dx \cdot x^3/(e^x - 1) = \pi^4/15^2$). If we include the vanishing chemical potential μ in equation (6.7) through $e^{\beta\mu - \beta\varepsilon}$, where $\beta = 1/T$ and $\varepsilon = \hbar\omega$, we get the mean occupation number

$$n_{\mathbf{k}} = \frac{1}{e^{\hbar\omega/T} - 1} \tag{6.10}$$

from $n_{\mathbf{k}} = -\partial F_{\mathbf{k}}/\partial\mu$, where $F = \sum_{\mathbf{k}} F_{\mathbf{k}}$; the mean phonon energy is

$$\varepsilon_{\mathbf{k}} = \hbar\omega n_{\mathbf{k}} = \frac{\hbar\omega}{e^{\hbar\omega/T} - 1} \tag{6.11}$$

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[1] C. Kittel, *Quantum Theory of Solids*, Wiley, NY (1963); C. Kittel, *Introduction to Solid State Physics*, Wiley, NY (1986); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford (1954).

[2] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier (1980).

and the total energy is

$$E = \frac{V\hbar}{2\pi^2 c^3} \int d\omega \cdot \frac{\omega^3}{e^{\hbar\omega/T} - 1} \ . \tag{6.12}$$

In all these summations we restrict ourselves to the first Brillouin zone; it is convenient to define a cutoff frequency ω_D, through

$$N = \sum_{\mathbf{k}} 1 = \frac{V}{2\pi^2 c^3} \int_0^{\omega_D} d\omega \cdot \omega^2 = \frac{V\omega_D^3}{6\pi^2 c^3} \ , \tag{6.13}$$

such that the energy becomes

$$E = 3NT(T/\hbar\omega_D)^3 \int_0^{\hbar\omega_D/T} dx \frac{x^3}{e^x - 1} \ . \tag{6.14}$$

We can see that at low temperature $E \sim T^4$ (and the specific heat (at constant volume) goes like T^3 - this is known as the Debye law[3]), while at high temperature $E \sim T$ (and the specific heat is constant - this is known as the Dulong-Petit law, as for an ideal classical gas[4]). The cutoff frequency ω_D is known as the Debye frequency. Its order of magnitude is $10^2 - 10^3 K$.

We note that the occupation number is very high for acoustic phonons, especially in the long wavelength limit; it follows that these phonons may be treated quasi-classically, *i.e.* the displacement may be viewed as consisting of classical waves. We can use the thermodynamics of classical harmonic oscillators with the hamiltonian given by equation (6.3).[5] Moreover, since the wavelengths of these waves are longer than the inter-atomic distance, we may view them as classical elastic waves propagating in a solid with two elastic constants; we get one branch of longitudinal waves and two branches of transverse waves. Also, it is worth noting that the wavevectors $\mathbf{k}$ (momenta $\hbar\mathbf{k}$) or the energies $\hbar\omega$ are statistical variables. We give here the hamiltonian

$$H = \int d\mathbf{r} \left(\frac{1}{2}\rho\dot{u}^2 + \frac{1}{2}\lambda u_{ii}^2 + \mu u_{ij}^2 \right) \tag{6.15}$$

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[3] P. Debye, "Zur Theorie der spezifischen Warmen", Ann. Phys. **39** 789 (1912).

[4] A. Einstein, "Theorie der Strahlung und die Theorie der spezifischen Warmen", Ann. Phys. **22** 180 (1907).

[5] L. Landau and E. Lifshitz, cited above.

of the elastic waves, where ϱ is the density of the solid, λ, μ are the elastic constants (Lame coefficients), $u_{ij} = \frac{1}{2}(\partial_i u_j + \partial_j u_i)$ is the strain tensor and $\mathbf{u}$ is the displacement vector; the equation of motion

$$\ddot{\mathbf{u}} = (c_l^2 - c_t^2) grad\, div \mathbf{u} + c_t^2 \Delta \mathbf{u} \tag{6.16}$$

leads to longitudinal and transverse waves propagating with velocities $c_l = \sqrt{(\lambda + 2\mu)/\rho}$ and $c_t = \sqrt{\mu/\rho}$, respectively.[6]

Also, we note that for an anisotropic solid, the extension of the Debye cutoff frequency to the whole phonon spectrum requires special procedures.[7] The summation over the wavevectors $\mathbf{k}$ implies

$$\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3} \int dS \frac{d\omega}{\mid grad \omega(\mathbf{k}) \mid} \quad , \tag{6.17}$$

where the surface $S(\mathbf{k})$ is given by $\omega(\mathbf{k}) = \omega$ and the integration is restricted to the Brillouin zone; the integral over S is the density of states; it may exhibit singularities, known as van Hove singularities.[8]

6.2 Phonon gas

The acoustic phonons exhibit a series of very interesting properties. (The optical phonons are not very relevant for the transport properties, so we leave them aside). First, we note that the wavelengths of the acoustic phonons $\lambda \simeq 1/k$ extend from a, the mean inter-atomic separation distance, to ∞. Actually, they are limited to the dimension L of the solid, the mode $\mathbf{k} = 0$ being a displacement of the solid as a whole (and, therefore, discarded). Moreover, the $\mathbf{k}$-states are very rare in the long wavelength limit, and very dense for finite values of the wavevector $\mathbf{k}$, as we can see from the state density $(V/2\pi^2)k^2 dk$. For instance, from $\omega_D/10$ to ω_D there are concentrated all the wavelengths from $10a$ to a (we may use a Debye wavevector $k_D = \omega_D/c \simeq 1/a$, as it can be seen from equation (6.13). A very large number of phonon states are concentrated in such a finite wavelength range.

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[6] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 7, *Elasticity*, Elsevier (1986).

[7] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier (1980).

[8] L. Van Hove, "The occurrence of singularities in the elastic frequency distribution of a crystal", Phys. Rev. **89** 1189 (1953); H. P. Rosenstock, "Dynamics of simple lattices", Phys. Rev. **97** 290 (1955).

The phonons can be viewed as quantum-mechanical particles (waves), in a certain, limited sense. From equations (6.2) and (6.5) we may view $e^{\frac{i}{\hbar}[-\hbar\omega(\mathbf{k})t+\hbar\mathbf{k}\mathbf{r}]}$ as phonon wavefunctions (noteworthy, these wavefunctions are defined for any $\mathbf{r}$); however, their energy should be $\pm\hbar\omega(\mathbf{k})$ and their momentum $\hbar\mathbf{k}$, with a hamiltonian $\pm\hbar\omega(-i\partial/\partial\mathbf{r})$. The negative energy and the deviation from a quadratic dependence on the momentum show that this formal quantum-mechanical view is limited. The limitation arises from the fact that the phonons are quasiparticles. The number of phonons is indefinite. The phonons are different from the quantum-mechanical motion of the atomic displacement $\mathbf{u}_i$ (or $\mathbf{u}_\mathbf{k}$), which is governed by the harmonic-oscillator hamiltonian given by equation (6.3); since the change in the energy of the motion of the atomic coordinates given by equation (6.6) is governed by a change $\delta n_\mathbf{k} = 1$ in the phonon occupation number, we may view the phonons as elementary excitations (quasiparticles) of the solid oscillations (vibrations). These excitations appear for many atoms, of the order of a macroscopic number of atoms, and reflect an emergent dynamics.[9]

While the phonons are purely quantum-mechanical waves (particles), the quantum-mechanical motion of the atoms is, in fact, a quasi-classical motion. Indeed, the thermal mean occupation number

$$n = \frac{1}{e^{\hbar\omega/T} - 1} \tag{6.18}$$

(where we omit the argument ω, or $\mathbf{k}$), shows that the phonons with $\hbar\omega \ll T$ are excited in large numbers, while those with higher energies do not bring relevant contributions.[10] Large number of excitations mean a quasi-classical description of the atomic coordinates given by equation (6.5). Moreover, equation (6.18) tells that temperatures T lower than very low energies $\hbar\omega$ are meaningless. In particular, the limit $T \to 0$ should be treated with caution (which, in fact, is a general trait of the low-temperature thermodynamics).

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[9] P. W. Anderson, "More is different: broken symmetry and the nature of the hierarchical structure of science", Science **177** 393 (1972); R. B. Laughlin, D.Pines, J. Schmalian, B. P. Stojkovich and P. Wolines, "The middle way", Proc. Nat. Acad. Sci. **97** 32 (2000).

[10] I. Pomeranchuk, "On the thermal conductivity of the dielectrics", Phys. Rev. **60** 820 (1941).

If we want to measure the wavevector $\mathbf{k}$ (momentum $\hbar\mathbf{k}$) of a phonon, then we need to see the content of $e^{i\mathbf{kr}}$ in a wavefunction which includes wavevectors $\mathbf{K}$; *i.e.*, we need to estimate the integral

$$\int d\mathbf{r} e^{i(\mathbf{k}-\mathbf{K})\mathbf{r}} \quad ; \tag{6.19}$$

if we integrate over the whole space we get the "momentum conservation" $\mathbf{k} = \mathbf{K}$ (from $\delta(\mathbf{k} - \mathbf{K})$); but it is sufficient to integrate over a region of dimension Δr equal to a few wavelengths $\lambda \simeq 1/k$ to get the wavevector $\mathbf{k} \simeq \mathbf{K}$ with an error $1/\triangle r$; this (well known) technical point can be seen from the integral

$$\int_{-\Delta x}^{\Delta x} dx e^{iqx} = \frac{2\sin q\Delta x}{q} \quad , \tag{6.20}$$

which is a function localized mainly over the region $\Delta q \simeq 1/\Delta x$. It follows that the wave (the phonon) with the wavevector $\mathbf{k}$ is delocalized over a region of the order $\lambda \simeq 1/k$ (its wavelength). As well known as this result is, its relevance is often overlooked. It tells that we cannot speak of a phonon (a wave) over a distance shorter than its wavelength; the phonon "exists and doesn't exist" over such distances. Obviously, a distance of the order λ may be viewed as the mean freepath of the wave (phonon).

Similar considerations hold for the frequency ω; the integral

$$\int dt e^{i(\omega-\Omega)t} \tag{6.21}$$

gives the "energy conservation" $\omega = \Omega$, but, what is more important, it shows that the period $1/\omega$ may be taken as the order of magnitude of the phonon lifetime. These mean that freepaths and lifetimes are related by the phase velocity $c = v/k$; in transport the connection is made by the group velocity, as we shall see shortly.

The quantum-mechanical coordinates $\mathbf{u_k}$ given by equation (6.5) and the atomic displacement $\mathbf{u}_i$ given by equation (6.2) are operators, with zero mean values; they are not determined, in the sense of measurable quantities; we may look for mean values over a superposition of quantum-mechanical (phonon) states for a fixed $\mathbf{k}$; then, they are determined, but are still small, on the quantum-mechanical scale. However, since there exists a macroscopic occupation of these states (for $\hbar\omega \ll T$), we may replace the creation and destruction operators in equation (6.5) by c-numbers; we may use a superposition of quantum states labelled by the occupation number; if the phases of this superposition are the same we have a coherent phonon state; but, usually, the phases are randomly distributed, so we have an incoherent superposition. In any case, the displacement $\mathbf{u}_i$ given by equation (6.2), with the temporal factor included, reads

$$\mathbf{u}_i = \sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}} e^{i[\mathbf{k}\mathbf{R}_i - \omega(\mathbf{k})t]} \ , \tag{6.22}$$

where $\mathbf{u}_{\mathbf{k}}$ are now determined from the initial conditions. For instance, if we have initially a uniform distribution of displacement on the atoms denoted by j,

$$\sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_i} = \sum_j \mathbf{u}_j \delta(\mathbf{R}_i - \mathbf{R}_j) \ , \tag{6.23}$$

we get

$$\mathbf{u}_{\mathbf{k}} = \frac{1}{V} \sum_j \mathbf{u}_j e^{-i\mathbf{k}\mathbf{R}_j} \ , \tag{6.24}$$

where $\mathbf{u}_j$ are given vectors. This way, we can follow the time evolution of the displacement $\mathbf{u}_i$. Obviously, we may extend the definition of $\mathbf{u}_i$ from $\mathbf{R}_i$ to any $\mathbf{r}$, which is convenient for the phonon transport. We can see from equation (6.22) that the spatial evolution of the wave is in the direction of $\mathbf{k}$. As long as we limit ourselves to long wavelengths, for which $\omega(\mathbf{k}) = ck$, we can define the velocity $\mathbf{v} = c\mathbf{k}/k$ and write

$$\mathbf{u} = \sum_{\mathbf{k}} \mathbf{u}_{\mathbf{k}} e^{i(\mathbf{r} - \mathbf{v}t)\mathbf{k}} \ , \tag{6.25}$$

which is the initial displacement distribution propagating with velocity $\mathbf{v}$. This is valid for long wavelength phonons, which have a low density of $\mathbf{k}$-states. For larger magnitudes of the wavevectors $\mathbf{k}$ the states are very dense and the contribution of any wavevector $\mathbf{k}$ is increased by the contributions of the neighbouring $\mathbf{k}$'s. Therefore, if we select a wavevector $\mathbf{k}_0$, then we write $\mathbf{k} = \mathbf{k}_0 + \mathbf{q}$ and

$$\omega(\mathbf{k}) = \omega(\mathbf{k}_0) + \mathbf{vq} + \frac{1}{2}\frac{\partial^2\omega}{\partial k_i k_j}\,|_{\mathbf{k}_0}\, q_i q_j + ... \quad , \tag{6.26}$$

where

$$\mathbf{v} = \frac{\partial\omega}{\partial\mathbf{k}}\,|_{\mathbf{k}_0} \tag{6.27}$$

is the group velocity. In the long wavelength limit ($\omega = ck$) we can see that $\mathbf{v}$ is $c\mathbf{k}/k$ defined above and coincides in magnitude with the phase velocity c. If we omit the second-order derivatives in equation (6.26) and higher-order terms in the expansion of $\mathbf{u}_\mathbf{k}$, we get

$$\mathbf{u} \simeq \mathbf{u}_{\mathbf{k}_0} e^{i(\mathbf{k}_0\mathbf{r} - \omega_0 t)} \sum_\mathbf{q} e^{i(\mathbf{r} - \mathbf{v}t)\mathbf{q}} \quad , \tag{6.28}$$

which shows that the $\mathbf{k}_0$-phonon has an envelope, more or less localized, which propagates with the group velocity $\mathbf{v}$. The spatial extension of the envelope is of the order $1/\Delta q$, where Δq is the range of q; it is limited by k_0, such that the extension is at least of the order $1/k_0 \simeq \lambda$. Therefore, we get again that the order of magnitude of the wavelength is comparable to the mean freepath of the phonons. Their lifetimes are of the order λ/v. We prefer to take the period $\tau_0 = 1/\omega$ as the phonon lifetime and to define the mean freepath as $\Lambda = v\tau_0$. We can see that $\Lambda = c/\omega = \lambda$ for $v = c$.

For a state with n phonons the lifetime, denoted τ_n, is defined by the mechanical action $n\hbar\omega\tau_n$ as $\tau_n = 1/n\omega = \tau_0/n$; it is the duration when the action is changed by the quantum $\hbar$. According to Matthiessen's rule[11] the effective lifetime τ is given by the interpolation formula

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_n} \quad , \tag{6.29}$$

i.e.

$$\tau = \frac{\tau_0}{1+n} \quad . \tag{6.30}$$

This relation has a formal resemblance with Einstein's emission coefficient (and the factor $\sqrt{n+1}$ in the matrix element of the creation operator a^+);[12] actually, τ_0 in these relations should correspond to the zero-energy $\hbar\omega/2$, which would give $\tau = 1/[\omega(1/2+n)]$; all these are estimations, and we prefer to use the estimation given by equation (6.30). It follows that at non-zero temperature the phonon lifetime is given by

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[11] A. Matthiessen, Rep. Brit. Ass. **32** 144 (1862).

$$\tau = \frac{1}{\omega(1+n)} = \frac{1}{\omega}\left(1 - e^{-\hbar\omega/T}\right) \quad , \tag{6.31}$$

where we have introduced the mean occupation number.[13] In the limit $T \to 0$ the lifetime goes like $\tau \simeq 1/\omega$, while in the limit $T \gg \hbar\omega$ the lifetime is $\tau \simeq \hbar/T$. The mean freepath is

$$\Lambda = v\tau = \frac{v}{\omega}\left(1 - e^{-\hbar\omega/T}\right) \quad . \tag{6.32}$$

In the limit $T \ll \hbar\omega$ the mean freepath is $\Lambda \simeq v/\omega$, while $\Lambda \simeq \hbar v/T$ for $T \gg \hbar\omega$, where v is the group velocity. For $v = c$ (phase velocity of the acoustic phonons) we get $\Lambda \simeq c/\omega \simeq \lambda$ (the wavelength) and $\Lambda \simeq \hbar c/T$, respectively. Since $n = T/\hbar\omega$ in this limit, we can see that $\Lambda = \lambda/n$. The dependence $\Lambda \sim 1/T$ in the range of high temperatures has been discovered by Debye.[14] The quantity $\Lambda = \hbar c/T$ is a characteristic length for phonons; at room temperature it is $\simeq 2.5\text{Å}$ ($c = 10^6 cm/s$). Since only frequencies which satisfy $\hbar\omega < T$ are relevant, it follows that only wavelengths which satisfy $\lambda > \hbar c/T$ are relevant, *i.e.* those wavelengths which satisfy $\lambda \gtrsim \Lambda$. We note that the lifetime τ given by equation (6.31) corresponds to an uncertainty in energy $\Delta\varepsilon \simeq \hbar\omega/\left(1 - e^{-\hbar\omega/T}\right)$, which, for high temperatures, may overcome the Debye frequency; this is an indication that the harmonic-oscillator approximation is not valid anymore.

The phonons, originally elastic waves and lattice vibrations (waves), are now, according to the discussion above, particles with energy, momentum, (group) velocity, lifetime and mean freepath; therefore, they may be viewed as a gas, the phonon gas. Their mean freepath arises from their original wavelength and their lifetime is related to the period of their oscillations. The mean freepath and their lifetime make them to be viewed as quasiparticles. Wavelengths and oscillation periods are exhibited by regular quantum-mechanical particles (waves) too. But these quantities are effective only for a large number of such particles (waves), which is precisely what happens for quasiparticles (elementary excitations). The elementary excitations have been introduced in condensed matter by Landau.[15]

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[12] A. Einstein, "Zur Quantentheorie der Strahlung", Phys. Z. **18** 121 (1917).

[13] M. Apostol, "On the lattice thermoconductivity of an ideal crystal", Fizika **A1** 175 (1992); "Phason contribution to the lattice heat capacity and thermoconductivity", Commun. Theor. Phys. **20** 249 (1993); *Transport Theory*, apoma, Magurele (2001).

[14] P. Debye, in *Vortrage uber die kinetische Theorie der Materie und der Elektrizitat*, Teubner, Berlin (1914) (contributors M. Planck, P. Debye, W. Nernst, M. Smoluchowski, A. Sommerfeld and H. A. Lorentz).

The summation

$$\sum_{\mathbf{k}} n_{\mathbf{k}} = \mathcal{N} \tag{6.33}$$

of the phonon occupation numbers $n_{\mathbf{k}}$ should give the total number of phonons $\mathcal{N}$; at zero temperature this is an indefinite number. Since the phonons are defined for any $\mathbf{r}$, the summation in equation (6.33) may be extended to infinity (it is not restricted to the Brillouin zone). At non-zero temperature the mean number of phonons is

$$3N(T/\hbar\omega_D)^3 \int_0^{\hbar\omega_D/T} dx \frac{x^2}{e^x - 1} = \mathcal{N} \ . \tag{6.34}$$

The integral $\int_0^\infty dx \cdot x^2/(e^x - 1)$ is $\simeq 2.4$.[16] We can see that the mean separation distance between the phonons is $a(\hbar\omega_D/T)$, which, for ω_D of the order c/a, is $\hbar c/T$ given above. The phonon gas resembles much an ideal classical gas, although there is no scattering cross-section in the definition of the mean freepath; the mean freepath is given, practically, by the mean phonon-phonon separation distance.

Equation (6.33) shows that $n_{\mathbf{k}}$ may be taken as the phonon distribution (at non-zero temperatures), with the normalization condition

$$\frac{V}{2\pi^2} \int dk \cdot k^2 \frac{1}{e^{\hbar\omega(\mathbf{k})/T} - 1} = \mathcal{N} \ ; \tag{6.35}$$

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[15] L. Landau, "The theory of a Fermi liquid", Sov. Phys.-JETP **3** 920 (1957) (ZhETF **30** 1058 (1956)); "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1957) (ZhETF **32** 59 (1957)); "On the theory of the Fermi liquid", Sov. Phys.-JETP **8** 70 (1959) (ZhETF **35** 97 (1958)).

[16] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier (1980).

or

$$\frac{1}{2\pi^2}\int d\mathbf{r}dk\cdot k^2\frac{1}{e^{\hbar\omega(\mathbf{k})/T}-1}=\mathcal{N}\quad, \tag{6.36}$$

if we allow for a spatial variation; this way, we may speak of a phonon density. The mean occupation number $n_{\mathbf{k}}$ (also denoted n_ω or, simply, n) may have a spatial variation through the temperature T, or the parameters in $\omega(\mathbf{k})$ (*e.g.*, phase or group velocity). A spatial variation of the frequency ω should be much smaller than the relevant phonon wavelengths, in order to preserve its analytical form; since such variations are at the macroscopic scale, this condition is fulfilled. The spatial dependence of the frequency ω implies that the energy $\varepsilon=\hbar\omega$ may act as the hamiltonian for the quasiparticles (phonons), with the equation of motion $\dot{\mathbf{p}}=\hbar\dot{\mathbf{k}}=-\partial\varepsilon/\partial\mathbf{r}$ (*i.e.*, $\dot{\mathbf{k}}=-\partial\omega/\partial\mathbf{r}$, and, of course, the group velocity $\mathbf{v}=\partial\varepsilon/\partial\mathbf{p}$, *i.e.* $\mathbf{v}=\partial\omega/\partial\mathbf{k}$). Therefore, the Boltzmann equation for phonons reads

$$\frac{dn}{dt}=\frac{\partial n}{\partial t}+\mathbf{v}\frac{\partial n}{\partial\mathbf{r}}-\frac{\partial\varepsilon}{\partial\mathbf{r}}\frac{\partial n}{\partial\mathbf{p}}=0\quad, \tag{6.37}$$

or

$$\frac{\partial n}{\partial t}+\frac{\partial\varepsilon}{\partial\mathbf{p}}\frac{\partial n}{\partial\mathbf{r}}-\frac{\partial\varepsilon}{\partial\mathbf{r}}\frac{\partial n}{\partial\mathbf{p}}=0\quad, \tag{6.38}$$

or

$$\frac{\partial n}{\partial t}+\frac{\partial\omega}{\partial\mathbf{k}}\frac{\partial n}{\partial\mathbf{r}}-\frac{\partial\omega}{\partial\mathbf{r}}\frac{\partial n}{\partial\mathbf{k}}=0 \tag{6.39}$$

(where local equilibrium is assumed); we can see that the spatial variations of ω and n should take place on a much larger scale than the phonon mean freepath. These equations describe the evolution of the phonon distribution; the effect of the external forces (or interactions) is included in the spatial dependence of the frequency $\omega(\mathbf{r})$. Evolution equations for mean quantities are obtained from the above equations. A summation over the branch label should be included for several phonon branches.

6.3 Second sound

Let us assume that the phonon density has a spatial dependence, through the temperature; equation (6.37) reads

$$\partial_t n + c\frac{k_i}{k}\partial_i n = 0 \tag{6.40}$$

(for acoustic phonons). On the other hand, since the energy distribution is $u = \hbar ckn$ and the momentum distribution is $\mathbf{p} = \hbar c\mathbf{k}n$, we get from equation (6.40)

$$\partial_t u + \hbar c^2 k_i \partial_i n = 0 \ , \ \ \partial_t p_i + \hbar c^2 \frac{k_i k_j}{k}\partial_j n = 0 \ . \tag{6.41}$$

These equations must be multiplied by $1/V$ and summed up over $\mathbf{k}$, in order to get the energy density U and the momentum density $\mathbf{P}$, respectively; since n depends only on k (an isotropic distribution) the product $k_i k_j$ gives $\frac{1}{3}k^2\delta_{ij}$, such that we get

$$\partial_t U + c\partial_i P_i = 0 \ , \ \ \partial_t P_i + \frac{1}{3}c\partial_i U = 0 \ \ , \tag{6.42}$$

or

$$\partial_t^2 U - \frac{1}{3}c^2\Delta U = 0 \ , \ \ \partial_t^2 \mathbf{P} - \frac{1}{3}c^2\Delta\mathbf{P} = 0 \ . \tag{6.43}$$

We can see that the phonon energy and momentum are propagated in a non-uniform phonon gas with the velocity $c/\sqrt{3}$; this is called the second sound (in order to distinguish it from the usual sound which propagates with velocity c, called the first sound).[17] The geometric factor $1/3$ appears also in the phonon thermoconductivity.

6.4 Thermoconductivity

It is convenient to define the phonon distribution $f(\mathbf{r},\mathbf{k}) = n/V$ from equations (6.35) and (6.36), where $\int d\mathbf{r}\sum_{\mathbf{k}} f = \mathcal{N}$. The quantity

$$\rho = \sum_{\mathbf{k}} f \tag{6.44}$$

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[17] J. C. Ward and J. Wilks, "III. Second sound and the thermo-mechanical effect at very low temperatures", Phil. Mag. **43** 48 (1952).

is the phonon density. We assume that f depends on position through temperature. The Boltzmann equation (6.37) gives

$$\frac{\partial f}{\partial t} + (\mathbf{v}grad)f = 0 \quad , \tag{6.45}$$

where $\mathbf{v}$ is the group velocity. For slight spatial variations

$$f = -\tau(\mathbf{v}grad)f \tag{6.46}$$

and

$$\mathbf{v}f = -\mathbf{v}\tau(\mathbf{v}grad)f \quad , \tag{6.47}$$

where τ is the phonon lifetime. We keep a fixed direction $\mathbf{s}$ of the velocity $\mathbf{v}$ in $\mathbf{v}f$ and get

$$\mathbf{i} = \mathbf{s}\sum_{\mathbf{k}} vf = -\mathbf{s}\sum_{\mathbf{k}} v\tau(\mathbf{v}grad)f \quad , \tag{6.48}$$

where $\mathbf{i}$ is the phonon flux (flow), *i.e.* the number of phonons per unit time which pass through the cross-sectional area in the $\mathbf{s}$-direction; this is a generalized Fick's law for phonons.

The energy is given by

$$E = \sum_{\mathbf{k}} \hbar\omega n = \int d\mathbf{r} \sum_{\mathbf{k}} \hbar\omega f \quad ; \tag{6.49}$$

it follows, from equation (6.46),

$$\hbar\omega f = -\hbar\omega\tau(\mathbf{v}grad)f \tag{6.50}$$

and

$$\mathbf{v}\hbar\omega f = -\mathbf{v}\hbar\omega\tau(\mathbf{v}grad)f \quad . \tag{6.51}$$

Therefore, the energy flow is

$$\frac{\partial Q}{\partial t} = -\mathbf{s}\sum_{\mathbf{k}} \hbar\omega v\tau(\mathbf{v}grad)f = -\mathbf{s}\sum_{\mathbf{k}} \hbar\omega v\tau(\mathbf{v}gradT)\frac{\partial f}{\partial T} \quad , \tag{6.52}$$

where Q is the energy flux. At constant volume this is the heat flux, and equation (6.52) is the law of phonon thermal conduction. In general, for an anisotropic phonon spectrum the distribution f, the phonon lifetime and the mean freepath are anisotropic, and we may have transport along any direction. For an isotropic phonon spectrum we can see from equation (6.52) that we have heat transport only along the direction of $gradT$; in this case we get

$$\frac{\partial Q}{\partial t} = -\left(\sum_{\mathbf{k}} \hbar\omega v_s^2 \tau \frac{\partial f}{\partial T}\right) \frac{\partial T}{\partial s} \quad , \tag{6.53}$$

where s denotes the coordinate along which the temperature varies; the quantity

$$K = \sum_{\mathbf{k}} \hbar\omega v_s^2 \tau \frac{\partial f}{\partial T} \tag{6.54}$$

is the thermoconductivity coefficient in the thermal-conduction law $\partial Q/\partial t = -K(\partial T/\partial s)$; the integration over the angular variables gives $v_s^2 = \frac{1}{3}v^2$ and

$$K = \frac{1}{3(2\pi^2)} \int dk \cdot k^2 \hbar\omega v^2 \tau \frac{\partial n}{\partial T} \quad . \tag{6.55}$$

For acoustic phonons $\omega = ck$ ($v = c$) we get the thermoconductivity

$$K = \frac{T^2}{6\pi^2 c\hbar^2} \int_0^{\hbar\omega_D/T} dx \frac{x^3}{e^x - 1} \quad ; \tag{6.56}$$

in the low-temperature limit $K = \pi^2 T^2/90c\hbar^2$ (the integral extended to infinity is $\pi^4/15$[18]). In the high-temperature limit $K = \hbar\omega_D^3/18\pi^2 cT$.

In the low-temperature limit only a few long-wavelength phonon states are excited, whose mean freepath is long and may overcome the spatial variations of the phonon distribution; consequently, the limit $T \to 0$ in thermoconductivity should be viewed with caution. In the region of low temperatures there exists another mean freepath which may compete with the thermal mean freepath, arising from the finite dimension of the solid (*e.g.*, its thickness); for instance, the thickness d of a solid may be shorter than the phonon long wavelengths, such that the mean freepath is of the order d (this is known as the boundary-scattering limit).[19] The competition between various mean freepaths (or lifetimes) is achieved by the Matthiessen interpolation formula. The $1/T$-law of thermoconductivity in the high-temperature limit was pointed out by Debye.[20] The thermoconductivity given by equation (6.56) has a maximum of the order $10^{-2}(\omega_D^2/c)$ for T of the order $\hbar\omega_D$. This value is much higher than the experimental values. The thermoconductivity given by equation (6.56) should be viewed within the following limits: first, the acoustic-phonon spectrum is limited to a cutoff frequency ω_0 much smaller than ω_D; second, the formula is valid for $T \gg \hbar\omega_0$, which, indeed, results in an appreciable reduction of the thermoconductivity.

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[18] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier (1980).

The thermoconductivity given above is the thermoconductivity of a perfect, infinite solid. In real solids the picture changes appreciably.

6.5 Anharmonic solids

At equilibrium, the phonon distribution $n = \left(e^{\hbar\omega/T} - 1\right)^{-1}$ gives vanishing energy and momentum flows, as expected. If a constant macroscopic velocity $\mathbf{V}$ were present, the distribution

$$n = \left(e^{\hbar\omega - \hbar\mathbf{V}\mathbf{k}/T} - 1\right)^{-1} \tag{6.57}$$

would be an equilibrium distribution, but, as it is sometimes argumented, a non-vanishing flow of energy and momentum would then be present; therefore, according to such an argument, we would have a heat flow without a temperature gradient, *i.e.* an infinite thermoconductivity; the perfect solid would have an infinite thermoconductivity. It would be necessary, the argument goes on, to assume the existence of momenta which would compensate the macroscopic momentum of the phonons. These momenta are provided by vectors of the reciprocal lattice (in crystals), which should imply umklapp processes of phonon scattering, arising from anharmonic atomic interactions. Such a reasoning led Peierls to assume the existence of phonon umklapp scattering, where the phonon wavevector changes by a reciprocal lattice vector, resulting in an exponential factor $\sim e^{\hbar\omega_D/T}$ in thermoconductivity, at intermediate temperatures.[21] Of course, the distribution function with a constant macroscopic velocity means nothing but the change of the reference frame, the phonons being indissolubly attached to the oscillating atoms. An infinite thermoconductivity would mean an infinite lifetime of phonons, as if the phonons would be classical free particles.

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[19] H. B. G. Casimir, "Note on the conduction of heat in crystals", Physica **5** 495 (1938).

[20] P. Debye, in *Vortrage uber die kinetische Theorie der Materie und der Elektrizitat*, Teubner, Berlin (1914) (contributors M. Planck, P. Debye, W. Nernst, M. Smoluchowski, A. Sommerfeld and H. A. Lorentz).

However, small anharmonic interactions are present in solids; for instance they are responsible for the thermal expansion of solids.[22] In the long wavelength limit they may change slightly the phonon spectrum, thus modifying the group velocity; such modifications are reflected in thermoconductivity. At low temperatures the lattice displacements are small and the effect of the anharmonic contributions may be neglected. At high temperatures the anharmonic contributions may be viewed as small corrections to the equilibrium thermodynamic quantities (like the specific heat, for instance). But the main effect of the anharmonic terms consists in destroying the notion of phonons as independent modes of mechanical motion, especially at short wavelengths. The change brought by anharmonicities in the heat transport in solids (thermoconductivity) was emphasized by Debye and Born.[23] The loss of the phonon states is reflected in phonon scattering, involving three, or more, phonons, with creation or destruction of phonons (e.g., phonon decay). The phonon-phonon scattering processes imply the momentum conservation and do not lead to a finite lifetime since the emission and absorption processes are at equilibrium; the vectors of the reciprocal lattice for umklapp processes

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[21] R. Peierls, "Zur kinetischen Theorie der Warmeleitung in Kristallen", Ann. Phys. **3** 1055 (1929).

[22] C. Kittel, *Introduction to Solid State Physics*, Wiley, NY (1986); *Quantum Theory of Solids*, Wiley, NY (1963); J. M. Ziman, *Electrons and Phonons, The Theory of Transport Phenomena in Solids*, Clarendon Press, Oxford (1960); *Principles of the Theory of Solids*, Cambridge University Press, Cambridge (1972).

[23] In *Vortrage uber die kinetische Theorie der Materie und Elektrizitat*, Teubner, Berlin (1914) (contributors M. Planck, P. Debye, W. Nernst, M. Smoluchowski, A. Sommerfeld and H. A. Lorentz).

(in crystals) are irrelevant for the phonon states.[24] The atomic motion cannot be viewed anymore as a correlated, collective motion, but, instead, we should view it as motion of independent, uncorrelated (or weakly correlated) atoms, about equilibrium positions (possibly displaced); obviously, the heat transport should diminish appreciably in this case. The mechanism of heat transport in the presence of anharmonicities is very different from the mechanism of heat transport by phonons.

According to this picture the mean freepath (of the atomic motion) can be estimated as for a classical gas: $\Lambda = (a/d)^2 a$, where a is the mean inter-atomic separation and for d^2 we can use the mean square displacement u^2 which is given by $M\omega^2 u^2 = T$, where $\omega = c/a$, c being, approximately, the sound velocity. It follows $u^2 = (T/Mc^2)a^2$ and $\Lambda = (Mc^2/T)a$. We can see that the $1/T$-dependence is preserved, though there is an important deviation from the phonon mean freepath $\Lambda = \hbar c/T$ (for high temperatures). This mean freepath can be used in estimating the thermoconductivity, which, from equation (6.52), can be written as

$$K = \frac{1}{3} C v \Lambda \quad , \tag{6.58}$$

where C is the specific heat (per unit volume, $C = 3/2a^3$). We get

$$K \simeq \frac{Mvc^2}{2a^2 T} \quad . \tag{6.59}$$

The thermoconductivity is appreciably reduced by the group velocity and the velocity c in $\omega = c/a$. At low temperature, where only long wavelengths phonons (with anharmonicities) are excited (and the specific heat goes like $C \sim T^3$), the mean freepath is still of the order of the phonon wavelengths, but it may be dominated by the size d of the solid, according to Casimir's law. In order to compare these results with experimental data an interpolation formula between low- and high-temperature limits is convenient.

The mean freepath $\Lambda = (Mc^2/T)a$ induces an energy uncertainty $\Delta\varepsilon \simeq \hbar T/Mca$; it is much smaller than the Debye energy $\hbar\omega_D$ for $T \ll Mc^2$ ($Mc^2 \simeq 10^3 A(K)$, where A is the mass number).

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[24] R. Peierls, *Surprises in Theoretical Physics*, Princeton University Press, Princeton, NJ (1979).

The heat conduction in solids is sometimes approached[25] by the Boltzmann equation

$$\frac{\partial n}{\partial t} + (\mathbf{v}grad)n = C(n) \quad , \tag{6.60}$$

where $C(n)$ is the collision integral; as if the transport were at non-equilibrium. Since the transport is viewed as being stationary, the term $\partial n/\partial t$ is neglected (though it is of the same order of magnitude as the spatial-derivative term), and equation (6.60), multiplied by energy $\hbar\omega$, leads to

$$Cv\frac{\partial T}{\partial s} = \frac{\Delta E}{\Delta t \cdot a^3} \quad , \tag{6.61}$$

where ΔE is the energy transported along the s-direction; multiplying this equation by Λ estimated above, we get

$$Cv\Lambda\frac{\partial T}{\partial s} = \frac{\Delta E}{\Delta t \cdot u^2} = \frac{\partial Q}{\partial t} \quad , \tag{6.62}$$

where Q is the heat flux; we get the law of thermal conduction (up to some immaterial factors), which shows that the cross-section through which the heat is transported is the mean square displacement u^2, which is reasonable. Although such an approach may have its range of applicability (for non-equilibrium transport), usually the transport is at equilibrium, because the relaxation time $\tau = \Lambda/c = Mca/T$ is very short in comparison with the macroscopic time scale.

6.6 Temperature waves

If the temporal and spatial variations of the temperature T in the distribution function of (acoustic) phonons are comparable with the phonon lifetime and mean freepath (at low temperatures), we should preserve the time derivative in equation (6.40), which reads

$$\partial_t T + \frac{c}{k}(\mathbf{k}grad)T = 0 \quad , \tag{6.63}$$

or

$$\partial_t^2 T - c^2\frac{k_i k_j}{k^2}\partial_i\partial_j T = 0 \quad ; \tag{6.64}$$

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[25] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 10, *Physical Kinetics*, Elsevier, Oxford (1981).

for an isotropic distribution, we get temperature waves propagating with velocity c; if the propagation is along one direction, the velocity is $c/\sqrt{3}$.

6.7 Sound attenuation

For slight variations of the phonon distribution function along the s-direction, the Boltzmann equation (6.37) leads to

$$n - n_0 + \Lambda \frac{\partial n}{\partial s} = 0 \quad , \tag{6.65}$$

whose solution is

$$n = n(s=0)e^{-s/\Lambda} + n(s=\infty)\left(1 - e^{-s/\Lambda}\right) \quad ; \tag{6.66}$$

this equation is valid over short distance; it only shows that the phonons have a mean freepath.

The sound frequencies are much lower than the phonon lifetime frequency, while, usually, the sound amplitude is large. This means that the sound makes the phonon frequency to acquire a spatial dependence, which amounts to keep in the Boltzmann equation (6.39) the force term proportional to $-\partial\omega/\partial\mathbf{r}$. However, the large amplitude of the sound makes its propagation a non-equilibrium process. The sound attenuation is given by lattice thermoconduction and viscosity in the non-equilibrium process of solid deformation. Technically, it is the ratio of the dissipated heat $T\dot{S}$, where S is the entropy per unit volume, to the sound energy flow (it is given in units cm^{-1}). We may assume that the non-equilibrium processes are governed by the phonon mean freepath; then, we may write

$$\lambda \frac{\partial n}{\partial t} \simeq -v \frac{\partial n}{\partial T} \frac{\Delta T}{\Lambda} \quad , \tag{6.67}$$

where the factor λ is proportional to the square of the deformation tensor (sound energy); it is reflected in the temperature difference ΔT. Multiplying by $\hbar\omega$, we get the rate of the dissipated heat (per unit volume)

$$\lambda \frac{\partial q}{\partial t} \simeq -\frac{K}{\Lambda^2} \Delta T \quad , \tag{6.68}$$

whence the absorption coefficient $\gamma \sim KT$, due to the thermoconduction (it is also proportional to the frequency square ω^2). At high temperature γ is a constant. The same formula is valid for viscosity at high temperatures; at lower temperatures, the short-range viscosity produces an additional strain variation which compensates the change in temperature, such that the absorption coefficient goes like $\gamma \sim K \sim 1/T$. The interaction of the phonons with the electrons in solids brings an additional mechanism of phonon absorption (sound attenuation), connected with electron conduction and electron viscosity. This mechanism is discussed in one of the next chapters.

6.8 Electron-phonon interaction

We estimate here the effect of the electron-phonon interaction in metals. In metals, there exists an electron liquid, with a Fermi sea, a chemical potential (Fermi energy) μ and a Fermi wavevector k_F of the order $k_F \simeq 1/a$, where a is the mean inter-atomic separation; the chemical potential is $\mu = \hbar^2 k_F^2/2m$, where m is the electron mass. The dynamics of the electron liquid is governed by elementary excitations of quasiparticle type, with low energy and momentum; they are quasielectrons excited slightly above the Fermi surface, extending in energy over a range of the order T, where T is the temperature.[26] We limit ourselves to moderate temperatures, because at low temperature the electronic structure of metals changes (*e.g.*, they become superconductors), while in the very high temperature range the metals soften and melt down. Usually, the interaction of the electrons with the phonons is considered as the interaction of the quasielectrons with the phonons; it consists in creation or destruction of a phonon and the corresponding change in the quasielectron; it implies small wavevectors and energies and leads to an attractive interaction between (quasi) electrons which is responsible of superconductivity in the low-temperature range.[27] This is a small interaction and for intermediate temperatures we may leave it aside. However, the same type of electron-phonon interaction may affect the electrons inside the Fermi sea; it is this type of electron-phonon interaction which gives a lifetime to the quasielectrons. Indeed, short wavelength phonons may change the wavevectors of the electrons inside the Fermi sea; the energy conservation requires that for a phonon and an electron a number n of quasielectrons to be created, since the chemical potential μ is much larger than phonon energy. It is easy to see that this number is of the order $n = \mu/Mc^2$, where M is the atom mass and c is a mean sound velocity. Indeed, short-wavelength phonons have an energy scale of the order $M\omega_D^2 u^2 \simeq Mc^2$, where ω_D is the Debye frequency and u is the atomic displacement. Therefore, we get a wavefunction $\sim e^{-\frac{i}{\hbar}n\hbar\varepsilon}$ for a quasielectron state with energy ε, which implies that its lifetime is τ_0/n, τ_0 being the original lifetime; this later quantity is of the order $\hbar/T$; we get the inverse of the electron-phonon lifetime

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[26] L. Landau, "The theory of a Fermi liquid", Sov. Phys.-JETP **3** 920 (1957) (ZhETF **30** 1058 (1956)); "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1957) (ZhETF **32** 59 (1957)); "On the theory of the Fermi liquid", Sov. Phys.-JETP **8** 70 (1959) (ZhETF **35** 97 (1958)).

$$\frac{1}{\tau_{e-ph}} = \frac{Tn}{\hbar} = \frac{T}{\hbar F} \quad , \tag{6.69}$$

where we introduced the notation $F = 1/n$.[28] The number n is estimated as follows:

$$F = \frac{1}{n} = \frac{Mc^2}{\mu} = \frac{M\omega_D^2 a^2}{\mu} = \frac{M\hbar^2\omega_D^2}{\mu\hbar^2 k_F^2} = \frac{M}{m}\left(\frac{\hbar\omega_D}{\mu}\right)^2 \quad . \tag{6.70}$$

Noteworthy, τ_{el-ph} is the lifetime of the (quasi) electrons caused by the electron-phonon interaction. The phonons are also affected by the electron-phonon interaction, such that a corresponding phonon lifetime τ_{ph-e}, caused by the electron-phonon interaction, exists; it is discussed in one of the next chapters. We shall use the lifetime τ_{e-ph} in one of the next chapters to estimate the effect of the electron-phonon interaction on the electron thermoconductivity in metals. The same effect in semiconductors will be discussed separately. Also, the electron-phonon interaction in polar (ionic) solids is a distinct subject. In general, lattice thermoconduction is affected by impurities, defects, disorder (like in amorphous solids), boundaries, contacts, various interactions with other elementary excitations, etc.

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[27] H. Frohlich, "Theory of the superconducting state. I. The ground state at the absolute zero of temperature", Phys. Rev. **79** 845 (1950); J. Bardeen, L. N. Cooper and J. R. Schrieffer, "Microscopic theory of superconductivity", Phys. Rev. **106** 162 (1957); "Theory of superconductivity", Phys. Rev. **108** 1175 (1957).

[28] A. H. Wilson, *The Theory of Metals*, Cambridge University Press, Cambridge (1953).

6.9 Dimensionality effects

We note that phonons with wavelengths longer than the dimension of the bodies are unphysical, since they imply a translation. For instance, in a slab with thickness d, transverse phonons with wavelengths longer than d are unphysical. The phonon gas becomes quasi-two-dimensional in this case. However, the elastic motion in a finite body should include surface effects, in particular boundary conditions, which transform the phonon motion in vibrations. For instance, in a slab, transverse vibrations with frequencies of the order c/d occur (limited by a Debye frequency). In computing thermodynamic quantities the summation over discrete frequencies cannot be transformed into integrals without errors; a Euler-Maclaurin formula is needed in this case, which leads to surface effects. It is easy to see that a crossover temperature of the order $T \simeq \hbar c/d$ may appear, from a three- to a two-dimensional regime. In addition, surface elastic waves (Rayleigh waves) appear in such structures, which should be taken into account.[29]

In two dimensions and one dimension another difficulty appears, related to the fluctuations of the displacement of the atomic constituents of the bodies; this displacement acquires a divergent behaviour, due to the long-wavelength phonons.[30] Actually, two- or one-dimensional bodies may only exist on substrates, or with contacts, or otherwise with position constraints, which remove such divergencies.[31] Specific elastic waves appear in layered structures (*e.g.*, Love waves), which complicates further the problem.

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[29] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 7, *Elasticity*, Elsevier (1986).

[30] R. Peierls, "Bemerkungen uber Umwandlungstemperaturen", Helv. Phys. Acta **7** , Suppl. 2, 81 (1934); Quelques propri*é*t*é*s typiques des corps solides, Ann. d'Institut Henry Poincar*é*, **5** 177 (1935); L. Landau, "On the theory of phase transitions", Part II, ZhETF **7** 627 (1937) (in Russian) (Phys. Zeit. Sowjetunion **11** 545 (1937); L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier (1980).

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[31] M. Apostol, "On the low-dimensional solids and their melting", Synth. Metals **79** 253 (1996).

7 Fermi Liquid

7.1 Quasiparticles

He^3 liquefies at 3.2K under normal pressure, with a mean inter-particle separation distance of a few angstroms, comparable with the range of the (weak) interaction potential; its thermal wavelength is about 2Å, such that the liquid He^3 is a quantum liquid of fermions, or a Fermi liquid (sometimes called a normal Fermi liquid). The motion of the He^3 atoms in the (repulsive) interaction potential is affected by inertia effects, *i.e.* the particles possess an effective mass; they obey the Fermi distribution, like an ideal Fermi gas. Quasiparticles are a class of elementary excitations in Fermi liquid; they are located near the Fermi level (of the order $10meV$; $1eV = 1.1 \times 10^4 K$). The states lying deeply in, or highly above, the Fermi sea require, on one hand, high excitation energies, and, consequently, they do not contribute much to the liquid properties (are not excited at low temperatures); on the other hand, they are not well-defined excitations, because the interaction may redistribute their energy and momentum, in many ways, and, consequently, it may affect them appreciably. It follows that the interaction does not affect the step-wise shape of the Fermi distribution, and the relevant quasiparticles may be viewed as slight distortions of the Fermi sea near its surface; this is especially true for high values of particle concentration, where the Fermi energy is high and the interaction effects are weak. Similarly, the temperature T smears out the stepwise Fermi distribution over a range of the order T, much smaller than the Fermi energy. This is Landau's theory of the Fermi liquid.[1]

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[1] L. Landau, "The theory of a Fermi liquid", Sov. Phys.-JETP **3** 920 (1957) (ZhETF **30** 1058 (1956)); "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1957) (ZhETF **32** 59 (1957)); "On the theory of the Fermi liquid", Sov. Phys.-JETP **8** 70 (1959) (ZhETF **35** 97 (1958)).

He^3 preserves its nature of a Fermi liquid over a certain, limited, range of parameters; at very low temperatures, for instance, weak attractive interactions of magnetic origin pair up the He^3 atoms into quasi-bosons, which exhibit superfluidity;[2] under pressure He^3 may even solidify at very low temperatures, in a rather disordered structure which requires additional entropy; He^3 may serve as a natural tool for reaching significantly low temperatures.

Another Fermi liquid is the electron liquid in metals. Although it is discussed in another chapter, its main characteristics of a normal Fermi liquid are included here.

The Fermi sea and the Fermi surface are defined by minimizing the ground-state energy with respect to the fermion occupancy under the constraint of a fixed number of particles N; the chemical potential μ is thereby obtained, as well as the Fermi momentum $\mathbf{p}_F$. The volume of the Fermi sea is determined by the concentration N/V of the particles, where V is the volume; for an isotropic liquid, $N/V = gp_F^3/6\pi^2\hbar^3$, where g is the spin weight ($g = 2$, He^3 and the electrons have spin $1/2$) . In general, the shape of the Fermi surface may be different from a sphere; we assume a spherical Fermi surface. The interaction does not change the volume of the Fermi sea, since the number of particles is conserved; an isotropic interaction preserves the shape of the Fermi sea, and, therefore, the Fermi momentum $\mathbf{p}_F$ is also preserved. The quasiparticle energy is a function $\varepsilon(\mathbf{p})$ of the momentum $\mathbf{p}$, and it can be written as

$$\varepsilon(\mathbf{p}) = \mu + \mathbf{v}_F(\mathbf{p} - \mathbf{p}_F) \quad , \tag{7.1}$$

where $\mathbf{v}_F = \partial\varepsilon/\partial\mathbf{p}_F$ is the Fermi velocity, and $\mathbf{p}$ is close to $\mathbf{p}_F$. These quasiparticles lie in a narrow region Δp around the Fermi surface; their uncertainty in momenta is $\sim (\Delta p)^2/p_F$, arising from the uncertainty in energy $\delta(p_F^2) \sim p_F\delta p = (\Delta p)^2$. This uncertainty comes from the nature (definition) of the quasiparticles; one can see that it is very small as long as the quasiparticles are located near the Fermi surface, *i.e.* as long as $\Delta p \ll p_F$. The corresponding lifetime of the quasiparticles is $\tau_0 \sim \hbar\mu/\left(\varepsilon - \mu\right)^2$ ($\hbar/[(\Delta p)^2/m]$, $\mu = p_F^2/2m$, where m is the particle mass). We can see that the range over which the quasiparticles are well-defined near the Fermi surface increases with increasing particle concentration. Similarly, the quasiparticles are spread across the Fermi surface over a Δp range due to the thermal effects, such that $\Delta p \sim T/v_F$; the corresponding uncertainty in momenta is $(\Delta p)^2/p_F \sim T^2/v_F^2 p_F \ll \mu T/v_F^2 p_F \sim \Delta p \ll \mu^2/v_F^2 p_F \sim p_F$, which means that the quasiparticle momenta are pretty well determined. Similarly, their uncertainty in energy is $\sim T^2/\mu$, such that their lifetime is $\tau_{th} \sim \hbar\mu/T^2$, much longer than the characteristic time of the Fermi level μ. The two uncertainties are competitive, and the net lifetime τ is given by $\tau^{-1} = \left(\tau_0^{-1} + \tau_{th}^{-1}\right) n$, where n is the Fermi distribution, according to the probabilistic nature of the quasiparticles.[3] We get

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[2] T. Leggett, "Interpretation of recent results on He^3 below $3mK$: A new liquid phase?", Phys. Rev. Lett. **29** 1227 (1972).

$$\frac{1}{\tau} = \frac{(\varepsilon - \mu)^2 + T^2}{\hbar\mu} \cdot \frac{1}{e^{(\varepsilon-\mu)/T} + 1} \ . \tag{7.2}$$

This lifetime can also be obtained by computing the transition probability in the second-order of the perturbation theory.[4] All these are consistent with the linear series expansion in equation (7.1) of the quasiparticle spectrum.

The lowest energy levels of a Fermi liquid consist of particle-hole excitations around the Fermi surface, given by

$$\varepsilon(\mathbf{p}) = \mathbf{v}_F\mathbf{p} \quad , \tag{7.3}$$

where $\mathbf{p}$ denotes the small variation in the momentum; noteworthy, this energy depends on the relative orientation of the Fermi velocity with respect to the momentum, and, incidentally, the "superfluidity" criterion $v < \mathbf{v}_F\mathbf{p}/p$ is not satisfied. We say that the excitations given by equation (7.3) form a particle-hole continuum; this is called a Fermi-type spectrum. In principle, the quasiparticle energy given by equation (7.1) may also depend on the particle spin $\mathbf{s}$. This dependence may only include contributions of the s^2- or $(\mathbf{sp})^2$-type; the former is irrelevant, while the latter splits the $2s+1$ degenerate levels into $(1/2)(2s+1)$ levels, each twofold degenerate; we can say that the quasiparticles have a one-half spin. The spin weight g accounts for the corresponding density of states in the subsequent calculations.

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[3] P. Morel and P. Nozieres, "Lifetime effects in condensed helium-3", Phys. Rev. **126** 1909 (1962).

[4] L. Landau, "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1957) (ZhETF **32** 59 (1957)).

It is worth noting that the term quasiparticle is used both for particles with energy given by equation (7.1) and excitations with energy given by equation (7.3); the notation $\varepsilon(\mathbf{p})$ in these two equations has a different meaning; the same is true for the notation $\mathbf{p}$.

The quasiparticles distort the Fermi distribution by a certain, small, amount $\delta n(\varepsilon)$, which implies a particle-hole pair; consequently, one may define the quasiparticle energy $\varepsilon(\mathbf{p})$ by the corresponding small change in the energy

$$\delta E = \frac{gV}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot\varepsilon\delta n(\varepsilon) \ \ , \tag{7.4}$$

while the entropy is the Fermi entropy

$$S = -\frac{gV}{(2\pi\hbar)^3}\int d\mathbf{p}\left[n\ln n + (1-n)\ln(1-n)\right] \ \ ; \tag{7.5}$$

it corresponds to the Fermi distribution

$$n = \frac{1}{\exp\left[(\varepsilon-\mu)/T\right]+1} \tag{7.6}$$

at thermal equilibrium and for a given number N of particles and a given energy. The distribution given by equation (7.6) is smeared out over a small T-range around the chemical potential μ, and the thermal effects can be computed in the same way as those for the ideal Fermi gas (including the change in the chemical potential due to the temperature). It remains to account for the interaction effects, especially in the density of states at the Fermi surface, *i.e.* the dependence $\varepsilon(\mathbf{p})$, which amounts, in principle, to determining the two parameters μ and v_F in equation (7.1). As in equation (7.4), small changes in the distribution determine small changes in the (quasi)-particle energies, which may be represented as

$$\varepsilon(\mathbf{p}) = p^2/2m + \frac{g}{(2\pi\hbar)^3}\int d\mathbf{p}'\cdot f(\mathbf{p},\mathbf{p}')\delta n(\varepsilon') \ \ ; \tag{7.7}$$

the momenta $\mathbf{p}$ and $\mathbf{p}'$ are close to the Fermi surface and the function $f(\mathbf{p},\mathbf{p}')$, which is symmetrical in its variables (and may also depend on spin), depends on the particle interaction. It is worth noting that

$\varepsilon(\mathbf{p})$ in equations (7.4)-(7.7) includes the chemical potential besides the excitation energy given by equation (7.3) (and the interaction). The energy $\varepsilon(\mathbf{p})$ is determined in equation (7.7) with the same accuracy as in equation (7.1); it is the hamiltonian of the quasiparticles, and it may depend on position for a slightly perturbed liquid, as in a quasi-classical description. It is worth noting here the self-consistent character of the equation above, together with the quasiparticle Fermi distribution given by equation (7.6) (the quasiparticle energy depends also on temperature, though in a higher-order approximation). The f-term in equation (7.7) accounts for the quasiparticle scattering (interaction); f is a scattering amplitude. This term dresses the free particles with interaction, the free particles being, therefore, bare particles. Solving for the interaction effects in terms of quasiparticles is also called the renormalization of the interaction, the quasiparticles being renormalized particles. The f-term in equation (7.7) represents also the reaction of the liquid to a particle excitation, and, in this respect, the theory of the Fermi liquid amounts to a linear response theory. It is important to notice in this case that the interaction integrals of the f-type in equation (7.7) include the density of the quasiparticle states at the Fermi surface; the latter is large for high values of the particle concentration (*i.e.*, for a well-defined quasiparticle picture). Indeed, the density of states $\mathcal{D}_F$ is given by

$$\begin{gathered} d\tau = g\tfrac{V}{(2\pi\hbar)^3}d\mathbf{p} = g\tfrac{V}{(2\pi\hbar)^3}\tfrac{dsd\varepsilon}{v_F} = \\ = g\tfrac{V}{(2\pi\hbar)^3}\tfrac{p_F^2}{v_F}dod\varepsilon = \mathcal{D}_F dod\varepsilon \quad , \end{gathered} \tag{7.8}$$

where $d\tau$ is the infinitesimal number of states, ds is the surface element, and $do = \sin\theta d\theta d\varphi$ is the infinitesimal solid angle; one can see that $\mathcal{D}_F$ increases with increasing p_F. The f-function (the interaction effects) must be weak, according to the perturbational character of the theory. Noteworthy, the small variations of the Fermi distribution at zero temperature, located at the Fermi surface, are $\delta n = -\delta(\varepsilon - \mu)\delta\varepsilon$. Also, we note

$$\delta(\varepsilon - \mu) = \int \frac{ds}{v_F}\delta\left(\mathbf{p} - \mathbf{p}_F\right) \quad . \tag{7.9}$$

From equation (7.7) we may infere the form

$$\mu = p_F^2/2m + \frac{g}{(2\pi\hbar)^3}\int d\mathbf{p}'\cdot f(\mathbf{p}_F, \mathbf{p}')n(\varepsilon') \tag{7.10}$$

for the chemical potential μ, to the first approximation.

7.2 Interaction

Interaction may affect appreciably the many-particle ensembles; for instance, a weak attraction between electrons binds them up in pairs, leading to superconductivity; interacting fermions in one dimension get bosonized;[5] anisotropic fermions with "nested" Fermi surfaces become non-homogeneous when interacting and develop charge- or spin-density waves.[6] All these are different phases, and appear as a symmetry breaking, spontaneous or induced; they are also called instabilities of the many-body ensembles, under interaction. Hints towards their nature are often obtained by studying the interacting two-particle problem, scattering included. We leave aside such cases.

By switching on the interaction we may preserve the nature of the particles, their statistics, the symmetries; such a (repulsive) interaction may be treated by perturbation-theory methods.[7] The ground-state should be treated distinctly from the low-energy excitations. The low energy of the latter may be comparable with the weak interaction effects, which may result in new kinds of elementary excitations, as compared with the non-interacting system. Probably, the most common case is provided by the quantum sounds in both interacting Bose and Fermi ensembles. The general perturbational scheme for the ground-state is based on the observation that the wavefunction does not change, to the lowest order of the perturbation theory, while the energy changes by the mean value of the interaction over the unchanged (non-perturbed) ground-state,

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[5] M. Apostol, "Jordan's boson representation for the one-dimensional two-fermion model", Phys. Lett. **A91** 177 (1982); "Bosonization of the one-dimensional two-fermion model: boson representation", J. Phys. **C16** 5937 (1983).

[6] M. Apostol and I. Baldea, "On the charge density wave state in the quasi-one-dimensional compound $K_2[Pt(CN)_4]Br_{0.3} \times 3.2H_2O$ (KCP)", Rev. Roum. Phys. **30** 605 (1985).

[7] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems*, Dover, NY (2003); D. Pines and P. Noziers, *The Theory of Quantum Liquids*, vol.1, *Normal Fermi Liquids*, Benjamin, NY (1966); D. Pines and P. Noziers, *The Theory of Quantum Liquids*, vol.2, *Superfluid Bose Liquids*, Westview Press, NY (1999); G. D. Mahan, *Many-Particle Physics*, Kluwer, NY (2000).

$$\psi = \psi_0 + ... \ , \ \ E = E_0 + (\psi_0, U\psi_0) + ... \ . \tag{7.11}$$

Therefore, the Fermi sea (as well as the one-particle plane waves), or the boson condensed ground-state, is not changed by interaction in this scheme, while a constant energy is acquired by each particle, as if each of them were moving in a constant, external potential. In addition, the individual fermions behave as if they would have, approximately, a different, effective mass. Indeed, the only free parameters in the hamiltonian of a free quantum particle are the particle mass and a constant potential (up to redefining momentum, occasionally). This perturbational scheme may be viewed as an approximation lower than the quasi-classical one. For the boson condensed ground-state the calculation of the energy correction within this scheme is carried out by means of the particle operators turned into c-numbers; a distinct particularity appears for the Fermi sea, namely the quantum exchange effect between the fermion states, seen in what is usually called the Hartree-Fock approximation; in both cases the particles react as a whole to the interaction, a feature called the random phase approximation; this reaction is either static or dynamic, the latter implying virtual excited states, retardation and damping effects; all these features have actually the aspect of an interacting mean-field; the difference between fermions and bosons originates in their distinct statistics.

Naturally, the question of the validity of this perturbational scheme arises, or, as this question is sometimes termed, the convergence of the perturbation theory for these "normal" many-body systems. Various orders of the perturbation theory may be viewed as containing factors of the form

$$\sum_s \frac{v(\mathbf{q})/V}{\varepsilon} \quad , \tag{7.12}$$

where the summation is extended over all the s states allowed by statistics, coupled by interaction to the ground-state; their "excitation" energy is denoted by ε in equation (7.12), where V stands for the volume of the ensemble; $v(\mathbf{q})$ is the Fourier transform

$$v(\mathbf{q}) = \int d\mathbf{r} \cdot v(\mathbf{r}) e^{-i\mathbf{qr}} \tag{7.13}$$

of the two-particle interaction potential (energy) $v(\mathbf{r})$. The "excited" states in equation (7.12) are connected to the ground-state through momentum ($\hbar\mathbf{q}$) and energy conservation (according to the invariance under the space and time translations). In addition, the states s are real, not virtual "excited" states, *i.e.* their energies are related to their momenta through the free-particle Galilean relationship (as for non-relativistic particles). The estimation of equation (7.12) is different for bosons and fermions, as well as for various space dimensions, but, before proceeding, one should emphasize the general model-like assumptions for many-body ensembles: particles are point-like and the potentials are Fourier-transformable; *i.e.*, distances shorter than the typical atomic length (Bohr radius) are meaningless, and the highly-repulsive hard-core atomic potentials are replaced by delta-type potentials, at most. Now, the most dangerous contribution to equation (7.12) comes from small $\mathbf{q}$ and ε, and for three-dimensional fermions this means $\varepsilon \sim \hbar^2 k_F q/m$, while the density of states is of the form $V \cdot q^2 dq$; the angular factors are rendered ineffective by the Fermi statistics, as one can see easily; k_F is the Fermi wavevector, and m denotes the fermion mass. In addition, $k_F \sim 1/a$, where a is the mean inter-particle distance. The interaction may be represented as $v(\mathbf{q} \sim 0) = \overline{v}a^3$, where $\overline{v}$ is a characteristic average interaction energy per particle, and the integration may be extended up to k_F; under these circumstances equation (7.12) gives $\overline{v}/(\hbar^2/ma^2)$ at most; it leads to

$$\overline{v}/(\hbar^2/ma^2) \ll 1 \tag{7.14}$$

i.e. the average interaction energy per particle must be much smaller than the particle localization energy over inter-particle distance. This is the typical condition for the perturbation scheme of the "normal" many-body ensembles. The condition holds for two-dimensional fermions too, while it diverges logarithmically for fermions in one dimension; as it is known, the perturbation scheme is not valid for the latter. For bosons $\varepsilon \sim \hbar^2 q^2/2m$: the condition given by equation (7.14) holds in three dimensions; the condensed ground-state of the bosons is stable under perturbations in three dimensions. On the contrary, the quantity in equation (7.12) diverges for bosons in two and one dimensions, and the corresponding condensed ground-state is destabilized by fluctuations in these cases. As in the one-dimensional case of fermions, the ground-state in these situations is the vacuum of the corresponding elementary excitations; these ensembles are not called anymore "normal" ensembles, though the term "normal" is not currently used for bosons, not even in three dimensions, in view of their Bose-Einstein condensation.

An ensemble of N identical particles of mass m and interacting through a two-particle potential v is described by the hamiltonian

$$H=\sum_i \mathbf{p}_i^2/2m+\frac{1}{2}\sum_{i\neq j} v(\mathbf{r}_i-\mathbf{r}_j) \quad , \tag{7.15}$$

where i, j are labels for particles and $\mathbf{p}_i$ denotes the particle momentum. For long-range potentials the stability of the ensemble must be ensured, as, for instance, in the case of Coulomb interacting electrons, where a uniform, neutralizing background of positive charges must be added (which may have its own dynamics as well; this is often called the "jellium" model of interacting electrons). The corresponding interaction

$$\frac{1}{2}nN\int d\mathbf{r}\cdot v(\mathbf{r})=\frac{1}{2}nN\cdot v(\mathbf{q}=0) \tag{7.16}$$

must then be subtracted from the hamiltonian, which amounts to removing the $\mathbf{q}=0$ Fourier component $v(0)$ of the potential; $n=N/V$ is the particle concentration. In metals, the cohesion is achieved by the interaction with the ions, such that the removal of $v(\mathbf{q}=0)$ is not necessary (the "jellium" model is not very realistic). The electrons in metals are quantum-mechanical particles, which form a normal Fermi liquid. The quantum-mechanical counterpart of equation (7.15) is written by means of the field operators

$$\psi(\mathbf{r})=\frac{1}{\sqrt{V}}\sum_{\mathbf{k}} c_{\mathbf{k}}e^{i\mathbf{k}\mathbf{r}} \quad , \tag{7.17}$$

where the second-quantization particle operators (of creation and annihilation) satisfy the commutation (anticommutation) relations

$$\left[c_{\mathbf{k}},c_{\mathbf{k}'}^{+}\right]=\delta_{\mathbf{k}\mathbf{k}'} \quad , \quad \left\{c_{\mathbf{k}},c_{\mathbf{k}'}^{+}\right\}=\delta_{\mathbf{k}\mathbf{k}'} \tag{7.18}$$

(and $c_{\mathbf{k}}$, $c_{\mathbf{k}'}$ commute or anticommute), corresponding to Bose and Fermi statistics, respectively; such that

$$\begin{gathered}[\psi(\mathbf{r}),\psi^{+}(\mathbf{r}')]=\delta(\mathbf{r}-\mathbf{r}') \ \ , \\ \{\psi(\mathbf{r}),\psi^{+}(\mathbf{r}')\}=\delta(\mathbf{r}-\mathbf{r}') \ \ , \ \ etc \ \ .\end{gathered} \tag{7.19}$$

The spin label should be introduced, or tacitly accepted, together with the position $\mathbf{r}$ and the wavevector $\mathbf{k}$. The number of particles is given by

$$N=\int d\mathbf{r}\cdot\psi^{+}(\mathbf{r})\psi(\mathbf{r})=\sum_{\mathbf{k}}c_{\mathbf{k}}^{+}c_{\mathbf{k}} \quad , \tag{7.20}$$

and the particle density

$$n(\mathbf{r})=\sum_{i}\delta(\mathbf{r}-\mathbf{r}_{i}) \tag{7.21}$$

becomes

$$\begin{gathered}n(\mathbf{r})=\int d\mathbf{r}_{i}\cdot\psi^{+}(\mathbf{r}_{i})\delta(\mathbf{r}-\mathbf{r}_{i})\psi(\mathbf{r}_{i})= \\ =\psi^{+}(\mathbf{r})\psi(\mathbf{r})=\tfrac{1}{V}\sum_{\mathbf{q}}n_{\mathbf{q}}e^{i\mathbf{q}\mathbf{r}} \quad ,\end{gathered} \tag{7.22}$$

where the Fourier components

$$n_{\mathbf{q}}=\sum_{\mathbf{k}}c_{\mathbf{k}}^{+}c_{\mathbf{k}+\mathbf{q}} \tag{7.23}$$

are called the particle-density fluctuations, for $\mathbf{q}\neq 0$. The hamiltonian given by equation (7.15) is written as

$$\begin{gathered}H=\int d\mathbf{r}\cdot\psi_{\alpha}^{+}(\mathbf{r})(\mathbf{p}^{2}/2m)\psi_{\alpha}(\mathbf{r})+ \\ +\tfrac{1}{2}\int d\mathbf{r}d\mathbf{r}'\cdot\psi_{\alpha}^{+}(\mathbf{r})\psi_{\beta}^{+}(\mathbf{r}')v_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\psi_{\beta}(\mathbf{r}')\psi_{\alpha}(\mathbf{r}) \quad ,\end{gathered} \tag{7.24}$$

where $\mathbf{p}=-i\hbar\partial/\partial\mathbf{r}$ and the spin labels have been written explicitly; summations over these labels are included. The potential may, in general, depend on the spin, with the natural symmetry properties; for instance, for one-half spin fermions the potential can be represented as $v_{\alpha\beta}=v+\alpha\beta\cdot u$, where $\alpha,\beta=\pm 1$. It is worth noting that the interaction can also be written as

$$U=\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\cdot v_{\alpha\beta}(\mathbf{r}-\mathbf{r}')n_{\alpha}(\mathbf{r})n_{\beta}(\mathbf{r}')-\frac{1}{2}v_{\alpha\alpha}(\mathbf{r}=0)N_{\alpha} \quad , \tag{7.25}$$

where the self-interaction is (redundantly) introduced; we agree to ignore it, occasionally, and use equation (7.25) as a more convenient form. Without spin labels the kinetic energy can also be written as

$$K = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c^{+}_{\mathbf{k}} c_{\mathbf{k}} \quad , \tag{7.26}$$

where $\varepsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m$, while the interaction can be represented as

$$\begin{aligned} U &= \tfrac{1}{2V} \textstyle\sum_{\mathbf{k}\mathbf{k}'\mathbf{q}} v(\mathbf{q}) c^{+}_{\mathbf{k}+\mathbf{q}} c^{+}_{\mathbf{k}'-\mathbf{q}} c_{\mathbf{k}'} c_{\mathbf{k}} = \\ &= \tfrac{1}{2V} \textstyle\sum_{\mathbf{q}} v(\mathbf{q}) n_{\mathbf{q}} n_{-\mathbf{q}} - \tfrac{1}{2} v(\mathbf{r}=0) N \quad , \end{aligned} \tag{7.27}$$

where the self-interaction has been written again. All this formalism being set up, one can continue now with the normal fermions (in three dimensions). Similar considerations hold also for bosons, care being taken of their distinct statistics, and of their condensed ground-state.

Assuming that the perturbation condition given by equation (7.14) is satisfied, *i.e.* the interaction is weak and short-ranged, one may take the average of the hamiltonian given, for instance, by equations (7.26) and (7.27) over the fermion ground-state, leading to the ground-state energy

$$\begin{aligned} E = &\textstyle\sum_{\mathbf{k}\alpha} \varepsilon_{\mathbf{k}} n_{\mathbf{k}\alpha} + \\ &+ \tfrac{1}{2V} \textstyle\sum_{\mathbf{k}\mathbf{k}'\alpha\beta} \left[v_{\alpha\beta}(0) - v_{\alpha\alpha}(\mathbf{k}-\mathbf{k}')\delta_{\alpha\beta} \right] n_{\mathbf{k}\alpha} n_{\mathbf{k}'\beta} \quad , \end{aligned} \tag{7.28}$$

where $n_{\mathbf{k}\alpha}$ is the fermion occupancy, and the explicit summation over the spin labels is restored. This is the Hartree-Fock approximation, the first interacting term being the Hartree (or direct) contribution, while the second one is the Fock contribution; obviously, the latter is due to the exchange effects.[8] The equation of motion can also be written for a one-particle state described by $c^+_{\mathbf{k}\alpha}$, and by averaging again over the ground-state one obtains

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[8] D. R. Hartree, "The wave mechanics of an atom with a non-Coulomb central field. Part I. Theory and methods, Part II. Some results and discussion", Proc. Cambr. Phil. Soc. **24** 89, 111 (1928); V. Fock, "Naherungsmethode zur Losung des quantenmechanischen Mehrkorperproblems", Z. Phys. **61** 126 (1930).

$$\begin{gathered}\varepsilon^{HF}_{\mathbf{k}\alpha}c^+_{\mathbf{k}\alpha}=\varepsilon_{\mathbf{k}}c^+_{\mathbf{k}\alpha}+\\ +\frac{1}{V}\sum_{\mathbf{k}'\beta}\left[v_{\alpha\beta}(0)-v_{\alpha\alpha}(\mathbf{k}-\mathbf{k}')\delta_{\alpha\beta}\right]n_{\mathbf{k}'\beta}c^+_{\mathbf{k}\alpha}\quad ,\end{gathered}\tag{7.29}$$

where $\varepsilon^{HF}_{\mathbf{k}\alpha}$ may be seen as the single-state energy. The same energy can be obtained by taking the variation of the average of the hamiltonian (7.15) over the antisymmetrized wavefunction $A\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)...$, where the φ-labels denote the one-particle states (this wavefunction is sometimes called a Slater determinant, A stands for antisymmetrization); we get

$$\begin{gathered}-\frac{\hbar^2}{2m}\Delta\varphi_{\mathbf{k}\alpha}+\\ +\sum_{\mathbf{k}'\beta}\left[\left(\varphi_{\mathbf{k}'\beta},v_{\alpha\beta}\varphi_{\mathbf{k}'\beta}\right)\varphi_{\mathbf{k}\alpha}-\delta_{\alpha\beta}\left(\varphi_{\mathbf{k}'\alpha},v_{\alpha\alpha}\varphi_{\mathbf{k}\alpha}\right)\varphi_{\mathbf{k}'\alpha}\right]=\\ =\varepsilon^{HF}_{\mathbf{k}\alpha}\varphi_{\mathbf{k}\alpha}\quad ,\end{gathered}\tag{7.30}$$

which are called the Hartree-Fock equations; obviously, they are identical with equations (7.29). The solutions of equation (7.30) are plane waves, since we start with orthogonal one-particle wavefunctions and the hamiltonian is translationally invariant. The single-state energies $\varepsilon^{HF}_{\mathbf{k}\alpha}$ and the corresponding plane waves do not describe independent particles; each particle state depends on the whole rest of one-particle states; for this reason we say that the Hartree-Fock equations describe self-consistently an interacting mean-field. In particular, the ground-state energy given by equation (7.28) is not the sum of the one-particle energies $\varepsilon^{HF}_{\mathbf{k}\alpha}$, but, on the contrary, a factor one-half must be introduced in the interacting contribution, in order not to count twice the same state (this observation is sometimes referred to as Koopman's "theorem"). The ground-state energy must be minimal not only under variations of one-particle wavefunctions, but also under the variations of the fermion occupancy, with the constraint of a fixed number N of particles. With the notation

$$f_{\alpha\beta}(\mathbf{k},\mathbf{k}')=v_{\alpha\beta}(0)-v_{\alpha\alpha}(\mathbf{k}-\mathbf{k}')\delta_{\alpha\beta}\quad ,\tag{7.31}$$

this leads to the variation of

$$
\begin{gathered}
E = \sum\nolimits_{\mathbf{k}\alpha} \varepsilon_{\mathbf{k}} n_{\mathbf{k}\alpha} + \tfrac{1}{2V} \sum\nolimits_{\mathbf{k}\mathbf{k}'\alpha\beta} f_{\alpha\beta}(\mathbf{k}, \mathbf{k}') n_{\mathbf{k}\alpha} n_{\mathbf{k}'\beta} - \\
-\mu \left(\sum\nolimits_{\mathbf{k}\alpha} n_{\mathbf{k}\alpha} - N \right) \quad ,
\end{gathered} \tag{7.32}
$$

where μ is the chemical potential, which yields

$$
\mu = \varepsilon_{\mathbf{k}} + \frac{1}{V} \sum_{\mathbf{k}'\beta} f_{\alpha\beta}(\mathbf{k}, \mathbf{k}') n_{\mathbf{k}'\beta} \;\; ; \tag{7.33}
$$

in this equation $\mathbf{k}$ is on the Fermi surface, since the small variations $\delta n_{\mathbf{k}\alpha}$ are localized there. The symmetry of the f-function is used in deriving equation (7.33). Equation (7.33) is an extremely important equation; it must be fulfilled together with the conservation of the number of particles,

$$
\sum_{\mathbf{k}\alpha} n_{\mathbf{k}\alpha} = N \;\; . \tag{7.34}
$$

In fact, it defines the Fermi surface, and shows, together with equation (7.34), that both the volume and the shape of the Fermi sea are preserved, *i.e.* the Fermi sea is preserved, as expected; this statement is sometimes known as Luttinger's "theorem", and, also, $\mu = \partial E / \partial N$ (for a change in the Fermi distribution at the Fermi surface) is known as van Hove's "theorem". The full variation of E with respect to the Fermi sea (determined in this way) gives the elementary excitations; this variation is

$$
\begin{gathered}
\delta E = \sum\nolimits_{\mathbf{k}\alpha} \varepsilon_{\mathbf{k}} \delta n_{\mathbf{k}\alpha} + \tfrac{1}{V} \sum\nolimits_{\mathbf{k}\mathbf{k}'\alpha\beta} f_{\alpha\beta}(\mathbf{k}, \mathbf{k}') n_{\mathbf{k}\alpha} \delta n_{\mathbf{k}'\beta} + \\
+ \tfrac{1}{2V} \sum\nolimits_{\mathbf{k}\mathbf{k}'\alpha\beta} f_{\alpha\beta}(\mathbf{k}, \mathbf{k}') \delta n_{\mathbf{k}\alpha} \delta n_{\mathbf{k}'\beta} \quad ,
\end{gathered} \tag{7.35}
$$

where it is important to remark that the $n\delta n$-term vanishes; indeed, the δn-variations take a particle from below the Fermi surface and put it above this surface, close to it, the excited states being thus "orthogonal" to the ground-state. Therefore,

$$
\delta E = \sum_{\mathbf{k}\alpha} \varepsilon_{\mathbf{k}} \delta n_{\mathbf{k}\alpha} + \frac{1}{2V} \sum_{\mathbf{k}\mathbf{k}'\alpha\beta} f_{\alpha\beta}(\mathbf{k}, \mathbf{k}') \delta n_{\mathbf{k}\alpha} \delta n_{\mathbf{k}'\beta} \quad , \tag{7.36}
$$

and the energy of an elementary excitation is

$$\widetilde{\varepsilon}_{\mathbf{k}\alpha} = \varepsilon_{\mathbf{k}} + \frac{1}{V}\sum_{\mathbf{k}'\beta} f_{\alpha\beta}(\mathbf{k}, \mathbf{k}')\delta n_{\mathbf{k}'\beta} \ ; \tag{7.37}$$

these are quasiparticles, lying in the vicinity of the Fermi surface (and having the fermion spin). Thus, we recover Landau's theory of the Fermi liquid, the f-function given by equation (7.31) being the scattering amplitude of this theory (interaction), to the first approximation. It is worth remarking here the quadratic structure of the quasiparticle energy given by equation (7.36). The quasiparticle elementary excitation is a particle-hole pair, *i.e.* a particle excited just above the Fermi surface and a hole left just below the Fermi surface; however, the Fermi sea may relax (with an insignificant change in the chemical potential for high densities), and we are left with a particle above the Fermi surface. As it is known, while the ordinary sound cannot propagate as local density oscillations through the ideal gas of quasiparticles with infinite viscosity at zero temperature, the liquid may oscillate as a whole through its quasiparticles, which now support a quasi-classical dynamics; in the sense that their energy, as described by equation (7.37), depends now both on momentum and position, the latter through the variations in the Fermi distribution. The temporal changes in the δn-coordinates are described by the energies $\widetilde{\varepsilon}_{\mathbf{k}\alpha}$, which play the role of the hamiltonian either in the Poisson brackets, or the Boltzmann equation, or in the quantum commutators; yielding in either case, besides the particle-hole excitations, the collective oscillations of the zero sound, which is the quantum guise the ordinary sound takes in Fermi liquids at zero temperature. In principle, these modes add their contribution to energy (and to wavefunctions); contribution that is, however, insignificant in this case.

For strong, or long-range interactions, the validity condition for the perturbation scheme expressed by equation (7.14) may not be fulfilled. While the former case is rather unphysical, the typical example for the latter is provided by the Coulomb interacting electrons. The perturbation scheme may not be valid in terms of the original coordinates of the individual particles, but the many-body ensembles possess additional type of coordinates, called collective coordinates, which describe the variations of particle density, for instance, and the motion of the ensemble as a whole. These collective modes, which correspond to the zero sound discussed above, and which in the case of the electrons are called plasmons, screen the long-range interaction, whose strong effects are spent on the plasmon zero-point oscillations. The remaining screened potential is short range, and the perturbation scheme may be valid for it. This particular effect is called the "random phase approximation";[9] obviously, it is not a perturbation effect, though it can be obtained by perturbation-theory techniques, *e.g.*, by summing up a sub-series of perturbations (which, however, is not, formally, convergent). Basically, the "random phase approximation" means the reduction of sums like

$$\sum_i e^{i\mathbf{q}\mathbf{r}_i} \quad , \tag{7.38}$$

where the summation is over all the randomly distributed particles, to

$$\sum_i e^{i\mathbf{q}\mathbf{r}_i} \cong N\delta_{\mathbf{q}0} \quad ; \tag{7.39}$$

the approximation is valid for high concentrations, affects the long-range components of the motion, and has the aspect of a (self-consistent) mean-field, since it does not depend anymore on the particle coordinates. A derivation of the (static) random phase approximation for fermions can be obtained in the following manner. Suppose that when the interaction is switched on, the particle density changes from n_0 to n by the amount δn; the corresponding change in the kinetic energy is

$$\delta K = \int d\mathbf{r} \cdot \mu\delta n \quad , \tag{7.40}$$

where μ is the chemical potential. According to the random phase approximation, this change may be written as

$$\mu\delta n_\alpha = (3/2)n_\alpha\delta\varepsilon_\alpha \quad , \tag{7.41}$$

since $\mu \sim \varepsilon \sim k_F^2$ and $n \sim k_F^3$; noteworthy, n_α in equation (7.41) is half the concentration, and, though not very relevant, the spin labels are introduced. The change in the kinetic energy corresponds to a variation $-\varphi$ of the potential energy (mean-field),

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[9] D. Bohm and D. Pines, "A collective description of electron interactions: III. Coulomb interactions in a degenerate electron gas", Phys. Rev. **92** 609 (1953); D. Pines, "A collective description of electron interactions: IV. Electron interaction in metals", Phys. Rev. **92** 626 (1953).

$$\delta K = \int d\mathbf{r} \cdot \mu \delta n = -\varphi = \int d\mathbf{r} \cdot n_{0\alpha} \delta \varepsilon_{\alpha} \quad , \tag{7.42}$$

where the spin summations are included. The total potential energy

$$\varphi + U = \varphi + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \cdot v_{\alpha\beta}(\mathbf{r} - \mathbf{r}') n_{0\alpha}(\mathbf{r}) n_{0\beta}(\mathbf{r}') \tag{7.43}$$

should be minimized (the form given by equation (7.25) is used for interaction, ignoring the self-interaction). The variation of equation (7.43) leads to

$$-\delta\varepsilon_{\alpha} + \int d\mathbf{r}' \cdot v_{\alpha\beta}(\mathbf{r} - \mathbf{r}') n_{0\beta}(\mathbf{r}') = 0 \ ; \tag{7.44}$$

obviously, the total energy $K + \delta K + \varphi + U = K + U$ is left unchanged. Using equation (7.41) we get

$$-\frac{2\mu}{3n_{\alpha}} \delta n_{\alpha} + \int d\mathbf{r}' \cdot v_{\alpha\beta}(\mathbf{r} - \mathbf{r}') n_{0\beta}(\mathbf{r}') = 0 \quad , \tag{7.45}$$

or

$$-\frac{2\mu}{3n_{\alpha}} \delta n_{\alpha} + \int d\mathbf{r}' \cdot v_{\alpha\beta}(\mathbf{r} - \mathbf{r}') \left[n_{\beta}(\mathbf{r}') - \delta n_{\beta}(\mathbf{r}') \right] = 0 \ . \tag{7.46}$$

The two equations above are easily solved for δn_{α} by Fourier transforms; though not very realistic, we assume, for the sake of some generality, $v_{\alpha\beta} = v + \alpha\beta \cdot u$, where $\alpha, \beta = \pm 1$ for one-half spin fermions; we get

$$\delta n_{\mathbf{q}\alpha} = \frac{3n_{\alpha}}{2\mu} v_{\alpha\beta}(\mathbf{q}) n_{0\mathbf{q}\beta} = \frac{3n_{\alpha}}{2\mu} \widetilde{v}_{\alpha\beta}(\mathbf{q}) n_{\mathbf{q}\beta} \quad , \tag{7.47}$$

where

$$\widetilde{v}(\mathbf{q}) = \frac{v(\mathbf{q})}{1 + 3nv(\mathbf{q})/2\mu} \tag{7.48}$$

and

$$\widetilde{u}(\mathbf{q}) = \frac{u(\mathbf{q})}{1 + 3nu(\mathbf{q})/2\mu} \ . \tag{7.49}$$

Using equation (7.47) the interaction given by equations (7.25) and (7.27) can be written as

$$\begin{aligned} U = \tfrac{1}{2}\int d\mathbf{r}d\mathbf{r}'\cdot v_{\alpha\beta}(\mathbf{r}-\mathbf{r}')n_{0\alpha}(\mathbf{r})n_{0\beta}(\mathbf{r}') \cong \\ \simeq \tfrac{1}{2}\int d\mathbf{r}d\mathbf{r}'\cdot \widetilde{v}_{\alpha\beta}(\mathbf{r}-\mathbf{r}')n_{\alpha}(\mathbf{r})n_{\beta}(\mathbf{r}') \end{aligned} \tag{7.50}$$

(up to the self-interaction), and the Fermi liquid theory can now be started as before, with the f-function given by

$$f_{\alpha\beta}(\mathbf{k},\mathbf{k}') = \widetilde{v}_{\alpha\beta}(0) - \widetilde{v}_{\alpha\alpha}(\mathbf{k}-\mathbf{k}')\delta_{\alpha\beta} \tag{7.51}$$

(in the "jellium" model the direct term $\widetilde{v}_{\alpha\beta}(0)$ is cancelled by the stabilizing background). We can see that the bare potential is replaced by the screened (or dressed) potential; remarkably, the dressing factor $nv(\mathbf{q})/\mu$ is, practically, the same as the parameter $\overline{v}/(\hbar^2/ma^2)$ by means of which the validity of the perturbation theory is assessed by equation (7.14). This is why the potential dressing is irrelevant for weak short-range interaction, while for strong, long-range interaction the validity of the perturbation theory may remain, in principle, to be checked for the dressed interaction; for Coulomb interacting electrons it does not hold (it is worth noting that the derivation of the random phase approximation given above is not perturbational). In general, higher-order contributions of the perturbation theory, beyond the Hartree-Fock approximation and random phase approximation, which imply what is called (interaction) vertex corrections, are not warranted, because they are associated with self-interaction.[10] In addition, we should note that both the Hartree-Fock approximation and the random phase approximation preserve the one-particle character of the theory (they renormalize separately the particles and the interaction), while the vertex corrections affect the particle interaction and destroy the one-particle nature of the theory. In this context we should remember that we use sums of separable products of one-particle wavefunctions (avoiding the entanglement of the wavefunctions); this procedure requires the results to be obtained in terms of quasiparticles and collective excitations (the latter being associated with the renormalization of the interaction). Therefore, going further with the perturbation theory, beyond the Hartree-Fock and random phase approximations, would mean corrections of the order of the lifetime of the elementary excitations, which is meaningless.[11]

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[10] M. Apostol, "On the vertex function method in the Tomonaga-Luttinger model", J. Phys. **C16** 665 (1983).

The Fourier transform of the Coulomb potential (interaction) is $v(q) = 4\pi e^2/q^2$, where e is the electron charge; we assume $u = 0$ (spin-independent interaction). Then,

$$\widetilde{v}(q) = \frac{4\pi e^2}{q^2 + 4\pi e^2(3n/2\mu)} \ ; \tag{7.52}$$

the quantity q_{TF} given by $q_{TF}^2 = 4\pi e^2(3n/2\mu)$ is known as the Thomas-Fermi vector (parameter); the Fourier transform of equation (7.52) gives a screened Coulomb potential $4\pi e^2 e^{-q_{TF}r}/r$. The change $\delta\mu$ in the chemical potential due to a slight spatial imbalance $\delta n(\mathbf{r})$ in the particle concentration is $\delta\mu = v_F \delta p_F = (\pi^2\hbar^3 v_F/p_F^2)\delta n$ (the total spatial variation of the Fermi distribution vanishes, such that the quasiparticle interaction does not contribute to this change); this change equals the potential energy $-e\varphi$, which must satisfy the Poisson equation $k^2\varphi = 4\pi e + 4\pi e\delta n = 4\pi e - (4e^2 p_F^2/\pi\hbar^3 v_F)\varphi$; hence, the Thomas-Fermi (Debye) screening of the Coulomb potential. Making use of the concentration $n = k_F^3/3\pi^2 = 1/a^3$ and the chemical potential (Fermi energy) $\mu = \hbar^2 k_F^2/2m$, where k_F is the Fermi wavevector and a is the mean inter-particle separation distance, we get $q_{TF} \simeq 2/\sqrt{aa_H}$, where $a_H = \hbar^2/me^2 \simeq 0.53\text{Å}$ is the Bohr radius ($\hbar \simeq 10^{-27} erg \cdot s$, $m \simeq 10^{-27} g$, $e = -4.8 \times 10^{-10} esu$). The separation distance a for electrons in metals is of the order a_H (concentration $\simeq 10^{22} - 10^{23} cm^{-3}$); therefore, q_{TF} is of the order k_F in this case. According to equation (7.51), the exchange effects introduce a spin-dependent interaction. For parallel spins, except for a small region where $\mathbf{k} \simeq \mathbf{k}^{'}$(an effect known as the "exchange hole"[12]), the function f given by equation (7.51) is of the order $f \simeq 4\pi e^2/k_F^2$, *i.e.* the same order of the function f for antiparallel spins. We can see that the "dressed" spin effect is small; on the other hand, according to equations (7.7) and (7.37), a constant function f (independent of the point on the Fermi surface), gives a vanishing contribution to the quasiparticles, since δn is of the form $\delta^{'}(\varepsilon-\mu)$ (particle-hole excitations). We can say that the screening of the long-range Coulomb potential, due to the long-range collective effects, provides a screened, short-range potential with small effects on the quasiparticles.

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[11] M. Apostol, *Electron Liquid*, apoma, Magurele (2000).

[12] J. C. Slater, *Quantum Theory of Molecules and Solids*, vol.1, *Electronic Structure of Molecules*, McGraw-Hill, NY (1963); "The electronic structure of metals", Revs. Mod. Phys. **6** 209 (1934).

As we can see from equation (7.52), the screening is effective for $q \rightarrow 0$: the long-range interactions reduce the electron interactions to a short-range potential. In the opposite limit $q \rightarrow \infty$ the potential $\widetilde{v}(q)$ remains unscreened, *i.e.* the short-range interactions do not affect the long-range potential. Apart from variations $\delta n_{\mathbf{k}} = \delta(c_{\mathbf{k}}^{+} c_{\mathbf{k}})$ of the fermion occupancy in the neighbourhood of the Fermi surface, which may be called individual (or quasiparticle) variations, because they are independent of one another, there exist other variations, of the form $n_{\mathbf{q}} = \sum_{\mathbf{k}} c_{\mathbf{k}} c_{\mathbf{k}+\mathbf{q}}$ (equation (7.23)), where the summation is carried out in the neighbourhood of the Fermi surface and $\mathbf{q}$ is small ($\mathbf{q} \rightarrow 0$); these latter variations may be called collective, because they involve summations over individual particle states. They correspond to (collective) excitations with energy $\mathbf{v}_F \mathbf{q}$ and interactions given by equations (7.25) and (7.27) (where $n_{\mathbf{q}}$ are the variations of the occupancy, *i.e.* they are similar with $\delta n_{\mathbf{k}}$). From equation (7.27) we get the function $f_{\alpha\beta} = v_{\alpha\beta}(\mathbf{q})$ for these excitations (where f depends on $\mathbf{k}-\mathbf{k}^{'}=\mathbf{q}$). The collective excitations are the second type of elementary excitations in Fermi liquids (and, in general, in condensed matter ensembles).

The zero-point contribution of the collective modes should be added to the ground-state energy (and to the wavefunction). A competition appears between the long-range oscillations of the collective modes and the short-range contribution of the individual motion of the particles; this competition may be resolved, in principle, by minimizing the ground-state energy with respect to this splitting of the total number of the degrees of freedom between quasiparticles and collective modes.

7.3 Effective mass

According to Galileo's principle of relativity the momentum of the liquid is given by

$$\int d\tau\cdot\mathbf{p}n=m\int d\tau\cdot\frac{\partial\varepsilon}{\partial\mathbf{p}}n\ \ ; \tag{7.53}$$

for a quasiparticle distortion δn we obtain

$$\begin{aligned}\int d\tau\cdot\mathbf{p}\delta n=m\int d\tau\cdot\tfrac{\partial\varepsilon}{\partial\mathbf{p}}\delta n+\tfrac{m}{V}\int d\tau d\tau'\cdot\tfrac{\partial f}{\partial\mathbf{p}}n\delta n'=\\ =m\int d\tau\cdot\tfrac{\partial\varepsilon}{\partial\mathbf{p}}\delta n-\tfrac{m}{V}\int d\tau d\tau'\cdot f\tfrac{\partial n'}{\partial\mathbf{p}'}\delta n\quad ,\end{aligned} \tag{7.54}$$

or

$$\frac{\mathbf{p}}{m^*}=\frac{\mathbf{p}}{m}-\frac{g}{(2\pi\hbar)^3}\int ds'\cdot\frac{\mathbf{v}'_F}{v'_F}f(\mathbf{p},\mathbf{p}'_F)\quad , \tag{7.55}$$

where m^*, defined by $\mathbf{v}=\partial\varepsilon/\partial\mathbf{p}=\mathbf{p}/m^*$, is the quasiparticle mass. For a spherical Fermi surface

$$\frac{1}{m^*}=\frac{1}{m}-g\frac{p_F}{(2\pi\hbar)^3}\int do\cdot\cos\theta\cdot f\quad , \tag{7.56}$$

where θ is the angle between $\mathbf{p}_F$ and $\mathbf{p}'_F$, $do=\sin\theta d\theta d\varphi$ and f depends on p_F and $\cos\theta$ (equation (7.8) is used in deriving equation (7.56)).

Let us calculate the effective mass of the electrons in metals. The direct term in the function f given by equation (7.51) ($\widetilde{v}(q=0)$) is a constant, which does not contribute to the effective mass. We are left with the exchange term

$$f_{\sigma\sigma'}=-\frac{4\pi e^2}{\left|\mathbf{k}-\mathbf{k}'\right|^2+q_{TF}^2}\delta_{\sigma\sigma'}\quad , \tag{7.57}$$

which gives

$$m^*=m\left\{1+\frac{1}{\pi a_H k_F}\left[2+\left(1+\frac{q_{TF}^2}{2k_F^2}\right)\ln\frac{q_{TF}^2/2k_F^2}{2+q_{TF}^2/2k_F^2}\right]\right\}\quad , \tag{7.58}$$

where $a_H=\hbar^2/me^2$ is the Bohr radius; for the electron concentrations in metals the correction brought by the Coulomb interaction to the electron mass is very small. If the term q_{TF}^2 is neglected in the denominator of the function $f_{\sigma\sigma'}$ and the integration is performed for $|\mathbf{k}-\mathbf{k}'| > k_c$, where k_c is a wavevector cut-off, we get

$$m^* = m\left\{1 + \frac{1}{\pi a_H k_F}\left[1 - \beta^2/4 + \ln(\beta/2)\right]\right\} \quad , \tag{7.59}$$

where $\beta = k_c/k_F$. For electrons at metallic concentrations $\beta \simeq 1$ from the minimum of the ground-state energy (zero-point plasmon contribution included), such that the electron mass is practically left undressed (sometimes, the separation between quasiparticles and plasmons is not complete, and an electron-plasmon coupling may arise, which brings a very small contribution to the electron effective mass).[13]

7.4 Zero sound

A displacement field $\mathbf{u}$ generates a volume change $\delta V = V\,div\mathbf{u}$; for sound, which is adiabatic, this implies a potential energy per unit volume $-(1/2V)(\partial p/\partial V)(\delta V)^2$, which obviously implies the (adiabatic) compressibility $\kappa = -(1/V)(\partial V/\partial p)$, where p denotes the pressure; this energy can further be written as $(\rho/2)(\partial p/\partial\rho)(div\mathbf{u})^2$, where $\rho = mN/V$ is the density; the corresponding kinetic energy per unit volume is $\rho\dot{\mathbf{u}}^2/2$, so that the sound velocity u is given by

$$u^2 = \partial p/\partial\rho = -\frac{V^2}{mN}\frac{\partial p}{\partial V} = \frac{1}{\rho\kappa} \quad . \tag{7.60}$$

Since $Nd\mu = Vdp - SdT$, we get for vanishing temperatures (where there is no need to distinguish between adiabatic and isothermal compressibility)

$$u^2 = -\frac{V}{m}\frac{\partial\mu}{\partial V} = \frac{N}{m}\frac{\partial\mu}{\partial N} \quad , \tag{7.61}$$

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[13] D. Bohm and D. Pines, "A collective description of electron interactions: III. Coulomb interactions in a degenerate electron gas", Phys. Rev. **92** 609 (1953); D. Pines, "A collective description of electron interactions: IV. Electron interaction in metals", Phys. Rev. **92** 626 (1953).

where we use the fact that the chemical potential μ depends only on the concentration N/V. This equation may serve to determine the chemical potential. Now,

$$\delta\mu = \frac{\partial\varepsilon}{\partial\mathbf{p}_F}\delta\mathbf{p}_F + \frac{1}{V}\int d\tau' \cdot f\delta n' \quad , \tag{7.62}$$

which agrees with equation (7.10), and where the effective mass m^* should be used (because it is a local change in the density); it is also worth remarking that the changes associated with the compressibility amount, naturally, to changes in the distribution at the Fermi surface. The first term in the right-hand side of equation (7.62) gives $\left[(2\pi\hbar)^3/4\pi gVm^*p_F\right]\delta N$ for an isotropic Fermi sea; the second term gives $\left[(1/4\pi V)\int do' \cdot f\right]\delta N$, such that

$$u^2 = \frac{p_F^2}{3mm^*} + \frac{N}{4\pi mV}\int do' \cdot f(\mathbf{p}_F, \mathbf{p}'_F) \quad , \tag{7.63}$$

or

$$u^2 = \frac{p_F^2}{3m^2} + \frac{gp_F^3}{3m(2\pi\hbar)^3}\int do' \cdot (1-\cos\theta)\, f(\mathbf{p}_F, \mathbf{p}'_F) \quad . \tag{7.64}$$

However, it is worth noting that the sound does not propagate in a Fermi liquid at vanishing temperatures, as a consequence of its total absorption by the particle-hole excitations; this is called the quasiparticle damping of the sound. Indeed, the absorption coefficient of the sound is defined as $\gamma \sim 1/\omega\tau_s \sim \lambda/l$, where ω is the sound frequency, λ is its wavelength, τ_s is the sound lifetime and l is the mean freepath of the sound; by definition l is proportional to the viscosity. For $\omega\tau \ll 1$, where τ is the quasiparticle lifetime, the frequency is so low that only the temperature effects govern the quasiparticles lifetime; consequently, the absorption rate is $\gamma \sim \omega^2/T^2$ (since, by using its probabilistic nature, $\tau_s \sim (1/\omega)(1/\omega\tau)(1/\omega)$, where a characteristic frequency due to the interaction processes appears in the last factor); hence, the sound cannot be propagated at vanishing temperatures, where the viscosity of the quasiparticles is infinite. For $\omega\tau \gg 1$ the thermal effects are negligible, and the absorption rate goes, obviously, like $\gamma \sim \omega^2$.[14] A minimum of γ appears evidently in-between, of the order of $\gamma \sim T^2$, which shows that a certain sound-type disturbance can be propagated even at vanishing temperature; obviously, this is nothing but a local perturbation in the quasiparticles density, *i.e.* a space-time perturbation of the Fermi distribution; this perturbation is called zero sound, in order to distinguish it from the ordinary, first, sound (and to distinguish it from the second sound which may propagate in superfluids; or in the phonon gas). The zero sound (like the superfluid sound u) is, in fact, ordinary sound propagating in the context of interaction and at low temperatures, *i.e.* the guise which the ordinary sound takes in quantum liquids.

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[14] I. Pomeranchuk, "On the theory of liquid He^3", ZhETF **20** 919 (1950) (in Russian); L. Landau, "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1057) (ZhETF **32** 59 (1957)).

The slight space-time changes in the particle distribution are described by the kinetic (Boltzmann) equation

$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial \mathbf{r}}\frac{\partial \varepsilon}{\partial \mathbf{p}} - \frac{\partial n}{\partial \mathbf{p}}\frac{\partial \varepsilon}{\partial \mathbf{r}} = 0 \quad , \tag{7.65}$$

where the collision rate of the quasiparticles is too low to be kept in the right-hand side; and obviously the motion must satisfy $\omega\tau \gg 1$, as being the motion of the quasiparticles. For $n = n_0 + \delta n$, where n_0 is the unperturbed Fermi distribution and δn is an ω, $\mathbf{k}$-wave, we get

$$(\omega - \mathbf{pk}/m^*)\,\delta n = \mathbf{pk}\frac{gp_F}{(2\pi\hbar)^3}\int do' \cdot f\delta n' \quad , \tag{7.66}$$

for a spherical Fermi surface. Noteworthy, the changes in the distribution are localized at the Fermi surface. This is a typical equation describing the self-consistent effects of interacting particles (and, in a different form, it is called the Bethe-Salpeter equation). In principle, the f-function may depend on spin, too, in which cases spin summations are included in the g factor. First, the equation is solved for the spin dependence of the change δn, the solution describing thus both particle- and spin-density waves. Thereafter, it is easy to see that we should use the scattering amplitude corresponding to the collective excitations, because δn in equation (7.66) is a density variation; this scattering amplitude is $f = v(\mathbf{q})$, $\mathbf{q} \to 0$; we denote it by $f(0)$ (spin effects can be included). Under these circumstances equation (7.66) amounts to

$$\frac{2\pi^2\hbar^3}{gm^*p_F f(0)} = \frac{1}{2}\int d\theta \cdot \sin\theta \frac{\cos\theta}{s - \cos\theta} \quad , \tag{7.67}$$

where $s = \omega/v_F k$; the integral is $-1-(s/2)\ln|(s-1)/(s+1)|$ (which, sometimes, is called the Lindhard function); equation (7.67) has solution only for $f(0) > 0$, which amounts to repulsive interaction, and for $s = \omega/v_F k > 1$; the latter condition ensures the absence of the excitation processes for the quasiparticles, *i.e.* the existence of the quasiparticles that propagate the zero sound. For small values of the left-hand side the solution is obtained for $s \to \infty$, where the integral goes like $1/3s^2$; we get

$$\omega = \left[\frac{2}{gm^*}\frac{N}{V}f(0)k^2\right]^{1/2} \quad . \tag{7.68}$$

The result given by equation (7.68) is particularly relevant for interacting electrons ($g = 2$), where $f(0) = 4\pi e^2/k^2$, *i.e.* the Fourier transform of the Coulomb potential; indeed, in the long wavelength limit $k \to 0$ this is a strong coupling, and the corresponding frequency

$$\omega = \left(\frac{4\pi ne^2}{m}\right)^{1/2} \tag{7.69}$$

is that of the particle-density waves called plasmons (due to the long-range correlations the bare mass of the electrons is practically left unchanged).

On the contrary, in the opposite limit of high values of the left-hand side of equation (7.67) we get the genuine zero sound frequency

$$\omega = v_F\left\{1 + 2\exp\left[-4\pi^2\hbar^3/gm^*p_F f(0)\right]\right\}k \quad , \tag{7.70}$$

where $f(0) = v(0)$, *i.e.* the long-wavelength limit of the (short-range) original particle interaction. Despite the fact that it appears as affecting only one-particle states (and in contrast with the quasiparticles), the zero sound (as well as the sound in superfluids) is, in fact, generated by the interaction with the other particles; therefore, they are collective modes of the liquid motion, like ordinary sound; and like the plasmons, where the long-range character of the Coulomb interaction affects all the particles.

7.5 Paramagnetic susceptibility

The magnetic momentum of an electron is $2\beta s = \beta\sigma$, where $\beta = e\hbar/2mc$ is the Bohr magneton (2 is the gyromagnetic factor, $s = 1/2$ is the spin and c is the light velocity). In a magnetic field H its energy changes by

$$\delta\varepsilon_\sigma = -\beta\sigma H + \frac{1}{(2\pi\hbar)^3}\sum_{\sigma'}\int d\mathbf{p}'\cdot f_{\sigma\sigma'}\delta n_{\sigma'} \quad ; \tag{7.71}$$

this change takes place at the Fermi surface, so that

$$\delta\varepsilon_\sigma = -\beta\sigma H - \frac{m^* p_F}{4\pi^2\hbar^3}\sum_{\sigma'}\int d\theta\cdot\sin\theta f_{\sigma\sigma'}\delta\varepsilon_{\sigma'} \quad , \tag{7.72}$$

whose solution is

$$\delta\varepsilon_\sigma = -\frac{1}{2}g\beta\sigma H \quad , \tag{7.73}$$

where

$$g^{-1} = \frac{1}{2}\left[1 + \frac{m^* p_F}{4\pi^2\hbar^3}\int d\theta\cdot\sin\theta(f_{\sigma\sigma} - f_{\sigma\overline{\sigma}})\right] \quad , \tag{7.74}$$

with $\overline{\sigma} = -\sigma$. The magnetization is given by

$$\begin{aligned} \chi H &= \tfrac{\beta}{(2\pi\hbar)^3}\textstyle\sum_\sigma \int d\mathbf{p}\cdot\sigma\delta n_\sigma = \\ &= -\tfrac{\beta m^* p_F}{2\pi^2\hbar^3}\textstyle\sum_\sigma \sigma\delta\varepsilon_\sigma = \tfrac{\beta^2 m^* p_F}{2\pi^2\hbar^3}gH \quad , \end{aligned} \tag{7.75}$$

whence the spin susceptibility

$$\chi = \frac{\beta^2 m^* p_F}{2\pi^2\hbar^3}g \quad . \tag{7.76}$$

Making use of equation (7.59) we get

$$\chi \simeq \frac{\beta^2 m p_F}{\pi^2\hbar^3}\left[1 + \frac{me^2}{\pi\hbar p_F}\ln(\beta/2)\right] \tag{7.77}$$

for electrons. This is called the Pauli paramagnetism[15] (the orbital motion of the electrons gives the Landau diamagnetism, which is minus one-third of the χ above[16]).

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[15] W. Pauli, "Uber Gasentartung und Paramagnetismus", Z. Phys. **41** 81 (1927).

[16] L. Landau, "Diamagnetismus der Metalle", Z. Phys. **64** 629 (1930)

7.6 Thermodynamics

The number of particles at finite temperatures is given by

$$N = g\frac{V}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot n \quad , \tag{7.78}$$

where n is the Fermi distribution. Let F be given through f by

$$F = g\frac{V}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot fn \ ; \tag{7.79}$$

according to the properties of the Fermi distribution it may be written as

$$\begin{gathered} F = g\tfrac{V}{(2\pi\hbar)^3}\int \tfrac{dsd\varepsilon}{v}\cdot fn = g\tfrac{V}{(2\pi\hbar)^3}\int dod\varepsilon\cdot\left(p^2f/v\right)n = \\ = g\tfrac{V}{(2\pi\hbar)^3}\int do\left[\int_0^\mu d\varepsilon\cdot\left(p^2f/v\right)+\tfrac{\pi^2T^2}{6}\left(p^2f/v\right)'_\mu+...\right] = \\ = F_0 + g\tfrac{V}{(2\pi\hbar)^3}\int do \\ \left[\left(p^2f/v\right)_{\mu_0}\delta\mu+\tfrac{\pi^2T^2}{6}\left(p^2f/v\right)'_{\mu_0}+...\right] \quad , \end{gathered} \tag{7.80}$$

where F_0 is the quantity F at zero temperature and μ_0 is the chemical potential at zero temperature. For a spherical Fermi surface and the conserved number of particles one obtains

$$\delta\mu = -\pi^2T^2m^*/6p_F^2 \ \ . \tag{7.81}$$

The change in energy can be written as

$$\delta E = g\frac{V}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot\varepsilon(n-n_0) \quad , \tag{7.82}$$

where n_0 denotes the Fermi distribution at zero temperature; by using equation (7.80) for a spherical Fermi surface one obtains

$$\delta E = g\frac{V}{12\hbar^3}m^*p_FT^2 = \frac{\pi^2T^2}{2p_F^2}m^*N \ ; \tag{7.83}$$

hence, the entropy

$$S = g\frac{V}{6\hbar^3}m^* p_F T \quad , \tag{7.84}$$

the free energy

$$\delta F = -g\frac{V}{12\hbar^3}m^* p_F T^2 \quad , \tag{7.85}$$

the heat capacity

$$C = g\frac{V}{6\hbar^3}m^* p_F T = S \quad ; \tag{7.86}$$

as well as the change in pressure

$$\delta p = g\frac{1}{18\hbar^3}m^* p_F T^2 \quad . \tag{7.87}$$

The thermodynamic potentials Ω and Φ change by

$$\delta\Omega = \delta\Phi = \delta F = -g\frac{V}{12\hbar^3}m^* p_F T^2, \tag{7.88}$$

when expressed in proper variables, *i.e.* μ instead of N, and p instead of V in δF. Noteworthy, $\delta\Omega_0 = -N\delta\mu$, such that the total change in Ω is $-(gV/18\hbar^3)m^* p_F T^2 = -2\delta E/3 = -\delta(pV) = -V\delta p$. Similarly, the change in Φ_0 is $V\delta p$, which together with equation (7.87) lead to a total change $-(gV/36\hbar^3)m^* p_F T^2 = \delta(\mu N) = N\delta\mu$ in Φ. From equation (7.87) one can see easily that $C_p - C_v \sim T^3$ (as expected from $S \sim T$); therefore, there is no need to distinguish between the two heat capacities (in particular, the zero sound contributes insignificantly to the thermodynamic properties). By using again equation (7.87) one finds the coefficient of thermal expansion $(1/V)(\partial V/\partial T)_p = -(gT/6V\hbar^3)\partial(m^* p_F)/\partial p$, with $\partial\Phi/\partial p = V$; one can see that its ratio to the heat capacity is independent of temperature (this is knwon as Gruneisen's law).

We note here dimensionality effects in fermion thermodynamics. For instance, the quantization along the transverse direction in a slab with thickness d introduces a series of discrete levels, with a characteristic energy $\hbar^2/md^2$. Consequently, a crossover temperature appears and an Euler-Maclaurin formula is used to estimate surface effects in thermodynamic quantities.[17] Also, the thermodynamics of fermions in two dimensions is the same as the thermodynamics of bosons in two dimensions.[18]

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[17] M. Apostol, "Fermions in a slab", J. Theor. Phys. **18** (1996); "Specific heat of charged fermions in magnetic field", J. Theor. Phys. **16** (1996).

Liquid He^3, under normal pressure, has a Fermi wavevector $p_F/\hbar \sim 0.8\text{Å}^{-1}$ (from density), an effective mass $m^* \sim 2.4m$ (from the heat capacity), and a sound velocity $u \sim 190$m/s (from compressibility).

The Landau theory of the Fermi liquid is described by Abrikosov and Khalatnikov;[19] the spin diffusion in He^3 is discussed by Hone.[20]

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[18] M. Apostol, "Dimensionality effects in the ideal Fermi and Bose gases", Phys. Rev. **E56** 4854 (1997).

[19] A. A. Abrikosov and I. M. Khalatnikov, "The theory of a Fermi liquid (the properties of He^3 at low temperatures", Reps. Progr. Phys. **22** 329 (1959).

[20] D. Hone, "Self-diffusion in He^3", Phys. Rev. **121** 669 (1961).

8 Electron Liquid

8.1 Introduction

This chapter is devoted to metals. We have seen in the "Kinetics of Plasma" chapter that the electrons are correlated with the ions, such that plasma can acquire a solid phase at sufficiently low electron temperature (but still high), sufficiently low ion temperature and sufficiently high densities (see Fig. 5.4 - Fig. 5.6). The thermodynamics of plasma is governed by ion thermodynamics. The plasma solid can be either classical or quantum-mechanical, with respect to the motion of the electrons. The individual ionic motion in the solid is quantum-mechanical (or quasi-classical quantum-mechanical); it is a collective motion which generates phonons. The classical plasmonic solid is little investigated. The relatively high electron temperature is transformed into mechanical motion in the quantum-mechanical solid, where the electrons are either absorbed into the atoms or form a Fermi sea, or both. The solid may be crystalline or amorphous, with a mean inter-atomic distance of the order of a few angstroms, within a range of temperatures up to a few thousands degrees.

The first question which appears for solids is their cohesion. The electrons can be transferred, totally or partially, between neighbouring atoms, giving rise to an ionic solid, where the electrons have a low mobility, with distortion of the ionic lattice. The electrons can be shared between neighbouring atoms, giving rise to covalent solids, like semiconductors. The atoms can be tied together by polarization forces, like in molecular solids; or they can form a solid by hydrogen bonds; etc. A special case occurs in metals, where the electrons are delocalized over all the atoms, giving rise to a Fermi sea; in crystalline metals they form energy bands (in amorphous solids, like alloys for instance, the electrons are localized, their mobility is low).

8.2 Metallic cohesion

Let us assume a set of $N \gg 1$ identical atoms. They may release a fraction z of their valence electrons, which may acquire a motion over the whole macroscopic ensemble, thus forming a Fermi sea; on each delocalized orbital there exists a fraction of electrons, the remaining electrons being located on atomic orbitals. The delocalized (plane wave) wavefunction of each state is connected to the atomic orbital of origin. Therefore, we have a set of N positive ions, each with charge ze, and a set of zN electrons, each with charge $-e$ ($e = 4.8 \times 10^{-10} esu$). The electron density is $n = k_F^3/3\pi^2$ and the Fermi level is $\mu = \hbar^2 k_F^2/2m$, where m is the electron mass and k_F is the Fermi wavevector ($\hbar = 10^{-27} erg \cdot s$ is Planck's constant). We assume point ions placed at positions R_i, $i = 1, 2, ...N$ (label j will also be used for ionic positions). It is convenient to describe the electrons in terms of the second-quantization operators $\psi_\alpha(\mathbf{r})$, $\psi_\alpha^*(\mathbf{r})$, where α is the spin label (β will also be used for spin). The Coulomb interaction energy is denoted by v.

The Hartree-Fock energy of the ground-state of the ensemble is given by

$$E = E_{kin} + E_{e-i} + E_{e-e,H} + E_{e-e,F} + E_{i-i} \quad , \tag{8.1}$$

where

$$E_{kin} = \sum_\alpha \int d\mathbf{r} \cdot [\psi_\alpha^* (\mathbf{p}^2/2m) \psi_\alpha] \tag{8.2}$$

is the kinetic energy of the electrons,

$$E_{e-i} = -ze^2 \sum_{i\alpha} \int d\mathbf{r} v(\mathbf{r} - \mathbf{R}_i) [\psi_\alpha^*(\mathbf{r}) \psi_\alpha(\mathbf{r})] \tag{8.3}$$

is the electron-ion Coulomb attraction,

$$E_{e-e,H} = \frac{1}{2} e^2 \sum_{\alpha\beta} \int d\mathbf{r} d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') [\psi_\alpha^*(\mathbf{r}) \psi_\alpha(\mathbf{r})][\psi_\beta^*(\mathbf{r}') \psi_\beta(\mathbf{r}')] \tag{8.4}$$

is the Hartree (direct) electron-electron Coulomb repulsion,

$$E_{e-e,F} = -\frac{1}{2} e^2 \sum_{\alpha} \int d\mathbf{r} d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') [\psi_\alpha^*(\mathbf{r}) \psi_\alpha(\mathbf{r}')][\psi_\alpha^*(\mathbf{r}') \psi_\alpha(\mathbf{r})] \tag{8.5}$$

is the Fock (exchange) electron-electron Coulomb attraction and

$$E_{i-i} = \frac{1}{2} z^2 e^2 \sum_{i \neq j} v(\mathbf{R}_i - \mathbf{R}_j) \tag{8.6}$$

is the ion-ion Coulomb repulsion. The brackets in the above equations indicate the mean values over the Fermi sea; $p = -i\hbar\partial/\partial\mathbf{r}$ is the electron momentum and the electron wavefunctions are plane waves. It is easy to see that for a uniform Fermi sea the electron-ion and the Hartree electron-electron energies are infinite. It is convenient to introduce the Hartree potential

$$\begin{aligned} \varphi(\mathbf{r}) = ze \textstyle\sum_i v(\mathbf{r} - \mathbf{R}_i) - e \sum_\alpha \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}')[\psi_\alpha^*(\mathbf{r}')\psi_\alpha(\mathbf{r}')] = \\ = ze \textstyle\sum_i v(\mathbf{r} - \mathbf{R}_i) - e \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') \ \ , \end{aligned} \tag{8.7}$$

where

$$n(\mathbf{r}) = \sum_\alpha [\psi_\alpha^*(\mathbf{r})\psi_\alpha(\mathbf{r})] \tag{8.8}$$

is the electron density (averaged over the Fermi sea). The potential $\varphi(\mathbf{r})$ consists of two parts; an ion (core) potential

$$\varphi_c(\mathbf{r}) = ze \sum_i v(\mathbf{r} - \mathbf{R}_i) \tag{8.9}$$

and an electron potential

$$\varphi_e(\mathbf{r}) = -e \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') \ ; \tag{8.10}$$

the electron-ion and Hartree electron-electron energies can be written as

$$\begin{aligned} E_{e-i} + E_{e-e,H} = -\tfrac{1}{2} e \int d\mathbf{r} \varphi_e(\mathbf{r}) n(\mathbf{r}) - e \int d\mathbf{r} \varphi_c(\mathbf{r}) n(\mathbf{r}) = \\ = -\tfrac{1}{2} e \int d\mathbf{r} [\varphi(\mathbf{r}) + \varphi_c(\mathbf{r})] n(\mathbf{r}) \ . \end{aligned} \tag{8.11}$$

By definition, the potential φ satisfies the Poisson equation

$$\Delta\varphi = -4\pi e z \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi e n(\mathbf{r}) \ ; \tag{8.12}$$

the equilibrium of the ions-electrons ensemble requires

$$\mu(\mathbf{r}) - e\varphi(\mathbf{r}) = 0 \ . \tag{8.13}$$

Equation (8.13) shows that the chemical potential μ should be non-uniform (equation (8.13) reflects the vanishing of the total chemical potential). Since μ depends on the electron density ($\mu = \hbar^2 k_F^2/2m$ and $n = k_F^3/3\pi^2$), it follows that the electron density and the Fermi wavevector k_F depend on position; moreover, equation (8.13) establishes a connection between the electron density n and the potential φ, which allows a solution of the Poisson equation (8.12) and gives the theory a self-consistent character. The connection between n and φ is $n = (2me\varphi/\hbar^2)^{3/2}$. This way, we get the Thomas-Fermi model.[1] However, if we use the 3/2-power dependence $n \sim \varphi^{3/2}$, we preserve the free-electron character of the Fermi sea in the context where the electron density has an abrupt variation in the vicinity of the ions (where the potential goes like $\varphi \sim 1/r$); in those regions the electron wavefunctions cannot be viewed as having a delocalized plane-wave shape. The 3/2-Thomas-Fermi model does not provide an ion-electron binding, as a consequence of the fact that the electrons are excessively accumulated on the ions. This is known as the "no-binding" theorem.[2]

In order to allow for the relaxation of the Fermi sea we should admit that the electron wavefunctions have a quasi-classical character, implying slight spatial variations, which leads to using a linear approximation of the type $\mu = (\hbar^2 \overline{k}_F/2m)k_F$, $n = (\overline{k}_F^2/3\pi^2)k_F$ and

$$n = \frac{q^2}{4\pi e}\varphi \ , \ q^2 = \frac{8me^2\overline{k}_F}{3\pi\hbar^2} = \frac{8\overline{k}_F}{3\pi a_H} \quad , \tag{8.14}$$

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[1] L. H. Thomas, "The calculation of atomic fields", Proc. Cambr. Phil. Soc. **23** 542 (1927); E. Fermi, "Un metodo statistico per la determinazione di alcune proprieta dell'atomo", Rend. Accad. Naz. Lincei **6** 602 (1927); E. Fermi, "Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente", Z. Phys. **48** 73 (1928); P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendungen*, Springer, Berlin (1949).

[2] E. Teller, "On the stability of molecules in the Thomas-Fermi theory", Revs. Mod. Phys. **34** 627 (1962); N. Balazs, "Formation of stable atoms within the statistical theory of atoms", Phys. Rev. **156** 42 (1967); see also L. Spruch, "Pedagogical notes on Thomas-Fermi theory (and on some improvements): atoms, stars and the stability of bulk matter", Revs. Mod. Phys. **63** 151 (1991).

where q^2 and the mean Fermi wavevector $\overline{k}_F$ should be treated as variational parameters;[3] $a_H = \hbar^2/me^2$ is the Bohr radius. Making use of this procedure, the Poisson equation (8.12) becomes

$$\Delta\varphi = -4\pi ez \sum_i \delta(\mathbf{r} - \mathbf{R}_i) + q^2\varphi \ \ , \tag{8.15}$$

whose solution is the screened Coulomb potential

$$\varphi(\mathbf{r}) = ez \sum_i \frac{e^{-q|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r} - \mathbf{R}_i|} \ \ . \tag{8.16}$$

We can see that the linearized Thomas-Fermi theory leads to a distorted (and non-uniform) Fermi sea, which is the result of a random phase approximation (compare with the "Fermi Liquid" chapter); indeed, the Fourier transform of equation (8.15) is

$$\varphi(k) = \sum_i \frac{4\pi ez}{k^2 + q^2} e^{-i\mathbf{k}\mathbf{R}_i} \ \ ; \tag{8.17}$$

the screening length $1/q = (3\pi a_H/8\overline{k}_F)^{1/2}$ is similar with the Debye-Huckel screening length $\lambda = a(aT/4\pi e^2)^{1/2}$, where T is the temperature and a is the mean inter-electron separation distance ($n \simeq 1/a^3$, $k_F \simeq 1/a$). We note that the delocalization of the electrons and the existence of the Fermi sea imply that the solid is a metal.

Having known the potential $\varphi(\mathbf{r})$ we can compute the energy

$$E_{e-i} + E_{e-e,H} = -\frac{q^2}{8\pi} \int d\mathbf{r}(\varphi + \varphi_c)\varphi \tag{8.18}$$

given by equation (8.11); the integrals in equation (8.18) are two-centre integrals; they can be effected by using the elliptic coordinates

$$\begin{gathered} |\mathbf{r} - \mathbf{R}_i| = \tfrac{1}{2}R_{ij}(\lambda + \mu) \ \ , \ \ |\mathbf{r} - \mathbf{R}_j| = \tfrac{1}{2}R_{ij}(\lambda - \mu) \ \ , \\ d\mathbf{r} = \left(\tfrac{1}{2}R_{ij}\right)^3 (\lambda^2 - \mu^2) d\lambda d\mu d\varphi \ \ , \end{gathered} \tag{8.19}$$

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[3] L. C. Cune and M. Apostol, "Ground-state energy and geometric magic numbers for homo-atomic metallic clusters", Phys. Lett. **A273** 117 (2000).

where $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ and $1 < \lambda < \infty$, $-1 < \mu < +1$, $0 < \varphi < 2\pi$.[4] Adding the ion-ion energy E_{i-i} (equation (8.6)), we get the potential energy

$$\begin{gathered} E_{pot} = E_{e-i} + E_{e-e,H} + E_{i-i} = \\ = -\tfrac{qz^2e^2}{4}\left[3N + \textstyle\sum_{i\neq j}\left(1 - \tfrac{2}{q|\mathbf{R}_i - \mathbf{R}_j|}\right)e^{-q|\mathbf{R}_i - \mathbf{R}_j|}\right] \quad . \end{gathered} \tag{8.20}$$

We can see that the ions acquire a self-energy ($\sim N$) and interact through the potentials

$$\Phi_{ij} = -\frac{1}{2}qz^2e^2\left(1 - \frac{2}{q\left|\mathbf{R}_i - \mathbf{R}_j\right|}\right)e^{-q|\mathbf{R}_i - \mathbf{R}_j|} \tag{8.21}$$

which are repulsive for short distances, attractive for long distances, and have a minimum value for $q\left|\mathbf{R}_i - \mathbf{R}_j\right| = 2.73$; these are, in fact, pseudo-potentials, which are valid for distances close to equilibrium. The minimization of the configurational energy $E_{conf} = \frac{1}{2}\sum_{i\neq j}\Phi_{ij}$ with respect to the parameters $\mathbf{x}_i = q\mathbf{R}_i$ gives the equilibrium configuration of the ion-electron ensemble. This is done (numerically) for metallic clusters with a number of ions up to $N = 800$.[5] The (meta-) stable configurations exhibit many isomers, separated from the ground-state by very small energies (of the order meV; $1eV = 1.6\times10^{-12}erg = 1.1\times10^4K$); for some magic numbers N the ground-state is well defined. The crystalline macroscopic configuration with translational symmetry is an open problem in the thermodynamic limit; at the centre of the cluster with $N = 800$ ions (a large cluster) an incipient ordered region can be seen. The vibration spectra (frequency ω) can also be calculated, by $det(\omega^2M\delta_{ij}\delta_{\alpha\beta} - D_{ij}^{\alpha\beta}) = 0$, where M is the ion mass and $D_{ij}^{\alpha\beta} = \partial^2E_{conf}/\partial X_{i\alpha}\partial X_{j\beta}$, α, β being labels for the cartesian coordinates $X_{i\alpha}$, $X_{j\beta}$ of the position vectors $\mathbf{R}_{i,j}$ (the derivatives being taken at the equilibrium positions). At equilibrium the potential energy has the form $-Bq$, where the coefficient B does not depend on q; for a uniform distribution of ions $\sum_j\Phi_{ij} = 0$, such that we may take $B = 3z^2e^2N/4$.

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[4] J. C. Slater, *Quantum Theory of Molecules and Solids*, vol. 1, *Electronic Structure of Molecules*, Mc-Graw-Hill, NY (1963).

[5] L. C. Cune and M, Apostol, *loc. cit.*

In a similar way we compute the kinetic energy (equation (8.2)) and the exchange energy (equation (8.5)). In the linearized Thomas-Fermi theory the kinetic energy $E_{kin} = V\hbar^2 k_F^5/10\pi^2 m$ of the electrons in volume V becomes

$$\begin{aligned} E_{kin} = \tfrac{\hbar^2 \overline{k}_F^4}{10\pi^2 m} \int d\mathbf{r} \cdot k_F = (3/8)^3 \tfrac{\pi\hbar^2 a_H^2 q^6}{5me} \int d\mathbf{r} \cdot \varphi = \\ = \tfrac{27\pi^2}{640} \tfrac{z\hbar^2 a_H^2}{m} N q^4 \ \ ; \end{aligned} \tag{8.22}$$

we denote this energy $E_{kin} = Aq^4/4$, where $A = 27\pi^2 z\hbar^2 a_H^2 N/160m$. The exchange energy[6] $E_{e-e,F} = -Ve^2 k_F^4/4\pi^3$ becomes

$$\begin{aligned} E_{e-e,F} = -\tfrac{e^2 \overline{k}_F^3}{4\pi^3} \int d\mathbf{r} \cdot k_F = \\ = -\tfrac{9ea_H q^4}{128\pi} \int d\mathbf{r} \cdot \varphi = -\tfrac{9}{32} z e^2 a_H N q^2 \ \ ; \end{aligned} \tag{8.23}$$

we denote $E_{e-e,F} = -Cq^2$, where $C = 9ze^2 a_H N/32$.

From equations (8.3) and (8.4) we can see that E_{e-i} and $E_{e-e,H}$ are functionals of the electron density $n(\mathbf{r})$; also, for slight spatial variations the kinetic energy is a functional of density; but the exchange energy (equation (8.5)) implies a delocalized interaction. Consequently, the variations of the parameter q, which govern the variations of the electron density should be taken only in the energy

$$E_{kin} + E_{pot} = Aq^4/4 - Bq \ \ ; \tag{8.24}$$

this energy has a minimum

$$\begin{aligned} E_{kin} + E_{pot} = -\tfrac{3}{4} B (B/A)^{1/3} = -\tfrac{3}{4} Bq = \\ = -\tfrac{3}{8} (15z/\pi^2)^{1/3} (z^2 e^2 N/a_H) \simeq -0.43 z^{7/3} (e^2 N/a_H) \end{aligned} \tag{8.25}$$

for

$$q = (B/A)^{1/3} = (40z/9\pi^2)^{1/3} \frac{1}{a_H} \simeq 0.77 \frac{z^{1/3}}{a_H} \tag{8.26}$$

($E_{kin} = -\frac{1}{4} E_{pot}$); the total energy is obtained by adding the exchange energy

$$E_{e-e,F} = -\frac{1}{8} (15z/\pi^2)^{2/3} (ze^2 N/a_H) \simeq -0.16 z^{5/3} (e^2 N/a_H) \tag{8.27}$$

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[6] M. Apostol, *Electron Liquid*, apoma, Magurele (2000).

(computed at equilibrium value of the parameter q). Using a mean value $x_{ij} = qR_{ij} = 2.73$ we get a mean ion-ion separation distance $R_{ij} = a = (2.73/0.77z^{1/3})a_H$. We can see that the linearized Thomas-Fermi theory provides the binding of the ion-electron ensemble.

It is worth estimating the errors involved in the computation scheme given above. If we separate an ion placed at $\mathbf{R}_i = 0$ and view the others uniformly distributed, we can write the potential φ given by equation (8.16) as

$$\varphi = ez\frac{e^{-qr}}{r} + ez\frac{4\pi}{a^3q^2} \quad , \tag{8.28}$$

where $a = R_{ij}$ is the mean ion-ion separation distance; we can see that the potential has a uniform part (which can be used to estimate the deviation of the average Fermi wavevector from the parameter $\overline{k}_F$ derived here by variational calculus). Since we have assumed slight spatial variations of the electron density, it is this uniform part which brings the main contribution to the electron dynamics. The abrupt part eze^{-qr}/r of the potential in equation (8.28) may be viewed as a correction; an estimation of this correction is

$$\frac{1}{a^3}\int_{r<a} ez\frac{e^{-qr}}{r} = \frac{4\pi ez}{a^3q^2}\left[1-(1+aq)e^{-qa}\right] \quad ; \tag{8.29}$$

this contribution should be compared with the uniform part $4\pi ez/a^3q^2$; we get the correction $(aq+1)e^{-qa}$, which, for q given by equation (8.26) and a given above ($aq = 2.73$) is $\simeq 24\%$. Such corrections (which may be called quantum-mechanical corrections to the quasi-classical description) can be included in the numerical results by solving the Hartree-Fock equations

$$\begin{gathered} -\tfrac{\hbar^2}{2m}\Delta\psi_\alpha - e\varphi\psi_\alpha - \\ -e^2\textstyle\sum_\beta \int d\mathbf{r}' \cdot \frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi^*_\beta(\mathbf{r}')\psi_\beta(\mathbf{r}) \cdot \psi_\alpha(\mathbf{r}') = \varepsilon_\alpha\psi_\alpha \quad ; \end{gathered} \tag{8.30}$$

it is convenient to estimate the Hartree and Fock (exchange) corrections to the ground-state energy, arising from the abrupt part of the potential φ and the Coulomb potential in the vicinity of an ion; these corrections are additional contributions to the main results obtained above; they preserve the Fermi-sea picture for the electrons, with a slightly modified q and an additional contribution to the exchange energy. Since such corrections are of the order of φ in the neighbourhood of an ion (24%), once included, we may say that we have an error $(0.24)^2$, *i.e.* 6%. Since such an error arises from higher-order terms in the perturbation theory (second-order), it is comparable with the quasiparticle lifetime; this is the accuracy limit of the theory of the electron liquid.

The estimation of the errors of the abrupt variation of the potential in the neighbourhood of an ion is similar with the same procedure in the linearized Thomas-Fermi theory for heavy atoms.[7] The 3/2-Thomas-Fermi model has been originally applied to heavy atoms, where it overestimates the atomic binding energy (due to the excess of electrons localized on the atomic nucleus). The linearized Thomas-Fermi theory gives the correct atomic binding energy, the so-called quantum-mechanical corrections (discussed above) included. Moreover, it provides a means of estimating the fraction z of the valence electrons participating in the metallic binding. Indeed, the screened potential in a heavy atom is $\varphi = eZe^{-qr}/r$, where Z is the atomic number and $q = 0.85Z^{1/3}/a_H$; the electron density is $n = q^2\varphi/4\pi e$, such that the fraction of the released electrons is

$$\alpha = \frac{1}{Z}\int_{r<R} d\mathbf{r}n = \frac{q^2}{4\pi}\int_{r<R} d\mathbf{r}\frac{e^{-qr}}{r} = (1+qR)e^{-qR} \quad , \tag{8.31}$$

where R is the atomic radius $R \simeq a_H$. The number of released electrons is $z = \alpha z_0$, where z_0 is the nominal valency; for instance, we get $z = 0.57$ for iron (Fe, $Z = 26$, $z_0 = 2$). The fractional valency is relevant for other electronic and magnetic properties of metals.[8]

8.3 Metals

According to the above discussion the energy of a metallic solid is

$$E = E_{kin} + E_{pot} + E_{conf} + E_{e-e,F} \quad , \tag{8.32}$$

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[7] M. Apostol, "Giant dipole oscillations and ionization of heavy atoms by intense electromagnetic fields", Roum. Reps. Phys. **67** 837 (2015).

[8] M. Apostol, *Electron Liquid*, apoma, Magurele (2000).

where

$$E_{kin} = \frac{1}{4}Aq^4 \ , \ A = \frac{27\pi^2}{160}z\frac{\hbar^2 a_H^2}{m}N \tag{8.33}$$

is the kinetic energy of the electrons,

$$E_{pot} = -Bq \ , \ B = \frac{3}{4}z^2e^2N \tag{8.34}$$

is the potential energy ($E_{e-i} + E_{e-e,H} + E_{i-i}$), of the electron-ion ensemble,

$$\begin{gathered} E_{conf} = \tfrac{1}{2}\sum_{i\neq j}\Phi_{ij} = q\sum_{i\neq j}F(qR_{ij}) \ , \\ F(qR_{ij}) = -\tfrac{1}{4}z^2e^2\left(1 - \tfrac{2}{q|\mathbf{R}_i - \mathbf{R}_j|}\right)e^{-q|\mathbf{R}_i - \mathbf{R}_j|} \end{gathered} \tag{8.35}$$

is the potential energy of the ion configuration and

$$E_{e-e,F} = -Cq^2 \ , \ C = \frac{9}{32}ze^2a_HN \tag{8.36}$$

is the electron exchange energy. The configurational equilibrium is realized for definite values of the parameters qR_{ij}, whose mean value is $c = qa$ ($c = 2.73$ for the minimum of the potentials Φ_{ij}) and the minimum of the energy $E_{kin} + E_{pot}$ is realized for $q = (B/A)^{1/3} = 0.77z^{1/3}/a_H$ (a is the mean value of the inter-ionic distance R_{ij}); the minimum values are $E_{kin} + E_{pot} = 0.43z^{7/3}(e^2N/a_H)$ (*i.e.*,$-\frac{3}{4}Bq$) and $E_{e-e,F} = -0.16z^{5/3}$. We may limit ourselves to the nearest neighbours g in the configuration energy, which becomes

$$E_{conf} = -\frac{1}{4}qNz^2e^2gf(qa) \ , \ f(x) = \left(1 - \frac{2}{x}\right)e^{-x} \ ; \tag{8.37}$$

the configuration energy at equilibrium is small in comparison with the other energies, such that we may neglect it. Leaving aside the configuration energy we get the total energy

$$E = -\frac{3}{4}Bq - Cq^2 \ . \tag{8.38}$$

The ion-electron ensemble looks like a "Wigner metal", *i.e.* a collection of "quasi-atoms", consisting of electric charges in equilibrium, with a self-energy and slightly interacting with one another; it is a model of a "universal" metal, based upon the screened Coulomb interaction.[9] Equation (8.32) gives reasonable values for the binding energy of metals; for instance, for Fe ($z_{\text{Fe}} = 0.57$) we get a binding energy per atom $E(Fe)/N \simeq -5eV$.

A displacement field $\mathbf{u}$ generates a volume change $\delta V = V\,div\mathbf{u}$; this implies a potential energy per unit volume $-(1/2V)(\partial p/\partial V)(\delta V)^2$, where the compressibility is $\kappa = -(1/V)(\partial V/\partial p)$ and p denotes the pressure; the compressibility κ can be obtained from equation (8.32) by making use of $c = aq$. The kinetic energy is $MN\dot{\mathbf{u}}^2/2$, where M is the ion mass; the sound velocity v_s is given by

$$\begin{aligned} v_s &= 1/\sqrt{\kappa M n} = \\ &= \left[\tfrac{1}{A}(0.43z^{*7/3} + +0.68z^{*5/3})\right]^{1/2} \cdot 1.7 \cdot 10^4 m/s \quad , \end{aligned} \tag{8.39}$$

where n is the atom concentration and A is the atomic mass; for Fe ($A = 56$) we get $v_s \sim 1400m/s$.

The sound waves contribute a T^4-energy (and T^3-entropy) for low temperatures T; the heat capacity is given by the T^3-Debye law, and there is no need to distinguish between the heat capacity at constant volume and the heat capacity at constant pressure; also, there is no need to distinguish between the two compressibilities, at constant temperature and at constant entropy (the sound is an adiabatic process); in addition, Gruneisen's law holds, *i.e.* the ratio of the coefficient of thermal expansion $(1/V)(\partial V/\partial T)_p$ (at constant pressure) to the specific heat is independent of temperature;[10] similar considerations are valid at higher temperatures (typically $\geq 10 - 100$K), where the heat capacity is constant, according to the Dulong-Petit law.

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[9] E. Wigner and F. Seitz, "On the constitution of metallic sodium", Phys. Rev. **43** 804 (1934); "On the constitution of metallic sodium. II", **46** 509 (1934); J. C. Slater, *The Calculation of Molecular Orbitals*, Wiley, NY (1979); E. Wigner, "On the interaction of electrons in metals", Phys. Rev. **46** 1002 (1934); "Effects of the electron interaction on the energy levels of electrons in metals", Trans. Faraday Soc. **34** 678 (1938).

[10] E. Gruneisen, "Theorie des festen Zustandes einatomiger Elemente", Ann. Phys. **344** 257 (1912).

The general form of the energy

$$E_{kin} + E_{pot} + E_{conf} = Aq^4/4 - Bq + q\sum_{i\neq j} F(qR_{ij}) \tag{8.40}$$

can be expanded with respect to the (local) variations δq and $\delta\mathbf{R}_i$ around the equilibrium; the δq-variations are related to the changes in the electron density, while $\delta\mathbf{R}_i$ are changes in the ionic positions. The first-order variation of the energy vanishes at equilibrum, while the second-order variations give an electron-electron interaction ($\sim \delta q^2$), an ion-ion interaction ($\sim \delta R_i^\alpha \delta R_j^\beta$, which leads to atomic vibrations, α, β being cartesian labels) and an electron-phonon interaction ($\sim \delta q \delta R_i^\alpha$). These are elementary excitations, associated with the density motion (both electronic and atomic). The frequencies of the atomic motion are computed according to the equations of motion $\det(\omega^2 M\delta_{ij} - D_{ij}^{\alpha\beta}) = 0$, where M denotes the atomic mass and $D_{ij}^{\alpha\beta} = \partial^2 E_{conf}/\partial R_i^\alpha \partial R_j^\beta$ is the dynamic matrix; typical atomic frequencies are $\sim$ 10meV. In the limit of long wavelengths these frequencies give the "bare" sound velocity, with typical values of the order $10^3 m/s$; equation (8.39) gives the "dressed" sound velocity, renormalized by the electron-phonon interaction (the displacement $\mathbf{u}$ of the sound is related to the variations $\delta\mathbf{R}_i$). Apart from plasmons the electron-electron contribution ($\sim \delta q^2$) may bring a small quadratic correction to the plasmon spectrum; within the linearized Thomas-Fermi theory this correction is however uncertain, and it merely indicates the range of validity of the plasmon spectrum. Apart from "dressing" the sound, the electron-phonon interaction brings small changes of the order of $\sqrt{m/M}$, where m is the electron mass and M is the atomic mass; it contributes to transport, especially the electron transport, and gives rise to superconducting instabilities, as well as to other electron-ions instabilities, like charge-density waves (Peierls-Frohlich transition) in anisotropic materials (for instance in quasi-one-dimensional materials).

8.4 Electronic elementary excitations

The electronic elementary excitations of the electron liquid are given by the second-order variation of the Hartree-Fock energy (equations

(8.2)-(8.6)); the first-order variation ensures the equilibrium; the Hartree-Fock functional of electron density preserves the Fermi-sea picture, with slight spatial variations; higher-order contributions of the interaction are irrelevant in the quasiparticle picture (they destroy the particle concept, a circumstance included by the quasiparticle picture in the concept of lifetime). The two interaction terms which contribute to the electronic excitations are the Hartree (direct) and the Fock (exchange) interactions given by

$$\begin{gathered} E_{e-e,H}=\frac{1}{2}e^2\sum_{\alpha\beta}\int d\mathbf{r}d\mathbf{r}'v(\mathbf{r}-\mathbf{r}')\cdot \\ \cdot[\psi_\alpha^*(\mathbf{r})\psi_\alpha(\mathbf{r})][\psi_\beta^*(\mathbf{r}')\psi_\beta(\mathbf{r}')]\ , \\ E_{e-e,F}=-\frac{1}{2}e^2\sum_{\alpha}\int d\mathbf{r}d\mathbf{r}'v(\mathbf{r}-\mathbf{r}')\cdot \\ \cdot[\psi_\alpha^*(\mathbf{r})\psi_\alpha(\mathbf{r}')][\psi_\alpha^*(\mathbf{r}')\psi_\alpha(\mathbf{r})] \end{gathered} \tag{8.41}$$

(equations (8.4) and (8.5)). The Hartree term leads to two types of interaction for the excitations. First, for variations of the density $n_{\mathbf{q}}=\sum_{\mathbf{k}\alpha}c_{\mathbf{k}\alpha}^+c_{\mathbf{k}+\mathbf{q}\alpha}$ the scattering amplitude of the theory of the normal Fermi liquid is

$$f(\mathbf{k}-\mathbf{k}^{'})=e^2v(q)\ ,\ \ \mathbf{k}-\mathbf{k}^{'}=\mathbf{q}\ \ , \tag{8.42}$$

where $\mathbf{k}$, $\mathbf{k}^{'}$ are in the vicinity of the Fermi surface and $\mathbf{q}$ is small ($v(q)=4\pi/q^2$ is the Fourier transform of the Coulomb potential $1/r$); the variations $\delta n_{\mathbf{q}}$ are collective excitations (plasmons). Second, for $\mathbf{q}=0$ the Hartree term gives a (direct) contribution

$$f_d(\mathbf{k}-\mathbf{k}^{'})=e^2v(0)\ \ , \tag{8.43}$$

which corresponds to variations of the electron occupancy $n_{\mathbf{k}}=$ $=\sum_\alpha c_{\mathbf{k}\alpha}^+c_{\mathbf{k}\alpha}$; these are the quasiparticles. Similarly, the Fock term leads to the exchange contribution

$$f_{ex,\alpha\beta}(\mathbf{k}-\mathbf{k}^{'})=-e^2v(\mathbf{k}-\mathbf{k}^{'})\delta_{\alpha\beta}\ \ ; \tag{8.44}$$

therefore, the scattering amplitude of the quasiparticles is

$$f_{\alpha\beta}(\mathbf{k}-\mathbf{k}^{'})=e^2\left[v(0)-v(\mathbf{k}-\mathbf{k}^{'})\delta_{\alpha\beta}\right]\ \ . \tag{8.45}$$

For the Coulomb potential the random phase approximation is necessary in order to get a finite scattering amplitude; it is given in the "Fermi Liquid" chapter, where the coefficient $3n/2\mu$ must now be replaced by n/μ ($n = \overline{k}_F^2 k_F/3\pi$, $\mu = \hbar^2\overline{k}_F k_F/2m$); therefore, the dressed potential

$$\widetilde{v}(\mathbf{q}) = \frac{v(\mathbf{q})}{1 + e^2 n v(\mathbf{q})/\mu} \tag{8.46}$$

must be used in equations (8.43)-(8.45). Making use of equation (8.14), we get

$$\widetilde{v}(\mathbf{q}) = \frac{v(\mathbf{q})}{1 + v(\mathbf{q})\overline{q}^2/4} = \frac{4\pi}{q^2 + q_0^2} \quad , \tag{8.47}$$

where $\overline{q} = 0.77 z^{1/3}/a_H$ and $q_0 = \sqrt{\pi}\overline{q} = 1.36 z^{1/3}/a_H$; we can see that the Coulomb potential is screened by a wavevector of the order $1/a_H$, where a_H is the order of the atomic dimension (this is the Thomas-Fermi parameter in the linearized Thomas-Fermi theory). The quasiparticle scattering amplitude becomes

$$f_{\alpha\beta}(\mathbf{k} - \mathbf{k}^{'}) = \frac{4\pi e^2}{q_0^2} - \frac{4\pi e^2}{(\mathbf{k} - \mathbf{k}')^2 + q_0^2}\delta_{\alpha\beta} \quad . \tag{8.48}$$

8.5 Effective electron mass

The effective electron mass can be computed by the same procedure as in the "Fermi Liquid" chapter; using the scattering amplitude given by equation (8.48) (the direct term does not contribute), we get

$$m^* = m\left\{1 + \frac{1}{\pi a_H \overline{k}_F}\left[2 + \left(1 + \frac{q_0^2}{2\overline{k}_F^2}\right)\ln\frac{q_0^2/2\overline{k}_F^2}{2 + q_0^2/2\overline{k}_F^2}\right]\right\} \quad , \tag{8.49}$$

where k_F is replaced by $\overline{k}_F$ in the linearized equations $n = \overline{k}_F^2 k_F/3\pi$, $\mu = \hbar^2\overline{k}_F k_F/2m$ (indeed, making use of equation (8.28), we can see that the uniform contributions govern the electron dynamics; rigorously speaking, the effective mass depends on position). A similar estimation of the effective mass can be obtained by neglecting the term q_0^2 (*i.e.,* neglecting the plasmon contribution at this level) and integrating for $|\mathbf{k}-\mathbf{k}'| > k_c$, where k_c is a cut-off wavevector;[11] we get

$$m^* = m\left\{1+\frac{1}{\pi a_H \overline{k}_F}\left[1-\beta^2/4+\ln(\beta/2)\right]\right\} \quad , \tag{8.50}$$

where $\beta = k_c/\overline{k}_F$. For electrons at metallic concentrations $\beta \sim 1$ from the minimum of the ground-state energy (zero-point plasmon contribution included, the plasmon contribution being re-introduced at this level). In both cases the effective mass differs little from the bare mass (sometimes, the separation between quasiparticles and plasmons is not complete, and an electron-plasmon coupling may arise, which brings another, very small, contribution to the electron effective mass). Since the plasmons are obtained in the long wavelength limit ($\mathbf{q} \to 0$), their contribution to the energy (zero-point energy) may be neglected; therefore, equation (8.49) is preferable.

8.6 Electronic properties. Plasmons

The valence atomic orbitals contribute plane waves to the chemical-bond orbitals, in the first approximation; the occupancy of the plane-waves orbitals is given by the parameter z. The quantum-mechanical corrections, brought about by the electron motion in the self-consistent field φ (exchange energy included), modify slightly the plane-waves orbitals, and the corresponding single-particle energies; also, they may split the energy levels, leading to energy bands in crystalline solids. Each band consists of N twofold degenerate orbitals, each with a fractional occupancy; they may give electric conductors, or insulators, according to the number of orbitals in the band affected by the (fractional) electron filling, along one or other direction in space. The fractional occupancy of the orbitals may be viewed as a "strong renormalization", caused by electron-ion interaction.

The fractional occupancy is relevant for the magnetic moment and Hund's rule; for instance, an amount of 0.57 spin-paired electrons go to the chemical-bond orbitals for Fe, such that $4+1.43$ electrons are left in the d^6-atomic orbitals; 2×0.43 electrons get now paired, such that 4.57 remain unpaired; we may say that the magnetic moment of atomic-Fe aggregates is 4.57 electron magnetic moments (Bohr magnetons μ_B), $\mu_{\mathrm{Fe}}=4.57\mu_B$. The uniform part of the potential φ given by equation (8.28) ($4\pi ez/a^3q^2$) gives the Fermi level $\mu=e\varphi$ (equilibrium equation (8.13)); the chemical-bond electrons have a vanishing ionization potential; however, they are only a fraction α of the total number of electrons, the fraction $1-\alpha$ being left in ions (equation (8.31)); this fraction contributes the atomic ionization potential of the ion-electron aggregate. On the other hand, the periodicity of the lattice potential in crystals introduces an additional interaction which lowers the effective chemical potential $\mu-e\varphi=0$.

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[11] D. Bohm and D. Pines, "A collective description of electron interactions: III. Coulomb interactions in a degenerate electron gas", Phys. Rev. **92** 609 (1953); D. Pines, "A collective description of electron interactions: IV. Electron interaction in metals", Phys. Rev. **92** 626 (1953).

The thermodynamics of the electrons in metals is given in the "Fermi Liquid" chapter; it implies the effective electron mass (the electronic compressibility and the thermal expansion coefficient are not seen experimentally, since the electrons cannot be decoupled from ions). The electronic sound (with velocity $u\simeq v_F^0/\sqrt{3}$, where $v_F^0\simeq 3z^{*2/3}\cdot 10^6 m/s$ is the bare Fermi velocity) is immersed in the continuum of electron-hole excitations, such that it does not exist at low temperatures (Landau's damping). The zero-sound for electrons becomes plasmons. The quasiparticle lifetime τ is given by

$$\frac{1}{\tau}=\frac{1}{\hbar\mu}\cdot\frac{(\varepsilon-\mu)^2+T^2}{e^{(\varepsilon-\mu)/T}+1}\ \ . \tag{8.51}$$

The Pauli paramagnetic susceptibility is given in the "Fermi Liquid" chapter; its "renormalization" by interaction is very small. The free susceptibility is $\chi=(1/4)g^2\mu_B^2\rho$, where g ($\simeq 2$) is the electronic gyromagnetic factor and μ_B ($=e\hbar/2mc$) is the Bohr magneton (the Zeeman energy $\mu_B H\simeq 0.67K$ for a magnetic field $H=1Ts=10^4Gs$; 1eV$\simeq 1.1\times 10^4K\simeq 1.6\cdot 10^{-12}erg$; $m\simeq 10^{-27}g$; $\hbar\simeq 10^{-27}erg\cdot s$).

The long-wavelength variations of the electron density lead to a vanishing first-order variation of the Hartree-Fock energy functional (equations (8.1)-(8.6)), according to the self-consistent quasi-classical equilibrium equation (8.13); the second-order variation gives a potential energy

$$U=\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\cdot\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\delta n(\mathbf{r})\delta n(\mathbf{r}')\ \ ; \tag{8.52}$$

a displacement field $\mathbf{u}$ generates the change $\delta n = -n div \mathbf{u}$ of the density n, and a kinetic hamiltonian

$$T = \frac{1}{2} \int d\mathbf{r} \cdot nm\dot{\mathbf{u}}^2 \quad ; \tag{8.53}$$

hence, we get the plasma frequency $\omega = (4\pi ne^2/m)^{1/2}$. The same result is obtained from the zero-sound, in the "Fermi Liquid" chapter (the mass renormalization is left aside); typical values are $\omega \sim 5eV$. The quasiparticle lifetime restricts the finite-$\mathbf{q}$ extension of the plasmon spectrum.

8.7 Polarizability and diamagnetic susceptibility

A uniform and constant external electric field $\mathbf{E}$ produces an additional potential energy $e\mathbf{E}\mathbf{r}$, for the electrons and a change δn in the equilibrium electron density; since $\int \delta n = 0$, the kinetic energy (equation (8.22)) does not change, while the potential energy (equation (8.11)) gives

$$-\frac{4\pi e^2}{q^2} n\delta n - \frac{1}{2} e\varphi_c \delta n + e\mathbf{E}\mathbf{r}n = 0 \quad , \tag{8.54}$$

and

$$\delta n = \frac{q^2}{4\pi e} \frac{\varphi}{\varphi + \varphi_c/2} \mathbf{E}\mathbf{r} \quad ; \tag{8.55}$$

the net change in energy is therefore

$$\delta \mathcal{E} = -\frac{q^2}{4\pi} \int d\mathbf{r} \left(\frac{\varphi}{\varphi + \varphi_c/2} \right)^2 (\mathbf{E}\mathbf{r})^2 \quad ; \tag{8.56}$$

hence we can get the polarizability. For a uniformly distributed ionic charge Nze in a sphere of radius R, we may use $\varphi = 4\pi ze/q^2 a^3$ (equation (8.16)) and $\varphi_c = 2\pi zeR^2/a^3$, where a is the average inter-ionic distance; the change in energy is $\delta\mathcal{E} = -[16/15(aq)^2]a^2RE^2$, and the polarizability $\chi_e = \left[8/5\pi(aq)^2\right] a^2/R^2$ (per unit volume); as expected, it vanishes for large R. The electric polarization is a surface contribution, which is not included in the above calculations.

The electrons in a uniform magnetic field $\mathbf{H}$ have a diamagnetic energy

$$\delta\mathcal{E} = -\frac{e^2}{8mc^2}\sum_\alpha \overline{(\mathbf{H}\times\mathbf{r}_\alpha)^2} \quad , \tag{8.57}$$

where the summation extends to all the electrons and c is the light velocity; hence,

$$\delta\mathcal{E} = -\frac{e^2H^2}{12mc^2}\sum_\alpha \overline{r_\alpha^2} = -\frac{e^2H^2}{12mc^2}\int d\mathbf{r}\cdot r^2 n \quad ; \tag{8.58}$$

with a uniform distribution of ionic charges, we get

$$\delta\mathcal{E} = -\frac{\pi z e^2}{15ma^3c^2}R^5H^2 \tag{8.59}$$

and the diamagnetic susceptibility

$$\chi_d = -\frac{ze^2}{10ma^3c^2}R^2 = -\frac{z}{10}\left(\frac{e^2}{\hbar c}\right)^2\frac{R^2a_H}{a^3} \quad , \tag{8.60}$$

where we can see the fine structure constant ($e^2/\hbar c = 1/137$). The quantum-mechanical motion of the electrons replaces the parameter R by the mean separation distance between the electrons.

8.8 Electronic thermoconductivity

The kinetic equation

$$\frac{\partial n}{\partial t} + \mathbf{v}\frac{\partial n}{\partial \mathbf{r}} = 0 \tag{8.61}$$

for electrons can also be written as

$$\frac{\partial n}{\partial t} + \mathbf{v} gradT \frac{\partial n}{\partial T} = 0 \quad , \tag{8.62}$$

where n is the Fermi distribution; we note that the derivative with respect to the temperature T accounts, in fact, for the quasiparticles, such that we may replace the velocity $\mathbf{v}$ by the Fermi velocity $\mathbf{v}_F$; since the variations in equation (8.62) are small, the interaction term in the energy of the quasiparticles is neglected. The energy density transported by the quasiparticles along the direction of the $gradT$ is

$$\frac{2}{V}\sum_{\mathbf{p}}\frac{\partial(\varepsilon n)}{\partial t}=-\frac{2}{V}\sum_{\mathbf{p}}\mathbf{v}_F gradT\frac{\partial(\varepsilon n)}{\partial T} \quad , \tag{8.63}$$

where 2 is the spin factor. Since the transport is performed by quasiparticles with a finite lifetime τ_e, much smaller than the transport time, we may write this equation as

$$\frac{2}{V}\sum_{\mathbf{p}}\varepsilon n=-\frac{2}{V}\sum_{\mathbf{p}}\tau_e\mathbf{v}_F gradT\frac{\partial(\varepsilon n)}{\partial T} \quad . \tag{8.64}$$

Therefore, the energy flow along an $\mathbf{s}$-direction is given by

$$\begin{aligned}\frac{\partial\mathbf{q}}{\partial t}&=-\tfrac{2}{V}\textstyle\sum_{\mathbf{p}}\tau_e\mathbf{v}_{Fs}\left(\mathbf{v}_F gradT\right)\tfrac{\partial(\varepsilon n)}{\partial T}=\\&=-\tfrac{2}{(2\pi\hbar)^3}\textstyle\int d\mathbf{p}\tau_e\mathbf{v}_{Fs}\left(\mathbf{v}_F gradT\right)\tfrac{\partial(\varepsilon n)}{\partial T} \quad ,\end{aligned} \tag{8.65}$$

where $\mathbf{q}$ is the heat transported per unit time and unit area along the direction $\mathbf{s}$; we can see that the energy flows only along the direction opposite to the direction of the gradient of the velocity, as expected; we denote this direction by T and write the above equation as

$$\frac{\partial\mathbf{q}}{\partial t}=\frac{2}{(2\pi\hbar)^3}\int d\mathbf{p}\tau_e v_{FT}^2\frac{\partial(\varepsilon n)}{\partial T}gradT \quad ; \tag{8.66}$$

therefore, the electronic thermoconductivity is given by

$$K=\frac{p_F^2 v_F}{2\pi^2\hbar^3}\int d\theta\sin\theta\cos^2\theta\int d\varepsilon\tau_e\frac{\partial(\varepsilon n)}{\partial T} \quad . \tag{8.67}$$

The quasiparticle lifetime τ_e is given by equation (8.51) above. At any finite temperature the main contribution to the excitations is brought by $(\varepsilon-\mu)^2\ll T^2$, including the vanishing temperature $T\longrightarrow 0$; it follows that we may use for τ_e the approximation given by

$$\frac{1}{\tau_e}=\frac{T^2}{2\hbar\mu} \quad ; \tag{8.68}$$

we can see that the electronic lifetime and thermoconductivity are infinite at $T \longrightarrow 0$. However, various other lifetime mechanisms appear in this limit, like, for instance, the one generated by the finite size of the sample[12] (leaving aside that at zero temperature the nature of the electron liquid may be completely changed). This is why we introduce a cutoff lifetime τ_0 and use

$$\tau = \frac{2\hbar\mu}{T^2+\Theta^2} \ , \ \Theta^2 = 2\hbar\mu/\tau_0 \tag{8.69}$$

for the electronic lifetime (where μ is the chemical potential (Fermi level)). The thermoconductivity becomes

$$\begin{gathered} K = -\tfrac{2p_F^2 v_F\mu}{3\pi^2\hbar^2}\tfrac{1}{T(T^2+\Theta^2)}\int d\varepsilon\cdot\varepsilon(\varepsilon-\mu)\tfrac{\partial n}{\partial\varepsilon} = \\ = \tfrac{2p_F^2 v_F\mu}{3\pi^2\hbar^2}\tfrac{1}{T(T^2+\Theta^2)}\int d\varepsilon\cdot(2\varepsilon-\mu)n \ . \end{gathered} \tag{8.70}$$

The integral in equation (8.70) is computed according to[13]

$$\int d\varepsilon\cdot fn = \int_0^\mu d\varepsilon\cdot f + \frac{\pi^2T^2}{6}f^{'}(\mu) + ... \tag{8.71}$$

(for any function f); we get

$$K = \frac{2p_F^2 v_F\mu}{9\hbar^2}\frac{T}{T^2+\Theta^2} \ ; \tag{8.72}$$

we can see that the electronic thermoconductivity goes like T at vanishing temperatures and $1/T$ at high temperatures, with a maximum $K \simeq p_F^2 v_F\mu/9\hbar^2\Theta$ for $T=\Theta$. Typically, the electronic thermoconductivity is smaller than the phonon thermoconductivity (except in the limit $T \longrightarrow 0$ for a perfect solid). Making use of the specific heat $C = mp_FT/3\hbar^3$ of the electron liquid (leaving aside the effective mass), we can write $K=\frac{1}{3}Cv_F\Lambda$, where $\Lambda = 2\hbar v_F\mu/(T^2+\Theta^2)$ ($\simeq 2\hbar v_F\mu/T^2$) is a mean freepath; for metals at room temperature

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[12] H. B. G. Casimir, "Note on the conduction of heat in crystals", Physica **5** 495 (1938).

[13] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol. 5, *Statistical Physics*, Elsevier (1980).

Λ is of the order $10^{-4}cm$. This representation of the thermoconductivity is the same for electrons, phonons and classical gases (it was suggested by Drude[14]); it shows that the heat is transported with the velocity of the quasiparticles reduced by the factor Λ/l, where l is the length of the sample.

In the "Phonons in Solids" chapter the electron lifetime

$$\frac{1}{\tau_{e-ph}} = \frac{T}{\hbar F} \ , \ F = \frac{M}{m}\left(\frac{\hbar\omega_D}{\mu}\right)^2 \tag{8.73}$$

caused by the electron-phonon interaction is derived (acoustic phonons). This lifetime should be combined with τ_e and τ_0 (Matthiessen's rule); it leads to an electronic thermoconductivity

$$K = \frac{2p_F^2 v_F \mu}{9\hbar^2}\frac{T}{T^2+\Theta^2+T\Theta_1} \ , \ \Theta_1 = \frac{2\mu}{F} \ ; \tag{8.74}$$

the electron-phonon interaction decreases the electronic thermoconductivity, as expected. For typical metals the orders of magnitude are $\mu \simeq 10^4 K$, $\hbar\omega_D \simeq 10^2 K$, such that $F \simeq 10-100$; if the temperature Θ is controlled by the finite size of the sample, then it is usually smaller than Θ_1, which means that the electron-phonon interaction governs the electronic thermoconductivity.

8.9 Thermopower

A temperature gradient along an x-direction generates an electric field

$$E = Q\frac{\partial T}{\partial x} \tag{8.75}$$

in an electron liquid, where Q is the thermoelectric power. The corresponding voltage U is

$$U = -\int dx \cdot E = -\int dT \cdot Q = Q\Delta T \quad , \tag{8.76}$$

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[14] P. Drude, "Zur Elektronentheorie der Metalle", Ann. Phys. **306** 566 (1900).

where ΔT is the difference of temperature. This is known as the Seebeck (or thermoelectric) effect.[15] The opposite effect, where an electric field generates a temperature difference, is known as the Peltier effect.[16] (Similar effects in magnetic field are the Nernst and the Ettingshausen effects; the generation of an electric polarization by a temperature difference is called pyroelectricity; a galvanic cell with electrodes at different temperatures is a thermogalvanic cell).

A local change δT in the temperature gives rise to a change

$$\begin{aligned}\delta n_T = -\tfrac{2}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot(\partial n/\partial\varepsilon)[(\varepsilon-\mu)/T]\delta T = \\ = -\tfrac{1}{\pi^2\hbar^3}\int d\varepsilon\cdot(p^2/v)(\varepsilon-\mu)(\partial n/\partial\varepsilon)(\delta T/T) \quad ,\end{aligned} \tag{8.77}$$

in the quasiparticle density, where n denotes the Fermi distribution (and v stands for the Fermi velocity); the integral in (8.77) can be estimated straightforwardly (the first derivative of the density of states $(p^2/v)'$ on the Fermi surface brings the main contribution); we get

$$\delta n_T = \frac{\pi^2}{4}n\frac{T\delta T}{\mu^2} \quad , \tag{8.78}$$

where n denotes the electron concentration, $\mu = p_F^2/2m$ is the chemical potential (Fermi level), and m is the electron mass. The chemical potential undergoes a change $\delta\mu$ given by

$$\delta n_\mu = -\frac{2}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot(\partial n/\partial\varepsilon)\delta\mu = \frac{3}{2}n\frac{\delta\mu}{\mu} \quad , \tag{8.79}$$

in order to preserve the number of electrons. Therefore,

$$\delta n_T + \delta n_\mu = 0 \quad , \tag{8.80}$$

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[15] Th. J. Seebeck, "Magnetische Polarisation der Metalle und Erze durch Temperatur-Differenz", Abh. Konig. Akad. Wiss. Berlin 265 (1822); see also A. Volta, "Nuova memoria sull'elettricita animale", Annali di Chimica e Storia Naturale **5** 132 (1794).

[16] J. Ch. A. Peltier, "Nouvelles experiences sur la caloricite des courants electrique", Ann. Chimie & Physique **56** 371 (1834); W. Thomson (Lord Kelvin), "On a mechanical theory of thermoelectric currents", Proc. Roy. Soc. Edinburgh **3** 91 (1851).

and

$$\delta\mu = -\frac{\pi^2}{6}\frac{T}{\mu}\delta T \quad . \tag{8.81}$$

The change $\delta\mu$ in the chemical potential is equivalent with a change $-\delta\mu$ in the energy levels; therefore, an electric potential U appears, given by

$$-eU = -\delta\mu = \frac{\pi^2}{6}\frac{T}{\mu}\delta T \quad , \tag{8.82}$$

where $-e$ is the electron charge; or

$$U = -\frac{\pi^2}{6}\frac{T}{e\mu}\delta T \quad . \tag{8.83}$$

This is the origin of the thermoelectric effect; by comparing it with equation (8.76), we get the thermopower

$$Q = -\frac{\pi^2}{6}\frac{T}{e\mu} \quad . \tag{8.84}$$

It is worth noting that the thermoelectric effect is a second-order effect in comparison with the thermal conduction, which is a first-order effect, because both the voltage drop U and the change in the electron density δn_T (therefore the electric flow) are proportional to the temperature imbalance δT, such that the corresponding electric energy is proportional to $(\delta T)^2$; while the energy transported in the thermal conduction is proportional to δT. The change in energy per unit volume is

$$\delta E = C\delta T = (\pi^2/2\mu)nT\delta T \tag{8.85}$$

where $C = (\pi^2/2\mu)nT$ is the heat capacity of the electrons (per unit volume). One can also note that the thermopower does not depend on the quasiparticle lifetime.

According to equation (8.84), for typical values $\mu \sim 1eV = 11.6 \cdot 10^3$K we get at room temperature a thermopower of a few microvolts per Kelvin degree. It is worth remarking that the opposite Peltier effect compensates, during the time, the thermopower and the electric flow of the Seebeck effect.

It is worth comparing the thermopower of an electron liquid given by equation (8.84) with the thermopower of a classical gas of electric charges given by

$$Q = -\frac{1}{e}\left(\frac{3}{2} - \frac{\mu}{T}\right) \tag{8.86}$$

("Transport in Gases" chapter), where $\mu = \frac{3}{2}T\ln(2\pi\hbar^2/Tma^2)$ (where m is the particle mass and a is the mean separation distance between the charges).

8.10 Electrical conductivity, 1

Let an electron liquid be at thermal equilibrium in a macroscopic sample. A voltage U is applied along the sample, such as to give rise to a steady, continuous electric flow. Any other flow of energy, as, for instance, a heat flow, is disregarded.

A quasiparticle with energy ε carries a charge density

$$-e\delta n = e^2\frac{\partial n}{\partial \varepsilon}\delta U \quad , \tag{8.87}$$

where $-e$ is the electron charge, n is the Fermi distribution, and δU is the local voltage. This charge is carried along the x-direction with the velocity v_x, such that the charge flux (charge per unit area) is given by

$$e^2\frac{\partial n}{\partial \varepsilon}\cdot v_x\tau\cdot\delta U \quad , \tag{8.88}$$

where τ is the quasiparticle lifetime. (We recognize here the kinetic equation). The total electric flow (or current, *i.e.* charge per unit area and per unit time) is given by

$$\begin{aligned} j = \tfrac{\partial Q}{\partial t} &= \tfrac{2}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot e^2\tfrac{\partial n}{\partial \varepsilon}\cdot v_x^2\tau\cdot\tfrac{\partial U}{\partial x} = \\ &= -\tfrac{2}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot e^2\tfrac{\partial n}{\partial \varepsilon}\cdot v_x^2\tau\cdot E \quad , \end{aligned} \tag{8.89}$$

where E is the electric field (and Q is the charge per unit area); hence, the electrical conductivity

$$\sigma = -\frac{2e^2}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot\frac{\partial n}{\partial \varepsilon}v_x^2\tau \tag{8.90}$$

(in the international system of units it is measured in $(C^2/m^2s)(m/J)$ $= CA/mJ = A/mV = 1/m\Omega$, where the ohm-meter Ωm is the unit for resistivity $\rho = 1/\sigma$). Making use of the lifetime given by equation (8.69) we get the conductivity

$$\sigma = \frac{4e^2 p_F \mu^2}{3\pi^2\hbar^2} \cdot \frac{1}{T^2 + \Theta^2} \ . \tag{8.91}$$

It is worth noting the residual electrical conductivity at vanishing temperature

$$\sigma_0 = \frac{2e^2 p_F \mu \tau_0}{3\pi^2\hbar^3} = \frac{e^2 n \tau_0}{m} \quad , \tag{8.92}$$

which can be obtained from the equation of motion $mv/\tau = -eE$). Using the thermoconductivity K given by equation (8.72) we get the Wiedemann-Franz law

$$\frac{K}{\sigma T} = \frac{\pi^2}{3e^2} \tag{8.93}$$

(a universal constant);[17] this ratio, denoted by L, is called the Lorenz number.[18]

According to equation (8.89), the electric flow through a sample of transverse area A is given by

$$I = \sigma \tfrac{U}{l} A = \tfrac{e^2}{h} \left(\tfrac{A}{a^2}\right) \tfrac{\lambda_F}{l} \tfrac{\Theta^2}{T^2+\Theta^2} \cdot U \quad , \tag{8.94}$$

where a is the mean separation distance between the electrons and λ_F is the Fermi wavelength; hence the quanta e^2/h of electrical conductance.[19]

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[17] R. Franz and G. Wiedemann, "Uber die Warme-Leitungsfahigkeit der Metalle", Ann. Phys. **165** 497 (1853); see also H. A. Lorentz, "The motion of electrons in metallic bodies. I, II, III", Proc. Acad. Sci. Amst. **7** 438, 585, 684 (1905) (with Boltzmann distribution); A. Sommerfeld, "Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik", Z. Phys. **47** 1 (1928) (with Fermi statistics; the first paper which derived the specific heat of the electrons).

[18] L. Lorenz, "Bestimmung der Warmegrade in absoluten Maasse", Ann. Phys. Chem. **147** 429 (1872); "Uber das Leitungsvermogen der Metalle fur Warme und Elektrizitat", **13** 422 (1881); see also A. H. Wilson, *The Theory of Metals*, Cambridge University Press, Cambridge (1953).

[19] M. Apostol, "A new approach to the quantized electrical conductance", Phys. Lett. **A372** 5093 (2008).

If we include the electron-phonon lifetime (equation (8.73)), the conductivity becomes

$$\sigma = \frac{4e^2 p_F \mu^2}{3\pi^2\hbar^2} \cdot \frac{1}{T^2 + \Theta^2 + T\Theta_1} \quad , \tag{8.95}$$

where Θ_1 is given by equation (8.74); the Wiedemann-Franz law is not affected by the electron-phonon interaction. For $T \ll \Theta_1$ and $\Theta^2 \ll T\Theta_1$ we get the Bloch law $\sigma \sim 1/T$.[20]

Making use of equation (8.87) the electrical conductivity given by equation (8.90) may also be written as $\sigma = e(\delta n/\delta U)v_F\Lambda$, where δn is the change of the quasiparticle concentration, v_F is the Fermi velocity and Λ is the quasielectron mean freepath ($\Lambda = 2\hbar v_F\mu/(T^2 + \Theta^2 + T\Theta_1)$); it is worth noting that $e(\delta n/\delta U)$ is the electric capacitance (per unit volume). On the other hand, charge $dQ = -\sigma(\partial U/\partial x)dt$ is carried in time dt through the unit area of the cross-section of the sample, according to equation (8.89); since the total amount of electric charge per unit area of the cross-section is $\Delta Q \sim e(\delta n/\delta U)l\Delta U$, it follows that $e(\delta n/\delta U)l\Delta U = \sigma(\Delta U/l)\Delta t$, where Δt is the time necessary for this charge to flow through the sample with length l; making use of $\sigma = e(\delta n/\delta U)v_F\Lambda$, we get the velocity of the charge transport $l/\Delta t \sim v_F(\Lambda/l)$, *i.e.* the electric charge is carried with a velocity much smaller than the Fermi velocity v_F (as expected).

The thermopower Q is defined by $U = Q\delta T$, the electrical conductivity σ is given by $I = \sigma AU/l$ and the thermoconductivity K is defined through $\partial\delta E/\partial t = KA\delta T/l$; the electric power is therefore $P_e = UI = \sigma Q^2 A(\delta T)^2/l$, and we can see that the thermoelectric effect is indeed a second-order effect, while the caloric power is $P_{cal} = \partial\delta E/\partial t$, *i.e.* a first-order effect; therefore, we can write the efficiency quotient as

$$\eta = \frac{\sigma T}{K} Q^2 \eta_C \quad , \tag{8.96}$$

where $\eta_C = \delta T/T$ is the Carnot quotient; the ratio $K/\sigma T = L$ is the Lorenz number, which is independent of temperature, according to Wiedemann-Franz law; for ideal conditions $L = \pi^2/3e^2$; on the other hand, the ideal thermopower is given by $Q = -(\pi^2/6e)(T/\mu)$ (for

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[20] F. Bloch, "Zum elektrischen Wiederstandsgesetz bei tiefen Temperaturen", Z. Phys. **59** 208 (1930).

$T/\mu \ll 1$), according to (8.84), so that the efficiency quotient above becomes $\eta = (\pi^2/12)(T/\mu)^2\eta_C$. The main part of the heat δE is carried by thermal conduction, and only the small, second-order part, is transported by the the electric flow;[21] $ZT = Q^2\sigma T/K$ is called the figure of merit of the thermoelectric generators.

8.11 Electrical conductivity, 2

The electric flow $\mathbf{j}$ is an electric charge passing across the unit area of the cross-section in unit time; it is a charge flux per unit time, *i.e.* a charge flow; it may be represented as a charge density multiplied by a velocity. For a steady flow the conservation of the electric charge requires

$$div\mathbf{j} = 0 \;\; ; \tag{8.97}$$

in addition, the electric field $\mathbf{E}$ is such that

$$curl\mathbf{E} = 0 \quad , \tag{8.98}$$

according to Maxwell's equations, such that there is an electric potential φ, $\mathbf{E} = -grad\varphi$. Since both $\mathbf{j}$ and $\mathbf{E}$ are small enough they are connected through[22]

$$\mathbf{j} = \sigma\mathbf{E} \quad , \tag{8.99}$$

where σ is the electrical conductivity, or, in general,

$$j_i = \sigma_{ik}E_k \quad , \tag{8.100}$$

where σ_{ik} is the electrical conductivity tensor (a symmetric tensor); this is Ohm's law. Obviously, $div\mathbf{E} = 0$, and Laplace equation $\Delta\varphi = 0$ holds for a homogeneous conductor, as expected, since there is no charge in a conductor. At the separation interface between two conductors the normal component of the flow and the tangent component of the electric field are continuous,

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[21] M. Apostol, "Generalized theory of thermoelectric figure of merit", J. Appl. Phys. **104** 053704 (2008).

[22] L. Landau and E. Lifshitz, *Course of Theoretical Physics*, vol.7, *Electrodynamics of Continuous Media*, Elsevier (1995).

$$\begin{aligned} j_{n1} = \sigma_1 E_{n1} = j_{n2} = \sigma_2 E_{n2} \ \ , \\ E_{t1} = j_{t1}/\sigma_1 = E_{t2} = j_{t2}/\sigma_2 \ \ ; \end{aligned} \tag{8.101}$$

while at the separation interface between a conductor and a non-conductor $j_n = 0$, $E_n = 0$.

The electric flow dissipates heat

$$q = \mathbf{jE} = \mathbf{j}^2/\sigma \tag{8.102}$$

per unit volume and unit time; this is Joule-Lenz heat. Under the constraint $div\mathbf{j} = 0$ the dissipated heat is minimal. Indeed, the variation of

$$\int d\mathbf{r} \cdot (\mathbf{j}^2/\sigma - 2\varphi div\mathbf{j}) \quad , \tag{8.103}$$

where φ is a Lagrange's multiplier, leads to $\mathbf{j}/\sigma = -grad\varphi = \mathbf{E}$ (and $curl\mathbf{E} = 0$). The release of entropy per unit time is therefore

$$\partial S/\partial t = \int d\mathbf{r} \cdot (\mathbf{j}^2/\sigma T) \quad , \tag{8.104}$$

where T is the temperature; hence, the conductivity is positive. In general, at constant energy, the density of entropy s may be expanded as

$$s = -\sum X_a x_a \quad , \tag{8.105}$$

where x_a are parameters, or variables, of the thermodynamic state, and X_a the corresponding generalized forces; for small variations the approach to equilibrium requires a time evolution given by

$$\partial x_a/\partial t = -\sum \gamma_{ab} X_b \quad , \tag{8.106}$$

where γ_{ab} are called kinetic coefficients. It follows that

$$\partial S/\partial t = -\int d\mathbf{r} \cdot \sum X_a (\partial x_a/\partial t) = \int d\mathbf{r} \cdot \sum \gamma_{ab} X_a X_b \quad , \tag{8.107}$$

and the kinetic coefficients are symmetric, $\gamma_{ab} = \gamma_{ba}$; this is Onsager's symmetry "principle".[23] By comparing equations (8.104) and (8.107) we may identify $\partial\mathbf{x}/\partial t = \mathbf{j}$, $\mathbf{X} = -\mathbf{j}/\sigma T = -\mathbf{E}/T$, and $\gamma = \sigma T$.

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[23] L. Onsager, "Reciprocal relations in irreversible processes, I.", Phys. Rev. **37**

8.12 Hall effect

In the presence of a magnetic field **H** the kinetic coefficients, like conductivity, acquire a **H**-dependence and their symmetry is not preserved anymore. Indeed, interchanging the electric field components E_i and E_k in heat equation (8.102), or in entropy production (equation (8.107)) amounts to spatial reflections; but, under such reflections, the magnetic field, which is not a polar, but an axial vector, changes sign; consequently, the kinetic coefficients must satisfy the symmetry relations $\gamma_{ab}(\mathbf{H}) = \gamma_{ba}(-\mathbf{H})$, and

$$\sigma_{ik}(\mathbf{H}) = \sigma_{ki}(-\mathbf{H}) \tag{8.108}$$

for conductivity. Since σ_{ik} is a sum of a symmetric tensor plus an antisymmetric one,

$$\sigma_{ik} = s_{ik} + a_{ik} \quad , \tag{8.109}$$

the latter must obey the following symmetry conditions:

$$\begin{aligned} s_{ik}(\mathbf{H}) &= s_{ki}(-\mathbf{H}) = s_{ik}(-\mathbf{H}) \quad , \\ a_{ik}(\mathbf{H}) &= a_{ki}(-\mathbf{H}) = -a_{ik}(-\mathbf{H}) \quad , \end{aligned} \tag{8.110}$$

i.e. the symmetric conductivity must be an even function of **H**, while the antisymmetric one must be an odd function of **H**. Since any antisymmetric tensor a_{ik} can be represented by a vector **a**, through

$$a_{xy} = a_z \quad , \quad a_{yz} = a_x \quad , \quad a_{zx} = a_y \quad , \tag{8.111}$$

it follows that $a_{ik}E_k = (\mathbf{E} \times \mathbf{a})_i$, such that Ohm's law in magnetic field reads

$$j_i = s_{ik}E_k + (\mathbf{E} \times \mathbf{a})_i \quad . \tag{8.112}$$

The Joule-Lenz heat is given by

$$q = \mathbf{jE} = s_{ik}E_iE_k \quad , \tag{8.113}$$

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405 (1931); "Reciprocal relations in irreversible processes, I.", Phys. Rev. **38** 2265 (1931); H. B. Callen, "The application of Onsager's reciprocal relations to thermoelectric, thermomagnetic and galvanomagnetic effects", Phys. Rev. **73** 1349 (1948).

i.e. only by the symmetric part of the conductivity. To the first-order contributions we may write

$$a_i = \alpha_{ik} H_k \tag{8.114}$$

(odd function of **H**), where α_{ik} is a polar tensor, and

$$s_{ik} = \sigma^0_{ik} + \beta_{ik,lm} H_l H_m \tag{8.115}$$

(even function of **H**), where $\beta_{ik,lm}$ is symmetric both with respect to ik and lm. The main effect in **H** is therefore a purely kinetic effect arising from the antisymmetric conductivity. As one can see from equation (8.112) this effect consists in an electric flow along a direction perpendicular to the electric field, whose magnitude is proportional to the magnetic field. This is the Hall effect. It is worth noting however, that, in general, there may exist an electric flow perpendicular to the electric field which is not a Hall flow.

Conversely, the reciprocal tensor σ^{-1}_{ik} in

$$E_i = \sigma^{-1}_{ik} j_k \tag{8.116}$$

can be decomposed into a symmetric part ρ_{ik}, which is called the resistivity tensor, and an antisymmetric part described by a vector **b**; their properties are similar with those of the tensor s_{ik} and vector **a**, respectively. One may write down consequently

$$E_i = \rho_{ik} j_k + (\mathbf{j} \times \mathbf{b})_i \quad ; \tag{8.117}$$

the Hall effect described by the last term in equation (8.117) is an electric field perpendicular to the electric flow, whose magnitude is proportional to the magnetic field.

For a homogeneous conductor the vectors **a** and **b** are directed along **H**, say, H_z; the only non-vanishing components of the resistivity tensor are $\rho_{xx} = \rho_{yy} = \rho_\perp$ and $\rho_{zz} = \rho_\parallel$, *i.e.* the transverse and longitudinal resistivity, respectively. Equation (8.116) reads then

$$E_x = \rho_\perp j_x \quad , \quad E_y = -b j_x \quad , \quad E_z = \rho_\parallel j_z \quad ; \tag{8.118}$$

in this case the Hall field is perpendicular on the magnetic field too. The coefficient b is such that

$$\mathbf{b} = -R\mathbf{H} \quad , \tag{8.119}$$

where R is the Hall constant; it may have either positive or negative values. As regards the quadratic terms in magnetic field entering the resistivity, we can see that the only vectors that may be constructed with $\mathbf{j}$ and $\mathbf{H}$, linear in $\mathbf{j}$ and quadratic in $\mathbf{H}$, are $\mathbf{H}(\mathbf{j} \times \mathbf{H})$ and $\mathbf{j}H^2$. It follows

$$\mathbf{E} = \rho^0\mathbf{j} + R(\mathbf{H} \times \mathbf{j}) + \beta_1\mathbf{j}H^2 + \beta_2\mathbf{H}(\mathbf{H}\mathbf{j}) \tag{8.120}$$

for a homogeneous conductor. The dependence of the resistivity on the magnetic field is the magnetoresistance.

It is worth computing the reciprocal tensor σ_{ik}^{-1} in terms of the direct tensor s_{ik} and direct vector $\mathbf{a}$. For the principal axes σ is given by the determinant

$$\begin{aligned} \sigma = \begin{vmatrix} s_{xx} & a_z & -a_y \\ -a_x & s_{yy} & a_x \\ a_y & -a_x & s_{zz} \end{vmatrix} = \\ = s_{xx}s_{yy}s_{zz} + s_{xx}a_x^2 + s_{yy}a_y^2 + s_{zz}a_z^2 \quad ; \end{aligned} \tag{8.121}$$

in general,

$$\sigma = s + s_{ik}a_ia_k \quad , \tag{8.122}$$

where $s = \det(s)$. Similarly, for principal axes,

$$\begin{aligned} \sigma_{xx}^{-1} = \rho_{xx} = \tfrac{1}{\sigma}(s_{yy}s_{zz} + a_x^2) \quad , \\ \sigma_{xy}^{-1} = \rho_{xy} + b_z = \tfrac{1}{\sigma}(a_xa_y + a_zs_{zz}) \quad , \end{aligned} \tag{8.123}$$

etc, such that, in general, we get

$$\begin{aligned} \rho_{ik} = \tfrac{1}{\sigma}(s_{ik}^{-1}s + a_ia_k) \quad , \\ b_i = \tfrac{1}{\sigma}s_{ik}a_k \quad . \end{aligned} \tag{8.124}$$

8.13 Contact potential

The mechanical work needed for extracting at equilibrium a charged particle from a condensed body is called the work function. It has positive values, and is equal with the mechanical work released on adding a charged particle to a condensed body. The work function depends on surface and on the nature of the particle. The electric potential W corresponding to extracting a positively-charged particle is also called work function, or extraction potential. Close to the surface the electronic and atomic charges are delocalized over distinct length scales, so that a double layer appears at the surface, with the charge density ρ. Poisson's equation reads

$$d^2\varphi/dx^2 = -4\pi\rho \quad , \tag{8.125}$$

so that

$$d\varphi/dx = -4\pi\int_{-\infty}^{x}\rho dx \ ; \tag{8.126}$$

for $x \to -\infty$ the derivative of the potential φ vanishes. Integrating equation (8.126) by parts, we get

$$\varphi(x) - \varphi(-\infty) = 4\pi\int_{-\infty}^{x} x\rho dx \quad , \tag{8.127}$$

since the charge far away of the surface and the total charge vanish rapidly. It follows that the work function $W = \varphi(\infty) - \varphi(-\infty)$ is given by the dipole momentum of the surface double layer,

$$W = 4\pi\int_{-\infty}^{\infty} x\rho dx \ . \tag{8.128}$$

At the interface of separation between two conductors the electrons pass over from the one with a higher work function to the one with a lower work function, until the potential difference equilibrates the difference in the work functions. This is the contact potential. Let AOC be the conductor a and BOC be the conductor b, with OC denoting the shared interface. At equilibrium the sum of the mechanical work for a cyclic motion of a charged particle must be zero, *i.e.*

$$W_a + \varphi_{ab} - W_b = 0 \quad , \tag{8.129}$$

hence the contact potential

$$\varphi_{ab} = W_b - W_a \quad , \tag{8.130}$$

where $\varphi_{ab} = \varphi_b - \varphi_a$. For a series of conductors in contact the total contact potential is equal with the contact potential between the two end conductors. Close to the common interface between two conductors, and outside them, the potential obeys Laplace equation

$$\frac{1}{r}\frac{\partial}{\partial r}(r\partial\varphi/\partial r) + \frac{1}{r^2}\partial^2\varphi/\partial\theta^2 = 0 \quad , \tag{8.131}$$

where θ is the angle measured from AO. The main contribution comes from the lowest power in r, for small r; this is $\varphi = const \cdot \theta$, or

$$\varphi = \frac{\varphi_{ab}}{\alpha}\theta \quad , \tag{8.132}$$

where α is the angle between the two free surfaces AO and BO. The corresponding electric field is

$$E = -\frac{1}{r}\frac{\partial\varphi}{\partial\theta} = -\frac{\varphi_{ab}}{\alpha}\frac{1}{r} \quad ; \tag{8.133}$$

the equipotential surfaces are planes of $\theta = const$ and the force lines are circles of $r = const$. Ionized particles are usually attracted by the free surfaces in the neighbourhood of the common interface, such as to neutralize the contact potential. The contact potentials exist also between two neighbouring free surfaces of the same crystal.

8.14 Galvanic cell

Two metals A and B in an electrolyte X produce an electromotive force $\mathcal{E}$. It arises from the dissociation of the electrolyte, and, being a non-equilibrium process, it involves the chemical potentials μ. Cation A^+ passes over into electrolyte, joining the anion X^-, and the cation B^+ is released by the electrolyte X^+C^- into metal B, where it acquires the electron lost by cation A^+ through the external circuit. Consequently, the associated energy is

$$e\mathcal{E} = (\mu_{AX} - \mu_A) + (\mu_B - \mu_{BX}) \quad , \tag{8.134}$$

where e is the electron charge. A similar relationship holds for a battery of galvanic cells, *i.e.* $\mathcal{E}_{AC} = \mathcal{E}_{AB} + \mathcal{E}_{BC}$. The heat released is given by

$$Q = -T^2\partial(e\mathcal{E}/T)/\partial T \quad , \tag{8.135}$$

usually at constant pressure; the electromotive force is a free energy (actually, Gibbs' free energy for pressure, temperature and number of particles). Obviously, it equilibrates all the voltage drops, both in the external and internal circuits,

$$\mathcal{E} = I\sum R \quad , \tag{8.136}$$

where I is the electric current, *i.e.* the charge flux per area S and per unit time, and R denotes the electric resistance; obviously, $I = jS$ and $R = \rho l/S$, as the work $\mathcal{E}I$ per unit time is given by $jESl = RI^2$, where l is the length of the circuit. It is worth noting that the electromotive force is also given by the total sum of the contact potentials,

$$\mathcal{E} = \sum \varphi_{ab} = \varphi_{AX} + \varphi_{XB} \quad , \tag{8.137}$$

which, however, is not the contact potential φ_{AB}, due to the chemical reactions in electrolyte. A battery of cells may therefore have identical metal electrodes but distinct electrolytes.

8.15 Electrocapillarity

Let S be the separation interface between two liquid metals (electrolytes) with electric potentials $\varphi_{1,2}$, and the double layer with charges $e_1 = e$, $e_2 = -e$. At constant pressure and temperature the surface thermodynamic potential $\widetilde{\Phi}$ obeys

$$d\widetilde{\Phi} = \alpha dS - e_1 d\varphi_1 - e_2 d\varphi_2 = \alpha dS - ed\varphi \quad , \tag{8.138}$$

where α is the surface tension and $\varphi = \varphi_1 - \varphi_2$. It follows

$$\alpha = (\partial\widetilde{\Phi}/\partial S)_\varphi \tag{8.139}$$

as a function of φ. Consequently, $\widetilde{\Phi} = \alpha S$, such that $e = -S(\partial\alpha/\partial\varphi)$, or the charge $\sigma = e/S$ of the unit area is given by

$$\sigma = -(\partial\alpha/\partial\varphi)_{p,T} \quad ; \tag{8.140}$$

this is known as the Lippman-Gibbs equation. At equilibrium $\widetilde{\Phi}$ is minimal as a function of e for a given φ,

$$\partial\widetilde{\Phi}/\partial e = 0 \ \ , \ \ \partial^2\widetilde{\Phi}/\partial e^2 > 0 \quad ; \tag{8.141}$$

introducing Φ through

$$\widetilde{\Phi} = \Phi - e\varphi \tag{8.142}$$

we get

$$\partial\Phi/\partial e - \varphi = 0 \tag{8.143}$$

and

$$\partial^2\Phi/\partial e^2 = \partial\varphi/\partial e = \partial\varphi/S\partial\sigma > 0 \quad , \tag{8.144}$$

i.e.

$$\partial\varphi/\partial\sigma > 0 \ \ . \tag{8.145}$$

Indeed, the double layer is a condenser of capacity $\partial e/\partial\varphi$, and the stability condition (8.145) is expected. From equation (8.140) we have

$$\partial\sigma/\partial\varphi = -(\partial^2\alpha/\partial\varphi^2)_{p,T} > 0 \quad , \tag{8.146}$$

i.e. $\alpha(\varphi)$ is maximal for $\partial\alpha/\partial\varphi = -\sigma = 0$. Therefore, the double layer diminishes the surface tension.

8.16 Thermoelectricity

Let $gradT$ be a small temperature gradient along a conductor, such that the charge carriers are in local equilibrium, but they are not in global equilibrium. The chemical potential changes locally, such that a local electric potential, an electric field and an electric flow appear. If an external electric field **E** is also present, the electric flow may, therefore, be written as

$$\mathbf{j} = \sigma(\mathbf{E} - Q\,gradT) \quad , \tag{8.147}$$

where σ denotes the conductivity and Q is the thermopower. It shows that a temperature gradient may produce an electric flow even in the absence of an external electric field. This is the thermoelectric, or Seebeck, effect. Conversely,

$$\mathbf{E} = \frac{1}{\sigma}\mathbf{j} + Q\,gradT \ \ . \tag{8.148}$$

In general, Q is a tensor, like the electric conductivity. Similarly, the heat flow $\mathbf{q}$, *i.e.* the heat flowing across the unit area of the cross-section per unit time, minus the electric energy $\varphi\mathbf{j}$ is proportional to the two gradients $grad\varphi = -\mathbf{E}$ and $gradT$,

$$\mathbf{q} - \varphi\mathbf{j} = \beta\mathbf{E} - \gamma gradT \ \ ; \tag{8.149}$$

obviously, γ is related to the thermoconductivity K in $\mathbf{q} = -K gradT$; the two coefficients β and γ are determined below.

Heat density per unit time is $-div\mathbf{q}$, so that the entropy production is

$$\partial S/\partial t = -\int d\mathbf{r} \cdot \frac{div\mathbf{q}}{T} \ \ ; \tag{8.150}$$

on the other hand,

$$\begin{gathered} \tfrac{1}{T} div\mathbf{q} = \tfrac{1}{T}[div(\mathbf{q} - \varphi\mathbf{j}) + div(\varphi\mathbf{j})] = \\ = \tfrac{1}{T} div(\mathbf{q} - \varphi\mathbf{j}) - \mathbf{jE}/T \ \ ; \end{gathered} \tag{8.151}$$

we get

$$\partial S/\partial t = \int d\mathbf{r} \cdot (\mathbf{jE}/T) - \int d\mathbf{r} \cdot [(\mathbf{q} - \varphi\mathbf{j})/T^2] gradT \ \ . \tag{8.152}$$

It follows that $\mathbf{j}$ and $\mathbf{q} - \varphi\mathbf{j}$ correspond to the $\partial x_a/\partial t$-velocities, and $-\mathbf{E}/T$, $(1/T^2)gradT$ correspond to the generalized forces X_a. Equations (8.147) and (8.149) can, therefore, be rewritten as

$$\mathbf{j} = -\sigma T(-\mathbf{E}/T) - \sigma Q T^2 (\frac{1}{T^2} gradT) \ \ , \tag{8.153}$$

and

$$\mathbf{q} - \varphi\mathbf{j} = -\beta T(-\mathbf{E}/T) - \gamma T^2 (\frac{1}{T^2} gradT) \ \ , \tag{8.154}$$

where the canonical form of the kinetic coefficients is identified. According to the symmetry of these kinetic coefficients $\beta T = \sigma Q T^2$, *i.e.* $\beta = \sigma Q T$. It follows $\mathbf{q} - \varphi\mathbf{j} = \sigma Q T\mathbf{E} - \gamma gradT$; making use of equation (8.148), or equation (8.153), we get finally

$$\mathbf{q} = (\varphi + QT)\mathbf{j} - K gradT \ \ , \tag{8.155}$$

where the thermoconductivity $K=\gamma-\sigma Q^2T$ has been introduced. Introducing equations (8.148) and (8.155) into equation (8.152) we get

$$\partial S/\partial t=\int d\mathbf{r}\cdot[(\mathbf{j}^2/\sigma T)+K(gradT)^2/T^2] \quad , \tag{8.156}$$

which requires the positivity of the electric and thermal conductivities. It is worth noting that the kinetic coefficients are the electric conductivity σ, the thermopower Q, and the thermoconductivity K. In addition, contributions proportional to *gradp*, where p is the pressure (or similar contributions in density), arising from inhomogeneities, are unphysical in the basic equations (8.148) and (8.155), as they would lead to negative terms in the entropy production.

From equation (8.155) we can compute the density of heat per unit time,

$$q=-div\mathbf{q}=\mathbf{Ej}-\mathbf{j}grad(QT)+div(K\,gradT) \quad , \tag{8.157}$$

or, making use of equation (8.148),

$$q=\mathbf{j}^2/\sigma-T\mathbf{j}gradQ+div(K\,gradT) \quad ; \tag{8.158}$$

the first contribution to equation (8.158) is the Joule-Lenz heat; the second contribution comes from thermoelectric effects, while the third one is due to the thermal conduction. From equation (8.147) $div\mathbf{j}=0$ implies that σ, and even Q and $gradT$, are constant, as expected, and so should be K; therefore, both the thermoelectric heat and the thermoconducted heat are fully transported. Nevertheless, the spatial variation of the thermopower is written as $gradQ=(dQ/dT)gradT$, the derivative being taken at constant pressure, as usually. Therefore, the heat produced per unit time in the unit volume by the thermoelectric effects is

$$q=-T(dQ/dT)\mathbf{j}gradT=-\tau\mathbf{j}gradT \quad ; \tag{8.159}$$

this is called Thomson's effect,[24] where

$$\tau=T(dQ/dT) \tag{8.160}$$

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[24] W. Thomson (Lord Kelvin), "On a mechanical theory of thermoelectric currents", Proc. Roy. Soc. Edinburgh **3** 91 (1851); Lord Kelvin (Sir W. Thomson), *Collected Papers*, Cambridge (1882, 1884).

is Thomson's coefficient. It is worth noting that Thomson's effect is proportional to the electric flow $\mathbf{j}$, in contrast with the Joule-Lenz heat; Thomson's heat may either be released or absorbed; the thermopower Q itself may have both signs (for electrons $Q = -\pi^2 T/6e\mu$, where μ is the chemical potential; electron charge is $-e$). It is also noteworthy that Thomson's heat does not produce volume entropy, while the thermoconducted heat may do.

In equation (8.155) φ, T and the normal components of $\mathbf{q}$, $\mathbf{j}$ are continuous across a contact between two conductors; it follows that

$$-Tj_x(Q_2 - Q_1) = -\Delta[K(\partial T/\partial x)] \tag{8.161}$$

along the x-axis of the conductors. Therefore, a variation of temperature appears at a conducting junction, as a consequence of an electric current flowing through it. This is the Peltier effect. The quantity $q_x = -\Delta[K(\partial T/\partial x)]$ is the heat released at the contact per unit area and unit time; therefore

$$q_x = -Tj_x(Q_2 - Q_1) = \Pi_{12} j_x \quad , \tag{8.162}$$

where

$$\Pi_{12} = -T(Q_2 - Q_1) \tag{8.163}$$

is called the Peltier coefficient; we can see that it is additive, $\Pi_{13} = \Pi_{12} + \Pi_{23}$. Like Thompson's effect, the Peltier effect is proportional to the electric flow j_x normal to the junction, and may have both signs. In addition,

$$\tau_1 - \tau_2 = T\frac{d}{dT}(\Pi_{12}/T) \quad , \tag{8.164}$$

as we can see by comparing equations (8.160) and (8.163).

Let a conductor serial 121 with the two junctions 12 and 21 at temperatures $T_{1,2}$ and the end (identical) conductors $1, 1$ at temperature T. The electromotive force is given by

$$\mathcal{E} = \int E dx = \int Q(\partial T/\partial x) dx = \int_{T_1}^{T_2} (Q_2 - Q_1) dT \quad ; \tag{8.165}$$

on the other hand,

$$\mathcal{E} = -\int_{T_1}^{T_2} (\Pi_{12}/T) dT \quad , \tag{8.166}$$

making use of equation (8.163). Equations (8.164) and (8.166) are called Thomson's equations.

Finally, the two basic thermoelectricity equations (8.148) and (8.155) read

$$\begin{gathered} E_i = \sigma_{ik}^{-1} j_k + Q_{ik}(\partial T/\partial x_k) \ \ , \\ q_i - \varphi j_i = T Q_{ik} j_k - K_{ik}(\partial T/\partial x_k) \end{gathered} \tag{8.167}$$

in their general form. The electric and thermal conductivity tensors σ_{ik} and K_{ik} are symmetric; the thermoelectric tensor Q_{ik} may not be symmetric, in general.

8.17 Thermomagnetoelectricity

The flows are $\mathbf{j}$ (electric flow) and $\mathbf{q} - \varphi\mathbf{j}$, where $\mathbf{q}$ is the heat flow and φ is the electric potential; the generalized forces are $-\mathbf{E}/T$ and $(1/T^2) gradT = -grad(1/T)$, where $\mathbf{E}$ is the electric field and T is the temperature. Therefore, Onsager's equations read

$$\begin{gathered} j_i = a_{ik}(E_k/T) + b_{ik}\partial(1/T)/\partial x_k \ \ , \\ q_i - \varphi j_i = c_{ik}(E_k/T) + d_{ik}\partial(1/T)/\partial x_k \ \ ; \end{gathered} \tag{8.168}$$

in the presence of a magnetic field $\mathbf{H}$ the kinetic coefficients depend on $\mathbf{H}$ and obey the symmetry equations

$$\begin{gathered} a_{ik}(\mathbf{H}) = a_{ki}(-\mathbf{H}) \ \ , \ \ d_{ik}(\mathbf{H}) = d_{ki}(-\mathbf{H}) \ \ , \\ b_{ik}(\mathbf{H}) = c_{ki}(-\mathbf{H}) \ \ . \end{gathered} \tag{8.169}$$

One can also write

$$\begin{gathered} E_i = \sigma_{ik}^{-1}(\mathbf{H}) j_k + Q_{ik}(\mathbf{H})(\partial T/\partial x_k) \ \ , \\ q_i - \varphi j_i = T Q_{ki}(-\mathbf{H}) j_k - K_{ik}(\mathbf{H})(\partial T/\partial x_k) \ \ , \end{gathered} \tag{8.170}$$

where the electric conductivity σ and the thermoconductivity K satisfy

$$\sigma_{ik}(\mathbf{H}) = \sigma_{ki}(-\mathbf{H}) \ \ , \ \ K_{ik}(\mathbf{H}) = K_{ki}(-\mathbf{H}) \ \ , \tag{8.171}$$

according to equation (8.169); the thermopower Q has also been identified; the latter is not necessarily symmetric under **H**-reversal.

Splitting up the above kinetic tensors into symmetric and antisymmetric parts we get vector-like contributions from the antisymmetric parts of σ and K, similarly with the Hall effect (therefore, first-order contributions in **H**); for a homogeneous conductor the only **H**-contribution to the thermopower comes from its antisymmetric part, such that all these contributions to equation (8.170) are vectorial products of **H** by electric flow and of **H** by temperature gradient, respectively. Therefore, we get

$$\begin{gathered}
\mathbf{E} = \mathbf{j}/\sigma + Q\,gradT + \\
+R(\mathbf{H}\times\mathbf{j}) + N(\mathbf{H}\times gradT) \ , \\
\mathbf{q} - \varphi\mathbf{j} = TQ\mathbf{j} - K\,gradT + \\
+NT(\mathbf{H}\times\mathbf{j}) + L(\mathbf{H}\times gradT) \ .
\end{gathered} \tag{8.172}$$

Apart from the Hall effect expressed by R in equation (8.172), it appears the Nernst effect, as expressed by the coefficient N, and the Leduc-Righi effect given by the coefficient L. It is worth noting that N comes from the expansion of the thermopower Q, while L arises from the expansion of the thermoconductivity K (as R comes from the expansion of the electrical resistivity σ^{-1}). By comparing with equation (8.165), we can see that the N-Nernst effect represents the effect of the magnetic field on the electromotive force, while the L-Leduc-Righi effect represents the effect of the magnetic field upon the thermoconduction. The normal components of **q** and **j** on a junction are continuous, such that the normal component of the vector

$$TQ\mathbf{j} - K\,gradT + NT(\mathbf{H}\times\mathbf{j}) + L(\mathbf{H}\times gradT) \tag{8.173}$$

is also continuous at that interface; it follows that the N-contribution given above is the effect of the magnetic field upon the Peltier effect; it is called the Ettingshausen effect.

The heat per unit volume and unit time $q = -div\mathbf{q}$ can be computed from equation (8.172); to the first-order contributions we get

$$\begin{gathered} q=\mathbf{j}^2/\sigma - T\mathbf{j}\,gradQ + div(K\,gradT)+ \\ +(1/\sigma T)\frac{d}{dT}(\sigma NT^2)(\mathbf{j}\times\mathbf{H})gradT \quad ; \end{gathered} \tag{8.174}$$

here, $curl\mathbf{H}=0$ (*i.e.* the magnetic field produced by the electric flow is neglected), $curl(\mathbf{j}/\sigma)\approx curl\mathbf{E}=0$, and, of course, $div\mathbf{j}=0$. The last term in equation (8.174) represents the effect of the magnetic field upon Thomson's coefficient given by equation (8.160).

8.18 Electrodiffusion

An electrolyte consists of n_1 solute particles per unit volume, of mass m_1 and electric charge z_1, and n_2 solvent particles per unit volume, of mass m_2 and electric charge z_2. The electrolyte mass concentration c is the ratio of the solute mass to the solution mass; for a unit mass of solution $n_1m_1+n_2m_2=1$ the concentration is given by $c=n_1m_1$. The thermodynamic potential Φ per unit mass of solution gives the (mass) chemical potential

$$\begin{gathered} \mu=\partial\Phi/\partial c=(\partial\Phi/\partial n_1)(\partial n_1/\partial c)+(\partial\Phi/\partial n_2)(\partial n_2/\partial c)= \\ =\mu_1/m_1-\mu_2/m_2 \end{gathered} \tag{8.175}$$

at constant pressure p and constant temperature T, where $\mu_{1,2}$ are the chemical potentials of the components; in equilibrium the chemical potentials are constant.

The electrolyte is neutral, so that the total charge $z=n_1z_1+n_2z_2=0$ vanishes. The electric potential is given by $\varphi=\rho\partial\Phi/\partial z$, at constant p,T,c and for $z=0$, where ρ is the density of solution. The electric flow is proportional, in general, to the gradients of the two (chemical and electric) potentials

$$\mathbf{j}=\sigma(\mathbf{E}-\beta grad\mu) \tag{8.176}$$

at constant temperature and pressure, such that

$$\mathbf{E}=\mathbf{j}/\sigma+\beta grad\mu \quad , \tag{8.177}$$

where β is a kinetic coefficient. The gradient of the chemical potential corresponds to a concentration gradient and a pressure gradient, through

$$grad\mu = (\partial\mu/\partial c)_{p,T} grad c + (\partial\mu/\partial p)_{c,T} grad p \quad , \tag{8.178}$$

at constant temperature, *i.e.* it corresponds to a gradient of concentration and a gradient of temperature in equation (8.176) (besides the gradient of the electric potential, *i.e.* the electric field), as expected; but the gradient of pressure does not enter equation (8.176), because it would not lead, in general, to an entropy production. The pressure is not associated directly with a transport.

Let **i** denotes the solute (electrolyte) mass flow; its atomic part is $\mathbf{i} - \rho c\mathbf{v}$, where **v** is a macroscopic velocity; one may neglect it here. According to equation (8.176), under similar conditions, we may write down

$$\mathbf{i} = \gamma\mathbf{E} - \delta grad\mu \quad , \tag{8.179}$$

where the coefficients γ and δ are determined below. The entropy production per unit time is given by

$$\partial S/\partial t = \int d\mathbf{r}\cdot(\mathbf{jE}/T) - \int d\mathbf{r}\cdot(\mathbf{i} grad\mu)/T \ ; \tag{8.180}$$

hence, **j** and **i** are flows, and $-\mathbf{E}/T$ and $(grad\mu)/T$ are generalized forces. Equations (8.176) and (8.179) read

$$\begin{aligned} \mathbf{j} &= -\sigma T(-\mathbf{E}/T) - \beta\sigma T(grad\mu)/T \ , \\ \mathbf{i} &= -\gamma T(-\mathbf{E}/T) - \delta T(grad\mu)/T \quad , \end{aligned} \tag{8.181}$$

and, consequently, $\gamma = \beta\sigma$. We obtain finally equation (8.177) and

$$\mathbf{i} = -(\delta - \beta^2\sigma) grad\mu + \beta\mathbf{j} \ ; \tag{8.182}$$

we can see that the entropy production has positive values. The coefficient $\delta - \beta^2\sigma$ can be easily identified. In the absence of the electric flow, and making use of equation (8.178), equation (8.182) becomes

$$\mathbf{i} = -(\delta - \beta^2\sigma)(\partial\mu/\partial c)_{p,T} grad c \tag{8.183}$$

at constant pressure (and temperature); on the other hand, according to Fick's law of diffusion, $\mathbf{i} = \rho c\mathbf{v} = m_1 n_1 \mathbf{v} = -D grad m_1 n_1 = -\rho D grad c$, where D is the diffusion coefficient; therefore,

$$\delta - \beta^2\sigma = \rho D/(\partial\mu/\partial c)_{p,T} \quad , \tag{8.184}$$

such that, in general,

$$\mathbf{i} = -\frac{\rho D}{(\partial\mu/\partial c)_{p,T}} grad\mu + \beta\mathbf{j} \ ; \tag{8.185}$$

or

$$\mathbf{i} = -\rho D grad c + \beta\mathbf{j} \ . \tag{8.186}$$

We can see that β is proportional to the ratio of the electric charge to the mass. Making use of equations (8.177), (8.185) and equation (8.186), the entropy production given by equation (8.180) can be written as

$$\partial S/\partial t = \int d\mathbf{r} \cdot \mathbf{j}^2/\sigma T + \int d\mathbf{r} \cdot \rho D(\partial\mu/\partial c)_{p,T}(grad c)^2/T \ ; \tag{8.187}$$

we can see that it has positive values.

8.19 Electrolysis

Let $\mathcal{E}$ be an electric field between the two metallic plates of an electrolysis cell; the metal dissolves from an electrode and passes over to the other electrode. The metal cation mass flow is $\rho\mathbf{v} = (m/e)\mathbf{j}$, where m and e is the cation mass and charge, respectively, and $\mathbf{j}$ is the electric flow. On the other hand

$$\begin{aligned}\rho\mathbf{v} = (m/e)\mathbf{j} = \mathbf{i} + \rho c\mathbf{v} = \mathbf{i} + c(m/e)\mathbf{j} = \\ = -\rho D grad c + \beta\mathbf{j} + c(m/e)\mathbf{j} \ ;\end{aligned} \tag{8.188}$$

hence,

$$\rho D(dc/dx) = [\beta - (m/e)(1-c)]j \quad , \tag{8.189}$$

and

$$jl = \int_{c_1}^{c_2} \frac{\rho D dc}{\beta - (m/e)(1-c)} \quad , \tag{8.190}$$

where $c_{1,2}$ are the concentrations on the two electrodes and l denotes the length between the two electrodes.

From the entropy production per unit time (equation (8.187)) we obtain the heat produced per unit time and unit area of the electrodes

$$q = T(\partial S/\partial t) = \int dx \cdot [j^2/\sigma + \rho D(\partial\mu/\partial c)(dc/dx)^2] = j\mathcal{E} \ \ ; \quad (8.191)$$

making use of equation (8.189) we get

$$\begin{gathered} \mathcal{E} = \int_{c_1}^{c_2} \frac{\rho D dc}{\sigma[\beta-(m/e)(1-c)]} + \\ + \int_{c_1}^{c_2} (\partial\mu/\partial c)[\beta-(m/e)(1-c)]dc \ \ . \end{gathered} \quad (8.192)$$

for a weak electric flow

$$jl = \frac{\rho D}{\beta-(m/e)(1-c)}\Delta c \quad (8.193)$$

and

$$\mathcal{E} = \frac{\rho D}{\sigma[\beta-(m/e)(1-c)]}\Delta c + (\partial\mu/\partial c)[\beta-(m/e)(1-c)]\Delta c \ \ ; \quad (8.194)$$

therefore, the resistivity of the solution is

$$\mathcal{E}/jl = 1/\sigma + \frac{1}{\rho D}(\partial\mu/\partial c)[\beta-(m/e)(1-c)]^2 \ \ ; \quad (8.195)$$

the second term in equation (8.195) is an electromotive force arising from the variation of the concentration.[25]

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[25] L. Landau and E. Lifshitz, cited above.

9 Magnetic Field

9.1 Electrons in magnetic field

The motion of a non-relativistic electron in a magnetic field **H** is described by the hamiltonian

$$\mathcal{H} = \frac{1}{2m}(\mathbf{p} + \frac{e}{c}\mathbf{A})^2 - g_m \mu_B \mathbf{sH} \quad , \tag{9.1}$$

where $m \simeq 10^{-27}g$ is the electron mass, $-e = -4.8 \cdot 10^{-10} esu$ ($-1.6 \cdot 10^{-19}$C) is the electron charge, $c = 3 \times 10^{10} cm/s$ is the speed of light in vacuum, $g_m = 2$ (2.0023) is the gyromagnetic factor of the electron, $\mu_B = e\hbar/2mc \simeq 0.9 \cdot 10^{-20} erg/Gs$ (1J$= 10^7 erg$, $1Ts$ (Tesla)$= 10^4 Gs$ (Gauss, Oerstedt, Oe)$= (1/4\pi) \cdot 10^7 A/m$) is the Bohr magneton, $\hbar \simeq 10^{-27} erg \cdot s$ is Planck's constant, and $s = \pm 1/2$ are the components of the 1/2-spin **s**; **p** denotes the electron momentum and **A** is the electromagnetic vector potential, such that $\mathbf{H} = curl\mathbf{A}$; the electric field is given by $\mathbf{E} = -(1/c)\partial\mathbf{A}/\partial t$, and it is assumed to be zero, *i.e.* **A** does not depend on time (also, the scalar potential φ in $\mathbf{E} = -grad\varphi - (1/c)\partial\mathbf{A}/\partial t$ is set equal to zero). The first term in the hamiltonian given by equation (9.1) is usually called the orbital term, while the latter is called the Zeeman contribution. Noteworthy, the $1/c$-electromagnetic contributions bring only small effects to the non-relativistic motion of the electron.

The classical equations of motion

$$\dot{\mathbf{r}} = \mathbf{v} = \frac{1}{m}(\mathbf{p} + \frac{e}{c}\mathbf{A}) \tag{9.2}$$

and

$$\begin{gathered}\dot{\mathbf{p}} = -\tfrac{e}{mc}((\mathbf{p} + \tfrac{e}{c}\mathbf{A})grad)\mathbf{A} - \tfrac{e}{mc}(\mathbf{p} + \tfrac{e}{c}\mathbf{A}) \times curl\mathbf{A} = \\ = -\tfrac{e}{c}(\mathbf{v}grad)\mathbf{A} - \tfrac{e}{c}\mathbf{v} \times \mathbf{H} = -\tfrac{e}{c}d\mathbf{A}/dt - \tfrac{e}{c}\mathbf{v} \times \mathbf{H} \quad ,\end{gathered} \tag{9.3}$$

i.e. the Lorentz force law

$$m\dot{\mathbf{v}} = -\frac{e}{c}\mathbf{v} \times \mathbf{H} \quad , \tag{9.4}$$

follow readily from equation (9.1); the same equation of motion follows straightforwardly for the quantum-mechanical momentum $\mathbf{p} = -i\hbar grad$. It is worth remarking that the vector potential is defined up to the gradient of a function f (gauge symmetry of the electromagnetic field equations), which requires a corresponding change in the classical momentum $\mathbf{p}$ and the phase factor $\exp(ief/c\hbar)$ in the wavefunction.

For a uniform magnetic field H along the z-axis the vector potential may be taken as $\mathbf{A} = (-Hy, 0, 0)$, such that Schrodinger's equation reads

$$\left[\frac{1}{2m}(p_x - \frac{eH}{c}y)^2 - \frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2m}p_z^2 - g_m\mu_B sH\right]\psi = E\psi \quad . \tag{9.5}$$

The wavefunctions are

$$\psi = \frac{1}{\sqrt{L_x L_z}} \exp\left[\frac{i}{\hbar}(p_x x + p_z z)\right]\chi(y) \quad , \tag{9.6}$$

where $L_{x,z}$ (and L_y) are the dimensions of the spatial region where the motion is confined to, and

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega_c^2(y - y_0)^2\right]\chi = \varepsilon_\perp \chi \quad ; \tag{9.7}$$

this is Schrodinger's equation for a harmonic oscillator with cyclotron frequency

$$\omega_c = \frac{eH}{mc} \quad , \tag{9.8}$$

displaced by

$$y_0 = \frac{c}{eH}p_x \quad , \tag{9.9}$$

and the energy

$$\varepsilon_\perp = E - p_z^2/2m + g_m\mu_B sH \quad . \tag{9.10}$$

Introducing the new variable $\xi = \sqrt{m\omega_c/\hbar}(y-y_0)$, the displaced harmonic oscillator becomes

$$\chi'' + (2\varepsilon_\perp/\hbar\omega_c - \xi^2)\chi = 0 \quad , \tag{9.11}$$

or

$$\varphi'' - 2\xi\varphi' + (2\varepsilon_\perp/\hbar\omega_c - 1)\varphi = 0 \quad , \tag{9.12}$$

where $\chi = \exp(-\xi^2/2)\varphi$. Vanishing solutions at infinity are obtained for

$$\varepsilon_\perp = \hbar\omega_c(n+1/2) \ \ , \ \ n = 0,1,2,... \quad , \tag{9.13}$$

and $\varphi = H_n(\xi)$,

$$\begin{aligned} H_n(\xi) = (-1)^n e^{\xi^2} \tfrac{d^n}{d\xi^n} e^{-\xi^2} = (2\xi)^n - \tfrac{n(n-1)}{1}(2\xi)^{n-2} + \\ + \tfrac{n(n-1)(n-2)(n-3)}{1\cdot 2}(2\xi)^{n-4} + ... \quad , \end{aligned} \tag{9.14}$$

being the Hermite polynomials. One obtains the Landau levels.[1]

$$E_{ns}(p_z) = \hbar\omega_c(n+1/2) + p_z^2/2m - g_m\mu_B sH \ \ , \ \ n = 0,1,2... \ \ , \tag{9.15}$$

and the wavefunctions

$$\chi = \sqrt{\frac{2}{\pi}}\frac{1}{\xi_c}\frac{1}{\sqrt{2^n n!}}\exp\left[-(y-y_0)^2/\xi_c^2\right] H_n\left[\sqrt{2}\frac{y-y_0}{\xi_c}\right] \quad , \tag{9.16}$$

where the cyclotron length

$$\xi_c = \sqrt{2\hbar/m\omega_c} = \sqrt{2c\hbar/eH} \tag{9.17}$$

is introduced.

The cyclotron frequency is given by $\omega_c \simeq 1.8 \cdot 10^7 H(Gs)s^{-1}$ and the corresponding energy is $\hbar\omega_c \simeq 10^{-8}H(Gs)eV \simeq 10^{-4}H(Gs)K$ ($1eV = 1.16 \times 10^4 K$); the same estimation holds for the Zeeman energy. For usual magnetic fields (of the order of, say, $10Ts$) both the orbital and the Zeeman quanta of energy are small ($\sim$ 10K). Similarly, the wavefunctions given by equation (9.16) are localized over cyclotron lengths $\xi_c \simeq \sqrt{12/H(Gs)} \cdot 10^4$Å; for usual fields these lengths are much longer than atomic distances (and much shorter than the size of the sample). All these indicate that the electrons in magnetic field admit a quasi-classical description. It is also worth noting the non-analytical character of the spectrum in the limit of vanishing field $H \to 0$. The electron spectrum in magnetic field acquires dimensionality effects.

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[1] L. Landau, "Diamagnetismus der Metalle", Z. Phys. **64** 629 (1930).

Since $g_m = 2$ the Landau levels (9.15) can also be represented as

$$\begin{aligned} E_{ns}(p_z) &= 2\mu_B H(n-s+1/2) + p_z^2/2m = \\ &= 2\mu_B H \cdot l + p_z^2/2m = E_l(p_z) \ , \ \ l = 0, 1, 2... \ \ , \end{aligned} \tag{9.18}$$

where the ground-state $l = 0$ is filled with spin-up electrons ($n = 0, s = 1/2$), while the upper levels $l = 1, 2, ...$ are filled with both spin orientations ($n, s = 1/2$ and $n-1, s = -1/2, n = 1, 2, ...$).

Landau's levels given by equation (9.15) have a spatial (or transverse) degeneracy given by

$$N_\perp = L_y/\Delta y_0 = L_y eH/c\Delta p_x = L_x L_y \frac{eH}{2\pi c\hbar} = L_x L_y/\pi\xi_c^2 \quad , \tag{9.19}$$

which shows that the magnetic flux

$$L_x L_y H = \frac{2\pi c\hbar}{e} N_\perp = \pi\xi_c^2 H N_\perp \tag{9.20}$$

is quantized by

$$\Phi_0 = 2\pi c\hbar/e = \pi\xi_c^2 H \quad , \tag{9.21}$$

i.e. $L_x L_y H = \Phi_0 N_\perp$. The flux quantum is

$$\Phi_0 = 2\pi c\hbar/e = ch/e \simeq 4.14 \cdot 10^{-7} Gs \cdot cm^2 \tag{9.22}$$

(flux unit $1Gs \cdot cm^2 = 1Mx\,(Maxwell) = 10^{-8}Wb\,(Weber)$). Therefore, the density of states per unit area is

$$n_\perp = N_\perp/L_x L_y = eH/2\pi c\hbar = H/\Phi_0 = 1/\pi\xi_c^2 \quad , \tag{9.23}$$

which is lower than the atomic density of states.

The summation over states includes this transverse degeneracy; it reads

$$\begin{aligned} \sum = N_\perp \textstyle\sum_{snk_z} &= \tfrac{L_x L_y L_z}{(2\pi\hbar)^2} \tfrac{eH}{c} \textstyle\sum_{sn} \int dp_z = \\ &= \tfrac{V}{(2\pi\hbar)^2} m\omega_c \textstyle\sum_{sn} \int dp_z \quad , \end{aligned} \tag{9.24}$$

where $k_z = p_z/\hbar = (2\pi/L_z) \times integer$ is the wavevector along the z-axis; for usual fields the dependence on n is smooth, and the summation over n may be replaced by integral; one can write

$$\sum = \frac{V}{(2\pi\hbar)^2} m\omega_c \sum_s \int dndp_z \quad . \tag{9.25}$$

Making use of the transverse energy $\varepsilon_\perp = \hbar\omega_c(n+1/2)$ from equation (9.13), we get $d\varepsilon_\perp = \hbar\omega_c dn$, such that equation (9.25) becomes

$$\sum = \frac{V}{(2\pi)^2\hbar^3} m \sum_s \int d\varepsilon_\perp dp_z \quad ; \tag{9.26}$$

the transverse energy can also be represented as $\varepsilon_\perp = (p_x^2+p_y^2)/2m = p_\perp^2/2m$, such that $d\varepsilon_\perp = p_\perp dp_\perp/m = (1/2\pi m)\oint dp_x dp_y$; the summation over states reads now

$$\sum = \frac{V}{(2\pi\hbar)^3} \sum_s \int d\mathbf{p} \quad , \tag{9.27}$$

which is identical with that of the free electrons; in addition, introducing $\varepsilon = \varepsilon_\perp + p_z^2/2m = p^2/2m$ we obtain

$$\sum = \frac{V}{4\pi^2}(2m/\hbar^2)^{3/2} \sum_s \int_0 d\varepsilon \cdot \varepsilon^{1/2} \quad . \tag{9.28}$$

It is worth noting that the Zeeman energy does not enter ε as defined here. Also, the effect of the orbital motion in the magnetic field does not appear in the bulk contribution to the summation over states, as expected.

Indeed, the magnetic field produces only a marginal effect, controlled by the ratio of the atomic distance to the cyclotron length, or the cyclotron frequency to the characteristic scale energy; it is obtained by including the next-order corrections in replacing summation over n by integrals. Expanding $f(n+\xi)$ in series of powers of ξ for $-1/2 <$

$\xi < 1/2$ we get

$$\begin{gathered}\int_{a-1/2}^{b+1/2} f(x)dx = \sum_{n=a}^{b} \int_{-1/2}^{1/2} d\xi \cdot \\ \cdot [f(n) + \xi f'(n) + (1/2)\xi^2 f''(n) + ...] = \\ = \sum_{n=a}^{b} f(n) + (1/24) \sum_{n=a}^{b} f''(n) + ... = \\ = \sum_{n=a}^{b} f(n) + (1/24) f'(x) \mid_{a-1/2}^{b+1/2} ... \ ; \end{gathered} \tag{9.29}$$

including the next-order terms in approximating the summation by integrals, we get

$$\begin{gathered}\sum_{n=a}^{b} f(n) = \int_{a-1/2}^{b+1/2} f(x)dx - (1/24) f'(x) \mid_{a-1/2}^{b+1/2} + \\ +(7/24 \cdot 240) f'''(x) \mid_{a-1/2}^{b+1/2} + ... \ ; \end{gathered} \tag{9.30}$$

in a more convenient form this equation reads

$$\sum_{n=a}^{b-1} f(n+1/2) = \int_a^b f(x)dx - (1/24) f'(x) \mid_a^b + ... \ . \tag{9.31}$$

For a function $f(E_{ns}(p_z))$ of energy $E_{ns}(p_z)$ given by equation (9.15) the summation over states is

$$\begin{gathered}\sum f = N_{\perp} \sum_{snk_z} f = \frac{V}{(2\pi\hbar)^2} m\omega_c \sum_{sn} \int dp_z f = \\ = \frac{V}{4\pi^2} (2m/\hbar^2)^{3/2} \sum_s \int_0^{\infty} d\varepsilon \cdot \varepsilon^{1/2} f(\varepsilon - g_m \beta s H) + \\ + \frac{1}{48} \frac{V}{4\pi^2} (\hbar\omega_c)^2 (2m/\hbar^2)^{3/2} \sum_s \int_0^{\infty} d\varepsilon \cdot \varepsilon^{-1/2} f'(\varepsilon) \end{gathered} \tag{9.32}$$

to the second-order in magnetic field H (with proper limits of integration and change of variables; in the last integral, for instance, $\varepsilon = p_z^2/2m$). We can see, indeed, that the effect of the orbital motion is included in the boundary term.

For cyclotron lengths and frequencies comparable, in some cases, to characteristic lengths and frequencies of the electrons, the magnetic field gives rise to characteristic oscillatory behaviour. Indeed,

$$f(x)=\sum_{s=-\infty}^{\infty}e^{-2\pi isx}g_s\ \ ,\ \ g_s=\int_n^{n+1}dx\cdot f(x)e^{2\pi isx}\quad , \tag{9.33}$$

and

$$f(n+1/2)=\sum_{s=-\infty}^{\infty}(-1)^s\int_n^{n+1}dx\cdot f(x)e^{2\pi isx}\ \ ; \tag{9.34}$$

therefore

$$\begin{gathered}\textstyle\sum_{n=0}^{\infty}f(n+1/2)=\sum_{s=-\infty}^{\infty}(-1)^s\int_0^{\infty}dx\cdot f(x)e^{2\pi isx}=\\ \textstyle=\int_0^{\infty}dx\cdot f(x)+2\sum_{s=1}^{\infty}(-1)^s\int_0^{\infty}dx\cdot f(x)\cos 2\pi sx\ \ ;\end{gathered} \tag{9.35}$$

integrating by parts twice in the second integral we get

$$\begin{gathered}\textstyle\sum_{n=0}^{\infty}f(n+1/2)==\int_0^{\infty}dx\cdot f(x)-2f'(0)\sum_{s=1}^{\infty}\frac{(-1)^s}{(2\pi s)^2}-\\ \textstyle-2\sum_{s=1}^{\infty}\frac{(-1)^s}{(2\pi s)^2}\int_0^{\infty}dx\cdot f''(x)\cos 2\pi sx\quad ,\end{gathered} \tag{9.36}$$

and we can check equation (9.31), since $\sum_1(-1)^s/s^2=-\pi^2/12$ (and $\sum_1 1/s^2=\pi^2/6$); f'' is typically peaked on some x, hence the oscillatory behaviour (in $1/H$).

9.2 Electron magnetism

As a consequence of their spatial extension the electrons in solids admit a quasi-classical description, to the first approximation. They interact both with the ionic cores and with themselves, screen off the Coulomb repulsion between the ions, and ensure, through their delocalization, the cohesion of the solids. They form a slightly inhomogeneous electron liquid in a self-consistent potential, and are described, within this approximation, by (quasi-) plane waves, according to Pauli's exclusion principle and Fermi statistics. The electron one-particle states are distributed into a (quasi-spherical, isotropic) Fermi sea, extending up to the Fermi level, or chemical potential, which, in this case, is given by the average self-consistent potential; it defines the Fermi surface. Due to the Fermi statistics, the single-electron states (and energies) are meaningful only for quasiparticle elementary excitations located in the neighbourhood of the Fermi surface. The quasiparticles have a finite lifetime (and mean freepath), a Fermi velocity, and all the other characteristics renormalized according to a (normal) Fermi liquid. For a Fermi liquid the relevant quantities are those obtained as small variations in the quasiparticle behaviour in the neighbourhood of the Fermi surface. In the next approximation, the electron states in crystalline solids are grouped into energy bands, separated by energy gaps and confined to Brillouin zones; some are fully occupied, giving rise to insulators, some others are only partially occupied, due to their spatial intersection, giving rise to conducting solids, like metals (or semiconductors); the Fermi sea and surface still hold in this case, at least at low temperatures, though, usually, they are anisotropic; the electron liquid is still described as a Fermi liquid. Typically, the characteristic electron energies are of the order of a few eV, and the characteristic electron distances are of the order of the atomic distances. However, for typical semiconductors, where the concentration of the charge carriers is low, the Boltzmann classical statistics applies, and the lifetime of the classical (quasi-) particles goes like $\tau \sim (a^2/\sigma)(1/\sqrt{T})$, where a is the average inter-particle separation, σ is the collision cross-section, and T denotes the temperature, for large values of both $a^2 T$ and a^2/σ (usually, the interaction with the atoms dominates, which leads to an effective $\sigma \simeq a^2$).

For macroscopic samples and usual magnetic fields the electron quasiparticles obey a quasi-classical description, according to Landau's levels (or magnetic bands) given by equations (9.15) and (9.18); the Fermi sea is filled band by band, satisfying the transversal degeneracy and gradually increasing the wavevector k_z, up to the Fermi level; the shape of the Fermi surface acquires a characteristic tubular aspect, with small striations, controlled by the (small) magnitude of the magnetic field.

A tight-binding energy band may be represented, for instance, as

$$\varepsilon = t_a(1-\cos ak_x) + t_b(1-\cos bk_y) + t_c(1-\cos ck_z) \quad , \qquad (9.37)$$

where $t_{a,b,c}$ are bandwidth parameters, a, b, c are unit cell sides, and the wavevector **k** is limited to the Brillouin zone $-\pi < ak_x, bk_y, ck_z < \pi$. A uniform magnetic field along the k_z-axis (not necessarily parallel with the z-axis) may suggest to replace $k_{x,y} = p_{x,y}/\hbar$ in equation (9.37) by $(p_{x,y} + eA_{x,y}/c)/\hbar$, in view of the hamiltonian role played by ε as a function of the momentum $\mathbf{p}$, and solve the resulting Schrodinger's equation;[2] (the direct space is spanned by $\mathbf{a}, \mathbf{b}, \mathbf{c}$ and the $\mathbf{k}$-reciprocal space is spanned by $2\pi(\mathbf{b} \times \mathbf{c})/v$, etc, where $v = \mathbf{a}(\mathbf{b} \times \mathbf{c})$ is the volume of the unit cell and $v^* = (2\pi)^3/v$ is the volume of the reciprocal unit cell (Brillouin zone)). However, the energy ε given by equation (9.37) is hamiltonian for quasiparticles only, which are close to the Fermi surface, and are described by a free-like hamiltonian with the corresponding effective-mass parameters. Therefore, the effect of the magnetic field is obtained similar to (quasi-) free electrons. The quadratic term in momentum deviation from the Fermi surface, which gives the uncertainty in the quasiparticle energy, and corresponds to the quasiparticle lifetime, may be included in such a treatment, since the quasiparticles on the Fermi surface live indefinitely. At finite temperatures, however, the scale energy associated with the magnetic field, *i.e.* the cyclotron frequency, must be larger than the uncertainty in the quasiparticle energy, *i.e.* the magnetic field must be sufficiently high. This uncertainty in the quasiparticle energy goes like T^2/μ, where T denotes the temperature and μ is the chemical potential, and is, in fact, very small in comparison with the cyclotron frequency associated with the usual magnetic fields, especially at low temperatures. Obviously, this criterion means that the quasiparticle lifetime is much longer than cyclotron time, *i.e.* the time needed for describing a quasi-classical cyclotron orbit, which is also the time required for a transition between two neighbouring cyclotron levels. In this connection it is worth emphasizing that, typically, there exist three characteristic scale energies and times which are relevant to the electron dynamics in magnetic field; first, there exists the thermal energy T, which must be larger than any other motion energy, in order to ensure equilibrium; it controls the fluctuations, and is associated with the statistical motion and the fluctuating time; second, there exists the uncertainty T^2/μ in the quasiparticle energy, which controls the quasiparticle lifetime and the collision rate; the former is always higher than the latter, the equilibrium being thus ensured by quasiparticles, and the latter being meaningful; and, finally, there exists the cyclotron frequency ω_c, which is usually smaller than T, *i.e.* $T \gg \hbar\omega_c$ (otherwise, for instance at very low temperatures, the equilibrium may not be attained). The situation described here corresponds to $\hbar\omega_c \gg T^2/\mu$, but the opposite situation $\omega_c \ll 1/\tau_{col}$, where τ_{col} is the collision time, may also be relevant, obviously. Turning back, for an anisotropic hamiltonian with mass parameters $m_{x,y}$ the cyclotron frequency is $\omega_c = eH/c\sqrt{m_x m_y}$ and the cyclotron length is $\xi_c = (m_x/m_y)^{1/4}\sqrt{2\hbar c/eH}$; the effective mass approximation to the energy spectrum is also appropriate for low concentrations of charge carriers, where the hamiltonian is a free-like one.

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[2] R. Peierls, "Zur Theorie des Diamagnetismus von Leitungselektronen", Z. Phys. **80** 763 (1933); "Zur Theorie des Diamagnetismus von Leitungselektronen. II Starke Magnetfelder", **81** 186 (1933); G. H. Wannier, "Dynamics of band electrons in electric and magnetic field", Revs. Mod. Phys. **34** 645 (1962).

Making use of equation (9.32), the number of electron states can be written as

$$N = \sum_s N_s - \frac{gV}{12(2\pi)^2} m\omega_c^2 \partial A/\partial\mu \quad , \tag{9.38}$$

where $g = 2s+1$,

$$N_s = \frac{V}{4\pi^2}(2m/\hbar^2)^{3/2} \int_0^\infty d\varepsilon \cdot \varepsilon^{1/2} \frac{1}{\exp(\varepsilon-\mu_s)\beta+1} \tag{9.39}$$

is the bulk contribution, with $\mu_s = \mu + \alpha_s$, $\alpha_s = g_m \mu_B s H$, $\beta = 1/T$, T being the temperature, and

$$A = \frac{1}{2}(2m/\hbar^2)^{1/2} \int_0^\infty d\varepsilon \cdot \varepsilon^{-1/2} \frac{1}{\exp(\varepsilon-\mu)\beta+1} \quad . \tag{9.40}$$

The Fermi integrals are estimated according to

$$\begin{gathered} \textstyle\int_0^\infty d\varepsilon \cdot f(\varepsilon) \frac{1}{\exp(\varepsilon-\mu)\beta+1} = \int_0^\mu d\varepsilon \cdot f(\varepsilon) + \\ + \frac{\pi^2 T^2}{6} f'(\mu) + \frac{7\pi^4 T^4}{360} f'''(\mu) + \dots \quad , \end{gathered} \tag{9.41}$$

valid for $\mu\beta \gg 1$. A series expansion is performed in equation (9.39) in powers of $\alpha_s\beta$, and $\sum_s \alpha_s^2 = g\alpha^2$ is introduced, where $\alpha^2 = (1/3)s(s+$

$1)(g_m\mu_B H)^2$. The number of particles given by equation (9.38) can now be written as

$$N=\tfrac{gV}{6\pi^2}(2mT/\hbar^2)^{3/2}(\ln z)^{3/2}\cdot$$

$$\cdot[1+\tfrac{1}{8}(\pi^2+\rho)\tfrac{1}{(\ln z)^2}+\tfrac{\pi^2}{64}(7\pi^2/10+\rho)\tfrac{1}{(\ln z)^4}+ \tag{9.42}$$

$$+\tfrac{49\pi^4}{3072}\rho\tfrac{1}{(\ln z)^6}] \quad ,$$

where

$$\rho=(f\beta)^2 \quad , \quad f^2=3\alpha^2-(\hbar\omega_c/2)^2 \quad , \tag{9.43}$$

and the fugacity $z=\exp(\mu\beta)$ has been introduced; it is obtained from equation (9.42) as

$$\begin{aligned}\ln z=(\beta\varepsilon_F)[1-\tfrac{1}{12}(\pi^2+\rho)\tfrac{1}{(\beta\varepsilon_F)^2}-\tfrac{\pi^2}{48}(3\pi^2/5+\rho)\tfrac{1}{(\beta\varepsilon_F)^4}-\\ -\tfrac{\pi^4}{4608}(49+581\pi^2/45+497\rho/15)\tfrac{1}{(\beta\varepsilon_F)^6}] \quad ,\end{aligned} \tag{9.44}$$

where the Fermi wavevector k_F has been introduced through $N=gVk_F^3/6\pi^2$, and the Fermi energy has been parametrized as $\varepsilon_F=\hbar^2k_F^2/2m$; it is noteworthy that the latter is the chemical potential at zero temperature in the absence of the magnetic field; and the chemical potential at zero temperature is changed by the magnetic field according to

$$\mu=\varepsilon_F[1-f^2/12\varepsilon_F^2] \quad ; \tag{9.45}$$

for $s=1/2$ one obtains $f^2=2(\mu_B H)^2$ ($\alpha=\hbar\omega_c/2=\mu_B H$) and $\mu=\varepsilon_F[1-(\mu_B H)^2/6\varepsilon_F^2]$ (and the change with the temperature is $\mu=\varepsilon_F(1-\pi^2T^2/12\varepsilon_F^2)$).

In a similar manner and within the same approximation it is found that the energy may be represented as

$$E=\sum_s E_s+\frac{gV}{24(2\pi)^2}m\omega_c^2A-\sum_s\alpha_sN_s \quad , \tag{9.46}$$

where

$$E_s=\frac{V}{4\pi^2}(2m/\hbar^2)^{3/2}\int_0^\infty d\varepsilon\cdot\varepsilon^{3/2}\frac{1}{\exp(\varepsilon-\mu_s)\beta+1} \quad . \tag{9.47}$$

The last term in equation (9.46) is

$$\sum_s \alpha_s N_s = \tfrac{gV}{4\pi^2\beta}(2mT/\hbar^2)^{3/2}(\ln z)^{1/2}\cdot$$
$$\cdot[1-\tfrac{1}{24}\tfrac{1}{(\ln z)^2}-\tfrac{7\pi^4}{384}\tfrac{1}{(\ln z)^4}](\alpha\beta)^2 \quad , \tag{9.48}$$

and the energy is given by

$$\beta E = \tfrac{gV}{10\pi^2}(2mT/\hbar^2)^{3/2}(\ln z)^{5/2}\cdot$$
$$\cdot[1+\tfrac{5}{8}(\pi^2-\rho/3)\tfrac{1}{(\ln z)^2}-\tfrac{\pi^2}{192}(7\pi^2/2-5\rho/3)\tfrac{1}{(\ln z)^4}+ \tag{9.49}$$
$$+\tfrac{35\pi^4}{9216}\rho\tfrac{1}{(\ln z)^6}] \quad .$$

Also, from equations (9.42) and (9.49) we get

$$\beta E/N = \tfrac{3}{5}(\ln z)[1+(\pi^2/2-\rho/3)\tfrac{1}{(\ln z)^2}-$$
$$-\tfrac{\pi^2}{24}(11\pi^2/5+2\rho/3)\tfrac{1}{(\ln z)^4}] \quad ; \tag{9.50}$$

hence, by using equation (9.44),

$$E/N = \frac{3}{5}\varepsilon_F + \frac{1}{4}(\pi^2-\rho)\frac{T^2}{\varepsilon_F} - \frac{3\pi^2}{80}(\pi^2+5\rho/9)\frac{T^4}{\varepsilon_F^3} \quad , \tag{9.51}$$

or

$$E/N = \tfrac{3}{5}\varepsilon_F + \pi^2T^2/4\varepsilon_F - 3\pi^4T^4/80\varepsilon_F^3 -$$
$$-\tfrac{f^2}{4\varepsilon_F}(1+\pi^2T^2/12\varepsilon_F^2) \quad . \tag{9.52}$$

The T^4-contribution is not relevant, as it is comparable with the quasiparticle uncertainty in energy; also, we can see that f^2-contribution must be larger than the T^2-contribution in order to be relevant, *i.e.* the cyclotron frequency (and Zeeman energy) should be larger than the quasiparticle uncertainty in energy.

The magnetization can be obtained from equation (9.52) as $M = -\partial E/\partial H$, hence the magnetic susceptibility per particle

$$\chi = (\mu_B^2/\varepsilon_F)(1+\pi^2T^2/12\varepsilon_F^2) = \mu_B^2/\mu \quad ; \tag{9.53}$$

the Zeeman contribution gives the Pauli paramagnetic spin susceptibility $\chi_p = 3\mu_B^2/2\mu$, while the orbital contribution is Landau's diamagnetic susceptibility $\chi_d = -\mu_B^2/2\mu$; we can see that the latter is one third of the former.

The paramagnetic spin susceptibility can also be obtained more directly from the variations of the chemical potential and the electron density; indeed, the former can be written as $\delta\mu_\pm = \pm(\hbar^2 k_F/m)\delta k_F \mp \mu_B H$ for both spin orientations, hence $\delta k_F = m\mu_B H/\hbar^2 k_F$ at equilibrium; on the other hand, the magnetization per unit volume is given by $M = \mu_B(\delta n_+ - \delta n_-) = \mu_B(k_F^2/\pi^2)\delta k_F$, and we get straightforwardly $\chi_p = 3\mu_B^2/2\mu$ for the paramagnetic susceptibility per particle. The corresponding energy for the Fermi liquid is obtained from $\delta E = (\mu - \mu_B H)\delta n_+ + (\mu + \mu_B H)\delta n_- = \mu\delta n - MH$, as expected, or $\delta E = \mu(k_F/\pi^2)(\delta k_F)^2 - \mu_B H(k_F^2/\pi^2)\delta k_F$; we obtain $\delta E/N = -3(\mu_B H)^2/4\mu$, which is the paramagnetic spin energy in equation (9.52). Also, from equation (9.18) we obtain the Fermi wavevectors along the z-direction as $k_{Fl} = [(2m/\hbar^2)(\mu - 2\mu_B Hl)]^{1/2}$, such that the number of spin-up electrons in the bottom band $l = 0$ is given by $N_+ = N_\perp(L_z/2\pi)\cdot 2k_{F0}$, and their number per particle is $N_+/N = 3\mu_B H/2\mu$; hence, again, the paramagnetic spin susceptibility $3\mu_B^2/2\mu$.

For localized atomic aggregates the diamagnetic contribution $(e^2/2mc^2)\sum_i A_i^2$ to the hamiltonian given by equation (9.1), where i denotes the electrons, can be treated as a perturbation; since the electromagnetic vector can be written as $\mathbf{A} = (1/2)(\mathbf{H}\times\mathbf{r})$, we obtain $(e^2H^2/8mc^2)\sum_i r_i^2\sin^2\theta_i$; for a radially symmetric density of electrons we get $(e^2H^2/12mc^2)N\overline{r^2}$, and the diamagnetic susceptibility $\chi_d = -(e^2/6mc^2)\overline{r^2}$ per particle, or $\chi_d = -(1/3)\mu_B^2(2m\overline{r^2}/\hbar^2)$; this is Langevin's diamagnetism. The linear **A**-contribution to the hamiltonian together with the spin contribution give the Zeeman atomic effect, generally anomalous, which involves a linear H-displacement of the energy levels; however, in the ground state this contribution may vanish, and the second-order perturbation theory for this linear H-term leads to a paramagnetic contribution which is higher than the diamagnetic one; this is van Vleck's paramagnetism; however, for high magnetic field the linear term still brings the main contribution; this is the Paschen-Back effect.

The classical motion of a charged particle exhibits diamagnetism (through Faraday-Lenz induction); indeed, the lagrangian of an electron in an external magnetic field is $L = mv^2/2 - (e/c)\mathbf{Av}$ ($\mathbf{p} = m\mathbf{v} - (e/c)\mathbf{A}$, and the hamiltonian is $H = mv^2/2 = (\mathbf{p} + e\mathbf{A}/c)^2/2m$); it reads also $L = mv^2/2 - (e/2c)(\mathbf{H}\times\mathbf{r})\mathbf{v}$, or $L = (m/2)[\mathbf{v} - (e/2mc)(\mathbf{H}\times\mathbf{r})]^2$, up to H^2-corrections, as for non-relativistic electrons, which shows that the electron turns about with the Larmor frequency $\Omega = eH/2mc$ (half of the cyclotron frequency). On the other hand, the equation of motion $m\dot{\mathbf{r}} = -(e/c)(\mathbf{v}\times\mathbf{H})$ vanishes when averaged over a finite motion, but the torque $\mathbf{M} = -(e/c)\mathbf{r}\times(\mathbf{v}\times\mathbf{H}) = -(e/c)\mathbf{v}(\mathbf{rH}) = \mathbf{m}\times\mathbf{H}$, where $\mathbf{m} = -(e/2c)(\mathbf{r}\times\mathbf{v})$ is the magnetic dipole (and the lagrangian can also be written as $L = mv^2/2 + \mathbf{mH}$), does not; it follows that the kinetic momentum moves according to $d\mathbf{L}/dt = \mathbf{m}\times\mathbf{H} = \overrightarrow{\Omega}\times\mathbf{L}$. *i.e.* it performs a Larmor precession about the turning axis. The induced electric current is $-e\Omega/2\pi$ and the magnetic moment $(-e\Omega/2\pi)\pi\overline{\rho^2}/c = -(e^2H/6mc^2)\overline{r^2}$, where ρ is the in-plane radius, such that the diamagnetic susceptibility is $\chi_d = -(e^2/6mc^2)\overline{r^2}$, in agreement with the above results.

The paramagnetism is a quantum-mechanical effect; the Boltzmann distribution does not lead to diamagnetism, the latter being a quantum-mecahnical effect for ensembles of charged particles in equilibrium. The Boltzmann distribution gives, however, the magnetization of the magnetic moments; for $s = 1/2$ for instance, we obtain $M = \mu_B \tan(\mu_B H/T)$ and Curie's law for paramagnetic susceptibility $\chi_p = \mu_B^2/T$; similar results hold for any other magnetic moments, as well as for classical magnetic moments (which correspond to large quantum-mechanical magnetic moments); in the latter case the magnetization is given by the Brillouin function, and the Langevin function $L(x) = \coth x - 1/x$, for $x = \mu_B H/T$. It is worth noting the formal substitution of the temperature T by the characteristic scale energy μ on passing from the Fermi to Boltzmann distribution.

9.3 Heat capacity

From equation (9.52) we obtain the heat capacity

$$c=\frac{\pi^2}{2}(1-f^2/12\mu^2)\frac{T}{\mu} \tag{9.54}$$

per particle (at constant volume); it can also be written as

$$c=\frac{\pi^2}{2}[1-(\mu_B H)^2/12\mu^2]\frac{T}{\mu}\ \ ; \tag{9.55}$$

we can see that the effect of the magnetic field is extremely small.[3] The grand-canonical potential $\Omega=-pV=-(1/\beta)\ln Q$, where p is the pressure and Q is the grand-partition function, is defined by

$$\beta\Omega=-\frac{V}{(2\pi\hbar)^2}m\omega_c\sum_{sn}\int dp_z\cdot\ln\{1+\exp[E_{ns}(p_z)-\mu]\}\quad , \tag{9.56}$$

where the energy is given by equation (9.15). By similar transformations it can be re-expressed as

$$\Omega=-\frac{2}{3}\sum_s E_s+\frac{gV}{12(2\pi)^2}m\omega_c^2 A\ \ ; \tag{9.57}$$

on the other hand, by taking the derivative in equation (9.56) with respect to β, we get

$$\Omega+\beta\partial\Omega/\partial\beta=E-\mu N\quad , \tag{9.58}$$

hence the entropy

$$\begin{gathered}S=\beta^2\partial\Omega/\partial\beta=\tfrac{5}{3}\beta E-N\ln z-\\ -\tfrac{gV}{9(2\pi)^2}m\omega_c^2\beta A+\tfrac{2}{3}\beta\textstyle\sum_s\alpha_s N_s\ \ .\end{gathered} \tag{9.59}$$

Making use of equations (9.48) and (9.51), and estimating A given by equation (9.40) by means of equation (9.41), we obtain that the entropy goes like $S \sim T$ for $T \rightarrow 0$; from Mayer's relationship $c_p - c_V \sim T^{2\alpha+1}$ between the heat capacity c_p at constant pressure and the heat capacity at constant volume c_V, where $S \sim T^\alpha$, we arrive at the conclusion that the two heat capacities coincide up to T^3-contributions, as expected, and as given in equation (9.54).

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[3] M. Apostol, "Specific heat of charged fermions in magnetic field", J. Theor. Phys. **16** (1996); see also "Fermions in a slab", J. Theor. Phys. **18** (1996).

It is also worth noting that $-MdH$ occurs in all the thermodynamic potentials, such that, for Gibbs's free energy $\Phi = F + pV = N\mu$, where F is the free energy, we can write

$$\begin{gathered}
-M_p = (\partial\Phi/\partial H)_{T,p,N} = \\
= (\partial F/\partial H)_{T,p,N} + p(\partial V/\partial H)_{T,p,N} = \\
= (\partial F/\partial H)_{T,V,N} + (\partial F/\partial V)(\partial V/\partial H)_{T,p,N} + \\
+p(\partial V/\partial H)_{T,p,N} = -M_V - p(\partial V/\partial H)_{T,p,N} + \\
+p(\partial V/\partial H)_{T,p,N} = -M_V \quad ,
\end{gathered} \tag{9.60}$$

i.e. the two magnetizations are the same.

9.4 Quasi-classical description

Quasiparticles located in the neighbourhood of the Fermi surface admit a quasi-classical description over large distances and long times, with a velocity given by

$$\mathbf{v} = \dot{\mathbf{r}} = \partial\varepsilon/\partial\mathbf{p} = (1/\hbar)\partial\varepsilon/\partial\mathbf{k} \quad , \tag{9.61}$$

where $\varepsilon(\mathbf{k})$ is their energy and $\mathbf{k}$ denotes the wavevector; this description is limited by atomic distances and quasiparticle lifetime; it holds also for various external perturbations, magnetic field included.

In the presence of a magnetic field $\mathbf{H}$ the momentum $\mathbf{p}$ is changed to $\mathbf{p}+e\mathbf{A}/c$, such that the wavevector $\mathbf{k}$ can be written as

$$\mathbf{k} = \frac{1}{\hbar}(\mathbf{p} + e\mathbf{A}/c) \ ; \tag{9.62}$$

the velocity is the same as that given by equation (9.61), and

$$\begin{aligned}\dot{\mathbf{p}} = -\partial\varepsilon/\partial\mathbf{r} = -\tfrac{e}{c\hbar}((\partial\varepsilon/\partial\mathbf{k})grad)\mathbf{A}- \\ -\tfrac{e}{c\hbar}(\partial\varepsilon/\partial\mathbf{k})\times curl\mathbf{A} = \\ = -\tfrac{e}{c}(\mathbf{v}grad)\mathbf{A} - \tfrac{e}{c}\mathbf{v}\times\mathbf{H} = \\ = -\tfrac{e}{c}d\mathbf{A}/dt - \tfrac{e}{c}\mathbf{v}\times\mathbf{H} = -\tfrac{\mathbf{e}}{\mathbf{c}}\mathbf{v}\times\mathbf{H} \quad ,\end{aligned} \tag{9.63}$$

i.e. the law of motion according to Lorentz force; and

$$\dot{\mathbf{k}} = -\frac{e}{c\hbar}\mathbf{v}\times\mathbf{H} \quad ; \tag{9.64}$$

it is assumed that the vector potential does not depend on time.

For a uniform magnetic field the wavevector **k** moves on the Fermi surface by

$$dk = \frac{eH}{c\hbar}v_{\perp}dt \quad , \tag{9.65}$$

according to equation (9.64), where

$$v_{\perp} = (1/\hbar)\partial\varepsilon/\partial k_{\perp} \tag{9.66}$$

is the velocity in the orbit plane perpendicular to the magnetic field; for a closed orbit the wavevector rotates on the Fermi surface with the cyclotron frequency $\omega_c = eH/mc$, according to equation (9.65), since $v_{\perp} = \hbar k_{\perp}/m$; the mass parameter m is, in fact, the corresponding quasiparticle effective mass m^*, which follows from equation (9.65) as

$$m^* = \frac{\hbar}{2\pi}\oint\frac{dk}{v_{\perp}} \quad ; \tag{9.67}$$

it can also be written as

$$m^* = \frac{\hbar^2}{2\pi}\oint(\partial k_{\perp}/\partial\varepsilon)dk = \frac{\hbar^2}{2\pi}(\partial\mathcal{A}/\partial\varepsilon) \quad , \tag{9.68}$$

where $\mathcal{A}$ is the area of the cross-section of the Fermi sea enclosed by the orbit.

From equation (9.64) we obtain also

$$d\mathbf{k} = -\frac{e}{c\hbar} d\mathbf{r} \times \mathbf{H} \quad , \tag{9.69}$$

hence the trajectory (perpendicular to the magnetic field) is the same as the **k**-trajectory on the Fermi surface, only rotated by $-\pi/2$ about **H**. Indeed, equation (9.64) has the solutions

$$\begin{aligned} k_x &= k_{0x} \cos \omega_c t + k_{0y} \sin \omega_c t \quad , \\ k_y &= -k_{0x} \sin \omega_c t + k_{0y} \cos \omega_c t \end{aligned} \tag{9.70}$$

for $\mathbf{v}_\perp = (1/\hbar)\partial\varepsilon/\partial\mathbf{k}_\perp = \hbar\mathbf{k}_\perp/m = \hbar(k_x, k_y)/m$; therefore, from equation (9.61) we obtain

$$\begin{aligned} \dot{x} &= (\hbar k_{0x}/m) \cos \omega_c t + (\hbar k_{0y}/m) \sin \omega_c t \quad , \\ \dot{y} &= -(\hbar k_{0x}/m) \sin \omega_c t + (\hbar k_{0y}/m) \cos \omega_c t \quad , \end{aligned} \tag{9.71}$$

and the trajectory

$$\begin{aligned} x &= (\hbar k_{0x}/m\omega_c) \sin \omega_c t - (\hbar k_{0y}/m\omega_c) \cos \omega_c t + x_0 \quad , \\ y &= (\hbar k_{0x}/m\omega_c) \cos \omega_c t + (\hbar k_{0y}/m\omega_c) \sin \omega_c t + y_0 \quad , \end{aligned} \tag{9.72}$$

which is circular, centered at (x_0, y_o), and with radius $r_\perp = \hbar k_\perp/m\omega_c = v_\perp/\omega_c$; a centripetal force $F = \hbar\omega_c k_\perp = m\omega_c^2 r_\perp$ acts upon it.
The quasi-classical quantization reads

$$\oint \mathbf{p} d\mathbf{r} = h(n + \gamma) \quad , \tag{9.73}$$

where γ is the phase defect (for the harmonic oscillator $\gamma = 1/2$); making use of equation (9.62), we get

$$\hbar \oint \mathbf{k} d\mathbf{r} - \frac{e}{c} \oint \mathbf{A} d\mathbf{r} = h(n + \gamma) \quad , \tag{9.74}$$

or, using equation (9.69),

$$\begin{aligned} \tfrac{c\hbar^2}{eH} \oint k_\perp dk - \tfrac{e}{c} \int H dS &= \tfrac{c\hbar^2}{eH} \oint d\mathcal{A} - \tfrac{e}{c} \int H dS \\ &= h(n + \gamma) \end{aligned} \tag{9.75}$$

for the transverse motion, where dS is the elementary area swept by the position vector; we can see that the flux HS of the magnetic field through the area of the cross-section enclosed by the trajectory is quantized by flux quanta $\Phi_0 = hc/e$, and, similarly, the area $\mathcal{A}$ of the cross-section enclosed by the **k**-orbit is quantized by the transverse degeneracy $(2\pi)^2H/\Phi_0 = N_\perp/(S/(2\pi)^2)$ (according to equation (9.19)).[4] In addition, the transverse energy is quantized by $\Delta\varepsilon_\perp = (\hbar^2/m)k_\perp\Delta k_\perp = (\hbar^2/2\pi m)\Delta\mathcal{A} = (\hbar^2/2\pi m)(2\pi eH/c\hbar)$ as follows from the quantization of $\mathcal{A}$, such that $\Delta\varepsilon_\perp = \hbar(eH/c\hbar) = \hbar\omega_c$, *i.e.* the Landau levels; similarly, the rotation energy $m\omega_c^2r_\perp^2/2$ gives $\Delta\varepsilon_\perp = m\omega_c^2r_\perp dr_\perp = (m\omega_c^2/2\pi)\Delta S = (m\omega_c^2/2\pi)(ch/eH) = \hbar\omega_c$. This is the cyclotron resonance.[5]

9.5 Magnetic oscillations

The statistical distribution $\exp(\mu-\varepsilon)\beta$ leads to the free energy $F = E - TS$ in canonical partition function $\exp(-\beta F)$ and to the grand-canonical potential $\Omega = F - \mu N$ in the grand-partition function $\exp(-\beta\Omega)$; the latter is given by $\prod[1+\exp(\mu-\varepsilon)\beta]$ for electron states, such that

$$F = \mu N - T\sum \ln[1+\exp(\mu-\varepsilon)\beta] \;\; ; \tag{9.76}$$

in the presence of a magnetic field it reads

$$\begin{gathered} F = \mu N - T\tfrac{gV}{(2\pi\hbar)^2}m\omega_c\cdot \\ \cdot\int dp_z\sum_{n=0}^{\infty}\ln[1+\exp(\mu-\varepsilon)\beta] \quad , \end{gathered} \tag{9.77}$$

according to the transverse degeneracy given by equation (9.19) and the energy $\varepsilon = E_n(p_z) = \hbar\omega_c(n+1/2) + p_z^2/2m$ as given by equation (9.15), where the paramagnetic spin contribution is omitted for simplicity; the summation over spins is included in $g = 2s+1$. Making use of equation (9.36) the free energy can be written as $F = F_b + F_m + F_{osc}$,

where

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[4] L. Onsager, "Interpretation of the de Haas-van Alphen effect", Phil. Mag. **43** 1006 (1952).

[5] C. Kittel, *Introduction to Solid State Physics*, Wiley, NY (2005); C. Kittel, *Quantum Theory of Solids*, Wiley, NY (1987).

$$F_b = \mu N - T\tfrac{gV}{4\pi^2}(2m/\hbar^2)^{3/2}\cdot$$

$$\cdot \textstyle\int d\varepsilon \cdot \varepsilon^{1/2} \ln[1+\exp(\mu-\varepsilon)\beta] = \tag{9.78}$$

$$== \mu N - \tfrac{gV}{6\pi^2}(2m/\hbar^2)^{3/2} \textstyle\int d\varepsilon \cdot \varepsilon^{3/2} f(\varepsilon)$$

is the bulk contribution, with $f(\varepsilon) = [\exp(\varepsilon-\mu)\beta+1]^{-1}$ the Fermi distribution;

$$F_m = \frac{gV}{24(2\pi)^2} m\omega_c^2 (2m/\hbar^2)^{1/2} \int d\varepsilon \cdot \varepsilon^{-1/2} f(\varepsilon) \tag{9.79}$$

is the marginal H^2-contribution; and

$$F_{osc} = -\frac{2gV}{(2\pi)^2\hbar} m\omega_c^2 \sum_{s=1}^{\infty} \frac{(-1)^s}{(2\pi s)^2} \int dp_z dx f'(x) \cos 2\pi s x \tag{9.80}$$

is the oscillatory part of the free energy; both F_b and F_m coincide with the corresponding contributions to equations (9.57) and (9.40). The derivative $f'(x)$ of the Fermi distribution is centered on x given by $\hbar\omega_c x + p_z^2/2m = \mu$ and falls rapidly to zero away from this x-value; therefore, we can write approximately

$$F_{osc} = -\tfrac{2gV}{(2\pi)^2\hbar} m\omega_c^2 \cdot I \cdot$$

$$\cdot \textstyle\sum_{s=1}^{\infty} \tfrac{(-1)^s}{(2\pi s)^2} \int dp_z \cos(s \cdot \hbar\mathcal{A}/m\omega_c) \quad , \tag{9.81}$$

where

$$I = \textstyle\int_{-\infty}^{+\infty} dx f'(x) \cos 2\pi s x =$$

$$= \textstyle\int_{-\infty}^{\infty} dz \cdot \left(\tfrac{1}{e^z+1}\right)' \cos(2\pi s z T/\hbar\omega_c) \tag{9.82}$$

and $\mathcal{A} = \pi p_\perp^2/\hbar^2 = (2\pi m/\hbar^2)(\mu - p_z^2/2m) = (2\pi m/\hbar^2)\hbar\omega_c x$ is the area of the orbit cross-section; though $f'(x)$ varies abruptly, the cosine varies, however, much more rapidly, and $\int dz[e^z/(e^z+1)^2]\cos az = \pi a/\sinh \pi a$ by the double poles at $z = i\pi \times odd\, integer$. Therefore, we obtain

$$F_{osc} = \tfrac{2gV}{(2\pi)^2\hbar} \cdot m\omega_c^2 \cdot \textstyle\sum_{s=1}^{\infty} \tfrac{(-1)^s}{(2\pi s)^2} \tfrac{2\pi^2 Ts/\hbar\omega_c}{\sinh(2\pi^2 Ts/\hbar\omega_c)} \cdot$$

$$\cdot \textstyle\int dp_z \cos(s \cdot \hbar\mathcal{A}/m\omega_c) \ ; \tag{9.83}$$

the remaining integral is a Fresnel integral, leading finally to

$$F_{osc}=\frac{2gV}{(2\pi)^4}(\hbar\omega_c)^{3/2}(m/\hbar^2)^{3/2}\cdot$$
$$\cdot\sum_{s=1}^{\infty}\frac{(-1)^s}{s^{5/2}}\frac{2\pi^2Ts/\hbar\omega_c}{\sinh(2\pi^2Ts/\hbar\omega_c)}\cos(2\pi\mu s/\hbar\omega_c+\pi/4)\ \ . \tag{9.84}$$

From equation (9.79) the marginal correction to the free energy $F_m\sim(\hbar\omega_c/\mu)^2F_b$ is of the order of H^2, while the oscillatory correction is $F_{osc}\sim(\hbar\omega_c/\mu)^{3/2}F_b$; however, this is so only in the limit of vanishing temperature and high magnetic field; since $T\gg\hbar\omega_c$ the oscillatory correction is exponentially small in fact, and, in any case, the $1/H$-oscillations are quite slow; the typical $1/H$-oscillations, as seen in the magnetization $M=-\partial F/\partial H$ and in the corresponding diamagnetic susceptibility, are the de Haas-van Alphen oscillations; similar oscillations may appear in various other physical properties, involving statistical integrals; for instance, the $1/H$-oscillations in the electric conductivity in the presence of the magnetic field are the Shubnikov-de Haas oscillations; they always involve closed orbits on the Fermi surface and give indications about the area of the orbit cross-section, as well as the curvature of the Fermi surface in the neighbourhood of its p_z-stationary points.

9.6 Magnetic effects

The absorption of an electromagnetic wave can be seen, in principle, at cyclotron frequency, in radio- and microwaves spectrum, especially at low temperatures; this is the cyclotron resonance, seen especially in semiconductors, though usually not quite well resolved; the magnetic field is perpendicular to the surface, and the electric field of the electromagnetic wave is parallel to the surface, such as to impinge the rotating electron state above the Fermi surface; in addition, the circular polarization of the electromagnetic wave must be the right one, in the sense of the rotating electron state, such as to produce the resonance; a reversely polarized wave will not be absorbed. Apart from being or not being absorbed the waves are delayed through dissipation, differently for different polarizations; therefore, the two circularly polarized components in a linearly polarized wave will rotate distinctly from each other, and the polarization plane of the wave will rotate while propagating in the magnetic field; this is the Faraday effect.

In metals however, as a consequence of the screening, the electromagnetic wave penetrates little and its action is limited to the metallic surface; this is the skin effect, and, for good metals, the anomalous skin effect, where the penetration depth is particularly small; consequently, the cyclotron resonance is hard to be seen. However, for a magnetic field applied parallel to the surface, the spiralling electron states will pass periodically through the penetration depth of the wave, and cyclotron resonance may appear, even at higher harmonics; this is the Azbel-Kaner effect.[6] The propagation of the electron state along the spiral trajectory must, however, bring the rotations in phase, in order to resonate; which happens for extremal trajectories on the Fermi surface, where the wavevectors dispersion is vanishing.

An ultrasound wave produces a transverse electric field, which may excite cyclotron resonances; indeed, say, for instance, that the electric field is $E_y \sim e^{ikx}$; then it will act upon the electron along its velocity v_y on the cyclotron trajectory, and the electric field must be maximal for electron velocity parallel to the electric field, and vanishing at the trajectory centre; absorption will appear therefore for the radius $r_\perp$ (along the x-axis) equals $\lambda/4 + n\lambda$, where λ is the sound wavelength; from equation (9.72) $r_\perp = \hbar k_\perp / m\omega_c$, such that ultrasound attenuation will oscillate as $1/H \sim n+1/4$; this is the magneto-acoustic effect, reflecting the geometry of the electron trajectory in the presence of the magnetic field.

At low temperatures and for small concentration of charge carriers, as in semiconductors, the equilibrium is attained with difficulty in high magnetic fields; the electrons motion is almost mechanical, and classical; an electric flow j_x is deviated by Lorentz force ev_xH/c which gives rise to the corresponding electric field $E_y = -v_x H/c$; hence, $j_x = -env_x = (enc/H)E_y = \sigma_{xy}E_y$, and the lateral conductivity $\sigma_{xy} = enc/H$, where n is the electron concentration; this is the Hall effect, and for holes a minus sign appears naturally in the Hall conductivity (and the propagation of an electromagnetic wave in a Hall-like experimental set-up acquires a particular quadratic dispersion relation, corresponding to what are called helicons). The y-flow is deviated along the x-direction, giving rise to an additional flow $j_x \sim j_y H$, so that $\sigma_{xy}E_y \sim \sigma_{yy}E_y H$, hence $\sigma_{yy} \sim \sigma/H \sim 1/H^2$, and similarly $\sigma_{xx} \sim 1/H^2$; this is the magneto-conductivity, transverse to the magnetic field, and the corresponding inverse tensor gives the magnetoresistance; while $\rho_{xy} = (\sigma^{-1})_{xy}$ is the Hall resistance; for anisotropies, similar Hall-like conductivities appear for $\sigma_{zx} \sim 1/H$, etc; the off-diagonal tensor of conductivities must be antisymmetric, as required by the symmetry under field reversal. In general, the conductivity tensor may be written as[7]

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[6] M. Ia. Azbel and E. A. Kaner, "The theory of cyclotron resonance in metals", Sov. Phys.-JETP **3** 772 (1956) (ZhETF **30** 811 (1956)); A. B. Pippard, "A proposal for determining the Fermi surface by magneto-acoustical resonance", Phil. Mag. **2** 1147 (1957); E. A. Kaner, V. G. Peschanskii and I. A Privorotskii, "Contribution to the theory of magnetoacoustic resonance in metals", Sov. Phys.-JETP **13** 147 (1961) (ZhETF **40** 214 (1961); Yu. M. Galperin, S. V. Gantsevich and V. L. Gurevich, "Giant oscillations of sound absorption by metals in the case of open trajectories", Sov. Phys.-JETP **29** 926 (1969) (ZhETF **56** 1728 (1969)).

$$\sigma = \begin{pmatrix} A_{xx}/H^2 & A_{xy}/H & -A_{zx}/H \\ -A_{xy}/H & A_{yy}/H^2 & A_{yz}/H \\ A_{zx}/H & -A_{yz}/H & A_{zz} \end{pmatrix} \quad , \qquad (9.85)$$

and one can see that the conductivity along the field is not affected ($A^{'}$s are constants). It is easy to check that the transverse magnetoresistance saturates with increasing field, while the Hall resistance $\rho_{xy} \sim H$. All these hold for closed orbits, but for open orbits the results are altered. An orbit opens where the Fermi surface touches the boundary of the Brillouin zone, and the electron state moves repeatedly along it by Bragg reflexions, or indefinitely along the extended zone scheme; open orbits lie along the symmetry axes, but, large, even aperiodic orbits may appear in the neighbourhood. For such an orbit, say, along the y-direction, there will be no reaction along x, such that $\sigma_{xx} \sim B_{xx}$ (a constant) will not depend on the field; similarly, σ_{zx} will not depend on the field, while σ_{yy}, σ_{xy} and σ_{yz} will remain the same; the conductivity tensor looks like

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[7] J. M. Ziman, *Electrons and Phonons, The Theory of Transport Phenomena in Solids*, Clarendon Press, Oxford (1960).

$$\sigma = \begin{pmatrix} B_{xx} & A_{xy}/H & -B_{zx} \\ -A_{xy}/H & A_{yy}/H^2 & A_{yz}/H \\ B_{zx} & -A_{yz}/H & A_{zz} \end{pmatrix} \quad , \tag{9.86}$$

and one can check that ρ_{xx} saturates, but the transverse magneto-resistance ρ_{yy} in the direction of an open orbit increases with field, $\rho_{yy} \sim H^2$; this is a giant magneto-resistance. It is worth noting that such derivations are based on the equation of motion of the form $m(d/dt+1/\tau)\delta\mathbf{v} = -e(\mathbf{E}+\delta\mathbf{v}\times\mathbf{H}/c)$, where τ is the (quasi-) particle lifetime.

Finally, a large magnetic field may even induce inter-band transitions, for small energy gaps E_g; the probability can be obtained by comparing the perturbation E_g^2/μ to the magnetic quanta $\hbar\omega_c$; indeed, the time $\hbar\mu/E_g^2$ must be longer than the cyclotron period $1/\omega_c$, hence $\hbar\omega_c\mu/E_g^2 > 1$ can be taken as the criterion of magnetic breakthrough; this is similar to Zener effect for inter-band transitions under the action of an electric field (dielectric breakdown).

Electrical conductance $\mathcal{S}$ is quantized; indeed, from Ohm's law $I = \mathcal{S}U$, where the electric flow through area S is given by $I = envS = e(1/a^3)(a/\tau)S$, we obtain $I = (e/\tau)(S/a^2)$ and $\mathcal{S} = (e^2/\varepsilon\tau)(S/a^2)$, where $n = 1/a^3$ is the electron concentration, a is the mean electron separation, τ is the electron life-time, and ε is the associated uncertainty in energy; since $\varepsilon\tau = h$ one may write $\mathcal{S} = (e^2/h)\cdot\nu$, where ν is the number of electrons per area S; it follows that the conductance $\mathcal{S}$ is quantized by quanta e^2/h, and conductivity $\sigma = \mathcal{S}(l/S) = (e^2/h)\cdot\nu\cdot(l/S)$.[8] Such quanta of conductivity (and electrical resistance) can be seen more conveniently in a magnetic field applied perpendicular to the surface; indeed, the Hall conductivity $\sigma_{xy} = enc/H$ includes the concentration $n = N/Sd = (n_\perp/d)\cdot\nu$, where $n_\perp = eH/ch$ is the transverse degeneracy, d is the thickness of the sample, and ν is the number of fully occupied Landau's levels; we obtain $\sigma_{xy} = (e^2/h)\cdot\nu\cdot(1/d)$; this is the quantum Hall effect,[9] discovered on inversion layers at metal-oxide-semiconductors (MOS) interfaces, in high magnetic fields (18Ts) and low temperatures (~ 1K). The number ν of quanta above may also be rational fractions; this is the fractional quantum Hall effect,[10] seen in high magnetic fields on semiconductor interfaces (GaAs/AlGaAs, for instance) at low temperatures. The origin of the effect consists in the interaction of the electrons, which leads to a fractionally cyclic boundary condition on the one-electron wavefunction encircling another electron; energy subbands appear in Landau's levels, and ν may get fractional values; vortices of magnetic flux are attached to electrons, which alter the statistics of these composite particles, and lead to elementary excitations of fractional electron charge.

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[8] See also M. Apostol, "A new approach to the quantized electrical conductance", Phys. Lett. **A372** 5093 (2008).

[9] K. von Klitzing, G. Dorda and M. Pepper, "New method for high-accuracy determination of the fine-structure constant based on quantized Hall resistance", Phys. Rev. Lett. **45** 494 (1980).

9.7 Magnetic transport

The magnetic field brings a lateral contribution to the transport coefficients in condensed matter, as a consequence of the Lorenz force acting upon the electron elementary excitations which possess a velocity; such contributions may be called lateral, or transverse, conductivities. The lateral conductivities are controlled by the lifetime of the electron quasiparticles. Typically, the considerations are made upon a homogeneous sample at thermal equilibrium, subjected to small, continuous and constant gradients of temperature and voltage along the x-axis, and placed into a constant magnetic field H directed along the z-axis; the lateral conductivities appear along the y-axis, and, for small, usual magnetic fields, they are linear in H; in addition, second-order contributions appear in the usual, longitudinal conductivities along the x-axis.

The basic equations of the thermomagnetoelectricity read

$$\mathbf{E} = \mathbf{j}/\sigma + Q\,gradT + R(\mathbf{H}\times\mathbf{j}) + N(\mathbf{H}\times gradT) \quad , \tag{9.87}$$

and

$$\mathbf{q} = \varphi\mathbf{j} + TQ\mathbf{j} - K\,gradT + NT(\mathbf{H}\times\mathbf{j}) + L(\mathbf{H}\times gradT) \quad , \tag{9.88}$$

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[10] D. C. Tsui, H. L. Stormer and A. C. Gossard, "Two-dimensional magnetotransport in the extreme quantum limit", Phys. Rev. Lett **48** 1559 (1982); "Anomalous quantum Hall effect: an incompressible quantum fluid with fractionally charged excitations", R. B. Laughlin, Phys. Rev. Lett. **50** 1395 (1983).

where $\mathbf{E}$ is the external electric field, $\mathbf{j}$ is the electric flow (charge per unit area of the cross-section per unit time), σ is the electric conductivity, Q is the thermopower, T denotes the temperature and $gradT$ is the temperature gradient, $\mathbf{q}$ is the heat flow (heat per unit area of the cross-section per unit time), φ is the voltage ($\mathbf{E} = -grad\varphi$, $div\mathbf{E} = div\mathbf{j} = 0$), and K represents the thermoconductivity; R is the Hall resistance, and represents the effect of the magnetic field on the electric resistance (or conductivity), N is the Nernst coefficient, and represents the effect of the magnetic field on the thermopower (or upon the Seebeck effect), and L is the Leduc-Righi coefficient, corresponding to the effect of the magnetic field on the thermoconductivity; N represents also the effect of the magnetic field upon the Peltier heat, which is called also the Ettingshausen effect. Making use of the reference frame given above, equations (9.87) and (9.88) can also be written as

$$E_x = j_x/\sigma + Q(\partial T/\partial x) \ , \ \ q_x = \varphi j_x + TQj_x - K(\partial T/\partial x) \ \ , \tag{9.89}$$

and

$$E_y = RHj_x + NH(\partial T/\partial x) \ , \ \ q_y = NTHj_x + LH(\partial T/\partial x) \ ; \tag{9.90}$$

the transverse character of the lateral conductivities is obvious in the above equations.

The cyclotron frequency is given by $\omega_c = eH/mc$, where $-e$ is the electron charge, m is the electron mass, and c denotes the light velocity; typical values for $\hbar/\tau_c = \hbar\omega_c$, where τ_c is the cyclotron time, are $\hbar/\tau_c \simeq 1 - 10\mathrm{K}$, corresponding to $H = 10^4 - 10^5 Gs$.

It is customary to represent the electron quasiparticle lifetime τ_e in the (slightly inhomogeneous) electron liquid as[11]

$$\frac{\hbar}{\tau_e} = 2B^2(\rho^3/n)\frac{(\varepsilon-\mu)^2 + T^2}{e^{(\varepsilon-\mu)/T}+1} \ \ , \tag{9.91}$$

where $B = 4\pi e^2/k_F^2$, $\rho = mp_F/\pi^2\hbar^3$ is the state density at the Fermi level, and n ($= k_F^3/3\pi^2$) is the electron concentration; k_F is the Fermi wavevector and $p_F = \hbar k_F$ is the Fermi momentum. Since, at finite temperatures, we may set $\varepsilon = \mu$, we get

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[11] P. Morel and P. Nozieres, "Lifetime effects in condensed helium-3", Phys. Rev. **126** 1909 (1962).

$$\frac{\hbar}{\tau_e} = B^2(\rho^3/n)T^2 \ ; \tag{9.92}$$

we can also write $\hbar/\tau_e = (4/3\pi)^2\varphi^2(\rho/n)^3T^2 \simeq (\varphi/\mu)^2(T^2/\mu)$, where $\varphi = e^2k_F$ is the Coulomb localization energy and μ is the chemical potential (Fermi level); since $\varphi \simeq \mu$, we get $\hbar/\tau_e = T^2/\mu$; typical values are $\hbar/\tau_e \simeq 10^{-4}T^2K$ (for $\mu = 1eV$), and one can see that $\hbar/\tau_e > \hbar/\tau_c$ for usual fields (though the inequality is reversed at low temperatures). The electron-phonon interaction brings the quasiparticle lifetime τ_{e-ph} given by $\hbar/\tau_{e-ph} = T/F$, where $F \simeq (M/m)(\hbar\omega_D/\mu)^2$, M being the atomic mass and ω_D being the Debye frequency; typically, $F \sim 10-100$, and we can see that τ_{e-ph} may easily dominate the electron lifetime (the lifetimes add according to Matthiessen's rule $1/\tau = 1/\tau_e + 1/\tau_{e-ph}$), especially on decreasing the temperature; for low magnetic fields the inequality $\hbar/\tau > \hbar/\tau_c$ still holds, where τ is the total quasiparticle lifetime, but again the inequality may be reversed at lower temperatures and higher fields. The geometric quasiparticle lifetime given by $1/\tau_g \sim d/v$, where v is the Fermi velocity (and d denotes the mean transverse size of the sample), contributes also, especially at low temperatures (Casimir geometric effect), as, for instance, $\hbar/\tau_g \sim 10$K for $d = 1\mu$m. Therefore, for low magnetic fields and normal temperatures one may admit that $\hbar/\tau \gg \hbar/\tau_c$, or $\omega_c\tau \ll 1$, where τ is the quasiparticle lifetime (or collision time). Under these circumstances the quasi-classical motion of the quasiparticle momentum

$$\begin{aligned} \widetilde{p}_x &= p_x\cos\omega_c t + p_y\sin\omega_c t \quad , \\ \widetilde{p}_y &= -p_x\sin\omega_c t + p_y\cos\omega_c t \end{aligned} \tag{9.93}$$

is limited to the lifetime τ, *i.e.* $t = \tau$ in equation (9.93), and the transport is performed in the limit $\omega_c\tau \ll 1$, such that the continuum limit may be applied, and, consequently, the continuity equation.

On the contrary, in the opposite limit $\omega_c\tau \gg 1$ the electrons get localized by the magnetic field, and their motion is subjected to the Lorentz force as for a classical particle; though they may still acquire a local equilibrium, there will not be a thermal transport, since the continuity of the equilibrium is destroyed; however, a drift velocity appears under the action of an electric field, so that there will be an electric transport, and a corresponding electrical conductivity. This circumstance may appear more frequently in semiconductors, where the lifetime τ of the charge carriers is given by $1/\tau = (\sigma/a^3)\sqrt{T/m}$, where σ is the scattering cross-section and a is the mean electron separation (the interaction with the atoms leads to an effective $\sigma \simeq a^2$); we can see easily that the inequality $\omega_c\tau \gg 1$ can be fulfilled for such a dilute electron liquid, and high fields.

In addition, it is also worth noting that transport is performed under local, continuous equilibrium and global non-equilibrium, and consequently, the effect of the magnetic field upon the equilibrium thermodynamic functions is not relevant for transport phenomena.[12] On the contrary, the quasi-classical motion in magnetic field does apply for transport, either for quasiparticles or, where appropriate, for localized classical electrons, endowed with velocity.

9.8 Lateral thermoconductivity

The quasiparticles with momentum $\mathbf{p}$ near the (quasi-spherical) Fermi surface and energy ε transport the energy density

$$\frac{\partial}{\partial T}(\varepsilon n) \cdot \Delta T \quad , \tag{9.94}$$

where n is the Fermi distribution of the quasiparticles and ΔT is the local variation of temperature; this energy is carried along the y-axis with velocity $\widetilde{v}_y = \widetilde{p}_y/m$; heat flux (heat per unit area of the cross-section) along the y-axis is

$$\frac{\partial}{\partial T}(\varepsilon n) \cdot \widetilde{v}_y\tau \cdot \Delta T \quad , \tag{9.95}$$

where τ is the quasiparticle lifetime; in local equilibrium, for small τ and long times, this flux is transported along the x-axis with velocity

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[12] Such an attempt was discussed by S. Titeica, "Uber die Wiederstandsanderung von Metallen in Magnetfeld", Ann. Physik **414** 129 (1935).

$v_x = p_x/m$, such that the heat flow is given by the continuity equation

$$q_y = \frac{2}{(2\pi\hbar)^3} \int d\mathbf{p} \cdot \frac{\partial}{\partial T}(\varepsilon n) \cdot \widetilde{v}_y v_x \tau \cdot (\partial T/\partial x) \;\; ; \tag{9.96}$$

hence the lateral thermoconductivity

$$K_{yx} = \frac{2}{(2\pi\hbar)^3} \int d\mathbf{p} \cdot \frac{\partial}{\partial T}(\varepsilon n) \cdot \widetilde{v}_y v_x \tau \;\; . \tag{9.97}$$

It is worth noting that the transport velocity is $v_x = p_x/m$ (not affected by the magnetic field), according to the quasi-classical motion and the local thermal equilibrium. Making use of equation (9.93) to the first order in H one obtains by straightforward calculations

$$K_{yx} = -\frac{\pi^2}{3} \frac{\omega_c n \tau^2}{m} T \quad , \tag{9.98}$$

and, consequently, the Leduc-Righi coefficient in equation (9.90)

$$L = -\frac{\pi^2}{3} \frac{e n \tau^2}{m^2 c} T \;\; . \tag{9.99}$$

It is worth noting that the thermoconductivity derived here holds in the absence of the electric flow, and electric field; in addition, it is easy to see that $K_{yx} = -K(\omega_c \tau)$, as expected, where K is the longitudinal thermoconductivity. The latter has a second-order correction arising from $\widetilde{v}_x v_x$, such that $K_{xx} = K[1 - (\omega_c \tau)^2/2]$.

9.9 Lateral electrical conductivity and thermopower

Similarly, a quasiparticle with energy ε carries a charge density

$$-e\delta n = e^2(\partial n/\partial \varepsilon) \cdot \delta U \quad , \tag{9.100}$$

where δU is the local voltage; the charge flux

$$e^2(\partial n/\partial \varepsilon) \cdot \widetilde{v}_y \tau \cdot \delta U \tag{9.101}$$

along the y-axis is carried along the x-axis at the rate

$$j_y = -\frac{2}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot e^2(\partial n/\partial\varepsilon)\cdot\widetilde{v}_y v_x\tau\cdot E_x \quad , \tag{9.102}$$

hence the lateral conductivity

$$\sigma_{yx} = -\frac{2}{(2\pi\hbar)^3}\int d\mathbf{p}\cdot e^2(\partial n/\partial\varepsilon)\cdot\widetilde{v}_y v_x\tau \ ; \tag{9.103}$$

to the first order in H we obtain straightforwardly

$$\sigma_{yx} = -\frac{e^2\omega_c n\tau^2}{m} \ ; \tag{9.104}$$

similarly, $\sigma = \sigma_{xx} = e^2 n\tau/m$ (up to H^2-corrections) and $\sigma_{yx} = -\sigma(\omega_c\tau)$. The Hall resistance is obtained from $RH = -\sigma_{yx}/\sigma^2 = m\omega_c/e^2n$, according to equations (9.89) and (9.90), as $R = 1/enc$. It is worth remarking that the lateral conductivities are antisymmetric tensors, because the magnetic field must be reversed. We may note also that the transverse Lorenz number $L_{yx} = K_{yx}/\sigma_{yx}T = \pi^2/3e^2$ equals the longitudinal Lorenz number $L = K/\sigma T = \pi^2/3e^2$, as expected.

From equations (9.89) and (9.90), for a vanishing electric field, the longitudinal electric flow is given by $j_x = -\sigma Q(\partial T/\partial x)$, such that $NH = RH\sigma Q = -(\sigma_{yx}/\sigma)Q = Q(\omega_c\tau) = -(\pi^2/6)(T/\mu)(\omega_c\tau)$, since the (longitudinal) thermopower is given by $Q = -(\pi^2/6e)(T/\mu)$; hence the Nernst coefficient

$$N = \frac{e\tau}{mc}Q = -\frac{\pi^2}{6}\frac{\tau}{mc}\frac{T}{\mu} \ . \tag{9.105}$$

We can remark finally that the lateral conductivities are the longitudinal ones reduced by $\omega_c\tau$.

10 Semiconductors

10.1 Lifetime

In typical semiconductors the concentration n of the charge carriers is $4-5$ orders of magnitude lower than in metals (from $10^{22}cm^{-3}$ in metals to $10^{17}-10^{18}cm^{-2}$ in semiconductors); these charge carriers are either electrons or holes, provided by doping impurities, like in extrinsic semiconductors, or both electrons and holes, like in intrinsic semiconductors, arising from thermal excitations across a small (narrow) energy gap; semimetals, with a slight superposition of energy bands, belong to the same class. Due to their low concentration the charge carriers in semiconductors move slowly on atomic positions, being much localized on the atoms. They possess an effective mass denoted by m (close to the electron mass), arising from their motion in the potential of the crystalline lattice (band mass, due to the interaction with the lattice), and a $\pm e$ charge, where $-e$ is the electron charge. The computations for holes are similar with those for electrons, with due care for the origin of energy and the corresponding chemical potentials; such computations are illustrated below for electrons.

In this extreme limit of very low concentrations the charge carriers (which are excitations across the Fermi surface) are described by the Boltzmann statistics for any usual temperature. The charge carriers behave like a classical gas of particles, and the characteristic quantum-mechanical energy $\varepsilon_q = \hbar^2/ma^2$, where $\hbar$ is Planck's constant and a ($\sim 1/n^{1/3}$) is the mean electron separation, is much smaller than the temperature T; the criterion for classical behaviour is $\hbar^2/ma^2 \ll T$, and typical values for a are $a \sim 100$Å. For such a dilute electron gas the electrons are localized, and have trajectories, their mechanical states being described by position $\mathbf{r}$ and velocity $\mathbf{v} = \dot{\mathbf{r}}$. For a classical gas the temperature T is high enough for statistical motion to localize the particles over thermal wavelengths $\lambda_{th} = \sqrt{\hbar^2/mT} \ll a$, much shorter than the average particle separation. Such thermal lengths are of the order of 10 inter-atomic distances. However, in comparison with their atomic localization the temperature produces rather a delocalization over thermal lengths.

Being so localized, the electrons interact weakly with the long-wavelength phonons, but they interact more with the atomic vibrations.[1] The corresponding cross-section is of the order of the square of the inter-atomic distance. In addition, they collide with themselves, with a cross-section of the same order of magnitude. According to the Boltzmann distribution the particle state density is given by

$$dn = \frac{2}{(2\pi\hbar)^3} e^{(\mu-\varepsilon)/T} d\mathbf{p} d\mathbf{r} \quad , \tag{10.1}$$

where μ is the chemical potential, $\varepsilon = p^2/2m$ and momentum $\mathbf{p} = m\mathbf{v}$; we get $\mu = T \ln[n(2\pi\hbar^2/mT)^{3/2}/2]$, spin included; therefore,

$$dn = \frac{n}{(2\pi mT)^{3/2}} e^{-\varepsilon/T} d\mathbf{p} d\mathbf{r} \quad . \tag{10.2}$$

The number of particles with velocity $\mathbf{v}$ moving (along z-axis) per unit time per unit area is given by

$$d\nu = n(m/2\pi T)^{3/2} e^{-mv^2/2T} v_z dv_x dv_y dv_z \quad ; \tag{10.3}$$

the density of particles having the velocity $\mathbf{v}$ with respect to one particle is therefore given by

$$d\nu = n\frac{\pi}{2}(m/\pi T)^{3/2} e^{-mv^2/4T} v^2 dv \quad , \tag{10.4}$$

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[1] It is worth comparing this situation with the electron-phonon interaction in the electron liquid; due to the delocalization of both the electron quasiparticles and the phonons, this interaction brings a factor $\sim (m/M)^{1/2}(\mu/\hbar\omega_D)$ to its matrix elements, where μ is the electron Fermi level and M is the atomic mass; consequently, the uncertainty in the electron energy is $\sim T(m/M)(\mu/\hbar\omega_D)^2$, hence the lifetime τ given by $1/\tau \sim T/\hbar F$, where $F = (M/m)(\hbar\omega_D/\mu)^2$; the effect of the electron-phonon interaction upon the phonons is less relevant, as the short-wavelength phonons (that are denser) are much less thermally activated, while the long-wavelength ones are very dilute. It is worth noting that the above estimation is valid for high ω_D, such that the adiabatic coefficient m/M is able to ensure the thermal equilibrium of the electrons with the phonons.

where the relative mass $m \rightarrow m/2$ is used. The collision cross-section σ is the ratio of the number of collisions per unit time (collision rate) to the flux of the incoming particles, *i.e.* their density multiplied by their velocity: $\sigma = d\nu_{coll}/vd\nu$; it follows that the total number of collisions suferred by a particle per unit time is

$$\nu_{coll} = n\frac{\pi}{2}(m/\pi T)^{3/2} \int e^{-mv^2/4T} \sigma v^3 dv = 4n\sigma(T/\pi m)^{1/2} \quad ; \quad (10.5)$$

since $\sqrt{T/m}$ is the mean square velocity v along one direction, one may write more conveniently $\nu_{coll} = n\sigma(T/m)^{1/2} = n\sigma v$, where $\sigma \rightarrow 4\sigma/\sqrt{\pi}$ is a cross-section. The (quasi-) particle lifetime is given by $\tau = 1/\nu_{coll}$. (The difference from a classical gas comes from the electron localization). The above derivation holds also for electron-atom collisions, only that the number of collisions is increased in this case by the factor a^2/σ, accounting for the higher density of atoms. This factor leads to an effective cross-section a^2, which is by far higher than σ, such that (according to Matthiessen's rule) it dominates the number of collisions. The number of collisions can therefore be written as

$$\nu_{coll} \simeq \frac{1}{a}(T/m)^{1/2} \quad , \quad (10.6)$$

and the corresponding lifetime

$$\tau = 1/\nu_{coll} = \sqrt{ma^2/T} = \hbar/\sqrt{\varepsilon_q T} \; ; \quad (10.7)$$

the corresponding uncertainty in energy is $\hbar/\tau \sim \sqrt{\varepsilon_q T}$, and the mean freepath is $\Lambda \sim v\tau \sim a$. The difference with respect to the standard classical gas of particles (where $\Lambda \sim a^3/\sigma$) comes from the electron-phonon interaction. In this respect the low-concentration electrons in semiconductors may be called a dilute electron liquid. The mobility B under a force $F = mv/\tau = v/B$ is obtained as $B = \tau/m = \sqrt{a^2/mT}$.

The corresponding mean freepath is much longer than the inter-atomic distances, and the thermal energy T (and fluctuation energy as well) is much larger than the (quasi-) particle energy $\sqrt{\varepsilon_q T}$, such that the thermal equilibrium is attainable, as expected.[2]

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[2] It is worth recalling that the thermal time (th), fluctuating time (f), elementary excitation lifetime (ex) and, externally observable time (e) are ordered through $\tau_{th} \leq \tau_f \ll \tau_e \ll \tau_{ex}$.

The (small) effect of the electron-phonon interaction in semiconductors, both on the phonons and the electrons (charge carriers), is discussed in one of the next chapters.

10.2 Transport coefficients

The density of particles with momentum $\mathbf{p}$ is given by

$$f = \frac{n}{(2\pi mT)^{3/2}} e^{-\varepsilon/T} \quad ; \tag{10.8}$$

these particles transport an energy density

$$\frac{\partial}{\partial T}(\varepsilon f) \cdot \Delta T \quad , \tag{10.9}$$

where ΔT is the temperature drop along the sample (z-axis); the density of energy is transported with velocity $v_{\parallel} = v \cos\theta$ along the sample, such that the heat flux is given by

$$\frac{\partial}{\partial T}(\varepsilon f) \cdot v_{\parallel}\tau \cdot \Delta T \quad ; \tag{10.10}$$

for $v_{\parallel}\tau \ll l$ (and the transverse size of the sample much smaller than l), where l is the sample length; we obtain the total heat flow

$$\frac{\partial Q}{\partial t} = \int d\mathbf{p} \cdot \frac{\partial}{\partial T}(\varepsilon f) \cdot v_{\parallel}^2 \tau \cdot \frac{\partial T}{\partial z} \quad , \tag{10.11}$$

and the thermoconductivity

$$K = \int d\mathbf{p} \cdot \frac{\partial}{\partial T}(\varepsilon f) \cdot v_{\parallel}^2 \tau \quad . \tag{10.12}$$

The effect of the sample boundaries is less relevant at high temperatures, such that we may use for τ the lifetime given by (10.7); we obtain easily

$$K = \frac{5n\tau T}{m} = \frac{5}{a^2}\sqrt{T/m} \quad ; \tag{10.13}$$

since the heat capacity per unit volume is $C = (3/2)(1/a^3)$, we may also write a typical representation $K = (10/3)Cv\lambda$ for thermoconductivity; another representation is $K \sim v/\sigma$, where σ denotes the cross-section.

The above computations are valid for a constant number of particles; for constant chemical potential, *i.e.* using

$$f = \frac{2}{(2\pi\hbar)^3} e^{(\mu-\varepsilon)/T} \quad , \tag{10.14}$$

we obtain similarly the thermoconductivity[3]

$$K = \frac{5n\tau T}{2m}(7/2 - \mu/T) = \frac{5}{2a^2}\sqrt{T/m}(7/2 - \mu/T) \quad , \tag{10.15}$$

where the chemical potential is given by

$$\mu = T \ln[\frac{n}{2}(2\pi\hbar^2/mT)^{3/2}] \;\; ; \tag{10.16}$$

it can also be written as

$$\mu/T \simeq -3\ln(a/\lambda_{th}) + 2 \quad , \tag{10.17}$$

where $\lambda_{th} = \left(\hbar^2/mT\right)^{1/2}$ is the thermal wavelength; the logarithm is a slow function, and for typical values of temperature and charge carrier concentration in semiconductors $-\mu/T \simeq 2$.

The charge density per (quasi-) electron is

$$-e\delta f = e^2 \frac{\partial f}{\partial \varepsilon} \cdot \delta U \quad , \tag{10.18}$$

where δU is the local voltage; the charge flux is

$$e^2 \frac{\partial f}{\partial \varepsilon} \cdot v_{\parallel}\tau \cdot \delta U \quad , \tag{10.19}$$

such that the electric flow is given by

$$j = \frac{\partial Q}{\partial t} = \int d\mathbf{p} \cdot e^2 \frac{\partial f}{\partial \varepsilon} \cdot v_{\parallel}^2 \tau \cdot \frac{\partial U}{\partial z} \;\; ; \tag{10.20}$$

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[3] For an electron liquid such a difference is irrelevant, because the chemical potential varies slowly with temperature in that case.

hence the electrical conductivity

$$\sigma = -\int d\mathbf{p} \cdot e^2 \frac{\partial f}{\partial \varepsilon} \cdot v_{\parallel}^2 \tau \ \ ; \tag{10.21}$$

it is the same either for a constant number of particles or for a constant chemical potential;[4] under the same conditions as above we get straightforwardly

$$\sigma = \frac{e^2 n\tau}{m} = \frac{e^2}{a^2} \cdot \frac{1}{\sqrt{mT}} \ \ ; \tag{10.22}$$

it may also be represented as $\sigma = (e^2/aT) \cdot v/a = (e^2/aT) \cdot (1/\tau)$. A Lorenz number can be defined as $L = K/\sigma T = 5/e^2$ from equations (10.13) and (10.22), or $L = (5/2e^2)(7/2 - \mu/T)$ from equations (10.15) and (10.22).

The variation of the chemical potential given by equation (10.16) is given by

$$\delta\mu = (\mu/T - 3/2)\delta T \ \ ; \tag{10.23}$$

it is equivalent with a change $-\delta\mu$ in particle energies, *i.e.* a voltage δU, such that

$$-e\delta U = -\delta\mu = (3/2 - \mu/T)\delta T \ \ ; \tag{10.24}$$

it follows that the thermopower $Q = \delta U/\delta T$ is given by

$$Q = -\frac{1}{e}(3/2 - \mu/T) \ \ . \tag{10.25}$$

In a typical thermoelectric circuit operated at equilibrium the electric flow $\mathbf{j}$ and the heat flow $\mathbf{q}$ are given by the fundamental equations of the thermoelectricity

$$\begin{aligned} \mathbf{j} &= -\sigma Q\, gradT \quad , \\ \mathbf{q} &= QT\mathbf{j} - K\, gradT \end{aligned} \tag{10.26}$$

(in the absence of the electric field). The heat density is obtained from these equations as

$$-div\mathbf{q} = -Q\mathbf{j}\, gradT + div(K\, gradT) = \mathbf{j}^2/\sigma + div(K\, gradT) \tag{10.27}$$

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[4] The charge transport is not a thermal transport.

(since $div\mathbf{j} = 0$), where we can identify the dissipated Joule-Lenz heat $\mathbf{j}^2/\sigma$ (per unit volume and unit time) and the thermoconducted heat $K\,gradT$ (per unit area of the sample cross-section); one can check also that the entropy increases in time, *i.e.* $\partial S/\partial t = -\int d\mathbf{r}\cdot(div\mathbf{q})/T > 0$. The efficiency coefficient is given by

$$\eta = \frac{\mathbf{j}^2/\sigma \cdot Al}{\mathbf{j}^2/\sigma \cdot Al - QT\mathbf{j}\mathbf{A} + K\mathbf{A}gradT} \quad , \tag{10.28}$$

where $\mathbf{A}$ is the sample cross-section (and l denotes the sample length); we obtain easily

$$\eta = \frac{\eta_c}{\eta_c + (K + Q^2\sigma T)/Q^2\sigma T} \quad , \tag{10.29}$$

where $\eta_c = \Delta T/T$ is the efficiency coefficient of the Carnot cycle, and

$$ZT = \frac{Q^2\sigma T}{K + Q^2\sigma T} = \frac{Q^2}{L + Q^2} \tag{10.30}$$

is called the figure of merit of the thermoelement; we can see that ZT is always lower than unity, its maximum value; the Lorenz number in equation (10.30) corresponds to the thermoconductivity computed at constant chemical potential.

10.3 Thermodynamics

Let f be the Fermi or Boltzmann distribution per unit volume for electron quasiparticles, or (quasi-) electrons possessing velocity, as in a quasi-classical description, such that the particle density is given by $n = \sum f$, the summation being extended over all momentum states. For constant chemical potential the transported particle density is given by $\delta n = \sum(\partial f/\partial T)\delta T$, where T is the temperature and δT is the local variation of temperature; the particle flux is $\sum(\partial f/\partial T)\mathbf{v}\tau\delta T$, where $\mathbf{v}$ is the velocity and τ denotes the quasi-particle lifetime; for small τ, such as to ensure the local equilibrium and the continuity of the transport over large-scale distances and times, the particle flow is given by the continuity equation, such that we may write down

$$\sum(\partial f/\partial T)\mathbf{v}\tau(\mathbf{v}gradT) \tag{10.31}$$

for the particle flow lost in the direction of the temperature gradient; for a homogeneous sample and in the absence of the magnetic field it is easy to see that we get the longitudinal particle flow

$$-\sum(\partial f/\partial T)v^2\tau gradT \quad , \tag{10.32}$$

representing the number of particles crossing the unit area of the cross-section per unit time. The electric flow is now easily obtained as

$$\mathbf{j} = e\sum(\partial f/\partial T)v^2\tau gradT = -\sigma Q gradT \quad , \tag{10.33}$$

where the electrical conductivity σ is introduced for convenience, and Q is the thermopower. This is the first of the two equations of the thermoelectricity (in the absence of external electric fields). It is easy to see that the electric flow in equation (10.33) arises from a (thermo-) electric field $\mathbf{E} = -Q gradT$, and a (thermo-) voltage drop $\varphi = QT$; consequently, an electric energy flow $\varphi\mathbf{j} = QT\mathbf{j}$ appears (which is also called the Peltier heat), and a corresponding density of electric energy $\mathbf{jE} = \mathbf{j}^2/\sigma$ is produced per unit time and per unit volume; the latter is the dissipated Joule-Lenz heat. On the other hand, besides the electric flow of energy $QT\mathbf{j}$, there exists the transported internal energy, whose density is $\sum\varepsilon(\partial f/\partial T)\delta T$; the corresponding flux is $\sum\varepsilon(\partial f/\partial T)\mathbf{v}\tau\delta T$, and the lost flow is $\sum\varepsilon(\partial f/\partial T)\mathbf{v}\tau(\mathbf{v} gradT)$; therefore, the longitudinal energy flow is given by

$$-\sum\varepsilon(\partial f/\partial T)v^2\tau gradT = -K gradT \quad , \tag{10.34}$$

where K is the thermoconductivity; it is the heat passing through the unit area of the cross-section per unit time. Therefore, the total heat flow $\mathbf{q}$ is given by

$$\mathbf{q} = QT\mathbf{j} - K gradT \ ; \tag{10.35}$$

this is the second equation of the thermoelectricity. The heat produced per unit time and unit volume is $-div\mathbf{q} = \mathbf{j}^2/\sigma + div(K gradT)$ (which amounts in fact to the dissipated Joule-Lenz heat $\mathbf{j}^2/\sigma$, since the charge conservation in the stationary flow $div\mathbf{j} = 0$ implies $gradT = const$ from equation (10.33); and the transport coefficients are constant for a homogeneous sample). One can also check the increase of entropy with time, $\partial S/\partial t = -\int d\mathbf{r}\cdot(div\mathbf{q})/T = \int d\mathbf{r}\cdot(\mathbf{j}^2/\sigma T +$

$K(gradT)^2/T^2) > 0$ (in fact $\int d\mathbf{r} \cdot \mathbf{j}^2/\sigma T > 0$). It is worth noting that both the Peltier heat and the thermoconducted heat in equation (10.35) are conducted heats.

The heat produced in the sample per unit time is $(\mathbf{j}^2/\sigma) \cdot Al = Q^2 \sigma \Delta T \cdot gradT \cdot A$, where A is the area of the sample cross-section ($\mathbf{A}$), l denotes the length of the sample and ΔT is the temperature drop along the sample; the thermoconducted heat per unit time is $\mathbf{A} K gradT$ and the Peltier (thermoelectric) heat is $-QT\mathbf{jA} = Q^2\sigma T \cdot \mathbf{A} gradT$; we get easily the efficiency coefficient given by equation (10.28).

Similarly, for an external voltage φ the transported density of electrons is $\sum(\partial f/\partial\varepsilon)(-e\varphi)$, the flux is $\sum(\partial f/\partial\varepsilon)\mathbf{v}\tau(-e\varphi)$ and the lost flow is $\sum(\partial f/\partial\varepsilon)\mathbf{v}\tau(-e\mathbf{v} grad\varphi) = e\sum(\partial f/\partial\varepsilon)\mathbf{v}\tau(\mathbf{vE})$, where $\mathbf{E}$ is the external electric field; longitudinally, it is $-e\sum(\partial f/\partial\varepsilon)v^2\tau\mathbf{E}$, since $\mathbf{vE} = -vE$; therefore, we obtain the particle flow as $e\sum(\partial f/\partial\varepsilon)v^2\tau\mathbf{E}$ and the corresponding electric flow

$$\mathbf{j} = -e^2 \sum(\partial f/\partial\varepsilon)v^2\tau\mathbf{E} = \sigma\mathbf{E} \quad , \tag{10.36}$$

where σ is the electrical conductivity; the first equation of the thermoelectricity becomes $\mathbf{j} = \sigma\mathbf{E} - \sigma Q gradT$, while the corresponding energy must be added to the second equation of the thermoelectricity, *i.e.* $\mathbf{q} = \varphi\mathbf{j} + QT\mathbf{j} - K gradT$.

The change in the particle density is given by $\delta n = \sum(\partial f/\partial T)\delta T - \sum(\partial f/\partial\varepsilon)\delta\mu = 0$; on the other hand, $\delta\mu = -\delta\varepsilon = e\delta\varphi$, such that $\sum(\partial f/\partial T)\delta T - e\sum(\partial f/\partial\varepsilon)\delta\varphi$; hence the thermopower

$$Q = \delta\varphi/\delta T = \frac{1}{e}\sum(\partial f/\partial T)/\sum(\partial f/\partial\varepsilon) \ ; \tag{10.37}$$

it is consistent with that obtained from equations (10.33) and (10.36),

$$\begin{aligned} Q = -e\sum(\partial f/\partial T)v^2\tau/\sigma = \\ = \tfrac{1}{e}\sum(\partial f/\partial T)v^2\tau/\sum(\partial f/\partial\varepsilon)v^2\tau \ . \end{aligned} \tag{10.38}$$

Also, from equation (10.32) we obtain the particle flow

$$\mathbf{i} = -\sum(\partial f/\partial T)v^2\tau gradT \ ; \tag{10.39}$$

on the other hand, $grad n = \sum(\partial f/\partial T) grad T$, such that

$$\mathbf{i} = -[\sum(\partial f/\partial T)v^2\tau / \sum(\partial f/\partial T)] grad n = -D_{th} grad n \quad , \qquad (10.40)$$

where D_{th} is the thermodiffusion coefficient, according to Fick's law; it transports mass, momentum and energy. Similarly, under the variation of the chemical potential there appears a change in the particle density $\delta n = -\sum(\partial f/\partial \varepsilon)\delta\mu$, a flux of particles $-\sum(\partial f/\partial\varepsilon)\mathbf{v}\tau\delta\mu$ and a particle flow

$$\begin{gathered} \mathbf{i} = \sum(\partial f/\partial\varepsilon)v^2\tau grad\mu = \\ = -[\sum(\partial f/\partial\varepsilon)v^2\tau / \sum(\partial f/\partial\varepsilon)] grad n = -D grad n \end{gathered} \qquad (10.41)$$

where D is the diffusion coefficient; it contributes to electrodiffusion.

10.4 Magnetic transport

For high temperatures and low magnetic fields H, as long as $\omega_c\tau \ll 1$, where $\omega_c = eH/mc$ is the cyclotron frequency and τ is the (quasi-) electron lifetime, the lateral conductivities are the longitudinal ones multiplied by $\omega_c\tau$; specifically, the transverse thermoconductivity $K_{yx} = LH = -K(\omega_c\tau)$, the transverse electrical conductivity $\sigma_{yx} = -\sigma(\omega_c\tau)$ (and the Hall resistance R is given by $RH = -\sigma_{yx}/\sigma^2 = (1/\sigma)(\omega_c\tau)$), and the transverse thermopower $NH = Q(\omega_c\tau)$; the longitudinal coefficients K, σ and Q are those computed above, L is the Leduc-Righi coefficient and N is the Nernst coefficient, according to the basic equations of the thermomagnetoelectricity.

For high magnetic fields and low temperature $\omega_c\tau \gg 1$, the charge carriers become localized, the cyclotron length $\xi_c = \sqrt{2c\hbar/eH} = \sqrt{12/H(Gs)} \cdot 10^4$Å becomes comparable or shorter than the mean electron separation, and the continuity of the local equilibrium, and, consequently, the transport becomes problematic. However, under the action of an electric field $\mathbf{E}$ the electrons acquire small drift velocities, according to the law of motion

$$\frac{m}{\tau}\mathbf{v} = -e(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{H}) \quad ; \qquad (10.42)$$

solving for velocities and introducing the electric flow $\mathbf{j} = -en\mathbf{v}$ one obtains the conductivity tensor

$$\widetilde{\sigma} = \frac{\sigma}{1+(\omega_c\tau)^2}\begin{pmatrix} 1 & -\omega_c\tau & 0 \\ \omega_c\tau & 1 & 0 \\ 0 & 0 & 1+(\omega_c\tau)^2 \end{pmatrix} \quad , \tag{10.43}$$

where $\sigma = e^2 n\tau/m$, and the resistivity tensor

$$\rho = \frac{1}{\sigma}\begin{pmatrix} 1 & -\omega_c\tau & 0 \\ \omega_c\tau & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad ; \tag{10.44}$$

if, however, the motion is blocked along, say, y-direction, as for a corresponding open cyclotron orbit, then the longitudinal resistivity $\rho_{xx} \sim H^2$, as for a giant magneto-resistance.

11 Electron-Phonon Interaction

11.1 Introduction

The cohesion of solids is caused by the ion-ion, electron-electron and ion-electron Coulomb interaction; once the cohesion is established, we can determine the thermodynamics of the solids, in particular the thermodynamics of their excited states. The excited states are determined by changes δn in electron density and displacement $\mathbf{u}$ in ionic positions, as well as changes in other interacting physical quantities (like magnetic moments, for instance). The first-order variations with respect to the cohesion state are vanishing, since this state is an equilibrium state. The second-order changes in the ionic positions give the vibrations of the solid, which, at least in the long-wavelength limit, can be analzyed in terms of phonons. The second-order changes in the electron density give an interaction between the electrons. The second-order combined change in electron density and ionic positions gives the electron-phonon interaction.

In metals the change δn in electron density leads to quasiparticle elementary excitations (quasi-electrons) and collective elementary excitations (plasmons). Since the quasi-electron energies are low, the quasi-electrons interact with (longitudinal) acoustic phonons. In general, such an interaction implies the product $\delta n\varphi$, where φ is the potential generated by the ion displacement. Since the quasi-electrons are mobile, they screen the ionic potential, such that the ionic potential is proportional to the ionic change in density, *i.e.* it is proportional to $div\mathbf{u}$, where $\mathbf{u}$ is the displacement field. Due to the Fermi statistics, we may replace δn by n; the electron-phonon interaction in metals reads

$$H_{e-ph} = -C \int d\mathbf{r} \cdot n(\mathbf{r}) div\mathbf{u} = -\frac{C}{\sqrt{N}} \sum_{\mathbf{kq}} i\mathbf{q}\mathbf{u}_{\mathbf{q}} c^{+}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} \quad , \tag{11.1}$$

where we use the Fourier transforms

$$\mathbf{u}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \mathbf{u}_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \tag{11.2}$$

for the longitudinal acoustic phonons and

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \tag{11.3}$$

for the electron annihilation operators; N denotes the number of ions, V denotes the volume and the summation over spin is included. In equation (11.1) $C > 0$ is a constant. The minus sign accounts for the attractive nature of this interaction.

The electron density

$$n(\mathbf{r}) = \sum_{i} \delta(\mathbf{r} - \mathbf{r}_i) \tag{11.4}$$

becomes in the second quantization

$$\begin{aligned} n(\mathbf{r}) = \psi^{+}(\mathbf{r})\psi(\mathbf{r}) = \tfrac{1}{V} \textstyle\sum_{\mathbf{kq}} c^{+}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} e^{-i\mathbf{q}\mathbf{r}} = \\ = \tfrac{1}{V} \textstyle\sum_{\mathbf{k}} c^{+}_{\mathbf{k}} c_{\mathbf{k}} + \tfrac{1}{V} \textstyle\sum_{\mathbf{kq}\neq 0} c^{+}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} e^{-i\mathbf{q}\mathbf{r}} \quad , \end{aligned} \tag{11.5}$$

whence we can see that $c^{+}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}}$, $\mathbf{q} \neq 0$, is associated with density variations.

The interaction given by equation (11.1) can also be obtained by taking the mixed second-order change in the energy of the electron liquid given in the "Electron Liquid" chapter. The cohesion theory of the metals given in that chapter offers the possibility of estimating the constant C, which is of the order $10^{-2}\mu$, where μ is the chemical potential of the electrons. An approximate estimation is provided by the change in the Fermi level $\delta\mu = -2\mu(\delta a/a) = -\frac{2}{3}\mu(\delta V/V)$, by using

$\delta V/V = -\delta n_i/n_i = div\mathbf{u}$, where a is the mean separation distance between the electrons, which is taken equal with the mean separation distance between the ions with density n_i; hence $C = 2\mu/3$. Since the effective ion charge is ze, where z is of the order $z = 10^{-1}$ (and $-e$ is the electron charge), it is easy to see that the interaction $\sim z^2$ is reduced by a factor of the order 10^{-2}.

First, we note that the electron-phonon energy, which is of the order C, is higher than the quasi-electron energy uncertainty T^2/μ, where T denotes the temperature; therefore, it makes sense to treat H_{e-ph} as an interaction. Similarly, C is higher than the uncertainty in the phonon energy $\hbar T/Mca$, where M is the ion mass, c is the sound velocity (actually the phonon group velocity) and a denotes the mean separation distance between the ions; the corresponding inequality is $T < \frac{M}{m}\hbar\omega_D$, where m is the electron mass and ω_D is the Debye frequency. Again we arrive at the conclusion that we may treat the electron-phonon coupling as an interaction, which does not disturb the main picture of phonons and quasi-electrons; this means that we may treat the electron-phonon interaction within the first orders of the perturbation theory.

However, if we look carefully at the electron-phonon interaction hamiltonian given by equation (11.1), we can see a few interesting things. First we note that the first contribution to energy arises from this hamiltonian in the second-order of the perturbation theory, where the well-known denominator which involves energy differences may be negative; this may lead to a pairing instability at low temperature, which changes completely the electron-liquid structure and is the cause of the superconductivity.[1] Moreover, this result tells us that at higher temperatures, where the pairing instability is not effective, the electron-phonon interaction has a small effect on the quasi-electrons, except for inducing an uncertainty in their energy given by $\hbar/\tau_{e-ph} = T/F$, $F = \frac{M}{m}(\hbar\omega_D/\mu)^2$ (given in the "Phonons in Solids" chapter). Also, since the electrons follow rapidly the ionic motion,[2] the effect of the electron-phonon interaction on the phonons is small.

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[1] H. Frohlich, "Theory of the superconducting state. I. The ground state at the absolute zero of temperature", Phys. Rev. **79** 845 (1950); L. Cooper, "Bound electron pairs in a degenerate Fermi gas", Phys. Rev. **104** 1189 (1956); J. Bardeen, L. N. Cooper and J. R. Schrieffer, "Theory of Superconductivity", Phys. Rev. **108** 1175 (1957).

[2] M. Born and J. R. Oppenheimer, "Zur Quantentheorie der Molekulen", Ann.

Second, we note that if the phonon wavevector **q** in equation (11.1) couples large portions of the Fermi surface (the so-called nesting portions, giving rise to macroscopic contributions), as in low-dimensional solids, then the electron-phonon interaction becomes large; as a consequence, it may lead to the Kohn anomaly[3] in the phonon spectrum and even to the Peierls-Frohlich distorted state of charge density waves,[4] where, again, the electron-liquid structure is completely changed (such a distorted state of the solid is similar with the Jahn-Teller effect, related to the interaction between electrons and molecular vibrations[5]).

Most of the covalent solids are insulators. When conducting, like semiconductors, the electron excitations are the charge carriers, with narrow energy bands and effective mass. The electron-phonon interaction given by equation (11.1) is applicable, but the coupling constant C is small. The energy uncertainty in semiconductors is $\Delta\varepsilon = \sqrt{\varepsilon_q T}$, where $\varepsilon_q = \hbar^2/ma^2$, a being the mean separation distance between the charge carriers (given in the "Semiconductors" chapter). The charge-carrier density is low, and a acquires large values (typically 100Å). We can see that $\Delta\varepsilon \ll C$, such that it makes sense to use the electron-phonon interaction within the charge-carrier picture. Since C is small, the perturbation theory is sufficient. The effect of the lifetime given by $\hbar/\tau_{e-ph} = T/F$, generated by the electron-phonon interaction, is small in comparison with the semiconducting lifetime $\hbar/\Delta\varepsilon$. Similarly, the effect of the electron-phonon interaction is small.

In ionic (polar) solids the situation is different. These solids exhibit optical phonons, which are localized vibrations and imply a polarization of the body. The electrons themselves have a small mobility.

Phys. **389** 457 (1927).

[3] W. Kohn, "Image of the Fermi surface in the vibration spectrum of a metal", Phys. Rev. Lett. **2** 393 (1959).

[4] H. Frohlich, "On the theory of superconductivity: the one-dimensional case", Proc. Roy. Soc. London **A223** 296 (1954); R. Peierls, *Quantum Theory of Solids*, Oxford University Press, Oxford (1955); see also M. Apostol and I. Baldea, "On the charge density wave state in the quasi-one-dimensional compound $K_2[Pt(CN)_4]Br_{0.3} \times 3.2H_2O$ (KCP)", Rev. Roum. Phys. **30** 605 (1985).

[5] H. A. Jahn and E. Teller, "Stability of polyatomic molecules in degenerate electronic states - I - Orbital degeneracy", Proc. Roy. Soc. London **A161** 220 (1937).

The interaction of these polarization modes with the electrons is proportional to $\delta n\varphi$, where φ is the Coulomb potential in a dielectric substance; on the other hand, the potential φ is related to the polarization, and the latter is given by the displacement of the ions. The electron-phonon interaction acquires the form

$$H_{e-ph} = -C^{'} \sum_{\mathbf{kq}} (i\mathbf{q}\mathbf{u}_{\mathbf{q}}/q^2) c^{+}_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} \tag{11.6}$$

(for longitudinal modes), where $C^{'}$ is a constant. The long-range Coulomb interaction in equation (11.6) is stronger than the local interaction in equation (11.1), such that the perturbation-theory calculations are questionable. The electrons get a large effective mass, their mobility is low and the solid is locally distorted; this elementary excitation is called polaron.[6]

11.2 Renormalization of velocity

The change δn in the electron density in equation (11.1) can be written as $\delta n = -ndiv\mathbf{v}$, where $\mathbf{v}$ is their displacement, with a slight spatial variation. The electron-phonon hamiltonian given by equation (11.1) generates an additional force which acts both on the ionic motion (displacement $\mathbf{u}$) and electron motion (displacement $\mathbf{v}$). The equations of motion for the Fourier transforms of the displacement can be written as

$$\begin{aligned} (\omega^2 - \omega_q^2)\mathbf{u} - \tfrac{Cn}{\rho} q^2 \mathbf{v} = 0 \ , \\ (\omega^2 - \omega_0^2)\mathbf{v} - \tfrac{C}{m} q^2 \mathbf{u} = 0 \ \ , \end{aligned} \tag{11.7}$$

where ρ is the mass density of the ions, $\omega_q = cq$ is the frequency of the longitudial phonons (c being the sound velocity and $\mathbf{q}$ the wavevector) and $\omega_0 = (4\pi ne^2/m)^{1/2}$ is the plasma frequency; $-e$ and m denote the electron charge and mass, respectively. It is worth noting the occurrence of the plasma frequency in these equations, due to the polarization generated by the charge motion; it corresponds to the Coulomb interaction between the electron collective excitations. The displacements **u** and **v** in these equations are not independent: due to the fast accommodation of the electrons to the ionic motion (the electrons follow rapidly the adiabatic ionic motion), the changes in the electron and ion densities are equal; *i.e.*, $n\mathbf{v} = (\rho/M)\mathbf{u}$ in equations (11.7), where ρ is the ion mass density and M is the ion mass. We get immediately

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[6] L. Landau and S. I. Pekar, "The effective mass of the polaron", ZhETF **18** 419 (1948) (in Russian); R. Feynman, "Slow electrons in a polar crystal", Phys. Rev. **97** 660 (1955); R. Feynman, R. W. Hellwarth, C. K. Iddings and P. M. Platzman, "Mobility of slow electrons in a polar crystal", Phys. Rev. **127** 1004 (1962).

$$\begin{gathered}\widetilde{\omega}_q^2 = \omega_q^2 + \tfrac{C}{M}q^2 = c^2\left(1 + \tfrac{C}{Mc^2}\right)q^2 \ \ , \\ \widetilde{\omega}_0^2 = \omega_0^2 + \tfrac{Cn}{mn_i}q^2\end{gathered} \tag{11.8}$$

for the renormalized frequencies, where n_i is the ion density. If we assume $C = \frac{2}{3}\mu$ and $n = n_i$, we get the renormalized sound velocity

$$\widetilde{c} = \left(1 + \frac{m}{3M}\frac{v_F^2}{c^2}\right)^{1/2} c \tag{11.9}$$

and the renormalized plasma frequency

$$\widetilde{\omega}_0^2 = \omega_0^2 + \frac{1}{3}v_F^2 q^2 \ \ , \tag{11.10}$$

where v_F is the Fermi velocity. We can see that the correction to the sound velocity is of the order m/M.[7] This is known sometimes as Migdal's theorem, since the energy conservation produces a ratio $p/P = \sqrt{m/M}$ of the electron momentum p to the ion momentum P.[8] We note that these corrections are very small (the constant C is much smaller than $2\mu/3$ and $n < n_i$), such that we may neglect them. In addition, the plasmons are well-defined in the limit $q \to 0$, such that the q^2-term in equation (11.10) is irrelevant.

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[7] J. Bardeen and D. Pines, "Electron-phonon interaction in metals", Phys. Rev. **99** 1140 (1955).

[8] A. B. Migdal, "Interaction between electrons and lattice vibrations in a normal metal", Sov. Phys.-JETP **7** 996 (1958) (ZhETF **34** 1438 (1958)).

11.3 Lifetime and interaction

The interaction introduces limitations on the physical properties of the particles. Typical examples of interaction are the electron-electron interaction in an electron liquid, or fermion-fermion interaction in a normal Fermi liquid, or electron-phonon interaction, or boson interaction in a Bose gas or a Bose liquid.[9] A convenient way of discussing interaction in ensembles of particles is Feynman's diagramatic theory of quantum electrodynamics.[10] The fundamental vertex is particle-interaction-particle, *e.g.* electron-phonon-electron. In the first order of the perturbation theory the particles are dressed with the Hartree-Fock approximation to the interaction. For the long-range Coulomb interaction the random phase approximation is needed for the interaction, which implies an infinite series of higher-order interaction terms. With this effective interaction, the theory looks like a first-order perturbation theory, which preserves the notion of particle (including the particle which carries the interaction). The effect is the renormalization of mass and interaction coupling constant. A unitary transformation may even eliminate the interaction and reduces the vertex to a second-order particle-particle coupling (though the electron wavefunctions are changed by the unitary transformation). All the internal lines in the diagrams corresponding to this approximation are virtual particles (as for any internal line), *i.e.* particles for which the relation between energy and momentum is not that of real particles; but the external lines in these diagrams, corresponding to renormalized particles, pertain to real particles. The f-function of Landau's theory of the normal Fermi liquid represents this approximation; not only the individual particles can be described this way, but also the collective modes.

The dressing of the vertex part changes this picture; a dressed vertex destroys the notion of particle, by mixing up interacting particles. Assuming that the perturbation theory gives finite results, these higher-order effects are included in a small contribution which is an uncertainty in energy, related to a lifetime. The particles have now a finite life, they are destroyed and created continuously, with a finite, short lifetime. They become elementary excitations of the quasi-particle type or collective modes. The lifetime can be computed by the transition probability, involving second-order perturbation theory (higher-order corrections, which would be corrections to corrections, are irrelevant). This is the notion of elementary excitations introduced by Landau. The probability transition (the scattering) involves real particles, with interaction which includes internal lines, *i.e.* virtual particles. If the perturbation series does not look formally convergent, it is a problem with its expansion; if it implies infinities, like in quantum electrodynamics, arising from self-interaction, they can be removed by renormalization techniques in each order of the perturbation theory (the quantum electrodynamics involves both infinities and non-convergence).

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[9] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems*, McGraw-Hill, NY (1971); G. D. Mahan, *Many-Particle Physics*, Kluwer, NY (1981).

[10] R. Feynman, "The theory of positrons", Phys. Rev. **76** 749 (1949); "Space-time approach to quantum electrodynamics", Phys. Rev. **76** 769 (1949); F. Dyson, "The radiation theories of Tomonaga, Schwinger and Feynman", Phys. Rev. **75** 486 (1949); "The S matrix in quantum electrodynamics", Phys. Rev. **75** 1736 (1949).

Summarizing, in an interacting ensemble of particles we have interaction effects of the first-order type (or second-order type effective-interaction effects), which renormalize the particles (*e.g.*, their mass) and finite lifetime effects, which are effects of the second-order type. An example of the former is the renormalization of the sound velocity in equation (11.9), while an example of the latter is the electron-phonon lifetime given above by $\hbar/\tau_{e-ph} = T/F$. The electron-phonon interaction does not renormalize the quasi-electrons, but it renormalizes the phonons and the plasmons (it couples the phonons to the collective modes of electron density); however, it affects the quasi-electron lifetime.

The uncertainty in energy $\Delta\varepsilon$ associated with a transition produced by an interaction V is of the order

$$\Delta\varepsilon \simeq \mid V \mid^2 \frac{1}{\delta\varepsilon}\Delta\nu \quad , \tag{11.11}$$

where $\mid V \mid^2$ stands for the square of the matrix element of the interaction, $1/\delta\varepsilon$ is the density of states per particle and energy and $\Delta\nu$ is the number of scattering possibilities. The state density for fermions with density n is $3n/2\mu$, such that we may take $1/\delta\varepsilon \simeq 1/\mu$

(per volume); each fermion has $\simeq T/\mu$ states for scattering, such that there is $\Delta\nu \simeq (T/\mu)^2$ scattering possibilities (per volume); we get $\Delta\varepsilon \simeq \mid V \mid^2 T^2/\mu^3$; for interacting electrons we may take $\mid V \mid^2 \simeq (e^2/a)^2$, where a is the mean separation distance between electrons; since $e^2/a \simeq \mu$, we get $\Delta\varepsilon \simeq T^2/\mu$ (at zero temperature T^2 is replaced by $(\varepsilon - \mu)^2$); the corresponding lifetime is the quasi-electron lifetime given by $1/\tau_e \simeq \Delta\varepsilon/\hbar \simeq T^2/\hbar\mu$.

For the electron-phonon interaction $\delta\varepsilon \simeq \hbar\omega_D$, where ω_D is the Debye frequency (acoustic phonons) and $\Delta\nu \simeq T/\hbar\omega_D$; we get $\Delta\varepsilon \simeq \mid V \mid^2 T/(\hbar\omega_D)^2$. For the interaction V we may take $\sqrt{m/M}\mu$, taking into account the energy conservation in the momentum exchange (where m is the electron mass and M is the ion mass); the energy uncertainty becomes $\Delta\varepsilon \simeq \frac{m}{M} T (\mu/\hbar\omega_D)^2$ and the lifetime given by $1/\tau_{e-ph} = T/\hbar F$, where $F = \frac{M}{m}(\hbar\omega_D/\mu)^2$.[11] At zero temperature T is replaced by $\hbar\omega_D$ (relaxation time of the electron).[12] It is worth noting that we estimate the interaction which affects the electron energy (and the quasi-electron lifetime caused by the electron-phonon interaction).

11.4 Ultrasound attenuation

The electron-phonon interaction provides a mechanism of phonon absorption, especially in metals. The free lagrangian of the acoustic phonons is

$$L_0 = \frac{1}{a^3} \int d\mathbf{r} \left[\frac{1}{2} M \dot{\mathbf{u}}^2 - \frac{1}{2} M c^2 (div\mathbf{u})^2 \right] \quad , \tag{11.12}$$

where a is the mean separation distance between the ions, M denotes the ion mass, $\mathbf{u}$ is the displacement and c is the sound velocity. Using the Fourier transform given by equation (11.2), we get the free hamiltonian

$$H_0 = \sum_{\mathbf{q}} \left(\frac{1}{2M} p_{\mathbf{q}} p_{-\mathbf{q}} + \frac{1}{2} M \omega^2 u_{\mathbf{q}} u_{-\mathbf{q}} \right) \tag{11.13}$$

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[11] A. H. Wilson, *The Theory of Metals*, Cambridge University Press, Cambridge (1953).

[12] C. Kittel, *Quantum Theory of Solids*, Wiley, NY (1963).

for longitudinal phonons, where $\omega = cq$ is the phonon frequency and $p_{\mathbf{q}}$ is the associated momentum. The quantization of this hamiltonian,

$$H_0 = \sum_{\mathbf{q}} \hbar\omega(a_{\mathbf{q}}^+ a_{\mathbf{q}} + 1/2) \quad , \tag{11.14}$$

is achieved by using

$$\begin{aligned} u_{\mathbf{q}} &= \sqrt{\tfrac{\hbar}{2M\omega}}\left(a_{\mathbf{q}}^+ + a_{-\mathbf{q}}\right) \quad , \\ p_{\mathbf{q}} &= i\sqrt{\tfrac{\hbar M\omega}{2}}\left(a_{\mathbf{q}}^+ - a_{-\mathbf{q}}\right) \quad , \end{aligned} \tag{11.15}$$

where $a_{\mathbf{q}}(a_{\mathbf{q}}^+)$ are phonon destruction (creation) operators. We note the commutation relation

$$[u(\mathbf{r}), p(\mathbf{r}')] = i\hbar\delta_{\mathbf{r},\mathbf{r}'} \ . \tag{11.16}$$

The hamiltonian of the electron-phonon interaction given by equation (11.1) becomes

$$\begin{aligned} H_{e-ph} &= -\tfrac{C}{\sqrt{N}}\textstyle\sum_{\mathbf{kq}} i\mathbf{q}\mathbf{u}_{\mathbf{q}} c_{\mathbf{k}+\mathbf{q}}^+ c_{\mathbf{k}} = \\ &= -\tfrac{C}{\sqrt{N}}\textstyle\sum_{\mathbf{kq}} iq\sqrt{\tfrac{\hbar}{2M\omega}}\left(a_{\mathbf{q}}^+ + a_{-\mathbf{q}}\right) c_{\mathbf{k}+\mathbf{q}}^+ c_{\mathbf{k}} \ . \end{aligned} \tag{11.17}$$

The probability of absorbing a phonon per unit time from n phonons is

$$w_- = \frac{2\pi}{\hbar} \cdot \frac{C^2}{N}\frac{\hbar q}{2Mc} n \cdot \sum_{\mathbf{k}} n(\mathbf{k})\left[1 - n(\mathbf{k}+\mathbf{q})\right]\delta(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}} - \hbar\omega) \quad , \tag{11.18}$$

where $n(\mathbf{k})$ is the Fermi distribution (number of electrons in the **k**-state) and $\varepsilon_{\mathbf{k}}$ is the electron energy (we perform the calculation for metals). Similarly, if a photon is emitted in the state with $n - 1$ phonons, the emission probability per unit time is

$$w_+ = \frac{2\pi}{\hbar} \cdot \frac{C^2}{N}\frac{\hbar q}{2Mc} n \cdot \sum_{\mathbf{k}} n(\mathbf{k})\left[1 - n(\mathbf{k}-\mathbf{q})\right]\delta(\varepsilon_{\mathbf{k}-\mathbf{q}} - \varepsilon_{\mathbf{k}} + \hbar\omega) \ . \tag{11.19}$$

The difference $w_- - w_+$ is the phonon loss rate. If the electron processes generate a slight spatial variation in the phonon number, *i.e.* if

$$\Lambda q \gg 1 \quad , \tag{11.20}$$

where Λ is the electron mean freepath, we may write the decay equation

$$\frac{dn}{dt} = -(w_- - w_+)n \quad , \tag{11.21}$$

where

$$\begin{aligned} \tfrac{1}{\tau_{ph-e}} &= (w_- - w_+) = \\ &= \tfrac{2\pi}{\hbar} \cdot \tfrac{C^2}{N} \tfrac{\hbar q}{2Mc} \textstyle\sum_{\mathbf{k}} n(\mathbf{k}) \cdot \\ \cdot \left[n(\mathbf{k}-\mathbf{q}) - n(\mathbf{k}+\mathbf{q})\right] &\delta(\hbar^2 \mathbf{kq}/m - \hbar\omega) \quad , \end{aligned} \tag{11.22}$$

or

$$\frac{1}{\tau_{ph-e}} = -\frac{2\pi C^2}{N} \frac{q}{Mc} \sum_{\mathbf{k}} n(k) \frac{\mathbf{kq}}{k} \frac{\partial n(k)}{\partial k} \delta(\hbar^2 \mathbf{kq}/m - \hbar\omega) \quad , \tag{11.23}$$

where we assume that $n(\mathbf{k})$ depends only on k and neglect the q^2-term in the energy differences, because it is too small; τ_{ph-e} is the phonon lifetime, caused by the interaction with the electrons. The integral in equation (11.23) can be reduced to

$$\frac{1}{\tau_{ph-e}} = -\frac{C^2 m^2 a^3}{\pi \hbar^3 Mc} \omega \int dk \cdot n(k) \frac{\partial n(k)}{\partial k} \tag{11.24}$$

(where the spin factor 2 is introduced). We get finally

$$\frac{1}{\tau_{ph-e}} = \frac{C^2 m^2 a^3}{2\pi \hbar^3 Mc} \omega \tag{11.25}$$

(leaving aside small temperature corrections). The attenuation coefficient is $\alpha = 1/c\tau_{ph-e}$. In this equation we may put $C = 2\mu/3$ for metals.

A more useful form of equation (11.25) is $1/\tau_{ph-e} \simeq (m/M)v_F q$, where v_F is the Fermi velocity. Since, usually, $(m/M)v_F \ll c$, we can see that the uncertainty in the phonon energy is much smaller than the phonon energy $\hbar\omega = \hbar cq$, as expected. On the other hand, we should compare the lifetime τ_{ph-e} with the intrinsic phonon lifetime $\tau_{ph} = Mca/T$, introduced in the "Phonons in Solids" chapter. For q close to $1/\Lambda$ these two times are comparable at room temperature, while for higher values of q ($\simeq 1/a$) the time τ_{ph-e} is shorter and may dominate the transport at room temperature; for very large temperatures the transport is still governed by τ_{ph}. This is why we need to use $1/\tau = 1/\tau_{ph} + 1/\tau_{ph-e}$ for the phonon transport time τ.

Similar considerations can be made for the electron-phonon interaction in semiconductors, where the density of the charge carriers is very low (and the interaction constant C is small); the phonons are little affected by this interaction.

11.5 Sound absorption

What happens in the long wavelength limit $\Lambda q \ll 1$, which corresponds to sound phonons? The phonon lifetime caused by the electron-phonon interaction is given in this case by

$$\tau_{ph-e} = \frac{T}{(\Lambda/\lambda)} = \frac{1}{\omega q \Lambda} \quad , \tag{11.26}$$

where T is the phonon period, λ is its wavelength and Λ is the electron mean freepath; this formula can be related to the electron viscosity η by

$$\tau_{ph-e} = \frac{1}{\omega q \Lambda} = \frac{\rho c^2}{\omega^2 \eta} \quad , \tag{11.27}$$

where ρ is the ion density; we can see that the ions move with velocity c (phonon velocity) through the electron gas; it follows

$$\frac{1}{\tau_{ph-e}} = \frac{\eta}{\rho c^2}\omega^2 \quad ; \tag{11.28}$$

since $\omega \to 0$, this contribution is very small; it may be used for semiconductors as well (also, it gives the sound absorbtion in gases).

The viscosity of the electron gas is $\eta = mnv_F^2\tau_e$, where τ_e is the electron lifetime; or $\eta = n\mu\tau_e$, such that we get

$$\frac{1}{\tau_{ph-e}} = \frac{n\mu}{\rho c^2}\tau_e\omega^2 \simeq \frac{\mu}{Mc^2}\tau_e\omega^2 \ ; \tag{11.29}$$

since $\tau_e \simeq \hbar\mu/T^2$, we can see that the sound is not propagated in the limit of zero temperature.[13] The above equations can be applied to semiconductors also, where $\tau_e = a\sqrt{m/T}$ (thermal velocity $v = \sqrt{T/m}$). We note that $1/\tau_{ph-e}$ is proportional to the conductivity $\sigma = ne^2\tau_e/m$. Also, the long wavelength lifetime given by equation (11.29) (sound lifetime) is the short-wavelength lifetime given by equation (11.25) (ultrasound lifetime) multiplied by $1/\Lambda q$.

We note that viscosity is one mechanism of sound absorption; another one is provided by thermoconduction (described in the "Phonons in Solids" chapter).

11.6 Electron lifetime

The electron-phonon interaction causes an electron lifetime τ_{e-ph}. The estimation for metals is $1/\tau_{e-ph} = T/\hbar F$, $F = \frac{M}{m}(\hbar\omega_D/\mu)^2$ (given in the "Phonons in Solids" chapter). It is generated by the absorption of a phonon from n phonons, or by emission of a phonon from $n-1$ phonons. According to the electron-phonon interaction given by equation (11.17), the transition probability per unit time is

$$\frac{1}{\tau_{e-ph}} = \frac{2\pi}{\hbar}\frac{C^2}{N}\sum_{\mathbf{q}}\frac{\hbar}{2M\omega}q^2 n\delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega) \ \ , \tag{11.30}$$

an equation which can be transformed as

$$\frac{1}{\tau_{e-ph}} = \frac{C^2a^3}{4\pi Mc}\int dq\cdot q^3 n\int du\delta(\frac{\hbar^2 kq}{m}u - \hbar cq) \ . \tag{11.31}$$

We can see that $u = c/v$, where $u = \cos\theta$, θ being the angle made by $\mathbf{k}$ and $\mathbf{q}$, and v is the electron velocity. For metals $v = v_F$ and

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[13] I. Pomeranchuk, "On the theory of liquid He^3", ZhETF **20** 919 (1950) (in Russian); L. Landau, "Oscillations in a Fermi liquid", Sov. Phys.-JETP **5** 101 (1057) (ZhETF **32** 59 (1957)).

$c/v_F \ll 1$; for semiconductors $v = \sqrt{T/m}$ and, usually, $c/v < 1$. Equation (11.31) leads to

$$\frac{1}{\tau_{e-ph}} = \frac{mC^2T^3}{4\pi M(\hbar\omega_D)^4}\frac{1}{\hbar(ak_F)}\int_0^{\hbar\omega_D/T} dx \cdot \frac{x^2}{e^x - 1} \ . \tag{11.32}$$

For $\hbar\omega_D/T \gg 1$ (low temperature) the integral is 2.4 and $1/\tau_{e-ph}$ goes like T^3; it is smaller than the inverse of the intrinsic electron lifetime ($1/\tau_e \simeq T^2/\hbar\mu$) in metals (the same situation is in semiconductors). For $\hbar\omega_D/T \ll 1$ (high temperature) we get

$$\frac{1}{\tau_{e-ph}} = \frac{T}{18\pi\hbar F}\frac{1}{(ak_F)} \ , \ F = \frac{M}{m}\left(\frac{\hbar\omega_D}{\mu}\right)^2 \tag{11.33}$$

for metals, which, for $ak_f \simeq 1$ is the well-known formula of the electron lifetime caused by the electron-phonon interaction given in the "Phonons in Solids" chapter.[14] The same formula can be used for semiconductors with a much smaller μ and $\hbar k_F$ replaced by $mv = \sqrt{mT}$; $1/\tau_{e-ph}$ goes like $\sqrt{T}$ in this case, which is the same temperature dependence as for the intrinsic electron lifetime τ_e. We get in this case $1/\tau = (1 + 1/18\pi F) \cdot 1/\tau_e$, which shows that the intrinsic electron lifetime is slightly renormalized by the electron-phonon interaction.

11.7 Non-equilibrium phenomena

The condition $\Lambda q \gg 1$, where Λ is the mean freepath of the electrons and $\mathbf{q}$ is the wavevector of the phonons, indicates that the electrons are not in equilibrium with the phonons. Indeed, since $\Lambda = v_F\tau$, where τ is the lifetime of the electrons (and v_F is the Fermi velocity, or the thermal velocity in semiconductors), this condition implies a long electron lifetime (for finite q). The lifetime ensures the equilibrium and, also, it is the non-equilibrium time. Therefore, it appears in the collision term of the Boltzmann equation, which is proportional to $1/\tau$. If τ is short, the collision term is large, and the equilibrium is achieved rapidly; such that we may use the equilibrium Boltzmann equation with a short lifetime, suitable for slow variations (which are also spatially slight). If τ is long, the equilibrium is achieved slowly, and we are, in fact, in non-equilibrium. The condition $\Lambda q \gg 1$ can also be written as $\frac{v_F}{c} \cdot \frac{\tau}{T} \gg 1$, which shows that the period of the phonons may be short; these phonons may generate non-equilibrium, and the electrons would not be able to respond quickly, in order to establish the equilibrium; this may happen at low temperatures. This condition may be satisfied for optical phonons too. A short-time perturbation, like that produced by ultrasound or optical phonons, may not be equilibrated quickly by slow electrons. In this case, the transport should be treated by using the Boltzmann equation with the collision term. We note that this is not valid in the long wavelength limit $q \to 0$ of the sound waves; the sound is not in equilibrium with the lattice (for reasons similar with those described above), but it may be in equilibrium with the electrons.

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[14] A. H. Wilson, *The Theory of Metals*, Cambridge University Press, Cambridge (1953).

The Boltzmann equation with collision term may generate a drag force on the electrons on behalf of the phonons, and may lead to the attenuation of the transverse phonons. Also, it describes the anomalous skin effect.[15] In this context, we note that the sound attenuation exhibits typical oscillations with $1/H$ in a magnetic field H.[16]

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[15] C. Kittel, *Quantum Theory of Solids*, Wiley, NY (1963).

[16] See also M. Apostol, "On the non-thermal relaxation time in the magnetic quantum tunneling", Fizika **A1** 231 (1992); "On a field-induced spin-density wave in Bechgaard salts", Acta Phys. Pol. **A85** 971 (1994);

12 Superconductivity

12.1 Introduction

Superconductivity was discovered in 1911, when it was noticed that the electrical resistance of mercury (Hg) disappears below some critical temperature $T_c \sim 3K$, comparable with the liquefaction temperature $\sim 2K$ of helium four (He^4).[1] Thereafter, it was noticed that some materials become superconductors below some low temperatures, while others do not. For instance magnetic impurities destroy the superconductivity.

Insights into superconductivity have been developed along the time.[2] The theory was given by Ginsburg and Landau in 1950[3] and by Bardeen, Cooper and Schrieffer (BCS) in 1957.[4]

The highest superconducting critical temperature was for a long time $\sim 20K$ for $Nb_3(Al_{0.8}Ge_{0.2})$. In 1986 there have been discovered cuprate oxides[5] with superconducting critical temperatures up to $\sim$

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[1] O. Kamerlingh Onnes, Akad. van Wetenschappen (Amsterdam) **13** 1107, 1274; **14** 113, 204 (1911); Commun. Leiden **119b**, **120b**, **122b**, **123a** (1911).

[2] C. J. Gorter and H. G. B. Casimir, "Zur Thermodynamik des supraleitenden Zustandes", Phys. Z. **35** 963 (1934); "Zur Thermodynamik des supraleitenden Zustandes", Z. Tech. Phys. **15** 539 (1934); F. London and H. London, "The electromagnetic equations of the supraconductor", Proc. Roy. Soc. London **A149** 71 (1935); "Supraleitung und Diamagnetismus", Physica **2** 341 (1935); F. London, *Superfluids*, Wiley, NY (1950); M. R. Schafroth, "Bemerkungen zur Frohlichschen Theorie der Supraleitung", Helv. Phys. Acta **24** 645 (1951); J. M. Blatt, *Theory of Superconductivity*, Academic Press, NY (1964).

[3] V. L. Ginsburg and L. Landau, "On the theory of superconductivity", ZhETF **20** 1064 (1950) (in Russian).

[4] J. Bardeen, L. N. Cooper and J. R. Schrieffer, "Microscopic theory of superconductivity", Phys. Rev. **106** 162 (1957); "Theory of superconductivity", Phys. Rev. **108** 1175 (1957).

[5] J. G. Bednorz and K. A. Muller, "Possible high T_c superconductivity in the $Ba-La-Cu-O$ system", Z. Phys. **B64** 189 (1986).

$40K$ ($La_{2-x}Sr_xCuO_4$) and latter on $\sim 90K$ ($YBa_2Cu_3O_7$) and $\sim 120K$ ($Bi_2Sr_2CaCu_2O_8$). It would be likely that the theory of high-T_c superconductivity is similar in its basic patterns with the standard superconductivity theory described herein.[6]

12.2 Cooper pair

The electron-phonon interaction may lead to an attractive electron-electron interaction which is relevant for superconductivity.[7] With usual notations we write the hamiltonian as

$$H = \sum_{\mathbf{k}\alpha} \varepsilon_{\mathbf{k}} c^{+}_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha} - (\lambda/V) \sum_{\mathbf{k}\mathbf{k}'\alpha} c^{+}_{\mathbf{k}\alpha} c^{+}_{-\mathbf{k}\bar{\alpha}} c_{-\mathbf{k}'\bar{\alpha}} c_{\mathbf{k}'\alpha} \ . \qquad (12.1)$$

The coupling constant λ (> 0) is an energy like $\varphi \sim e^2/a$ multiplied by volume $\sim a^3$ where a is the mean inter-electron distance. It does not depend on the momentum transfer, so it is equivalent with a δ-potential. It follows that the spins in the pair operators in equation (12.1) are opposite to each other ($\bar{\alpha} = -\alpha$) and the pair is an s-wave. The wavevectors $\mathbf{k}$'s are restricted to the neighbourhood of the Fermi surface.

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[6] See for instance M. Apostol, "On the mechanism of high-temperature superconductivity in $Ba - La(Y) - Cu - O$ type systems", Int. J. Mod. Phys. **B1** 957 (1987); M. Apostol and L. Vasiliu-Doloc, "High-temperature superconductivity from electron-lattice coupling", Int. J. Mod. Phys. **B6** 1539 (1992).

[7] H. Frohlich, "Theory of the superconducting state. I. The ground state at the absolute zero of temperature", Phys. Rev. **79** 845 (1950). Superconductivity has also been derived by starting directly with the electron-phonon interaction (G. M. Eliashberg, "Interaction between electrons and lattice vibrations in a superconductor", Sov. Phys.-JETP **11** 696 (1960) (ZhETF **38** 966 (1960)); see also L. P. Gorkov, "On the energy spectrum of superconductors", Sov. Phys.-JETP **7** 505 (1958) (ZhETF **34** 735 (1958)); Y. Nambu, "Quasi-particles and gauge invariance in the theory of superconductivity", Phys. Rev. **117** 648 (1960)) and the presumably high effect of the (screened) Coulomb repulsion was "renormalized" for pairing electrons by N. N. Bogoliubov, V. V. Tolmachev and D. V. Shirkov, *A New Method in the Theory of Superconductivity*, Consultants Bureau, NY (1959). Retardation and damping effects can then be dealt with (like in lead (Pb), for instance) without any qualitative change of the superconducting "picture" (except that the superconducting quasiparticles are not well defined anymore).

We introduce the pair operators $P^+_{\mathbf{k}\alpha} = c^+_{\mathbf{k}\alpha} c^+_{-\mathbf{k}\bar{\alpha}}$ and see that a non-trivial Schrodinger's equation

$$(2\varepsilon_{\mathbf{k}} - \varepsilon) P^+_{\mathbf{k}\alpha} = (2\lambda/V) \sum_{\mathbf{k}'} P^+_{\mathbf{k}'\alpha} \tag{12.2}$$

is obtained for one pair. The spectrum of this equation is given by

$$1 = (2\lambda/V) \sum_{\mathbf{k}} \frac{1}{2\varepsilon_{\mathbf{k}} - \varepsilon} \ . \tag{12.3}$$

It is easy to see that the solution of equation (12.3) is given by

$$\varepsilon = 2\varepsilon_F - 2\varepsilon_c e^{-1/\lambda\rho} \ , \tag{12.4}$$

where we have assumed that the interaction extends from ε_F to $\varepsilon_F + \varepsilon_c$, $\varepsilon_c \ll \varepsilon_F$, and $\rho = mk_F/2\pi^2\hbar^2 = 3n/4\varepsilon_F$ is the density of states per unit volume and per spin at the Fermi surface. The electron density is $n = k_F^3/3\pi^2 \sim 1/a^3$. We can see that the attractive interaction leads to a bound pair of electrons. This is the Cooper pair.[8] Since the attractive interaction originates in the exchange of virtual phonons we may take $\varepsilon_c \sim \hbar\omega_D$ where ω_D is the Debye frequency. For $\lambda \sim \varepsilon_F a^3$ we get $\lambda\rho \sim 1$ and ε_c can be taken as the order of magnitude of the pair binding energy.[9] Typical values are such that $e^{-1/\lambda\rho} \ll 1$.

There may exist therefore a "condensate" of electron pairs with density $\sim k_F^2\varepsilon_c/\hbar v_F \sim (\varepsilon_c/\varepsilon_F)n$, in accordance with an earlier hypothesis of two fluids (condensate and normal).[10] The size of a pair is of the order of $\sim \hbar v_F/\varepsilon_c \sim a(\varepsilon_F/\varepsilon_c)$. It can be taken as a "coherence" length of the condensate.

Obviously, the electron pairs conduct the electrical current without dissipation. Thus we have the superconductivity phenomenon.

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[8] L. N. Cooper, "Bound electron pairs in a degenerate Fermi gas", Phys. Rev. **104** 1189 (1956).

[9] $\lambda\rho = 1$ may be taken as the maximum value for the coupling parameter of the pairing theory leading to a maximum superconducting critical temperature. It is known as the "McMillan ceiling" (W. L. McMillan, "Transition temperature of strong-coupled superconductors", Phys. Rev. **167** 331 (1968); see also M. L. Cohen and P. W. Anderson, "Comments on the maximum superconducting temperature", AIP Conf. Proc. **4** 17 (1972); P. W. Anderson and C. C. Yu, in *Proc. Int. School Phys. "Enrico Fermi"*, eds F. Bassani, F. Fumi and M. Tosi, NH, Amsterdam (1983).

[10] C. J. Gorter and H. G. B. Casimir, *loc. cit.*

12.3 BCS theory

Following a method of Bogoliubov[11] and Valatin[12] we introduce

$$\Delta_\alpha^+ = \frac{\lambda}{V}\sum_{\mathbf{k}} \left\langle c_{\mathbf{k}\alpha}^+ c_{-\mathbf{k}\bar{\alpha}}^+ \right\rangle \ , \tag{12.5}$$

where the average is taken over the ground-state for one spin-orientation and write the hamiltonian given by equation (12.1) for a constant number of particles as

$$H = \sum_{\mathbf{k}\alpha} (\varepsilon_{\mathbf{k}} - \mu) c_{\mathbf{k}\alpha}^+ c_{\mathbf{k}\alpha} - \frac{1}{2}\sum_{\mathbf{k}\alpha} (\Delta_\alpha c_{\mathbf{k}\alpha}^+ c_{-\mathbf{k}\bar{\alpha}}^+ + h.c.) \ , \tag{12.6}$$

where μ is the chemical potential. We may assume the parameter Δ_α real, but note that $\Delta_\alpha = -\Delta_{\bar{\alpha}}$. The hamiltonian given by equation (12.6) is diagonalized by the canonical transformation

$$c_{\mathbf{k}\alpha} = u_{\mathbf{k}\alpha} a_{\mathbf{k}\alpha} + v_{\mathbf{k}\alpha} a_{-\mathbf{k}\bar{\alpha}}^+ \ , \ a_{\mathbf{k}\alpha} = u_{\mathbf{k}\alpha} c_{\mathbf{k}\alpha} - v_{\mathbf{k}\alpha} c_{-\mathbf{k}\bar{\alpha}}^+ \ , \tag{12.7}$$

where $u_{\mathbf{k}\alpha}$, $v_{\mathbf{k}\alpha}$ are real, $u_{\mathbf{k}\alpha}^2 + v_{\mathbf{k}\alpha}^2 = 1$, $u_{-\mathbf{k}\bar{\alpha}} = u_{\mathbf{k}\alpha}$ and $v_{-\mathbf{k}\bar{\alpha}} = -v_{\mathbf{k}\alpha}$. We get

$$u_{\mathbf{k}\alpha}^2 = \frac{1}{2}\left(1 + \frac{\varepsilon_{\mathbf{k}} - \mu}{E_{\mathbf{k}}}\right) \ , \ v_{\mathbf{k}\alpha}^2 = \frac{1}{2}\left(1 - \frac{\varepsilon_{\mathbf{k}} - \mu}{E_{\mathbf{k}}}\right) \tag{12.8}$$

and

$$u_{\mathbf{k}\alpha} v_{\mathbf{k}\alpha} = \frac{\Delta_\alpha}{2E_{\mathbf{k}}} \ , \tag{12.9}$$

where

$$E_{\mathbf{k}} = \sqrt{(\varepsilon_{\mathbf{k}} - \mu)^2 + \Delta_\alpha^2} \ . \tag{12.10}$$

These relations correspond to $\varepsilon_{\mathbf{k}} u_{\mathbf{k}\alpha} v_{\mathbf{k}\alpha} - \Delta_\alpha (u_{\mathbf{k}\alpha}^2 - v_{\mathbf{k}\alpha}^2)/2 = 0$. We can see that u and v do not depend on α, except for v which changes sign for $\alpha \to \bar{\alpha}$ as Δ_α does. We may omit the suffix α where it is irrelevant. The hamiltonian becomes

$$\begin{aligned} H = \textstyle\sum_{\mathbf{k}\alpha} &\left[(\varepsilon_{\mathbf{k}} - \mu) v_{\mathbf{k}}^2 - \Delta u_{\mathbf{k}} v_{\mathbf{k}}\right] + \\ &+ \textstyle\sum_{\mathbf{k}\alpha} \left[\varepsilon_{\mathbf{k}} (u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2) + 2\Delta u_{\mathbf{k}} v_{\mathbf{k}}\right] a_{\mathbf{k}\alpha}^+ a_{\mathbf{k}\alpha} \ , \end{aligned} \tag{12.11}$$

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[11] N. N. Bogoliubov, V. V. Tolmachev and D. V. Shirkov, *loc. cit.*

[12] J. Valatin, "Comments on the theory of superconductivity", Nuovo Cimento **7** 843 (1958).

or

$$H=\sum_{\mathbf{k}\alpha}\frac{1}{2}(\varepsilon_{\mathbf{k}}-\mu-E_{\mathbf{k}})+\sum_{\mathbf{k}\alpha}E_{\mathbf{k}}a^{+}_{\mathbf{k}\alpha}a_{\mathbf{k}\alpha}\ . \tag{12.12}$$

We can see that the energy of the ground state is lowered according to the first term in the *rhs* of this equation. The hamiltonian exhibits the structure of a gas of free quasiparticle excitations with energies $E_{\mathbf{k}}$ given by equation (12.10). The spectrum of the original quasiparticles exhibits a gap 2Δ at the Fermi level where $\varepsilon\sim\mu\pm\sqrt{(\varepsilon_{\mathbf{k}}-\mu)^2+\Delta^2}$ with the quadratic dependence $(\varepsilon_{\mathbf{k}}-\mu)^2$.

Similar results are obtained by using the original BCS ground-state wavefunction[13]

$$\psi_{BCS}\sim\prod_{\mathbf{k}\alpha}(1+g_{\mathbf{k}\alpha}P^{+}_{\mathbf{k}\alpha})\left|0\right\rangle\ \ , \tag{12.13}$$

where $P_{\mathbf{k}\alpha}$ are the pair operators introduced above, and minimizing the ground-state energy. We get $u^2_{\mathbf{k}}=(1+g^2_{\mathbf{k}})^{-1/2}$ and $v_{\mathbf{k}}=g_{\mathbf{k}}(1+g^2_{\mathbf{k}})^{-1/2}$.

12.4 The gap equation

Making use of equation (12.7) in equation (12.5) we get the gap equation

$$\Delta=\frac{\lambda}{V}\sum_{\mathbf{k}}u_{\mathbf{k}}v_{\mathbf{k}}=\frac{\lambda}{V}\sum_{\mathbf{k}}\Delta/2E_{\mathbf{k}}\ \ , \tag{12.14}$$

where the summation is extended from $-\varepsilon_c$ to ε_c. We get

$$1=\lambda\rho\int_0^{\varepsilon_c}d\varepsilon\cdot\frac{1}{\sqrt{\varepsilon^2+\Delta^2}} \tag{12.15}$$

and the gap

$$\Delta=2\varepsilon_c e^{-1/\lambda\rho}\ . \tag{12.16}$$

It is the same as the pair binding energy given by equation (12.4).

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[13] J. Bardeen, L. N. Cooper and J. R. Schrieffer, *loc. cit.*

12.5 Critical temperature

At finite temperature equations (12.5) and (12.7) give

$$\Delta = \frac{\lambda}{V}\sum_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}}(1-2f_{\mathbf{k}}) = \frac{\lambda}{V}\sum_{\mathbf{k}} \frac{\Delta}{2E_{\mathbf{k}}}\tanh(E_{\mathbf{k}}/2T) \ , \qquad (12.17)$$

where $f_{\mathbf{k}} = \left[\exp(E_{\mathbf{k}}/T)+1\right]^{-1}$ is the Fermi distribution for the quasiparticles. It can also be written as

$$\Delta = \lambda\rho\int_0^{\varepsilon_c} d\varepsilon\cdot\frac{\Delta}{\sqrt{\varepsilon^2+\Delta^2}}\cdot\tanh\left(\sqrt{\varepsilon^2+\Delta^2}/2T\right) \ . \qquad (12.18)$$

This equation has two distinct solutions. For low temperatures there is a finite gap Δ given by equation (12.16). For high temperatures the solution is $\Delta = 0$. The critical temperature is obtained by

$$1 = \lambda\rho\int_0^{\varepsilon_c} d\varepsilon\cdot\frac{1}{\varepsilon}\cdot\tanh\left(\varepsilon/2T\right) = \lambda\rho\int_0^{\varepsilon_c/2T} dx\cdot\frac{\tanh x}{x} \ . \qquad (12.19)$$

The integral in equation (12.19) is written as

$$I(C) = \int_0^C dx + \int_C^{\varepsilon_c/2T} dx/x = C + \ln(\varepsilon_c/2CT) \ . \qquad (12.20)$$

The minimum value of $I(C)$ is obtained for $C = 1$. The integral is $I = \ln(e\varepsilon_c/2T)$. We get the critical temperature

$$T_c \simeq 1.36\varepsilon_c e^{-1/\lambda\rho} \ . \qquad (12.21)$$

It is comparable with the gap given by equation (12.16) (the exact numerical factor in equation (12.21) is 1.14). Since $\varepsilon_c \sim \hbar\omega_D \sim M^{-1/2}$, where M is the atomic mass we get the isotopic shift $T_c \sim M^{-1/2}$ as emphasized originally by Frohlich.[14] Typical values for T_c of a few K's can be taken as an order of magnitude for the pair binding energy with a coherence length $l \sim a(\varepsilon_F/T_c) \sim 10^{-4}cm$.

We can expand equation (12.18) for $T < T_c$ in powers of $T_c - T$ and Δ^2. Making use of the C-cutoff method above we obtain $\Delta \simeq$

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[14] H. Frohlich, *loc. cit.*

$\sqrt{6}T_c(1-T/T_c)^{1/2}$. This is a typical temperature dependence of an order parameter (Δ) in the Landau theory of phase transitions (mean-field theory).[15] It follows that the superconductivity is a phase transition of the second kind.

12.6 Thermal properties

The ground-state energy of the superconducting phase given by equation (12.12) can be written as

$$E=\sum_{\mathbf{k}\alpha}\frac{1}{2}(\varepsilon_{\mathbf{k}}-\mu-E_{\mathbf{k}})=\rho\int_{-\varepsilon_c}^{\varepsilon_c}d\varepsilon\cdot\left(\varepsilon-\sqrt{\varepsilon^2+\Delta^2}\right) \tag{12.22}$$

(per unit volume). We get $E=-\rho\varepsilon_c^2-\rho\Delta^2\ln(2\varepsilon_c/\Delta)$. The change with respect to the normal state is $\Delta E=E-E(\Delta=0)=$ $=-\rho\Delta^2\ln(2\varepsilon_c/\Delta)$ or, making use of equation (12.16),

$$\Delta E=-\Delta^2/\lambda\ . \tag{12.23}$$

At finite temperature the energy is given by

$$E=\sum_{\mathbf{k}\alpha}\frac{1}{2}(\varepsilon_{\mathbf{k}}-\mu-E_{\mathbf{k}})+\sum_{\mathbf{k}\alpha}E_{\mathbf{k}}f_{\mathbf{k}}\ \ , \tag{12.24}$$

where $f_{\mathbf{k}}=\left[\exp(E_{\mathbf{k}}/T)+1\right]^{-1}$. The second term in equation (12.24) is the thermal energy E_{th}. For $\beta\Delta\gg 1$ (low temperature) the C-cutoff method employed above gives $E_{th}\simeq 4\rho\Delta^2e^{-\beta\Delta}$. For $\beta\Delta\ll 1$ (just below the critical temperature) the cutoff is $C\simeq 1/\beta\Delta$ and we get $E_{th}\simeq(4/e)\rho T^2$. It can be compared with a similar T^2-correction for the free-electron energy.

The entropy is given by

$$S=-\sum_{\mathbf{k}\alpha}\left[f_{\mathbf{k}}\ln f_{\mathbf{k}}+(1-f_{\mathbf{k}})\ln(1-f_{\mathbf{k}})\right]\ . \tag{12.25}$$

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[15] L. Landau, "Zur Theorie der Phasenumwandlungen I", Phys. Z. Sowjet. **11** 26 (1937) (ZhETF **7** 19 (1937)); "Zur Theorie der Phasenumwandlungen II", Phys. Z. Sowjet. **11** 545 (1937) (ZhETF **7** 627 (1937)).

It can be written as

$$S = -4\rho I + 4\rho\beta\frac{\partial}{\partial\beta}I \tag{12.26}$$

(per unit volume), where

$$I = \int_0^{\varepsilon_c} d\varepsilon \cdot \ln\left(1 + e^{\beta\sqrt{\varepsilon^2+\Delta^2}}\right) \ . \tag{12.27}$$

For $\beta\Delta \gg 1$ we can apply the C-cutoff method for $I - \beta(\partial I/\partial\beta)$. The result is $S \simeq 4\rho\beta\Delta^2 e^{-\beta\Delta}$. We can see that the entropy and the heat capacity $c_s = T(\partial S/\partial T)$ fall off exponentially in the low-temperature limit. For $\beta\Delta \ll 1$ (just below the critical temperature) the cutoff is $C \simeq 1/\beta\Delta$ and we get the entropy and the heat capacity (per unit volume) $S = c_s \simeq 4(3/e + \ln 2)\rho T$. It can be compared with the heat capacity for the free electrons $c_n = (2\pi^2/3)\rho T$. We can see that the heat capacity has a jump $c_s - c_n \simeq 0.32\rho T_c$ at the critical temperature.

12.7 Acoustic attenuation

With usual notations the electrons are coupled to phonons through a typical term of the form $gc^+_{\mathbf{k}'}c_{\mathbf{k}}b$ for a fixed phonon wavevector. We compute the rate of phonon absorption and emission by second-order theory of perturbations. Making use of equation (12.7), it is easy to see that the couple $c^+_{\mathbf{k}'}c_{\mathbf{k}}$ brings a "coherence" factor

$$n = uu' - vv' \ , \tag{12.28}$$

with simplified notations. The absorption rate is then

$$w_a = (4\pi g^2/\hbar)\sum n^2 f(1-f')N\delta(E' - E - \hbar\omega) \tag{12.29}$$

where N is the number of phonons with frequency ω. A factor 2 is included for spin. Similarly, the emission rate is given by

$$w_e = (4\pi g^2/\hbar)\sum n^2 f'(1-f)(N+1)\delta(E' - E - \hbar\omega) \ . \tag{12.30}$$

The phonons kinetics is governed by $w_a - w_e$ for absorption from N and emission from $N-1$ phonons, according to

$$dN/dt = -\alpha N \tag{12.31}$$

where

$$\alpha = (4\pi g^2/\hbar)\sum n^2(f-f')\delta(E'-E-\hbar\omega) \tag{12.32}$$

is the attenuation coefficient.

The summation in equation (12.32) is limited to $\mathbf{k}$ in the equatorial plane defined by $\mathbf{q}$ tangent to the Fermi surface, where $\mathbf{q}$ is the phonon wavevector. We have $\sum = (2\pi)^{-3}\pi k_F^2\Delta k = (\rho/4)\Delta\varepsilon = (\rho/4)\int d\varepsilon$ (per unit volume). On the other hand $\delta(\varepsilon-\varepsilon') = (1/\hbar v_F)\delta(k-k') = 1/\hbar v_F q$. We get $\sum = (\rho/4\hbar v_F q)\int d\varepsilon d\varepsilon'$. For $\rho = mk_F/2\pi^2\hbar^2$ we obtain $\sum = (m^2/8\pi^2\hbar^4 q)\int d\varepsilon d\varepsilon'$ and equation (12.32) becomes

$$\alpha = (m^2g^2/2\pi\hbar^5 q)\int d\varepsilon d\varepsilon'\cdot n^2(-\partial f/\partial E)\cdot\hbar\omega\cdot\delta(E'-E-\hbar\omega)\ . \tag{12.33}$$

The "coherence" factor gives

$$n^2 = \frac{1}{2}\left(1+\frac{\varepsilon\varepsilon'}{EE'}-\frac{\Delta^2}{EE'}\right) \tag{12.34}$$

and the $\varepsilon\varepsilon'$-contribution vanishes upon integration. Then we use $\varepsilon d\varepsilon = EdE$ and get

$$\begin{aligned}\alpha &= (m^2g^2\omega/4\pi\hbar^4 q)\cdot \\ &\cdot\int_\Delta dE\cdot\tfrac{EE'-\Delta^2}{\sqrt{E^2-\Delta^2}\sqrt{E'^2-\Delta^2}}(-\partial f/\partial E)\ ,\end{aligned} \tag{12.35}$$

or

$$\alpha = (m^2g^2\omega/4\pi\hbar^4 q)\cdot\frac{1}{e^{\beta\Delta}+1}\ . \tag{12.36}$$

The ratio

$$\alpha_s/\alpha_n = \frac{1}{e^{\beta\Delta}+1} \tag{12.37}$$

has a sudden drop at the critical temperature ($\Delta = 0$) and falls off exponentially below the critical temperature.[16]

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[16] On a related problem see M. Apostol, "Ultrasound attenuation in $(TaSe_4)_2$", Tr. J. Phys. **17** 995 (1993).

12.8 Microwave absorption

The microwave absorption is calculated in a similar way as the sound attenuation coefficient. According to equation (12.35) at zero temperature we can write[17]

$$\sigma_s/\sigma_n = \frac{1}{\hbar\omega}\int_{\Delta}^{\hbar\omega-\Delta} dE \cdot \frac{E(\hbar\omega - E) - \Delta^2}{\sqrt{E^2-\Delta^2}\sqrt{(\hbar\omega - E)^2 - \Delta^2}} \qquad (12.38)$$

for the ratio of the two conductivities. In the limit of small ω this ratio behaves like

$$\sigma_s/\sigma_n \sim \frac{1}{\hbar\omega}\int_{\Delta}^{\hbar\omega-\Delta} dE = 1 - 2\Delta/\hbar\omega \ . \qquad (12.39)$$

One can see that the conductivity vanishes for $\hbar\omega = 2\Delta$ (and absorption increases).

12.9 Nuclear spin relaxation rate

The flip of the nuclear spin is determined by a coupling of the form $\sim I_- c^+_{\mathbf{k}' up} c_{\mathbf{k} down}$ with the electrons, where $I_- = I_x - iI_y$ is the nuclear spin. The spin-flip rate is of the form

$$w \sim \sum l^2 f(1-f')\delta(E' - E - \hbar\omega)N_{up} \ , \qquad (12.40)$$

where the "coherence" factor is

$$l^2 = (uu' + vv')^2 = \frac{1}{2}\left(1 + \frac{\varepsilon\varepsilon'}{EE'} + \frac{\Delta^2}{EE'}\right) \qquad (12.41)$$

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[17] See for instance D. C. Mattis and J. Bardeen, "Theory of the anomalous skin effect in normal and superconducting metals", Phys. Rev. **111** 412 (1958); A. A. Abrikosov and L. P. Gorkov, "On the theory of superconducting alloys; I. The electrodynamics of alloys at absolute zero", Sov. Phys.-JETP **8** 1090 (1959) (ZhETF **35** 1558 (1958)); "Superconducting alloys at finite temperatures", Sov. Phys.-JETP **9** 220 (1959) (ZhETF **36** 319 (1959)).

and ω is the Zeeman frequency. The calculation of the decay rate goes similarly as the sound attenuation. We get

$$\begin{aligned}\alpha \sim \int_\Delta dE \cdot \tfrac{E}{\sqrt{E^2-\Delta^2}} \cdot \tfrac{E+\hbar\omega}{\sqrt{(E+\hbar\omega)^2-\Delta^2}} \cdot \\ \cdot \left[1+\tfrac{\Delta^2}{E(E+\hbar\omega)}\right] \cdot (-\partial f/\partial E)T\end{aligned} \tag{12.42}$$

and the ratio

$$\begin{aligned}\alpha_s/\alpha_n = \int_\Delta dE \cdot \tfrac{E}{\sqrt{E^2-\Delta^2}} \cdot \tfrac{E+\hbar\omega}{\sqrt{(E+\hbar\omega)^2-\Delta^2}} \cdot \\ \cdot \left[1+\tfrac{\Delta^2}{E(E+\hbar\omega)}\right] \cdot (-\partial f/\partial E)\ .\end{aligned} \tag{12.43}$$

We can see that the decay rate of the nuclear spins has a logarithmic singularity for $\omega = 0$. It increases abruptly below the critical temperature due to the high electron density of states and falls off exponentially with decreasing temperature.

12.10 Electron tunneling

Let us consider a $1-2$-junction. The tunneling hamiltonian can be written as

$$H_t = t \sum_{\mathbf{k}\mathbf{k}'} c^+_{2\mathbf{k}} c_{1\mathbf{k}'} + h.c. \tag{12.44}$$

where t is the tunneling amplitude.[18] We omit the spin suffix. We consider transitions between a state α with energy E_α in 1 and a state β with energy $E_\beta = E_\alpha - eV$ in 2 under a voltage V. The transition probability is given by

$$w = (2\pi t^2/\hbar) \sum_{\alpha\mathbf{k}'} \left|(c_{1\mathbf{k}'})_{0\alpha}\right|^2 \sum_{\beta\mathbf{k}} \left|(c^+_{2\mathbf{k}})_{\beta 0}\right|^2 \delta(E_\beta - E_\alpha + eV)\ . \tag{12.45}$$

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[18] J. Bardeen, "Tunneling from a many-particle point of view", Phys. Rev. Lett. **6** 57 (1961); "Tunneling into superconductors", Phys. Rev. Lett. **9** 147 (1962); M. H. Cohen, L. M. Falicov and J. C. Phillips, "Superconductive tunneling", Phys. Rev. Lett. **8** 316 (1962).

The electrical current is $I = -ew$. We introduce the spectral weight functions

$$N_1(E) = \sum_{\alpha\mathbf{k}'} \left|(c_{1\mathbf{k}'})_{0\alpha}\right|^2 \delta(E - E_\alpha) \tag{12.46}$$

and

$$N_2(E) = \sum_{\beta\mathbf{k}'} \left|(c^+_{2k})_{\beta 0}\right|^2 \delta(E_\beta - E) \tag{12.47}$$

and write the current as

$$I = -(2\pi t^2 e/\hbar) \int_0^{eV} dE \cdot N_1(E) N_2(E - eV) \ . \tag{12.48}$$

This is valid at zero temperature.

For a normal (n) metal 1 we get

$$N_1(E) = \sum_\alpha \delta(E - E_\alpha) = \rho \tag{12.49}$$

where ρ is the density of states at the Fermi surface. For a superconductor (s) 2 we use equations (12.7) and get

$$N_2(E) == \sum_\beta u^2_\beta \delta(E_\beta - E) = \rho \frac{|E|}{\sqrt{E^2 - \Delta^2}} \tag{12.50}$$

for $|E| > \Delta$; the ε-term does not contribute to integral. We get the $n - s$ current[19]

$$\begin{aligned} I = -(2\pi t^2 e/\hbar)\rho^2 \textstyle\int_0^{eV-\Delta} dE \cdot \frac{|E-eV|}{\sqrt{(E-eV)^2-\Delta^2}} = \\ = -(2\pi t^2 e/\hbar)\rho^2 \sqrt{(eV)^2 - \Delta^2} \ . \end{aligned} \tag{12.51}$$

We can see that the current occurs for $eV > \Delta$. At finite temperature there is also a current for $eV < \Delta$.[20] Also, there is a current of quasiparticles at the junction of two superconductors. In general the flow of an injected electrical current through a superconductor exhibits both a transmission and a reflection of quasiparticles. This is known as the Andreev reflection.[21]

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[19] See for instance J. R. Schrieffer, "Theory of electron tunneling", Revs. Mod. Phys. **36** 200 (1964).

[20] I. Giaever, "Energy gap in superconductors measured by electron tunneling", Phys. Rev. Lett. **5** 147, 464 (1960); "Electron tunneling between two superconductors", Phys. Rev. Lett. **5** 464 (1960); L. Esaki, "Long journey into tunneling", Revs. Mod. Phys. **46** 237 (1974).

12.11 Josephson current

The tunneling hamiltonian given by equation (12.44) induces also a pair tunneling between two superconductors. In the second order of the perturbation theory it gives a matrix element between states ψ_n and ψ_{n+1} where n is the number of pairs. The matrix elements can be calculated in a similar way as above. We consider a superposition

$$\psi_\alpha = \sum e^{i\alpha n}\psi_n \tag{12.52}$$

of states and notice that the transition rate contains factors $e^{\pm i\alpha}$. We can write the shift in the energy of the α-state as

$$E_\alpha = -\frac{1}{2}\hbar J\cos\alpha \tag{12.53}$$

where J is related to the transition rate. The change in pair population is

$$dn/dt = dE_\alpha/\hbar d\alpha = \frac{1}{2}J\sin\alpha \tag{12.54}$$

because $\hbar\alpha$ in equation (12.51) acts like a momentum. Equation (12.53) defines a velocity. The rate of changing the momentum is given by

$$d(\hbar\alpha)/dt = 2eV \tag{12.55}$$

where V is the voltage. We get therefore $\alpha = 2eVt/\hbar$ and the current

$$j = -2edn/dt = -eJ\sin(2eVt/\hbar)\ . \tag{12.56}$$

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[21] A. F. Andreev, "The thermal conductivity of the intermediate state in superconductors", Sov. Phys.-JETP **19** 1228 (1964) (ZhETF **46** 1823 (1964)). See also O. A. Dobrescu, L. C. Cune and M. Apostol, "Electric flow through a ferromagnet-superconductor junction", Roum. Reps. Phys. **60** 327 (2008); "Ferromagnet-superconductor junction", Roum. Reps. Phys. **60** 353 (2008); "Electric flow through an ideal ferromagnet-superconductor junction", Physica **C469** 273 (2009); M. Apostol and L. C. Cune, *Field-Controlled Superconducting Transistor*, apoma, MG (2003).

This is known as the Josephson current between two superconductors.[22] The voltage-rate of the oscillation frequency is $\nu = 2e/h \simeq 500MHz/\mu V$.

12.12 Ginsburg-Landau theory

We focus upon the onset of the superconductivity just below the critical temperature T_c. There appear (and disappear) electron pairs with an interacting energy φ and a binding energy $\Delta\varepsilon$ both of the order of T_c. It follows the coupling constant $\lambda = \varphi a^3 \sim \varphi/n \sim T_c/n$. According to equation (12.23) the energy (per unit volume) is diminished by $\Delta E = \Delta^2/\lambda \sim \Delta^2 n/T_c$. It is given by a pair density n_s multiplied by a pair energy $\Delta\varepsilon \sim T_c$. It follows $\Delta E \sim n_s T_c \sim \Delta^2 n/T_c$. Therefore we have $n_s \sim \Delta^2 n/T_c^2$ pairs per unit volume just below the critical temperature; and $\Delta \sim T_c(1 - T/T_c)^{1/2}$. This was Gorkov's result[23] for London's superconducting fluid[24] and Landau-Ginsburg's order parameter ψ.[25]

The pair condensate is described by a wavefunction ψ such that $|\psi|^2 = n_s \sim \Delta^2 n/T_c^2$. Therefore $\psi \sim \Delta\sqrt{n}/T_c$. It is an order parameter. It may have spatial and temporal variations. The density of free energy can be expanded in powers of $|\psi|^2$ just below the critical temperature. In addition, it contains a $|-i\hbar grad\psi|^2/2m^*$ term where $m^* = 2m$ is the pair mass. The internal magnetic field $\mathbf{h}$ may exist. The density of the free energy reads

$$\begin{aligned}\Delta F = \left|\left(-i\hbar grad + e^*\mathbf{A}/c\right)\psi\right|^2/2m^* + \\ + a\left|\psi\right|^2 + \tfrac{1}{2}b\left|\psi\right|^4 + \mathbf{h}^2/8\pi \ ,\end{aligned} \tag{12.57}$$

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[22] B. D. Josephson, "Possible new effects in superconducting tunneling", Phys. Lett. **1** 251 (1962). See also P. W. Anderson, in *Proc. Ravello Spring School*, vol.2, ed. E. R. Caianiello, Academic Press, NY (1964), p.113.

[23] L. P. Gorkov, "Microscopic derivation of the Ginsburg-Landau equations in the theory of superconductivity", Sov. Phys.-JETP **9** 1364 (1959) (ZhETF **36** 1918 (1959)); "The critical supercooling field in superconductivity theory", Sov. Phys.-JETP **10** 593 (1960) (ZhETF **37** 833 (1959)).

[24] C. J. Gorter and H. B. G. Casimir, *loc. cit.*; F. London, *loc. cit.*

[25] V. L. Ginsburg and L. Landau, *loc. cit.*

where $\mathbf{h} = curl\mathbf{A}$, $e^* = 2e$ is the pair charge and $\Delta F = F_s - F_n$ is the superconducting contribution with respect to the normal state. The coefficients are $a = a'(T - T_c)$, a', $b > 0$. In the presence of an external magnetic field $\mathbf{H}$ a term $-\mathbf{hH}/4\pi$ must be added, giving the Gibbs free energy.[26]

Variations with respect to ψ and $\mathbf{A}$ in equation (12.57) lead to

$$\left(-i\hbar grad + e^*\mathbf{A}/c\right)^2 \psi/2m^* + a\psi + b\left|\psi\right|^2 \psi = 0 \qquad (12.58)$$

and

$$\frac{c}{4\pi}curl\mathbf{h} = -\frac{e^*\hbar}{2m^*i}(\psi^* grad\psi - \psi grad\psi^*) - \frac{e^{*2}}{m^*c}\left|\psi\right|^2 \mathbf{A} = \mathbf{j} \ , \quad (12.59)$$

where $\mathbf{j}$ is the current density. It contains both the paramagnetic and diamagnetic contributions. In normal state these contributions cancel each other out, in the superconducting state they do not, due to the pair condensate. The resulting supercurrent expels an external magnetic field.

Equation (12.58) is a non-linear Schrodinger equation. Equation (12.59) is a Maxwell equation. The surface terms in the variations of equation (12.57) give the boundary conditions

$$\mathbf{n} \cdot \left(-i\hbar grad + e^*\mathbf{A}/c\right)\psi = 0 \qquad (12.60)$$

and

$$\mathbf{n} \times (\mathbf{h} - \mathbf{H}) = 0 \ , \qquad (12.61)$$

where $\mathbf{n}$ is the unit vector perpendicular to the surface. The first condition means that the current is parallel to the surface, while the second condition means that the tangential component of the magnetic field is continuous at the surface.

12.13 Phase transition

Let ψ be uniform and $\mathbf{h}$ be uniform. According to equations (12.58) and (12.59) $\mathbf{A} = 0$.

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[26] This is the basis of Landau's theory of phase transitions of the second kind (L. Landau, *loc. cit.*)

Equation (12.58) gives $\psi = 0$ for $T > T_c$ and

$$|\psi| = \left[a'(T_c - T)/b\right]^{1/2} \tag{12.62}$$

for $T < T_c$. Since $|\psi| \sim \Delta\sqrt{n}/T_c$, we have the gap $\Delta \sim T_c(1-T/T_c)^{1/2}$ and $a'/b \sim n/T_c$. The free energy is

$$\Delta F = -(a'^2/2b)(T_c - T)^2 \tag{12.63}$$

and the jump in the heat capacity is given by $\Delta c = -T(\partial^2 \Delta F/\partial T^2) = T_c(a'^2/b) \sim na'$. If we compare it with $\Delta c \sim \rho T_c$ we get $a' \sim \rho T_c/n$ and $b \sim \rho T_c^2/n^2$.

12.14 Meissner effect

Let ψ be uniform and **h** be uniform. Equation (12.59) shows that $\mathbf{h} = 0$ (and $\mathbf{A} = 0$). Equation (12.59) gives

$$\mathbf{j} = -\frac{e^{*2}}{m^* c} |\psi|^2 \mathbf{A} \ . \tag{12.64}$$

This is known as London's equation.[27] Since $curl \mathbf{h} = 4\pi\mathbf{j}/c$ we get

$$\Delta \mathbf{h} = \frac{4\pi e^{*2}}{m^* c^2} |\psi|^2 \mathbf{h} = \frac{1}{\lambda^2}\mathbf{h} \ , \tag{12.65}$$

where

$$\lambda = \left(m^* c^2/4\pi n_s e^{*2}\right)^{1/2} \tag{12.66}$$

is the penetration depth. Indeed, according to equation (12.65), $h = He^{-z/\lambda}$ where z is the coordinate perpendicular to a free plane surface at $z = 0$. It follows that the superconducting state expels external fields H. This is known as the Meissner effect.[28] There exists a "supercurrent" in equation (12.59) which creates a "diamagnetic" field which compensates the external magnetic field. The superconducting state is "rigid" with respect to an external magnetic field. This is known as London's "rigidity".

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[27] F. London, *loc. cit.*

[28] W. Meissner and R. Ochsenfeld, "Ein neuer Effekt bei eintritt der Supraleitfahigkeit", Naturwiss. **21** 787 (1933).

Since $|\psi|^2 = n_s = a'(T_c - T)/b$ we get the penetration length

$$\lambda = \left(mc^2 b/8\pi e^2 a' T_c\right)^{1/2} \cdot (1 - T/T_c)^{-1/2} \simeq \\ \simeq \left(mc^2/8\pi n e^2\right)^{1/2} \cdot (1 - T/T_c)^{-1/2} \ . \tag{12.67}$$

We can see that it diverges at the critical temperature. The prefactor is of the order of ~ 100Å.

The gain given by equation (12.63) in the free energy must be compensated by the energy of the expelled field.[29] It follows that there exists a critical magnetic field H_c given by

$$\Delta F = -(a'^2/2b)(T_c - T)^2 = -H_c^2/8\pi \ , \tag{12.68}$$

or

$$H_c = (4\pi a'^2/b)^{1/2} T_c (1 - T/T_c) \sim \rho^{1/2} T_c (1 - T/T_c) \tag{12.69}$$

just below the critical temperature. For $H > H_c$ the superconductivity is destroyed. The prefactor in equation (12.69) is of the order $\sim 100 Gs$.

12.15 Flux quantization

In general $\psi = |\psi|\, e^{i\varphi}$. The current given by equation (12.59) is

$$\mathbf{j} = -\frac{e\hbar}{m} n_s grad\varphi - \frac{2en_s}{mc}\mathbf{A} \ . \tag{12.70}$$

If we integrate this equation along a closed circuit we get

$$\int d\mathbf{f} \cdot \mathbf{h} + \frac{mc}{2en_s} \oint d\mathbf{l} \cdot \mathbf{j} = \frac{hc}{2e} n \ , \tag{12.71}$$

where n is an integer.[30] We can see that the flux of the magnetic field is quantized in $hc/2e$ units. It is $hc/2e \simeq 2 \times 10^{-7} Gs \cdot cm^2$.[31] We note the occurrence of the charge $2e$ in comparison with the charge e of the free electrons. The circulation of the current in equation (12.71) supports a similar quantization. In superconducting rings there may appear interference of the phase φ of the order parameter.[32]

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[29] F. London, "On the problem of the molecular theory of superconductivity", Phys. Rev. **74** 562 (1948).

[30] F. London, *loc. cit.*

[31] We recall that the electron charge is $-e = -4.8 \times 10^{-10} esu$ (for length in cm, energy in erg and magnetic field in Gs).

12.16 Coherence length

Equation (12.58) without magnetic field and for one z-coordinate reads

$$-\frac{\hbar^2}{2m^*}\cdot\frac{d^2}{dz^2}\psi+a\psi+b\left|\psi\right|^2\psi=0\ . \tag{12.72}$$

For $\psi=\psi(\infty)f=\left(|a|/b\right)^{1/2}f$ this equation becomes

$$-\frac{\hbar^2}{2m^*\left|a\right|}f''-f+f^3=0\ . \tag{12.73}$$

It has a characteristic length

$$\xi=\left(\hbar^2/2m^*\left|a\right|\right)^{1/2}\simeq a(\varepsilon_F/T_c)(1-T/T_c)^{-1/2}\ \ , \tag{12.74}$$

where a in the *rhs* of equation (12.74) is the mean inter-electron distance. The prefactor is of the order of $\sim 10^4$. ξ is a distance over which the condensate pairs may preserve their individuality; or it is the extent of a pair. The solution is $f(z)=\tanh(-z/\sqrt{2}\xi)$.

With equation (12.74) and making use of equations (12.67) and (12.69), we may write $H_c\simeq(hc/e)/\xi\lambda$.

12.17 Surface energy

Let us consider a normal-superconductor interface at $z=0$. The Gibbs free energy for the normal state per unit area amounts to

$$\int_{-\infty}^{\lambda}dz(-H_c^2/8\pi)\ \ , \tag{12.75}$$

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[32] B. D. Josephson, "Supercurrents through barriers", Adv. Phys. **14** 419 (1965).

while the Gibbs free energy for the superconducting state is

$$\int_{\xi}^{\infty} dz(-H_c^2/8\pi) \ . \tag{12.76}$$

The difference with respect to the normal state is therefore

$$\Delta\sigma = \int_{\lambda}^{\xi} dz \cdot H_c^2/8\pi = (\xi - \lambda)H_c^2/8\pi \ . \tag{12.77}$$

For $\kappa = \lambda/\xi < 1$ the interface is unstable and the sample is either normal or superconducting. For $\kappa > 1$ there exists such a normal-superconducting interface. It follows that in the latter case there exist two critical values of the magnetic fields: H_{c1}, when the sample breaks up in superconducting domains (with quantized flux) known as superconducting vortices, and $H_{c2} > H_{c1}$, when the superconducting state is completely destroyed. The actual critical value of κ is $1/\sqrt{2}$.[33] The superconductors with $\kappa > 1/\sqrt{2}$ are known as type-2 superconductors (or "hard" superconductors) and the vortex state is also known as the mixed state.

12.18 Comments and remarks

The superconductivity is pretty robust to chemical impurities ("dirty" superconductors), while it is quickly destroyed by magnetic impurities. This is so because the magnetic impurities destroy the symmetry of the pair mates under time reversal while the chemical ones do not.[34] The magnetic impurities may lead to "gapless" superconductivity[35] and the Kondo effect.[36]

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[33] A. A. Abrikosov, "On the magnetic properties of superconductors of the second group", Sov. Phys.-JETP **5** 1174 (1957) (ZhETF **32** 1442 (1957)).

[34] P. W. Anderson, "Theory of dirty superconductors", J. Phys. Chem. Solids **11** 26 (1959).

[35] A. A. Abrikosov and L. P. Gorkov, "Contribution to the theory of superconducting alloys with paramagnetic impurities", Sov. Phys.-JETP **12** 1243 (1961) (ZhETF **39** 1781 (1960)).

[36] J. Kondo, "Resistance minimum in dilute magnetic alloys", Progr. Theor. Phys. **32** 37 (1964); "Giant thermo-electric power of dilute magnetic alloys", Progr. Theor. Phys. **34** 372 (1965).

The coherence length ξ competes with the electron mean freepath l, such that a renormalized coherence length given by $1/\bar{\xi} = 1/\xi + 1/l$ might be relevant. The penetration depth increases with decreasing l[37] and, since it enters the equations as λ^2, the relevant renormalization is, probably, $\widetilde{\lambda} = \lambda(1 + \xi/l)^{1/2}$. London's equation $\mathbf{j} \sim \mathbf{A}$ is in general non-local.

The retardation and damping effects arise from electron-phonon interaction via the Green functions formalism. This formalism allows the consideration of the interacting effects produced by quasiparticles which do not obey the momentum-energy relationship (are not on the mass-shell). The diagram summation and the solution of the coupled Dyson equations in this context[38] lead to minor quantitative changes in the standard results, except, possibly, for explaining some deviations of the superconducting "bad actor" *Pb*. In particular, a possible electron interaction V like the Coulomb repulsion is renormalized as $\widetilde{V} = V - V\widetilde{V} \int \rho d\varepsilon/\varepsilon$ which gives $\widetilde{V} = V \left[1 + \rho V \ln(\varepsilon_F/\hbar\omega_D)\right]^{-1}$.[39]

The pairing theory breaks the gauge invariance under the transformation $\psi \rightarrow \psi e^{i\varphi}$ for the electron field operators. This is related to longitudinal electron-density modes. Plasmons do not affect the superconductivity,[40] but there are sound-like modes of the condensate which help restoring the gauge invariance.[41] The Coulomb interaction pushes them upward to the plasma frequency. Technically, the gauge invariance is related to the Ward identities for the vertex function of interaction.[42]

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[37] A. B. Pippard, "An experimental and theoretical study of the relation between magnetic field and current in a superconductor", Proc. Roy. Soc. London **A216** 547 (1953).

[38] P. Morel and P. W. Anderson, "Calculation of the superconducting state parameters with retarded electron-phonon interaction", Phys. Rev. **125** 1263 (1962); J. R. Schrieffer, D. J. Scalapino and J. W. Wilkins, "Effective tunneling density of states in superconductors", Phys. Rev. Lett. **10** 336 (1963); J. M. Rowell, P. W. Anderson and D. E. Thomas, "Image of the phonon spectrum in the tunneling characteristic between superconductors", Phys. Rev. Lett. **10** 334 (1963). See also J. Bardeen and J. R. Schrieffer, in *Progress in Low Temperature Physics*, ed. C. J. Gorter, North-Holland (1961), vol. 3 p. 203.

[39] N. N. Bogoliubov, V. V. Tolmachev and D. V. Shirkov, *loc. cit.*

[40] D. Pines and J. R. Schrieffer, "Gauge invariance in the theory of superconductivity", Nuovo Cimento **10** 496 (1958).

[41] P. W. Anderson, "Coherent excited states in the theory of superconductivity: gauge invariance and the Meissner effect", Phys. Rev. **110** 827 (1958); "Random-phase approximation in the theory of superconductivity", Phys. Rev. **112** 1900 (1958); "Plasmons, gauge invariance, and mass", Phys. Rev. **130** 439 (1963).

Superconducting vortices may be pinned down, may creep, flow and interact with themselves, dissipating supercurrents.[43]

The pairing theory has been applied to atomic nuclei.[44] Also, four-particle superconducting correlations have been considered in this case.[45]

12.19 Andreev reflection

With usual notations the motion of an electron destruction operator close to the Fermi surface is given by

$$i\hbar\partial c_{\mathbf{k}\alpha}/\partial t = (\mu - \hbar\mathbf{v}\mathbf{k}_F + h\mathbf{v}\mathbf{k})c_{\mathbf{k}\alpha} \ , \tag{12.78}$$

where $\mathbf{v}$ stands for the Fermi velocity. Leaving aside the chemical potential, we have

$$\begin{gathered} i\hbar\partial\psi_\alpha/\partial t = (-\hbar\mathbf{v}\mathbf{k}_F - i\hbar\mathbf{v}grad)\psi_\alpha + \\ + \int d\mathbf{r}' g(\mathbf{r}-\mathbf{r}')\psi^+_\beta(\mathbf{r}')\psi_\beta(\mathbf{r}')\psi_\alpha(\mathbf{r}) \end{gathered} \tag{12.79}$$

for the field operator with interaction. We assume a delta interaction $g(\mathbf{r}-\mathbf{r}')$=$\lambda\delta(\mathbf{r}-\mathbf{r}')$ and a non-vanishing average $F_\alpha = \lambda\left\langle\psi_{-\alpha}\psi_\alpha\right\rangle$.

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[42] Y. Nambu, "Quasi-particles and gauge invariance in the theory of superconductivity", Phys. Rev. **117** 648 (1960); see also M. Apostol, "Ward identity for non-relativistic fermions", Phys. Lett. **A78** 91 (1980); "On the vertex function method in the Tomonaga-Luttinger model", J. Phys. **C16** 665 (1983).

[43] See for instance P. W. Anderson and Y. B. Kim, "Hard superconductivity: Theory of the motion of Abrikosov flux lines", Revs. Mod. Phys. **36** 39 (1964).

[44] A. Bohr, B. R. Mottelson and D. Pines, "Possible analogy between the excitation spectra of nuclei and those of the superconducting metallic state", Phys. Rev. **110** 936 (1958).

[45] M. Apostol, "Four-fermion condensate", Phys. Lett. **A110** 141 (1985); M. Apostol, I. Bulboaca, F. Carstoiu, O. Dumitrescu and M. Horoi, "Alpha-like four nucleon correlations in superfluid phases of atomic nuclei", Nucl. Phys. **A470** 64 (1987).

Since $F_{-\alpha}=-F_\alpha$ and $F^*_{-\alpha}=F_\alpha$ by time-reversal symmetry, we have $F^*_\alpha=-F_\alpha$. We may write $F_\alpha=i\Delta_\alpha$. Equation (12.79) becomes

$$\begin{aligned} i\hbar\partial\psi_\alpha/\partial t &= (-\hbar\mathbf{v}\mathbf{k}_F - i\hbar\mathbf{v}grad)\psi_\alpha + i\Delta_\alpha\psi^+_{-\alpha} \ , \\ -i\hbar\partial\psi^+_{-\alpha}/\partial t &= (-\hbar\mathbf{v}\mathbf{k}_F - i\hbar\mathbf{v}grad)\psi^+_{-\alpha} + i\Delta_\alpha\psi_\alpha \ \ , \end{aligned} \tag{12.80}$$

or

$$\begin{aligned} i\hbar\partial c_{\mathbf{k}\alpha}/\partial t &= (-\hbar\mathbf{v}\mathbf{k}_F + h\mathbf{v}\mathbf{k})c_{\mathbf{k}\alpha} + i\Delta_\alpha c^+_{-\mathbf{k}-\alpha} \ , \\ -i\hbar\partial c^+_{-\mathbf{k}-\alpha}/\partial t &= (-\hbar\mathbf{v}\mathbf{k}_F + h\mathbf{v}\mathbf{k})c^+_{-\mathbf{k}-\alpha} + i\Delta_\alpha c_{\mathbf{k}\alpha} \ . \end{aligned} \tag{12.81}$$

These are Gorkov's equations of motion for the quasiparticles.[46] It is easy to see that the pairing theory can be obtained from equations (12.81).

We introduce the amplitudes $\varphi_\alpha=(\psi_\alpha)_{0;1\alpha}$ and $\chi_\alpha=(\psi^+_{-\alpha})_{0;1\alpha}$. The former represents a quasiparticle, the latter represents a pair or, equivalently, a quasi-hole besides the quasiparticle. Equations (12.80) give

$$\begin{aligned} i\hbar\partial\varphi_\alpha/\partial t &= (-\hbar\mathbf{v}\mathbf{k}_F - i\hbar\mathbf{v}grad)\varphi_\alpha + +i\Delta_\alpha\chi_\alpha \ , \\ -i\hbar\partial\chi_\alpha/\partial t &= (-\hbar\mathbf{v}\mathbf{k}_F - i\hbar\mathbf{v}grad)\chi_\alpha + i\Delta_\alpha\varphi_\alpha \ ; \end{aligned} \tag{12.82}$$

it is easy to check the continuity equation

$$\frac{\partial}{\partial t}\left(|\varphi_\alpha|^2+|\chi_\alpha|^2\right)+\mathbf{v}grad\left(|\varphi_\alpha|^2-|\chi_\alpha|^2\right))=0 \ . \tag{12.83}$$

A superconducting quasiparticle is therefore localized with probability $|\varphi_\alpha|^2+|\chi_\alpha|^2$ and flows with the current

$$\mathbf{j}=\mathbf{v}\left(|\varphi_\alpha|^2-|\chi_\alpha|^2\right) \ . \tag{12.84}$$

It acquires two distinct states: φ, as a quasiparticle and χ, as a quasi-hole. The quasi-holes flow backward according to equation (12.84).

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[46] L. P. Gorkov, "Microscopic derivation of the Ginsburg-Landau equations in the theory of superconductivity", Sov. Phys.-JETP **9** 1364 (1959) (ZhETF **36** 1918 (1959)); "The critical supercooling field in superconductivity theory", Sov. Phys.-JETP **10** 593 (1960) (ZhETF **37** 833 (1959)).

This is known as the Andreev reflection.[47] The transport processes in superconductors must include this particularity. It is easy to see that $\varphi \sim u^2$ and $\chi \sim iuv$ where u and v are the pairing-theory weights.

Since Δ_α and χ_α are odd functions of α we may drop out the suffix α in equations (12.82). We may also drop out the k_F-term in equation (12.82) and get the superconducting spectrum $\hbar\omega = \pm\sqrt{\hbar^2 v^2 k^2 + \Delta^2}$ and

$$\begin{aligned} \varphi &= \tfrac{C}{2}\sqrt{1+\mathbf{vk}/\omega} \ , \\ \chi &= \tfrac{-iC}{2}\sqrt{1-\mathbf{vk}/\omega} \end{aligned} \tag{12.85}$$

for $\hbar\omega > \Delta$ where C is a constant. The current given by equation (12.84) becomes

$$\mathbf{j} = C^2\mathbf{v}(\mathbf{vk}/\omega) \tag{12.86}$$

for both spin orientation. The incident current is $\mathbf{j}_{in} = A^2\mathbf{v}$ and the continuity provides $A = (C/\sqrt{2})\sqrt{1+\mathbf{vk}/\omega}$. Thus, we get finally the transmission coefficient

$$w = j/j_{in} = \frac{\mathbf{vk}/\omega}{1+\mathbf{vk}/\omega} \ , \tag{12.87}$$

or

$$w \simeq \sqrt{\hbar\omega/\Delta - 1} \tag{12.88}$$

for $\hbar\omega \gg \Delta$. This coefficient affects all the relevant transport rates.

For instance, the electrical conductivity[48]

$$\sigma \sim \int_\Delta d(\hbar\omega)\cdot\sqrt{\hbar\omega/\Delta - 1}\cdot e^{-\beta\hbar\omega} \sim \sqrt{T/\Delta}e^{-\Delta/T} \ . \tag{12.89}$$

A similar result holds for thermoconductivity.[49]

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[47] A. F. Andreev, "The thermal conductivity of the intermediate state in superconductors", Sov. Phys.-JETP **19** 1228 (1964) (ZhETF **46** 1823 (1964)).

[48] See for instance M. Apostol and L. C. Cune, *loc. cit.*

[49] See also J. Bardeen, G. Rickayzen and L. Tewordt, "Theory of the thermal conductivity of superconductors", Phys. Rev. **113** 982 (1959).

12.20 Comments on transport

The free electrons (fermions) have a ground state which is the Fermi sea and single-particle energies $\varepsilon(\mathbf{p}) = p^2/2m$, where $\mathbf{p}$ is momentum and m is the particle mass. This picture is changed, to some extent, by interaction. The Hartree-Fock approximation and the random phase approximation allow us to retain the single-particle picture for excited states in the neighbourhood of the Fermi surface; the change in the ground state remains, to a large extent, unknown, but the motion of the ensemble of particles and, in particular, the transport are governed by excitations. The two approximations imply corrections generated by virtual particles, which renormalize the particles and the interaction. The remaining part of the interaction, which renormalizes the interaction vertex, destroys, to some extent, this single-particle picture. The limitations brought about by this residual interaction are included in the finite lifetime of the particles; which, thereby, become quasiparticles (including their combinations which give the collective modes). This is the basic picture of Landau's elementary excitations (quasiparticles and collective modes) in a normal Fermi liquid. The temperature determines a behaviour similar to that generated by interaction, such that the temperature effects can be included in this picture.

A similar situation occurs for the elementary excitations of the superconducting state, with the energy spectrum

$$\widetilde{\varepsilon}(\mathbf{p}) = \pm\sqrt{\varepsilon^2(\mathbf{p}) + \Delta^2} \quad , \tag{12.90}$$

where $\varepsilon(\mathbf{p})$ stands now for $p^2/2m - \mu$, μ being the chemical potential, and Δ is the superconducting gap; similarly, $\widetilde{\varepsilon}(\mathbf{p})$ is measured from μ. We note that these excitations are both particles and holes. The superconducting spectrum is generated by the electron-phonon interaction and is constructed with quasiparticles, which have a finite lifetime; moreover, the superconducting gap depends on the temperature, which reflects again the quasiparticles as the basis of constructing the spectrum. In this respect the superconducting spectrum has the quantum-mechanical meaning only at zero temperature. This particularity, of deriving an energy spectrum which depends on the temperature, reflects the symmetry breaking (gauge symmetry) associated with the superconductivity. This shows that the superconductivity is a phase transition (with a critical temperature), according to the Ginsburg-Landau theory.

The electron quasiparticles and the phonons, including their lifetime, are independent particles; the electron-phonon interaction (with acoustic longitudinal phonons) couples them. In "Electron-Phonon Interaction" chapter we have seen that the effects of the electron-phonon interaction are larger than the lifetime effects, such that it is meaningful to treat the electron-phonon coupling as an interaction. Except for the renormalization of the phonon velocity (where the electron and phonon coordinates are not independent), the electron-phonon interaction brings a second-order coupling between the electrons. This effective coupling can be estimated in the second-order perturbation theory; it arises from virtual phonons. Let us write the hamiltonian of the electrons and phonons as

$$H = H_0 + H_1 \quad ,$$

$$H_0 = \sum\nolimits_{\mathbf{k}} \varepsilon_{\mathbf{k}} c^+_{\mathbf{k}} c_{\mathbf{k}} + \sum\nolimits_{\mathbf{q}} \hbar\omega a^+_{\mathbf{q}} a_{\mathbf{q}} \ , \tag{12.91}$$

$$H_1 = \sum\nolimits_{\mathbf{kq}} B_{\mathbf{q}} \left(a^+_{\mathbf{q}} + a_{-\mathbf{q}} \right) c^+_{\mathbf{k+q}} c_{\mathbf{k}}$$

where $B_{\mathbf{q}}$ =-$\frac{C}{\sqrt{N}} iq\sqrt{\hbar/2M\omega}$, with usual notations. We perform a canonical transformation $\widetilde{H} = e^{-S} H e^{S}$ with $H_1 = -[H_0, S]$, which leads to

$$\widetilde{H} = H_0 + \frac{1}{2}[H_1, S] + ... \ ; \tag{12.92}$$

it is easy to see that the one-phonon states are eliminated by the effective interaction

$$H_2 = \tfrac{1}{2}[H_1, S] = \tfrac{1}{2} \sum\nolimits_{\mathbf{kk'q}} \left|B_{\mathbf{q}}\right|^2 c^+_{\mathbf{k'+q}} c_{\mathbf{k'}} c^+_{\mathbf{k-q}} c_{\mathbf{k}} \cdot \\ \cdot \left(\tfrac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}} - \hbar\omega} - \tfrac{1}{\varepsilon_{\mathbf{k'}} + \hbar\omega - \varepsilon_{\mathbf{k'+q}}} \right) \ ; \tag{12.93}$$

if we group the ±**q**-terms we get

$$H_2 = \sum_{\mathbf{kk'q}} \left|B_{\mathbf{q}}\right|^2 \frac{\hbar\omega}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}})^2 - \hbar^2\omega^2} c^+_{\mathbf{k'+q}} c_{\mathbf{k'}} c^+_{\mathbf{k-q}} c_{\mathbf{k}} \ . \tag{12.94}$$

We note that the transformation used here corresponds to the Hartree-Fock approximation, which dresses the electrons with a cloud of phonons (polaronic cloud).

We can see that the effective interaction H_2 brings an electron-phonon contribution to the f-function of the collective excitations (plasmons) of the electron liquid; since the original contribution is the Coulomb interaction, this small additional contribution has negligible effects. However, a subset of states defined by

$$\mathbf{k}^{'} + \mathbf{q} = \mathbf{k}_1 \ , \ \mathbf{k}^{'} = \mathbf{k}_2 \tag{12.95}$$

and $\mathbf{k} = -\mathbf{k}_2$ deserves a special attention; it gives a reduced interaction

$$H_{2red} = \sum_{\mathbf{k}_1\mathbf{k}_2} |B_{\mathbf{k}_1-\mathbf{k}_2}|^2 \frac{\hbar\omega}{(\varepsilon_{\mathbf{k}_1} - \varepsilon_{\mathbf{k}_2})^2 - \hbar^2\omega^2} c^+_{\mathbf{k}_1} c^+_{-\mathbf{k}_1} c_{-\mathbf{k}_2} c_{\mathbf{k}_2} \ , \tag{12.96}$$

which, for $\mathbf{k}_{1,2}$ close to the Fermi surface, is

$$H_{2red} = -\frac{C^2}{2Mc^2N} \sum_{\mathbf{k}_1\mathbf{k}_2} c^+_{\mathbf{k}_1} c^+_{-\mathbf{k}_1} c_{-\mathbf{k}_2} c_{\mathbf{k}_2} \ ; \tag{12.97}$$

this is an attractive interaction of the form given by equation (12.1), which leads to the superconducting instability. We can see that it corresponds to an exchange of wavevectors $\mathbf{q}$ which are quasi-tangential to the Fermi surface, such that the superconducting instability is not affected by plasmons, nor the latter by the former. A comparison with the parameter $\lambda\rho$ in equation (12.4), for $C \simeq \mu$, indicates a pretty large coupling (gap and critical temperature), of the order of the Debye frequency. This rather strong superconducting coupling arises from the coherence of the Cooper pairs. Actually, there exists a serious restriction upon these estimations, which arises from the quasi-tangential correlations between $\mathbf{k}_1$and $\mathbf{k}_2$; this restriction introduces an additional factor of the order c/v_F in the estimation of ε_c from $\hbar\omega_D$.

The transport in the superconducting phase is performed both by quasiparticles and quasiholes; from equation (12.90) we can see that the group velocity of these excitations is small, such that they do not contribute much to transport. Moreover, their energy uncertainty is

$$\Delta\widetilde{\varepsilon} = \frac{\varepsilon \Delta\varepsilon}{\widetilde{\varepsilon}} \quad , \tag{12.98}$$

where $\Delta\varepsilon$ is the uncertainty in energy of the original quasi-electrons; we can see that $\Delta\widetilde{\varepsilon}$ is small, such that the lifetime of the superconducting quasiparticles is long. In addition, the energy uncertainty given by equation (12.98) is multiplied by the Fermi distribution $\left(e^{\widetilde{\varepsilon}/T}+1\right)^{-1}$, which, for quasiparticles, acquires very low values at low temperatures. Another source of energy uncertainty (and lifetime), both for Cooper pairs and quasiparticles, is the retardation of the interaction; the energy uncertainty is $\hbar/\tau = \hbar c/\xi$, where ξ is the coherence length; an overestimate is $\hbar/\tau \simeq \hbar^2\omega_D^2/\mu$.

The order parameter may have its own dynamics and relaxation. In charge-density waves the excitations of the order parameter are known as phasons and amplitudons.[50]

12.21 Concluding remarks

Superconductivity is a vast subject.[51] It includes fundamental concepts of the theory of condensed matter, like symmetry breaking, off-diagonal long-range order, macroscopic wavefunction of the condensate, order parameter and its dynamics, gauge invariance, flux quantization, magnetic effects, finite-size effects, etc. The BCS mechanism of superconductivity is still open to questions.[52]

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[50] M. Apostol and I. Baldea, "On the charge density wave state in the quasi-one-dimensional compound $K_2[Pt(CN)_4]Br_{0.3} \times 3.2H_2O$ (KCP)", Rev. Roum. Phys. **30** 605 (1985); M. Apostol, "Phason contribution to the lattice heat capacity and thermoconductivity", Commun. Theor. Phys. **20** 249 (1993); "Ultrasound attenuation in $(TaSe_4)_2$", Tr. J. Phys. **17** 995 (1993).

[51] D. Schoenberg, *Superconductivity*, Cambridge (1952); E. A. Lynton, *Superconductivity*, Methuen (1963); J. R. Schrieffer, *Theory of Superconductivity*, Benjamin (1964); G. Rickayzen, *Theory of Superconductivity*, Interscience (1965); P. G. de Gennes, *Superconductivity of Metals and Alloys*, Benjamin (1966); M. Tinkham, *Introduction to Superconductivity*, McGraw-Hill (1975).

[52] See for instance B. T. Matthias, Science **144** 378 (1964) and references therein.

13 Superfluidity

13.1 Introduction

We include here the basic elements of the theory of the superfluidity. The quantum-mechanical hydrodynamics and the quantum-mechanical nature of the vortices are discussed, and the essential role played by the crystaline-ordered superfluid ground state is emphasized; the vortex and roton spectrum of a superfluid is derived. It is shown that the quantum of vorticity is also the quantum of viscosity and the turbulence originates in quantum-mechanical vortices. The condensate wavefunction is introduced, allowing for the sound waves, vortices and rotons, and the quanta of these elementary excitations are thereby derived. The subject is also known as the Bose-Einstein condensation in dilute gases of alkali atoms.[1]

Atomic beams of ^{87}Rb or ^{23}Na, which have an integral spin and, therefore, we call them bosons, are slowed down by photons in laser beams, taking advantage of the frontal Doppler shift. Optical and magnetic fields provide magneto-optical traps for such cold atoms, while another laser beam or a rotating magnetic field polarizes the atomic spins in the traps. Dilute alkali gases of several thousands of atoms in a space region of about $1\mu m$ are thus obtained at a very low temperature of tens of $nK = 10^{-9}K$. Such temperatures are sufficiently low for the average inter-atomic separation (several hundred of Å) to make these atomic ensembles very dilute quantum-mechanical liquids of bosons undergoing Bose-Einstein condensation and superfluidity. Indeed, light scattering pictures the small, condensed liquid drop; splitting such a drop and thereafter bringing together the two fragments causes an interference, as for a coherent atomic state, and many vortices are also observed in these superfluid droplets. All these are signatures of a Bose-Einstein condensation and superfluidity.

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[1] M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman and E. A. Cornell, "Observation of Bose-Einstein condensation in a dilute atomic vapor", Science **269** 198 (1995); K. B. Davis, M.-O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn and W. Ketterle, "Bose-Einstein condensation in a gas of sodium atoms", Phys. Rev. Lett. **75** 3969 (1995).

All these may be interesting laboratory techniques, experimental methods and procedures. Bose-Einstein condensation and superfluidity are well-established and well-known, and He^4 superfluidity has been known since 1911.[2]

If we are to consider an elementary particle and still care about its internal structure, then its internal coordinates vanish, its internal momenta go to infinity, such that, besides the internal energy, we may have, at most, a finite internal angular momentum, as an internal prime integral. This is $\hbar s$, where $\hbar$ is Planck's constant and s is the spin of the particle. A spinning electron was suggested originally in connection with the Zeeman effect,[3] especially that a magnetic momentum is often associated with spinning particles (through the gyromagnetic factor), and assigned a quantum-mechanical number of one half.[4] Indeed, as an angular momentum, its projection along one axis has $2s + 1$ states, and $2s$ must be an integer; therefore, spin s may be an integer or half an integer. $2s + 1$ states are described by a symmetric tensor of rank $2s$ whose labels take two values; this is called a spinor; it rotates under a rotation about one axis. It is worth noting that spin vanishes in the quasiclassical description. Particles with an integral spin are described by Klein-Gordon-type equations; the energy in this case is a quadratic form in particle fields plus a quadratic form in hole fields; it is positive definite providing the fields commute; if the fields commute, the wavefunctions of identical particles are symmetric under particle permutations; if the wavefunctions are symmetric, the occupation number of one-particle states may take any positive, integral value; consequently, particles of integral spins obey the Bose-Einstein statistics and are called bosons. Particles with a half-integral spin are described by Dirac-type equations; the energy in this case is a quadratic form in particle fields minus a quadratic form in hole fields; it is positive definite providing the fields anticommute; the wavefunctions of identical particles are then antisymmetric under particle permutations and the occupation number of one-particle states may only take two values, zero and one. Consequently, such particles obey the Fermi statistics and are called fermions. This is the spin-statistics theorem.[5]

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[2] H. Kamerlingh Onnes, Proc. Roy. Acad. Amsterdam **13** 1107, 1274 (1911).

[3] See, for instance, G. E. Uhlenbeck and S. Goudsmit, "Ersetzung der Hypothese vom unmechanischen Zwang durch eine Forderung bezuglich des inneren Verhaltens jedes einzelnen Elektrons", Naturwissenschaften" **13** 953 (1925).

[4] W. Pauli, "Uber den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur des Spektren", Z. Phys. **31** 765 (1925).

The constituents of a composite particle have both a total orbital momentum **L** and a total spin **S**. The particle is invariant under rotations, such that its total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ is conserved; consequently, it is described by a symmetric spinor of rank $2J$, which has $2J + 1$ components; therefore, **J** is its spin. The hamiltonian of the particle may contain additional terms like $\sim \mathbf{J}^2$, and the ground state corresponds to the lowest value $|L - S|$ of J, or to the highest $|L + S|$, depending on the sign of such terms (since the energy has a lower bound, the internal structure of composite particles is non-relativistic, with relativistic corrections; such an additional term comes usually from the spin-orbit interaction). Frequently, the constituents of composite particles are identical particles, like electrons in atoms, or nucleons in atomic nuclei. The energy levels of identical particles are labelled by the irreducible representations of the permutations group. For identical particles with spin one-half these representations correspond to a well-determined total spin **S**, and the spin dependence of the energy levels of two identical fermions with spin one-half is the exchange interaction. The interacting particles building up a composite particle move in a self-consistent field, such that one-particle states are appropriate. The one-particle levels group themselves in energy shells, and the total spin and total orbital momentum in each shell is such as to minimize the energy, for the ground state of the composite particles. Consequently, for electrons, a shell has the highest possible spin and the highest possible orbital momentum (which is known as Hund's rule[6]), the corresponding symmetry of the wavefunction under permutations ensuring thereby as lowest an energy as possible, for the ground state. Closed shells have vanishing $\mathbf{L}$ and $\mathbf{S}$, while open shells have $J = |L - S|$ if they are less than half filled, and $J = L + S$ if they are more than half filled, according to the spin-orbit interaction. This way, having determined the energy shells, one may know the spin, the orbital momentum and the total angular momentum. For instance, ${}^{87}_{37}Rb$ has a $...3d^{10}4s^{2}4p^{6}5s^{1}$ succession of shells, labelled by the principal quantal number n, orbital quantal number l $(0, 1, 2...$ correspond to $s, p, d...)$, the superscript indicating the total number of electrons in the shell; consequently, the total spin of the electrons is $S = 1/2$, the total orbital momentum is $L = 0\,(S)$ and the total angular momentum is $J = |L - S| = 1/2$, as given by the open upper shell (the ground state is therefore labelled by the electronic term ${}^{2}S_{1/2}$, *i.e.* ${}^{2S+1}(L)_{J}$). Similarly, ${}^{23}_{11}Na$ has a ${}^{2}S_{1/2}$ ground state, with a $...2p^{6}3s^{1}$ upper shell. For nucleons the difference is made by the fact that the nuclear forces depend on spin, such that the self-consistent field gives rise to a stronger "spin-orbit" interaction, which, accordingly, classifies the energy bands by the angular momentum $\mathbf{j}$ of the nucleon. The nucleon states are labelled by nl_j, where the principal quantum-mechanical number $n = 1, 2, ...$ and the orbital quantal number $l = j \pm 1/2$ is well-defined, as the nucleon states have a well-defined parity. The nucleon shells are $(1s_{1/2})$, $(1p_{3/2},\, 1p_{1/2})$, $(1d_{5/2},\, 1d_{3/2},\, 2s_{1/2},\, 1f_{7/2})$, $(2p_{3/2},\, 1f_{5/2},\, 2p_{1/2},\, 1g_{9/2})$, etc.[7] The band filling is dictated by the nuclear pairing which couples nucleon pairs at a vanishing angular momentum, such that the even-even nuclei *(i.e.* an even number Z of protons and an even number $A-Z$ of neutrons) have a vanishing total angular momentum $J = 0$, odd-even nuclei have a total angular momentum $J = j$ of the upper unpaired nucleon, and the odd-odd nuclei have a total angular momentum $J = 2j$; indeed, in the latter case the isotopic spin $(T = 0)$ corresponds to an antisymmetric wavefunction and the rest of the wavefunction (spin and coordinate parts) must be symmetric. For instance, the 37 protons of ${}^{87}_{37}Rb$ are arranged in a closed shell of 28 and an open shell $...2p_{3/2}\, 1f_{5/2}\, 2p_{1/2}\, (1g_{9/2})$ with one unpaired proton on $1f_{5/2}$; consequently, the nuclear spin of ${}^{87}_{37}\mathrm{Rb}$ is $I = 5/2$. Similarly, ${}^{23}_{11}Na$ should have a nuclear spin $I = 5/2$;

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[5] W. Pauli, "The connection between spin and statistics", Phys. Rev. **58** 716 (1940).

[6] F. Hund, "Zur Deutung verwickelter Spektren, insbesondere der Elemente Scandium bis Nickel", Z. Phys. **33** 345 (1925); "Zur Deutung verwickelter Spektren. II.", **34** 296 (1925).

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[7] O. Haxel, J. H. D. Jensen and H. E. Suess, "On the "magic numbers" in nuclear structure", Phys. Rev. **75** 1766 (1949); M. G. Mayer, "On closed shells in nuclei. II.", Phys. Rev. **75** 1969 (1949).

however, it is an exception, it has $I = 3/2$ for its nuclear spin. The spin of the atom is therefore $\mathbf{F} = \mathbf{J} + \mathbf{I}$, which is conserved, and the hamiltonian contains the electron-nucleus hyperfine interaction $\sim \mathbf{F}^2$; this interaction always tends to anti-allign the spins, by the effect of the magnetic field, such that the atomic spin in the ground-state is $F = |J + I|$; therefore, for ${}^{87}_{37}Rb$ and ${}^{23}_{11}Na$ the atomic spins are $F = 2$ and $F = 1$, respectively.

The statistical distribution for identical particles with integral spin has been introduced by Bose.[8] Einstein noticed that at low temperatures such particles occupy the lowest energy level, in order to accommodate the macroscopic number of particles.[9] This is the Bose-Einstein condensation. Its connection with the superfluidity of He^4 has been suggested by London.[10] However, the Bose-Einstein condensation is a third-order phase transition, while the superfluidity is a second-order one. The superfluid transition is described by the Ginsburg-Landau theory,[11] while the theory of superfluidity was given by Landau.[12] It is the excitation spectrum of the condensate which is relevant for superfluid properties; it consists of sound-like phonons for long wavelengths and vortices and rotons for shorter wavelengths. The sound-like phonons were derived as long-wavelength elementary excitations of an interacting Bose-Einstein condensate,[13] while vortices and rotons are suggested, in a certain sense, by Gross-Pitaevskii equation.[14] The interaction of the Bose quantum liquid is repulsive, and the Bose-Einstein condensation is preserved for an interacting liquid of bosons.[15]

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[8] S. Bose, "Plancks Gesetz und Lichtquantenhypothese", Z. Phys. **26** 178 (1924).

[9] A. Einstein, "Quantentheorie des einatomigen idealen Gases. 2. Abhandlung", Sitzungsber. Preuss. Akad. Wiss. **3** 18 (1925).

[10] F. London, "On the Bose-Einstein condensation", Phys. Rev. **54** 947 (1938).

[11] L. Landau, "On the theory of phase transitions, I, II", ZhETF **7** 19, 627 (1937) (Phys. Z. Sowjet. **11** 26, 545 (1937)) (in Russian); V. L. Ginsburg and L. Landau, "On the theory of superconductivity", ZhETF **20** 1064 (1950) (in Russian).

[12] L. Landau, "The theory of superfluidity of helium II", ZhETF **11** 592 (1941) (J. Phys. USSR **5** 71 (1941)) (in Russian); "On the hydrodynamics of helium II", ZhETF **14** 112 (1944) (J. Phys. USSR **8** 1 (1944)) (in Russian); "On the theory of superfluidity of helium II", J. Phys. USSR **11** 91 (1947) (in Russian); "Theory of the superfluidity of helium II", Phys. Rev. **60** 356 (1941); "On the theory of superfluidity", Phys. Rev. **75** 884 (1949).

[13] N. Bogoljubov, "On the theory of superfluidity", J. Phys. USSR **11** 23 (1947).

[14] E. P. Gross, "Structure of a quantized vortex in boson systems", Nuovo Cimento **20** 454 (1961); L. P. Pitaevskii, "Vortex lines in an imperfect Bose gas", Sov.

The attractive part of the interaction of some kind of atoms may not be strong enough to solidify them under normal pressure even at vanishing temperatures, especially for lighter atoms; consequently, they form quantum liquids; the typical examples are He^4 below $\sim$ 2.17K and He^3 below $\sim$ 3.2K; the former is a Bose quantum liquid, while the latter is a Fermi quantum liquid. While the atoms in a quantum liquid move quasi-freely over most part of their paths, they may experience strong collisions with each other, due to the repulsive part of the interaction. Apart from such collisions the atoms are otherwise weakly interacting, which explains why the Bose-Einstein condensation is possible in an interacting quantum liquid of bosons and why the interaction effects are perturbation-like in a quantum liquid of fermions. However, the effects of the interaction are quite distinct for bosons and for fermions, as a consequence of their distinct statistics.

13.2 Landau's theory

Let such a quantum liquid of bosons be in its ground state, at vanishing temperature, where all the atoms are on the zero energy levels (on the same one-particle state with zero energy). Any interaction takes such a quantum liquid from its ground state to its excited states; the later are characterized by an energy and, sometimes, by a momentum; their quanta are called elementary excitations.[16] Small,

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Phys.-JETP **13** 451 (1961) (ZhETF **40** 646 (1961)); see also V. L. Ginsburg and L. P. Pitaevskii, "On the theory of superfluidity", Sov. Phys.-JETP **7** 858 (1958) (ZhETF **34** 1240 (1958)).

[15] R. Feynman, "The λ-transition in liquid helium", Phys. Rev. **90** 1116 (1953); "Atomic theory of the λ-transition in helium", Phys. Rev. **91** 1291 (1953); "Atomic theory of liquid helium near absolute zero", Phys. Rev. **91** 1301 (1953); "Atomic theory of the two-fluid model of liquid helium", Phys. Rev. **94** 262 (1954); R. Feynman, in *Progress in Low Temperature Physics*, ed. by C. J. Gorter, Interscience, NY (1955); R. Feynman and M. Cohen, "Energy spectrum of the excitations in liquid helium", Phys. Rev. **102** 1189 (1956).

[16] L. Landau, "The theory of superfluidity of helium II", ZhETF **11** 592 (1941) (J. Phys. USSR **5** 71 (1941)) (in Russian); "On the hydrodynamics of helium

long-wavelength, longitudinal disturbances of the liquid density may propagate above the ground state, governed by the repulsive interaction; they are quanta of sound and are the basic excitations of the Bose-Einstein condensate; they have momentum. For a given momentum there are no other excitations below the sound quanta in the Bose-Einstein condensate, and this is the basic point explaining the superfluidity. Indeed, a slightly excited atom would soon fall down in the condensate, as a consequence of the Bose-Einstein statistics, in contrast to the Fermi statistics where the fermions may assume individually excited states (or in contrast also to a classical liquid); in this latter case the excitations are quasiparticles, and they may have vanishing energies. Therefore, an excited Bose-Einstein condensate may only take an energy and a momentum corresponding to the dispersion relation of the sound quanta, *i.e.* internal motion with velocities smaller than the sound velocity are allowed without viscosity within the liquid; this is the superfluidity phenomenon. Indeed, a mass M of a fluid moving with velocity v has an energy $Mv^2/2$, and a small change δv in the velocity means an energy change $\varepsilon = M\mathbf{v}\delta\mathbf{v} = \mathbf{vp}$, where $\mathbf{p}$ is the momentum; in order to excite a sound quanta ε must be as large as the sound quanta of energy up at least, where u is the sound velocity; *i.e.* $vp > up$; for $v < u$ the motion proceeds without loss, *i.e.* without viscosity, *i.e.* the liquid is superfluid. It is easy to see also that heat is not propagated into a superfluid. However, for velocities v smaller than sound velocity u by a finite amount the superfluidity is destroyed, which suggests another kind of elementary excitations, lying close to a finite momentum and having a quadratic dispersion around an energy gap; such excitations were called rotons and the energy gap was assigned to localized vortices.

Indeed, the average inter-atomic separation a in a Bose liquid plays a relevant role. Since the bosons may assume identical states, the effect of their interaction is local, in contrast to fermions, where the interaction acts globally, in accordance with the fact that they assume only individual states. A localized effect of the interaction may lead to localized excitations for bosons, over distances of the order of

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II", ZhETF **14** 112 (1944) (J. Phys. USSR **8** 1 (1944)) (in Russian); "On the theory of superfluidity of helium II", J. Phys. USSR **11** 91 (1947) (in Russian); "Theory of the superfluidity of helium II", Phys. Rev. **60** 356 (1941); "On the theory of superfluidity", Phys. Rev. **75** 884 (1949).

a, obviously corresponding to a momentum of the order of $1/a$, and having a finite energy gap; the energy gap is of the order of $\hbar^2/ma^2$, where m is the atomic mass (and $\hbar$ denotes Planck's constant). Such excitations lie below the sound quanta in energy at that $1/a$ momentum, for obvious reasons (as for a liquid); such excitations are called vortices, for reasons to be seen shortly. Moreover, the excitations of such vortices, to say so, are called rotons and, obviously, they are particle-like excitations, *i.e.* their spectrum is $p^2/2\mu$ with respect to the vortices, where μ is an effective mass. Everything happens as if an atom is caught in a cage made of the surrounding atoms, where it moves around, together with its surrounding. It is also worth noting that the interaction is "removed" in such a picture, as if its effects were known.

The local effects of the interaction being important for a Bose liquid, it is then appropriate to view it as a quantum fluid, described by local quantities. Indeed, Landau quantized the motion of a fluid starting with a particle (mass) density $\rho = \sum m\delta(\mathbf{r}-\mathbf{R})$ and a (mass) flow of particles $\mathbf{j} = (1/2)\sum[\mathbf{p}\delta(\mathbf{r}-\mathbf{R}) + \delta(\mathbf{r}-\mathbf{R})\mathbf{p}]$, where the particles are placed at $\mathbf{R}$. Obviously, this is a $\psi(\mathbf{r})$-field theory, the particle density being $\psi^+(\mathbf{r})\psi(\mathbf{r})$ (mass density being $\rho(\mathbf{r}) = m\psi^+(\mathbf{r})\psi(\mathbf{r})$) and the mass flow being $\mathbf{j}(\mathbf{r}) = (1/2)[\psi^+(\mathbf{r})\cdot\mathbf{p}\psi(\mathbf{r}) - \mathbf{p}\psi^+(\mathbf{r})\cdot\psi(\mathbf{r})]$. A velocity field $\mathbf{v}(\mathbf{r}) = (1/2m)[\psi^+(\mathbf{r})\cdot\mathbf{p}\psi(\mathbf{r}) - \mathbf{p}\psi^+(\mathbf{r})\cdot\psi(\mathbf{r})]$ is also introduced,[17] and commutation relations

$$v_i(\mathbf{r})v_k(\mathbf{r}') - v_k(\mathbf{r}')v_i(\mathbf{r}) = -(i\hbar/2m)\delta(\mathbf{r}-\mathbf{r}')(curl\mathbf{v})_{ik} \qquad (13.1)$$

are found, where i,k denote the components of the velocities and $(curl\mathbf{v})_{ik} = \partial v_k/\partial x_i - \partial v_i/\partial x_k$. These are the basic equations which led Landau to substantiate the idea of vortices and rotons; their main characteristics are the inhomogeneity in velocities, *i.e.* the *lhs* of equation (13.1) is of second-order in velocities while the *rhs* of equation (13.1) is of first order in velocities; and, of course, the non-vanishing commutator in equation (13.1).

Before analyzing equation (13.1) with respect to vortices and rotons it is worth making some remarks. First, such a quantum hydrodynamics,

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[17] Actually, Landau ("The theory of superfluidity of helium II", ZhETF **11** 592 (1941) (J. Phys. USSR **5** 71 (1941)) (in Russian)) works in the "first quantization", and finds it more conveniently to use a "mean" velocity $\mathbf{v} = (1/2)[(1/\rho)\mathbf{j} + \mathbf{j}(1/\rho)]$.

i.e. a local field theory, is generally valid for any quantum liquid (equation (13.1) including). However, it is superfluous to a great deal of extent for fermions, because the excited states therein are delocalized, and the *curl* of a velocity near the (large) Fermi velocity is vanishing, since the change in such a velocity proceeds by vanishing changes in momenta. This is why one prefers to work with global quantities in the second quantization for fermions, *i.e.* with integrating densities of the type above over the whole volume of the liquid. The two formalisms, by the way, *i.e.* the local quantum hydrodynamics on one side, and the global second-quantized field theory on the other, already contain in themselves the solution of the interaction problem for bosons and fermions, which is remarkable. Second, it is worth noting that the field $\psi(\mathbf{r})$ is analyzed in plane waves, as usually, making the understanding of equation (13.1) much easier. Further on, it is worth stressing that the velocity $\mathbf{v}(\mathbf{r})$ introduced above is a field operator, *i.e.* an operator in the occupation number of plane waves. In particular, the average velocity $\mathbf{v} = (-i\hbar/2m)[\psi^*(\partial\psi/\partial\mathbf{r}) - (\partial\psi^*/\partial\mathbf{r})\psi]$, where $\psi \sim e^{i\Phi}$ is a wavefunction is $\mathbf{v} = \hbar grad\Phi/m$, and its *curl* is always vanishing ($curl\mathbf{v}$ is off-diagonal). Also, the velocity as defined above can be written as

$$\mathbf{v}(\mathbf{r}) = (\hbar/2m)\sum(2\mathbf{k}+\mathbf{q})a^+_{\mathbf{k}}a_{\mathbf{k}+\mathbf{q}}e^{i\mathbf{q}\mathbf{r}} \ , \tag{13.2}$$

where $a^+_{\mathbf{k}}$, $a_{\mathbf{k}}$ are creation and destruction operators of plane waves; now, one can see easily that a longitudinal wave has a vanishing *curl* of velocity, such that the sound waves are not affected by equation (13.1) (and the velocity of a quasiparticle excitation close to the Fermi surface has a vanishing *curl* too). Moreover, the *curl* of velocities is the highest for both $\mathbf{k}$ and $\mathbf{q}$ close to the highest relevant wavevectors, *i.e.* wavevectors of the order of $1/a$; it follows that equation (13.1) involves a motion localized over the average inter-atomic separation a and interaction processes that exchange momenta of the order $\hbar/a$; such a motion is relevant for bosons; it may be called a vortex, since the *curl* of its velocity is non-vanishing. It is also worth noting that such atomic movements are spatially disentangled from each other, since equation (13.1) is effective only at the same location. Also, it follows that any motion in the superfluid state, *i.e.* a motion with a velocity $\mathbf{v}$ low enough so as not to excite vortices, is a potential motion, *i.e.* irrotational, *i.e.* $curl\mathbf{v} = 0$. Indeed, if $curl\mathbf{v}$ is zero everywhere it commutes with everything, including the hamiltonian, and is conserved.

Indeed, the hamiltonian of an interacting ensemble of particles reads

$$H = \sum \mathbf{p}^2/2m + \frac{1}{2}\sum v(\mathbf{R} - \mathbf{R}') \tag{13.3}$$

(spin neglected), or

$$\begin{gathered} H = \sum (\mathbf{p}^2/2m) a^+_{\mathbf{p}} a_{\mathbf{p}} + \\ +(1/2V)\sum v(\mathbf{q}) a^+_{\mathbf{p}_1} a^+_{\mathbf{p}_2} a_{\mathbf{p}_2 - \hbar\mathbf{q}} a_{\mathbf{p}_1 + \hbar\mathbf{q}} \ \ , \end{gathered} \tag{13.4}$$

where $v(\mathbf{q}) = \int d\mathbf{r} \cdot v(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}}$ and V is the volume of the ensemble; one can easily recognize the density $n(\mathbf{r})$ in the interacting term in equations (13.3) and (13.4); in addition, a displacement field $\mathbf{u}(\mathbf{r})$ produces a change $\delta n = -ndiv\mathbf{u}$ in density; for bosons we get straightforwardly the frequency $\omega = [nv(\mathbf{q} = 0)/m]^{1/2} q$ of longitudinal sound waves; similarly, we can obtain sound for fermions too (where the contribution of kinetic energy must be included), but it is unstable against the quasiparticle excitations.[18] Further on, $curl\mathbf{v}$ does not commute with the kinetic hamiltonian (though it commutes with the density; and with itself!), such that it has not defined values for the elementary excitations, except for those which are longitudinal (where it vanishes); therefore, a vortex (with defined energy) has not a well-defined *curl*, and, conversely, a well-defined *curl* has not a well-defined energy. Moreover, $curl\mathbf{v} \neq 0$ requires a non-vanishing velocity in order to satisfy the inhomogeneous equation (13.1), such that such a vortex must have a finite energy, *i.e.* a gap in the excitations energy. (In addition, it is worth noting that the quantum hydrodynamics obeys the continuity equation and Euler's equation of motion for fluids). Obviously, a local non-vanishing velocity may only arise from interaction processes exchanging momenta of the order $\hbar/a$. For such interaction processes we obtain an average velocity $v \sim (\hbar/m)(\sin r/a)/r$ from equation (13.2), whose *curl* is $curl\mathbf{v} \sim (\hbar/ma)(\cos r/a)/r$ (having not a definite orientation, $\mathbf{v}$ does not come from a *grad*). The integral $\int d\mathbf{s}\cdot curl\mathbf{v}$ over any surface around the point is then the circulation $\oint d\mathbf{l}\cdot\mathbf{v}$ of the velocity around that point, and equals $\sim\hbar/m$. It is called vorticity and its quantum is h/m ($\hbar=h/2\pi$); it is the same as the quantum of viscosity,[19] for obvious reasons; indeed, the origin of viscosity is quantum-mechanical (it is worth noting in this connection that the quantum uncertainty in the fermion quasiparticle energy may originate in a vortex too); also, the classical turbulence is made of quantum vortices. In particular, one can notice that $curl\mathbf{v}\sim\mathbf{p}\times\mathbf{v}$, which is a purely quantum quantity.

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[18] Though global, delocalized density oscillations may propagate in ensembles of fermions, like the zero-sound of the quasiparticle states, or plasma oscillations of the electron ensemble.

The ground-state of a liquid consisting of identical interacting bosons is a crystaline-ordered state, characterized by a set of three reciprocal vectors $\mathbf{G}$, the atoms being placed at $\mathbf{R}_i$. Atoms, however, may oscillate within their atomic cages, with very low energies, and momenta $\hbar\mathbf{g}$, where $\mathbf{g}$ is a multiple $n\mathbf{G}$ of $\mathbf{G}$. The average of the structure factor $\sum e^{i\mathbf{qR_i}}$ gives $\mathbf{g}$-peaks decreasing like $1/q^3$, as for a genuine liquid with short-range order. Delocalized states, like an atom travelling with momentum $\hbar\mathbf{k}$, are therefore identical with "umklapp" scaterred states, in particular an atom travelling with a momentum $\hbar(\mathbf{k}+\mathbf{g})$; therefore, $a_{\mathbf{k}+\mathbf{g}}$ can be replaced by $a_{\mathbf{k}}$. Only $\mathbf{G}$-scattering processes should be kept in collisions, in view of the "short-range" character of the interaction, such that the velocity in equation (13.2) becomes

$$\mathbf{v}(\mathbf{r})=(\hbar/m)\mathbf{k}a^{+}_{\mathbf{k}}a_{\mathbf{k}}\sum e^{i\mathbf{Gr}} \tag{13.5}$$

for one particle, where the summation extends over $\mathbf{G}$'s; correspondingly, its *curl* is

$$curl\mathbf{v}=i(\hbar/m)\sum(\mathbf{k}\times\mathbf{G})a^{+}_{\mathbf{k}}a_{\mathbf{k}}e^{i\mathbf{Gr}}\ ; \tag{13.6}$$

one can see that, now, they are diagonal in the particle occupancy; and, of course, they do not commute anymore with the hamiltonian, in particular with the $\mathbf{G}$-interaction processes in equation (13.4). For a vortex, the particle momentum is $\mathbf{g}$ in principle (actually of the order of $\mathbf{G}$), and its (minimal) energy is of the order of $\Delta=\hbar^2/ma^2$ (for He^4 $\sim$ 9K from neutron scattering,[20] with $a\sim3.7$Å). A particle may escape a vortex after, at least, one planar loop involving 4 **G**-collisions; its energy is then $\hbar^2(k^2+4G^2)/2m$, and for $k\sim G$, it involves an effective mass $\mu\sim m/5=0.2m$ (the experimental value from neutron scattering is $0.16m$ for He^4). In addition, it is worth noting the position of the vortex gap at $G\sim 1/a$, actually at $2\pi/a=1.7\mathring{A}^{-1}$; the experimental location is $1.9\mathring{A}^{-1}$; and the roton energy $\mathbf{p}^2/2\mu$ which is quadratic in momenta. From equations (13.5) and (13.6) one can see again that the vorticity is $\sim nh/m$, *i.e.* it is quantized in quanta h/m; and *curl* is represented as $(\hbar/m)(\mathbf{g}\times\mathbf{G})$, where $\mathbf{k}\sim\mathbf{g}\,(\sim\mathbf{G})$.

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[19] $(curl\mathbf{v})_z=\partial(rv_\theta)/r\partial r-\partial v_r/r\partial\theta$; $(grad\Phi)_r=\partial\Phi/\partial r$, $(grad\Phi)_\theta=\partial\Phi/r\partial r$

[20] D. G. Henshaw and A. D. B. Woods, "Modes of atomic motions in liquid helium by inelastic scattering of neutrons", Phys. Rev. **121** 1266 (1961).

The ground-state of the hamiltonian given by equation (13.4) is a condensate with all $\mathbf{p}=0$; its elementary excitations consist of pairs of interacting particles; we get straightforwardly[21]

$$\begin{gathered}H=\tfrac{1}{2}Nnv(0)+\tfrac{1}{2}n^2\sum\tfrac{v^2(\mathbf{p})}{p^2/m}+\sum(\mathbf{p}^2/2m)a^+_{\mathbf{p}}a_{\mathbf{p}}+\\+\tfrac{1}{2}n\sum v(\mathbf{p})[a^+_{\mathbf{p}}a^+_{-\mathbf{p}}+a_{-\mathbf{p}}a_{\mathbf{p}}+2a^+_{\mathbf{p}}a_{\mathbf{p}}]\end{gathered}\tag{13.7}$$

for the hamiltonian of these excitations; it is worth noting that the excitation contributions are consistently included in equation (13.7) up to the second order of the perturbation theory, and the ground-state energy is, accordingly, renormalized by the second term in the *rhs* of equation (13.7). The diagonalization of the hamiltonian above is straightforward, and the excitation spectrum is given by

$$\varepsilon(\mathbf{p})=[nv(\mathbf{p})p^2/m+(p^2/2m)^2]^{1/2}\ ,\tag{13.8}$$

while the ground-state energy reads

$$\begin{gathered}E_0=\tfrac{1}{2}Nmu^2+\tfrac{1}{2}n^2\sum\tfrac{v^2(\mathbf{p})}{p^2/m}+\\+\tfrac{1}{2}\sum\{\varepsilon(\mathbf{p})-[p^2/2m+nv(\mathbf{p})]\}\ ,\end{gathered}\tag{13.9}$$

where $u=\sqrt{nv(0)/m}$ is the sound velocity ($\sim$ 240m/s); carrying out the integration in equation (13.9) we get $E_0=(1/2)Nmu^2[1+\alpha(mu)^3/2\pi^2\hbar^3n]$, where α is slightly smaller than the usual value

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[21] N. Bogoljubov, "On the theory of superfluidity", J. Phys. USSR **11** 23 (1947).

$\alpha = 2.3$ corresponding to a δ-type interaction ($v(\mathbf{p}) = v(0)$). For typical hard-core atomic potentials the experimental spectrum of excitations is obtained from equation (13.8); similarly, it is given by screened Coulomb potentials with oscillatory tails.[22] The excitation spectrum given by equation (13.8) can also be put in another form; indeed, denoting $\varepsilon_0 = p^2/2m$ one gets from equation (13.8) $\varepsilon = \varepsilon_0(1+nv(\mathbf{p})/\varepsilon_0)$ for large p; on the other hand, the pair distribution function is given by $S(\mathbf{q}) = (1/N)\sum e^{i\mathbf{q}(\mathbf{R_i}-\mathbf{R_j})} = \sum' e^{i\mathbf{q}\mathbf{R_i}}$ (where N is the number of atoms and prime means summation over neighbours), and the potential can be written as $\overline{v} = \sum v(\mathbf{r}-\mathbf{R_i}) \sim nv(\mathbf{q})S(\mathbf{q})$ for $q \sim 1/a$; therefore, $\varepsilon = \varepsilon_0(1 + \overline{v}/S(\mathbf{q})\varepsilon_0)$; in addition, the energy of the excitation can also be written approximately as $S\varepsilon_0 + \overline{v} = \varepsilon_0$ for the movement of an atom around its position $\mathbf{R_i}$, hence $\varepsilon = \varepsilon_0/S(\mathbf{q}) = \hbar^2 q^2/2mS(\mathbf{q})$, as suggested by Feynman (quoted above).

The excitations of the superfluid form its normal component, while the remaining part is the superfluid component; they have distinct densities, and a two-fluid picture holds for superfluidity, as suggested earlier.[23] Sound, vortices and rotons do scatter on each other in the normal part of the superfluid, and the corresponding cross-section can be estimated.[24] The superfluid flows frictionlessly through capillaries and narrow slits, in a rotating vessel the superfluid does not rotate, has not an inertia momentum (it is incapable of rotational flow), exerts no pressure on an immersed body (Euler's paradox); since the normal part and the superfluid part are in equilibrium, there is no entropy transfer between them, and, of course, no friction and no viscosity in the relative motion of the two fluids one against the other. The superfluid flows like an "ordered" fluid, without changing the entropy, and does not carry heat (and the superfluid motion is thermodynamically reversible); and, of course, it is so at zero temperature, practically; flowing out of vessels and carrying no heat, the superfluid leaves behind the heat which boils the remaining fluid (this is the thermomechanical effect). The heat is transported by the normal fluid, which flows to the cold temperatures, while the superfluid flows in compensation to the warmer temperatures; this out-of phase mutual flow of the two fluids may proceed by temperature waves, which are called the second sound, and whose velocity is $u/\sqrt{3}$ at vanishing temperature, in contrast to the usual u-sound which is called the first sound. Indeed, the interaction of the phonons with atoms gives Boltzmann's equation $\partial f/\partial t+(uq_i/q)\partial f/\partial x_i=I$ for their distribution function f, where I is the collision integral; introducing momentum $P_i=\int q_i f$ and energy $E=u\int(q_i^2/q)f$ one gets $\partial P_i/\partial t+(1/3)\partial E/\partial x_i=0$ as well as $\partial E/\partial t+u^2\partial P_i/\partial x_i=0$ (collisions do conserve the momentum and energy), hence $\partial^2 E/\partial t^2-(u^2/3)\partial^2 E/\partial x_i^2=0$ and the second sound velocity $u/\sqrt{3}$.

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[22] L. C. Cune and M. Apostol, "On the superfluid spectrum of He^4, J. Theor. Phys. **94** (2004).

[23] L. Tisza, "Transport phenomena in helium II", Nature **141** 913 (1938); "Sur la theorie des liquides quantiques. Application a l'helium liquid. I, II.", J. Phys. et Radium **1** 164, 350 (1940); "The theory of liquid helium", Phys. Rev. **72** 838 (1947); see also F. London, *Superfluids*, Dover, NY (1964).

[24] L. Landau and I. M. Khalatnikov, "The theory of the viscosity of helium II: I. Collisions of elementary excitations in helium II", ZhETF **19** 637 (1949) (in Russian); "The theory of the viscosity of helium II: II. Calculation of the viscosity coefficient", ZhETF **19** 709 (1949) (in Russian); I. M. Khalatnikov, *An Introduction to the Theory of Superfluidity*, Benjamin, NY (1965).

It is now worth turning back to vortices. One may notice for the beginning that vortices given by equations (13.5) and (13.6) do not commute with the hamiltonian (13.7). The wavefunction of a fluid moving with the velocity $\mathbf{v}$ has the form $\psi\sim\exp(im\mathbf{v}\sum\mathbf{R}/\hbar)$, and for a fluid rotating with the angular velocity ω the circulation of this velocity on a closed loop is of course $\oint\mathbf{dl}\cdot\mathbf{v}=(h/m)\times integer$ from the periodicity of the wavefunction, *i.e.* it is quantized by h/m, and its *curl* is 2ω; obviously, $v=\omega r=(L/m)/r$ in this case, and the vorticity is nothing but the quantization of the angular momentum L, and its *curl* is vanishing. Such a motion is called a "vortex" too, but of course $\mathbf{v}\sum\mathbf{R}=0$ in this case; it was suggested[25] that space is disconnected, and has a "hole", for instance at the centre, in which case ψ would go like $\psi\sim\exp(i\varphi(\mathbf{R})/\hbar)$; however $\mathbf{v}=(\hbar/m)grad\varphi$ would have no *curl* then, but, nevertheless, it is supposed further on that it may have a singularity at the "hole", where its *curl* might be non-vanishing, and Stokes' theorem would be used on the external loops only; in which case such a vortex might probably be better called a "circulating vortex", or an L-vortex, in contrast with a "*curl*, or an ω-, vortex".

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[25] L. Onsager, "Statistical hydrodynamics", Nuovo Cimento **6**, Suppl. 2, 279 (1949); R. Feynman, in *Progress in Low Temperature Physics*, ed. by C. J. Gorter, Interscience, NY (1955).

In any case, it has nothing to do with the superfluid excitations called vortices. Nonetheless, such an irrotational motion does exist of course, with $v = \omega r = L/mr$, and the energy associated with one quantum of rotating velocity is the centrifugal energy $\int \pi r dr \cdot nm(\hbar/mr)^2 d$, *i.e.* $\pi n(\hbar^2/m)\ln(b/a)$ per unit depth d of the liquid; which is not compensated by the surface tension of a real hole; however, many such "linear holes", *i.e.* cylinders, do appear in a rotating superfluid, whose free surface is finely rigged with them, such as to minimize the energy and conserve the angular momentum, and they are related to the capacity of the superfluid to create internal non-uniformities of a normal fluid, by exciting true vortices.

13.3 Wavefunction of the condensate

Let $\psi(\mathbf{r}, q)$ be the wavefunction of an ensemble of particles, for one particle at $\mathbf{r}$ and the rest with coordinates q. The one-particle density matrix $\rho(\mathbf{r} - \mathbf{r}') = \int dq\psi^*(\mathbf{r}, q)\psi(\mathbf{r}', q)$ has the Fourier transform $\int d\mathbf{R}\rho(\mathbf{R})e^{i\mathbf{kR}} = (1/V)\int dq \left|\psi(\mathbf{k}, q)\right|^2$, and $(1/V)\left|\psi(\mathbf{k}, q)\right|^2$ is the probability for one particle of being in the $\mathbf{k}$-state; for a condensed Bose liquid all the particles are deployed on the state $\mathbf{k} = 0$, such that $\rho(\mathbf{r})$ is finite at infinity; this is an off-diagonal long-range order.[26] What is more interesting is that the condensate has a field a_0, or, for a non-uniform condensate moving with some velocity, a field $\psi(\mathbf{r}) = a(\mathbf{r})e^{i\phi(\mathbf{r})}$, where $a(\mathbf{r})$ is the amplitude and $\Phi(\mathbf{r})$ is a phase; this is a classical field (though for a quantum object), and is called the wavefunction of the condensate; the velocity is $\mathbf{v} = (\hbar/m)grad\Phi$ and it is irrotational ($curl\mathbf{v} = 0$), as for a superfluid condensate. It is easy to see that $\psi(\mathbf{r})$ obeys

$$(-\frac{\hbar^2}{2m}\Delta - \mu)\psi(\mathbf{r}) + v(\mathbf{r} = 0)a^3\left|\psi(\mathbf{r})\right|^2\psi(\mathbf{r}) = 0 \qquad (13.10)$$

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[26] Note #11 and O. Penrose and L. Onsager, "Bose-Einstein condensation and liquid helium", Phys. Rev. **104** 576 (1956); C. N. Yang, "Concept of off-diagonal long-range order and the quantum phases of liquid *He* and superconductors", Revs. Mod. Phys. **34** 694 (1962); W. L. McMillan, "Ground state of liquid He^4", Phys. Rev. **138** 442 (1965).

for a δ-potential, which minimizes the classical energy for an average number of particles (μ is the chemical potential); this is the Gross-Pitaevskii equation,[27] and describes non-uniformities of a moving condensate; in particular, it gives a depletion of the superfluid near a wall (and the surface tension of the superfluid), as well as cylindrical "circulating vortices" for a rotating superfluid ($v_\theta \sim 1/r$); in the latter case ψ goes like $\psi \sim e^{i\theta}$ and it is $\psi \sim e^{iL\theta/\hbar}$, corresponding to an angular momentum $L = \hbar$; and the velocity reads $v_\theta = L/mr$; it has nothing to do with the true superfluid "*curl* vortices" (which, in particular, are associated with a hard-core potential). It is worth noting that the other two components of the angular momentum are vanishing as for a vanishing macroscopic rotation of the cylindrical vortex about the corresponding directions. Superfluid motion of non-uniform Bose condensates, as well as their long-wavelengths excitations, or macroscopic flows, superfluid hydrodynamics, including phase interference, Josephson-like oscillations of the flows, etc, are described by the Gross-Pitaevskii equation (13.10),[28] which amounts, for these reasons, to a mean-field theory; beyond this mean-field regime the picture is dominated by the atomic limit of the true *curl*-, quantum vortices.

Since the condensate does not conserve the number of particles (and its gauge symmetry $a_{\mathbf{p}} \rightarrow a_{\mathbf{p}} e^{i\varphi}$ is broken, as one can see, for instance, from equation (13.7)), and, in order to allow for the excitations in the condensate, it must be written as

$$\psi(\mathbf{r}) = \sqrt{n}(1 - \frac{1}{2} div\mathbf{u}) e^{i\Phi} \ , \tag{13.11}$$

where $\mathbf{u}$ is the slowly varying long-wavelengths sound field, while Φ is associated with all the rest of possible movements, macroscopic motion included. Indeed, $|\psi(\mathbf{r})|^2 = n(1 - div\mathbf{u})$ is the change in density, while Φ-motion does not change the density; of course, by including excitations the condensate wavefunction given by equation (13.11) has to be quantized; for the beginning, it may be viewed as a quasiclassical description. In addition, the macroscopic motion may be left aside, and the phase Φ may be viewed as varying abruptly over atomic distances near a given position; the direction of its variation changes continuously, and this is the sense in which it describes a quasiclassical motion; otherwise, due to its localization and to the uncertainty in the direction of its variation, it corresponds to a quantum motion. The energy can easily be derived from equation(13.3) as

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[27] E. P. Gross, "Structure of a quantized vortex in boson systems", Nuovo Cimento **20** 454 (1961); L. P. Pitaevskii, "Vortex lines in an imperfect Bose gas", Sov. Phys.-JETP **13** 451 (1961) (ZhETF **40** 646 (1961)); see also V. L. Ginsburg and L. P. Pitaevskii, "On the theory of superfluidity", Sov. Phys.-JETP **7** 858 (1958) (ZhETF **34** 1240 (1958)).

[28] F. Dalfovo, S. Giorgini, L. Pitaevskii and S. Stringari, "Theory of Bose-Einstein condensation in trapped gases", Revs. Mod. Phys. **71** 463 (1999).

$$\begin{gathered} H=\int d\mathbf{r}\cdot\psi^{+}(\mathbf{p}^{2}/2m)\psi+ \\ +\tfrac{1}{2}\int v(\mathbf{r}-\mathbf{r}')\psi^{+}(\mathbf{r})\psi^{+}(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})= \\ =\tfrac{\hbar^{2}n}{2m}\int d\mathbf{r}\cdot\left|grad\Phi\right|^{2}+ \\ +\tfrac{1}{2}n^{2}\int v+\tfrac{1}{2}n^{2}\int v\cdot(div\mathbf{u})(\mathbf{div'u})= \\ =\tfrac{\hbar^{2}n}{2m}\int d\mathbf{r}\cdot\left|grad\Phi\right|^{2}+\tfrac{1}{2}n^{2}V\sum v(\mathbf{q})+ \\ +\tfrac{1}{2}n^{2}V\sum v(\mathbf{q})q^{2}u_{\mathbf{q}}^{*}u_{\mathbf{q}}\ . \end{gathered} \tag{13.12}$$

With the kinetic term $\int d\mathbf{r}\cdot mn\left|\partial\mathbf{u}/\partial t\right|^{2}/2$ we get the sound quanta $\omega=\sqrt{nv(0)/m}q$ for the $\mathbf{u}$-motion in equation (13.12). For the Φ-phase in equation (13.11) we may take $\Phi=gu$ according to the discussion above, where u is the displacement along a wavevector $\mathbf{g}$ of the order of the reciprocal vector $\mathbf{G}$ (in which case the direction of the phase variation may also be quantized). The displacement u is developed in Fourier series as $u=\sum u_{\mathbf{g}}e^{i(\mathbf{g}+\mathbf{q})\mathbf{r}}$, where $\mathbf{q}$ is very small in comparison with $\mathbf{g}$ (such that $n\int d\mathbf{r}=1$). The gradient of the phase can be represented as $grad\Phi\sim-\mathbf{g}u/a+g\cdot gradu$, since $gradg\sim-\mathbf{g}/a$, such that the velocity is $\mathbf{v}\sim(\hbar/m)(-\mathbf{g}u/a+g\cdot gradu)$, and its $curl\mathbf{v}\sim-i(\hbar/ma)\sum\mathbf{g}\times\mathbf{g}'u_{\mathbf{g}'}e^{i\mathbf{g}'\mathbf{r}}$ is non-vanishing. The corresponding energy as estimated from equation (13.12) is given by

$$\begin{gathered} \tfrac{\hbar^{2}}{2m}(g^{2}\left|u_{\mathbf{g}}\right|^{2}/a^{2}+g^{2}\left|u_{\mathbf{g}}\right|^{2}/a^{2}+g^{2}q^{2}\left|u_{\mathbf{g}}\right|^{2})\simeq \\ \simeq\{\hbar^{2}(ag)^{2}/ma^{2}+(ag)^{2}p^{2}/2m\}a_{\mathbf{g}}^{+}a_{\mathbf{g}}\ \ , \end{gathered} \tag{13.13}$$

where $u_{\mathbf{g}}\sim aa_{\mathbf{g}}$; for $ag=\pi$ one obtains an energy $\Delta+p^{2}/2\mu$, where

$\Delta = \pi^2\hbar^2/ma^2 \simeq 8$K and $\mu = m/\pi^2 \simeq 0.1m$ for He^4, which is the rotons spectrum. (It is worth noting that $\sum \mathbf{gq} = 0$ in equation (13.13)). However, $curl\mathbf{v}$ does not commute with equation (13.13); it may be viewed as a spin $\mathbf{S}$ of magnitude unity, corresponding to the vector $\mathbf{g}$, in which case the energy is represented as $(\mathbf{Su_g})^2$, but still $\mathbf{S}$ is not determined. Rotons and the superfluid vortices are purely quantum particles. In addition, the phase is not determined, as for a determined number of atoms (one), and this is a phase diffusion.

It is energetically favourable for vortices to turn about the same direction in order to get together, forming larger vortices (and antivortices) which are classical, and are "*curl* vortices"; however, they create discontinuities in the superfluid velocity, associated with the surface tension, and the free surface of a rotating superfluid is rippled with such layers of discontinuity.[29] The superfluid velocity goes like $1/r$ in such a rotating fluid, for conserving the angular momentum (and like in Gross-Pitaevskii equation), and of course, it is irrotational (and flow conserving, $div\mathbf{v} = 0$); at least one true vortex exists at the centre.[30]

There is still another equivalent representation of the wavefunction given by equation (13.11). Indeed, the long wavelengths part can also be written as $\psi = \sqrt{n}e^{iu/a}$, and the density is given by $\psi^+(\mathbf{r} - i\mathbf{a}/2)\psi(\mathbf{r} + i\mathbf{a}/2) = n(1 - \mathbf{a}gradu/a) = n(1 - div\mathbf{a}u/a) = n(1 - div\mathbf{u})$; this form of the wavefunction shows up the condensate interference. A classical phase, *i.e.* a determined phase, corresponds to an undetermined number of particles, and these are so indeed, since the atomic distances are uncertain. As regards the vortex part of the wavefunction given by equation (13.11), the phase Φ may be written as $(1/\hbar)\int p_r dr + (1/\hbar)\int p_\theta r d\theta + (1/\hbar)\int p_\varphi r\sin\theta d\varphi$ in spherical coordinates, which means

$$(1/\hbar)\int p_r dr + (1/\hbar)\int L_\varphi d\theta - (1/\hbar)\int L_\theta \sin\theta d\varphi \ , \qquad (13.14)$$

where $\mathbf{L}$ is the angular momentum; in particular $L_\theta \sin\theta = L_z$, and

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[29] L. Landau and E. M. Lifshitz, "On the rotation of liquid helium", Dokl. Akad. Nauk SSSR **100** 669 (1955).

[30] See also M. Apostol, "Fluids, fluid vortices and the theory of electricity and magnetism", J. Theor. Phys. **135** (2006).

$L_\varphi = rp_\theta$, $L_\theta = -rp_\varphi$. Therefore,

$$grad\Phi = \frac{1}{\hbar}(p_r,\, L_\varphi/r,\, -L_\theta/r) = \frac{m}{\hbar}(v_r,\, r\omega_\varphi,\, r\sin\theta\cdot\omega_z) \ , \tag{13.15}$$

where angular frequencies $\omega_{\varphi,z}$ are introduced as for a free angular motion. One can see that $curl\mathbf{v} = (2\cos\theta\cdot\omega_z,\, -2\sin\theta\cdot\omega_z,\, 2\omega_\varphi)$, which is non-vanishing for a non-vanishing $\mathbf{L}$; in cartesian coordinates $curl\mathbf{v} = 2(-\omega_\varphi\sin\varphi,\, \omega_\varphi\cos\varphi,\, \omega_z)$. The energy given by equation (13.12) reads

$$\frac{\hbar^2 n}{2m}\int d\mathbf{r}\cdot|grad\Phi|^2 = \frac{1}{2m}p_r^2 + \frac{1}{2mr^2}\mathbf{L}^2 \ , \tag{13.16}$$

and its minimum value is $\Delta = (\pi^2+2)\hbar^2/ma^2$, corresponding to $r = a/\sqrt{2}$ and $l = 1$; it gives $9.6K$ for the vortex excitation in liquid He^4, in perfect agreement with the experimental data.[31] One can see that the vortices are not defined for a given energy (except for the L_z-component in the wavefunction). In addition, writing up $\Delta = p^2/2\mu$ with $p = \hbar(2\pi/4r) = \hbar(\pi/\sqrt{2}a)$, we get the effective mass $\mu = 0.2m$ for rotons, in good agreement with the experimental data. It is worth noting that even if L_z is determined, together with the vortex energy, the velocity and its *curl* are not, as a consequence of the quantum nature of the particle microscopic motion; or, conversely, if one allows for an undetermined energy of the vortex, and requires a well-determination of the wavefunction, or of velocity and its *curl*, it is again impossible, due to the quantum nature of the angular momentum components. However, there is one case where the quantum vortex is well defined, and this corresponds to a cylindrical rotator. The phase of the vortex reads then

$$(1/\hbar)\int p_z dr + (1/\hbar)\int L_z d\theta \ , \tag{13.17}$$

its gradient is given by

$$grad\Phi = \frac{1}{\hbar}(p_z,\, L_z/r) = \frac{m}{\hbar}(v_z,\, r\omega_z) \ , \tag{13.18}$$

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[31] D. G. Henshaw and A. D. B. Woods, "Modes of atomic motions in liquid helium by inelastic scattering of neutrons", Phys. Rev. **121** 1266 (1961).

and the energy reads

$$\frac{\hbar^2 n}{2m}\int d\mathbf{r}\cdot|grad\Phi|^2=\frac{1}{2m}p_z^2+\frac{1}{2mr^2}L_z^2\ . \tag{13.19}$$

The excitation energy diminishes a little (for $L_z = 1$), the roton mass increases slightly, the energy is defined together with the wavefunction, the *curl* of velocity is $2\omega_z$, but it is not defined (actually it vanishes) for a given momentum and energy, since $v_\theta = r\omega_z = L_z/mr$ in that case. Finally it is also worth noting that the condensate wavefunction is actually a field operator for vortices, as expected for such quantum objects. Also, a rigid body rotates with an angular velocity without conserving the local angular momentum ($v = \omega r$), and the local velocity has a non-vanishing *curl* (2ω), such that it has a rotational flow, in contrast with a superfluid that rotates with a constant distribution of angular momentum ($v = L/mr$), and no *curl* of velocity (potential flow); a classical fluid is capable of both a potential and a rotational flow (as an excited superfluid too), and the extent to which its flow is rotational expresses its resemblance to a rigid body and its developing turbulence.

14 Pulse Thermoelectricity

14.1 Figure of merit

It is well-known that thermoelements, which may be used either as Seebeck electric generators or as Peltier electric coolers, are characterized by a ”figure of merit”, according to which the Seebeck thermopower and the electrical conductivity must be as high as possible, while the thermoconductivity must be as low as possible, in order to get a high efficiency quotient.[1] We limit ourselves to the classical way of operating the thermoelectric circuits, where the local thermodynamic equilibrium is ensured, while small and continuous temperature and voltage gradients are established along the sample. In addition, the sample is assumed to be homogeneous on the macroscopic scale, as for a stable thermodynamical phase. Under these circumstances, the electric flow **j** and the heat flow **q**, *i.e.* the electric charge and the heat flowing across the unit area of the cross-section per unit time, are given by the basic equations of the thermoelectricity[2]

$$\mathbf{j} = \sigma \mathbf{E} - \sigma Q \mathrm{grad} T \tag{14.1}$$

and

$$\mathbf{q} = \varphi \mathbf{j} + QT\mathbf{j} - K grad T \ , \tag{14.2}$$

where σ is the electrical conductivity, **E** is the electric field, Q is the thermopower, T is the temperature, φ is the electric potential ($\mathbf{E} = -grad\varphi$), and, finally, K denotes the thermoconductivity; the gradient may be specialized to the x-direction, *i.e.* $grad = \partial/\partial x$. One can see from equation (14.1) that a temperature gradient gives rise to an electric field $\mathbf{E} = -QgradT$, controlled by the Seebeck thermopower coefficient Q; this is the Seebeck effect; while, from equation (14.2), the continuity of the flows across a junction leads to a released heat $-\Delta Q \cdot T\mathbf{j} = \Pi\mathbf{j} = -\Delta(KgradT)$ per unit time and per unit area of the junction, which is the Peltier effect, and $\Pi = -T\Delta Q$ denotes the Peltier coefficient. One can already notice from equations (14.1) and (14.2) that a high efficiency requires a high Q and σ and a low K.

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[1] D. M. Rowe and C. M. Bhandari, *Modern Thermoelectrics*, Holt-Technology, Reston, VA (1983); G. S. Nolas, J. Sharp and H. J. Goldsmid, *Thermoelectrics. Basic Principles and New Materials Developments*, Springer, NY (2001).

[2] See, for instance, L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics*, vol. 8, *Electrodynamics of Continuous Media*, Elsevier, Oxford (2004).

Indeed, heat per unit volume and unit time is given by

$$-div\mathbf{q} = \mathbf{Ej} - \mathbf{j}grad(QT) + div(KgradT) \tag{14.3}$$

from equation (14.2) (since $div\mathbf{j} = 0$, as for a steady flow which conserves the charge), or, making use of equation (14.1),

$$-div\mathbf{q} = j^2/\sigma - T\mathbf{j}gradQ + div(KgradT)\ . \tag{14.4}$$

We note that equation (14.4) holds irrespective of the presence or absence of the external electric field $\mathbf{E}$. In the *r.h.s.* of equation (14.4) the first term is the dissipated Joule-Lenz heat, the second term is the heat associated with thermoelectric effects, while the third contribution is the thermoconducted heat. Rigorously speaking, for an inhomogeneous sample there may be problems with establishing the thermodynamical equilibrium, so it is appropriate to restrict ourselves to homogeneous samples, as it was said above. For homogeneous samples at equilibrium σ, Q and K are constant, and the conservation of steady charges $div\mathbf{j} = 0$ in neutral conductors, *i.e.* $div\mathbf{E} = -\Delta\varphi = 0$, requires $gradT = const$ from equation (14.1), so the only heat is the dissipated heat j^2/σ. Under these circumstances there is no thermoelectric heat $-T\mathbf{j}gradQ$ and no volume contribution to the thermoconducted heat, $div(KgradT) = 0$; both the thermoelectric heat and the thermoconducted heat are fully transported through the sample. It is also worth noting that equations (14.1) and (14.2) correspond to small $\mathbf{j}$, $\mathbf{E}$, $gradT$ and $\mathbf{q}$; $\mathbf{j}$ and $\mathbf{E}$ are small in comparison with their counterpart on the atomic scale, since they are produced by macroscopic sources. Equations (14.1) and (14.2) should also be viewed as series expansions in $gradT$, which must be small in comparison with T; if not, the second-order contribution in $gradT$, which would lead to non-linear thermoelectrics equations, may imply unphysical temperature gradients, according to material constants, by the same reason of charge conservation. It is also worth stressing the fact that the density of heat per unit time given by equation (14.3) or (14.4) is a second-order effect, such that T in the $QT\mathbf{j}$-term in equation (14.2) must be viewed as the local temperature, and, consequently, position-dependent. This is related to Onsager's symmetry of kinetic coefficients, and ensures the increase in the entropy with time;[3] indeed, the time variation of entropy is easily obtained from equation (14.4) as

$$\partial S/\partial t = -\int d\mathbf{r}\frac{div\mathbf{q}}{T} = \int d\mathbf{r}\cdot[j^2/\sigma T + K(gradT)^2/T^2] > 0 \ , \quad (14.5)$$

and it is worth noting that the fully transported thermoconducted heat does not produce, in fact, entropy, since the volume term in equation (14.5) cancels out the surface contribution (the latter not written in equation (14.5); this assertion can also be verified directly by performing the integral $\int d\mathbf{r}div(KgradT)/T$ with $gradT = const$ and $K = const$). From such a standpoint, corresponding to a perfectly ideal situation, the only source of entropy, and the only true dissipation, is through the Joule-Lenz heat, as expected.

It is therefore appropriate to restrict ourselves to the linear equations of thermoelectricity (14.1) and (14.2) in the sense discussed above, which provide a consistent description of the thermoelectric phenomena in homogeneous samples; they imply also a small heat flow, in comparison with the internal energy of the sample, as expected, and in agreement with the macroscopic nature of the heat flows. Under these circumstances there is no internal (*i.e.* volume) thermoelectric or thermoconducted heat, as remarked before, and the only source of increasing the entropy is the Joule-Lenz dissipation. Nevertheless, in order to preserve some generality, though at the price of possible inconsistencies, it is customary to include the thermoconduction contribution to the increase in entropy in equation (14.5), and, similarly, one may admit localized inhomogeneities for material constants, as appropriate for junctions, for instance. In particular, Q may vary locally, as K may do as well (which does not mean that charge accumulates on, or disappears at junctions, as the normal components of the electric flow are continuous according to the boundary conditions). So, we are led to define the Thomson coefficient $\tau = T(\partial Q/\partial T)$, and get the Thomson thermoelectric heat in equation (14.4)

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[3] L. Onsager, "Reciprocal relations in irreversible processes. I.", Phys. Rev. **37** 405 (1931);"Reciprocal relations in irreversible processes. I.", Phys. Rev. **38** 2265 (1931); H. B. G. Casimir, "On Onsager's principle of microscopic reversibility", Revs. Mod. Phys. **17** 343 (1945); H. B. G. Callen, "The application of Onsager's reciprocal relations to thermoelectric, thermomagnetic, and galvanomagnetic effects", Phys. Rev. **73** 1349 (1948).

$$-T\mathbf{j}gradQ = -T\mathbf{j}(\partial Q/\partial T)gradT = -\tau\mathbf{j}gradT \ , \tag{14.6}$$

per unit time; τ is in fact closely related to Peltier coefficient through $\Delta\tau = -T\partial(\Pi/T)/\partial T$. However, one must be aware, for instance, that negative-valued non-vanishing surface contributions may appear in the entropy variations through a position-dependent Q, which would be unphysical; in fact, the Thomson heat must be viewed as corresponding to Peltier heat, expressed, however, in terms of volume contributions and not as discontinuities at a junction which has a slight spatial extension.

The critical analysis made above is meant to point out the kind of difficulties which may be encountered in practical operation of the thermoelements, as the practitioners are well aware of.

According to the above discussion we limit ourselves to the perfectly ideal situation, where the only volume heat is the dissipated Joule-Lenz heat j^2/σ per unit time and unit volume. This heat may, in principle, be used, as the heat produced by thermoelectric effects. Indeed, in addition, we assume that there is no external electric field, such that $\mathbf{j} = -\sigma QgradT$. Actually, as it is well-known, only half of this amount of heat, at most, may in fact be used in an external electric circuit; however, in principle, the whole amount j^2/σ may be used in an ideal situation where the thermoelement is at the same time both source and user of electricity. The same amount of energy is consumed by the thermoelement for establishing the electric flow; in addition, the thermoconducted heat injected at the hot end of the sample, and integrally recuperated at the cold end, is also a consumed energy; it is given by $KgradT$ from equation (14.4) per unit area of the cross-section and per unit time. It follows that the transformed energy can be written as $j^2/\sigma \cdot lA = Q^2\sigma(\Delta T)^2 \cdot A/l$ per unit time, where l is the length of the sample, A is the area of its cross-section and ΔT is the temperature drop along the sample. Similarly, the consumed thermoconduction heat is $K\left|gradT\right| \cdot A = K\Delta T \cdot A/l$ per unit time. In addition, according to equation (14.2), the Peltier heat $-QTj = Q^2\sigma T\left|gradT\right|$ per unit area of the cross-section and per unit time is also consumed; it can be written as $Q^2\sigma T\left|gradT\right| \cdot A = Q^2\sigma T\Delta T \cdot A/l$. Consequently, one may write down successively the efficiency coefficient

$$\begin{gathered}\eta = \frac{j^2/\sigma \cdot lA}{j^2/\sigma \cdot lA + Q^2\sigma T\left|gradT\right| \cdot A + K\left|gradT\right| \cdot A} = \\ = \frac{Q^2\sigma(\Delta T)^2 \cdot A/l}{Q^2\sigma(\Delta T)^2 \cdot A/l + Q^2\sigma T\Delta T \cdot A/l + K\Delta T \cdot A/l} = \\ = \frac{\Delta T}{\Delta T + T + K/Q^2\sigma} = \frac{\eta_c}{\eta_c + 1/ZT}\end{gathered} \tag{14.7}$$

of this perfect, ideal thermoelectric "machine", where $\eta_c = \Delta T/T$ is the efficiency coefficient of a perfect Carnot engine, and

$$ZT = Q^2\sigma T/(K + Q^2\sigma T) \tag{14.8}$$

is the "figure of merit" of the thermoelement; it can also be written as

$$ZT = \frac{Q^2}{L + Q^2} \quad , \tag{14.9}$$

where $L = K/\sigma T$ is the Lorenz number.[4]

Usually, $Q^2\sigma T/K$ is called "figure of merit",[5] but the definition given by equation (14.8) is more appropriate. From equations (14.8) and (14.9) we can see that ZT can never exceed unity, $ZT < 1$. Since η must be smaller than η_c, *i.e.* $\eta < \eta_c$, it follows also $ZT < 1/(1-\eta_c) = 1/(1-\Delta T/T)$ for any ΔT, which shows again that

$$ZT < 1 \quad . \tag{14.10}$$

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[4] M. Apostol, "Generalized theory of thermoelectric figure of merit", J. Appl. Phys. **104** 053704 (2008).

[5] A. F. Joffe, *Semiconductor thermopower and thermoelectric cooling*, Infosearch Ltd., London (1957).

Accordingly, the maximal value of the efficiency coefficient is $\eta = \eta_c/(1+\eta_c)$, which can never be attained. It is worth noting that, in contrast to the dissipated Joule-Lenz heat, any other amount of heat, like the Thomson heat, or the heat arising from thermoconduction are not utilizable in a thermoelectric thermal engine. It is worth noting that previous works focused on Joffe's definition of the figure of merit $ZT = Q^2\sigma T/K$.

14.2 Pulsed thermoelectricity

A special mechanism of thermoelectric transport is described here, consisting of pulses of charge carriers which "fly" periodically through the external circuit from the hot end of the sample to the cold end, with a determined duration of the "on" and "off" times of the electric contacts, while maintaining continuously the thermal contacts. It is shown that such a "resonant" ideal thermogenerator may work cyclically, with the same efficiency quotient as the ideal efficiency quotient of the thermoelectric devices operated in the usual stationary transport regime, but the electric flow and power are increased, as a consequence of the concentration of the charge carriers on pulses of small spatial extent. The process is reversible, in the sense that it can be operated either as a thermoelectric generator or as an electrothermal cooler.

It is well known that the classical way of operating the thermoelectric circuits consists in establishing small and continuous temperature and voltage gradients along a thermoelectric sample, while maintaining the local thermodynamic equilibrium. The sample is assumed to be homogeneous on the macroscopic scale, as for a stable thermodynamical phase. The physics and technology of the classical thermoelectricity is described in great detail in reference treatises, textbooks or handbooks. The electric flow **j** and the heat flow **q**, *i.e.* the electric charge and the heat flowing across the unit area of the cross-section per unit time, are given by the basic equations of the thermoelectricity

$$\mathbf{j} = \sigma\mathbf{E} - \sigma Q \mathrm{grad} T \tag{14.11}$$

and

$$\mathbf{q} = \varphi\mathbf{j} + QT\mathbf{j} - K grad T \ , \tag{14.12}$$

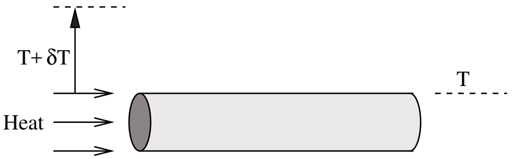

Figure 14.1: Heating a thermoelectric sample.

where σ is the electrical conductivity, $\mathbf{E}$ is the external electric field, Q is the thermopower, T is the temperature, φ is the electric potential ($\mathbf{E} = -grad\varphi$), and K denotes the thermoconductivity. The gradient may be specialized to the x-direction, *i.e.* $grad = \partial/\partial x$. One can see from equation (14.11) that a temperature gradient gives rise to an electric field $\mathbf{E} = -QgradT$, controlled by the Seebeck thermopower coefficient Q; this is the Seebeck effect. By equation (14.12), the continuity of the flows across a junction leads to a released heat $-\Delta Q \cdot T\mathbf{j} = \Pi\mathbf{j} = -\Delta(KgradT)$ per unit time and per unit area of the junction, which is the Peltier effect, and $\Pi = -T\Delta Q$ denotes the Peltier coefficient. One can already notice from equations (14.11) and (14.12) that high values of Q and σ and low values of K are desirable. Unfortunately, high values of electronic properties like σ and Q are usually related to a high K, which lowers the effectiveness of the thermoelectric devices.

There have been long and sustained efforts along the years to improve upon the performances of the thermoelectric devices. Particular emphasis was being given to designing new materials and devices, with high efficiency, engineering functionally graded materials, segmented or cascade devices, or assessing the compatibility of thermoelectric materials. Thermoelectric thin films, nanocomposites and nanostructured materials can enhance the efficiency, presumably by interface reflection of heat (which may not impede upon the electrical conductivity), or by highly-peaked electron density of states, as in low-dimensional materials. The inherent limitations of the classical mode of operating the thermoelectric devices originate in the small, continuous temperature gradient super-imposed along the whole length of the sample. This circumstance brings about both small currents and heat flows, on one hand, and may increase appreciably the risk of heat loss through a spatially-extended dissipation, on the other hand. In particular, the undesired effects of a high thermoconductivity are enhanced by a continuous temperature gradient extending over the whole length of the sample. We put forward here a different mechanism of thermoelectric transport, based on pulses of heat and current, which may circumvent, to some extent, the aforementioned limitations.[6] It leads to high electric pulses "flying" periodically through the external circuit. The objectives of the pulse thermoelectric device are to increase the delivered electric flow and power, by concentrating the charge carriers on pulses of small spatial extent.

14.3 Basic ingredients

Usually, the transport in condensed matter proceeds by quasiparticles. As it is well-known, quasiparticles are elementary excitations possessing velocity (momentum) and a finite lifetime τ. They obey either a Bose-Einstein distribution, like phonons (with a vanishing chemical potential), or a Fermi distribution, as for electron quasiparticles of the Fermi liquid in metals, or Boltzmann's distribution, as for the quasi-classical charge carriers (electrons and holes) in typical semiconductors. We adopt here a simple, general picture of this type of entities. For instance, we may assume that the electron quasiparticles of a Fermi liquid possess the Fermi velocity $\mathbf{v}_F$, while the quasi-classical charge carriers in semiconductors have a mean thermal velocity $\overline{v} = \sqrt{T/m}$, where T is the temperature and m denotes a mean effective mass. It is easy to see (by averaging over the solid angle) that the transport along one direction, say, the positive x-direction, proceeds with a mean transport velocity $v = \overline{v}/2$, or $v = \overline{v}_F/2$, respectively, where $\overline{v}_F$ denotes the average of the Fermi velocity (which may be anisotropic). The mean freepath of the quasiparticles can be represented as $\Lambda = v\tau$.

Under these conditions the local change $\partial n/\partial t + v_0 \partial n/\partial x$ in the quasiparticle density $n(x,t)$ at position x and time t, where v_0 is a transport velocity, is given by the local imbalance $(1/2\tau)[n(x+\Lambda,t)+n(x-\Lambda,t)-$

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[6] M. Apostol and M. Nedelcu, "Pulsed thermoelectricity", J. Appl. Phys. **108** 023702 (2010).

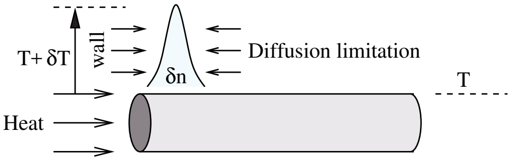

Figure 14.2: Diffusion limits the free transport.

$2n(x,t)]$ in the quasiparticle density,

$$\begin{aligned} \partial n/\partial t + v_0 \partial n/\partial x = (1/2\tau)[n(x+\Lambda,t) + n(x-\Lambda,t) - 2n(x,t)] = \\ = \tfrac{1}{2} v\Lambda \partial^2 n/\partial x^2 \ . \end{aligned} \tag{14.13}$$

This is the well-known diffusion equation. It describes a macroscopic, non-equilibrium transport (in contrast to the local equilibrium transport), for densities varying slowly over large distances and long times in comparison with the quasiparticle mean freepath and lifetime. It may also be generalized to an anisotropic spatial transport, and applied also to fluctuations (with the fluctuating time and length instead of quasiparticle lifetime and mean freepath), describing the approach to equilibrium. In this form, equation (14.13) has been used by Einstein in his classical analysis of the brownian motion.

For an initial δ-condition $n(x,t=0) = V\delta n \delta(x)$, where V is the original volume of the δ-peak and δn is the quasiparticle density in the δ-peak, equation (14.13) has the well-known gaussian solution

$$n(x,t) = \frac{V\delta n}{\sqrt{2\pi v\Lambda t}} e^{-(x-v_0 t)^2/2v\Lambda t} \ . \tag{14.14}$$

The gaussian pulse given by equation (14.14) may move as a whole with the transport velocity v_0, and has a spatial extension

$$l' = \sqrt{v\Lambda t} \tag{14.15}$$

(in one direction). This is taken as the pulse length. As one can see, it goes like the square root of the product of velocity by mean freepath by the duration, as it well konwn. The pulse τ flattens gradually on increasing the time, and vanishes in the limit of an infinite duration; in the opposite limit of a very short time the gaussian pulse reduces to the original δ-pulse, as expected. Indeed, for very short times and distances the diffusion term in equation (14.13) may be neglected, and we are left with the continuity equation whose solution is $V\delta n\delta(x - v_0 t)$ for the original $V\delta n\delta(x)$ peak. The total number of quasiparticles in the gaussian peak is $V\delta n$, and it may be represented as $2l'\overline{\delta n}$ (for a unit area of the cross-section), where $\overline{\delta n}$ is the average quasiparticle density; on the other hand, the maximum value of the density in the gaussian peak is $V\delta n/\sqrt{2\pi}l' = \sqrt{2/\pi}\overline{\delta n}$ from equation (14.14), whence one can see that the maximum value of the quasiparticle density is very close (up to a factor $\sqrt{2/\pi} = 0.8$) to the average quasiparticle density. Therefore, one may take, with a good approximation, $V\delta n$ for the total number of quasiparticles in a gaussian peak, where $V = 2l'$ (for unit area of the cross section) and δn is the maximum value of the quasiparticle density; this is identical with the representation of the δ-pulse, and it holds also for half a gaussian pulse, of course, where $V = l'$.

14.4 Thermal and charge pulses

Let a homogeneous conducting sample of length l and uniform cross-section, at temperature T, be uniformly heated at one end, such as to rise locally its temperature by the small amount δT, as shown in Fig. 14.1. We may neglect the small changes in volume, or pressure, and write $n = f(\mu, T)$ for the concentration n of the quasiparticles at equilibrium, where f is the integral over statistical distributions and μ denotes the chemical potential. As it is well known, for electron quasiparticles in metals $f(\mu, T) = [2/(2\pi\hbar)^3] \int d\mathbf{p} \cdot \{\exp[(\varepsilon - \mu)/T] + 1\}^{-1}$, *i.e.* the Fermi-Dirac distribution, while $f(\mu, T) = [2/(2\pi\hbar)^3] \exp(\mu/T) \cdot \cdot \int d\mathbf{p} \cdot \exp(-\varepsilon/T)$ is the Boltzmann distribution of the charge carriers in semiconductors; $\mathbf{p}$ denotes the quasiparticle momentum and $\varepsilon = \mathbf{p}^2/2m$ is the quasiparticle energy (for a spherical Fermi surface). At constant chemical potential the quasiparticle density changes by $\delta n = (\partial f/\partial T)\delta T$, as a consequence of the change in temperature. This change evolves in time and space according to equation (14.13), so the quasiparticle density is given by the gaussian in equation (14.14) for $\delta n = (\partial f/\partial T)\delta T$. The number of quasiparticles in the gaussian

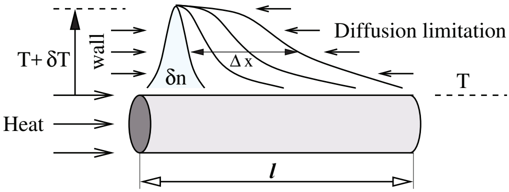

Figure 14.3: Diffusion of a gaussian pulse.

pulse increases in proportion to the extension l' of the pulse ($l' < l$), and, similarly, the temperature drop broadens in the same proportion, by continuously absorbing heat from the external source. It follows that both the quasiparticle density $\delta n(x, t)$ and the temperature drop $\delta T(x, t)$ can be represented by a gaussian of the form given by equation (14.12). The motion of the pulse as a whole is blocked in one direction by the sample end-wall, where the quasiparticles are continuously reflected, while its motion in the opposite direction along the sample is limited by diffusion; along this direction the pulse only broadens gradually by diffusion, which is a much slower process than the transport motion. Consequently, the pulse is in fact half of a gaussian pulse with its peak on the very hot end of the sample. Such a gaussian pulse is shown in Fig. 14.2.

Everywhere in this chapter we use, for the sake of the numerical illustration, a set of typical values for the basic physical quantities. For instance, we take the density $n = 10^{22}cm^{-3}$ for electrons in metals and the chemical potential $\mu = 1eV$. We take $v = 10^5 m/s$ for the Fermi velocity and $\Lambda = 10^3$Å for the electron mean freepath (at room temperature). We denote by $t' = \tau_{off}$ the time t in equation (14.15) needed to build up the pulse. From equation (14.15) we get $l^{'} = 10^5 \tau_{off}^{1/2} \mu m$ $(microns)$ for the spatial extension of the pulse, which is much smaller than the sample length l for sufficiently small τ_{off}. Its limiting value is of the order of the mean freepath Λ. For instance, for $\tau_{off} = 10^{-6}s$ we get $l' = 100\mu m$. For semiconductors we take $n = 10^{17}cm^{-3}$ as a typical value, corresponding to a chemical potential given by $\mu/T \simeq -5.7$ (this is easily derived from the Boltzmann distribution given above). In semiconductors we use $v = 10^4 m/s$ for velocity and $\Lambda = 10^2$Å (at room temperature) for the mean freepath. The spatial extent of the pulse is given by equation (14.15) as $l' = 10^4 \tau_{off}^{1/2} \mu m$. For $\tau_{off} = 10^{-6} s$ the spatial extent is $l' = 10 \mu m$. All these are typical figures for metals and semiconductors, which we use here in order to illustrate numerical estimations.

14.5 Heat and electric flows

A thermal pulse needs a build-up time t', according to $l' = \sqrt{v\Lambda t'}$, hence $t' = l'^2/v\Lambda$. During this time a heat flow (heat per unit area of the cross-section and per unit time) $q = cl'\delta T/t' = cv\Lambda(\delta T/l')$ is absorbed, where c is the heat capacity per unit volume; this heat flow may be represented as $\mathbf{q} = -cv\Lambda gradT = -KgradT$, where $K = cv\Lambda$ is a well-known representation for the thermoconductivity. Similarly, one can say that the heat flux (heat per unit area of the cross-section) absorbed by a gaussian pulse of extension l' is $\delta E = (Kl'/v\Lambda)\delta T$. In the limit of the δ-pulses, whose spatial extension is of the order of the mean freepath Λ, it reduces to $\delta E = (K/v)\delta T$, and one can see, as expected, that the heat absorbed by a pulse is proportional to its extension. In the opposite limit of a pulse as broad as the length of the sample, *i.e.* $l' = l$, the stationary transport regime starts to set up, where a small, uniform, continuous gradient of quasiparticle density and temperature extends over the whole length of the sample. This is valid for both charge carriers and phonons; the phonon thermoconductivity (as well as the thermoconductivity of other quasiparticles) must be added to the thermoconductivity K of the charge carriers given above. The diffusion of a gaussian pulse is shown in Fig. 14.3, the stationary transport is shown schematically in Fig. 14.4, and the pulse used in the pulsed mode of operation is shown in Fig. 14.5. For our models of metals and semiconductors used here (defined by the statistical distributions given above) it is easy to derive the heat capacity c and the thermoconductivity K. Although these expressions are not relevant for the subsequent discussion we note them here for the sake of a more detailed information. The heat capacity per unit volume is $c = \pi^2 nT/2\mu$ for metals (Fermi liquids) and $c = (3/2)(5/2 - \mu/T)n$ for semiconductors. The thermoconductivity can be represented as $K = \pi^2 nv\Lambda T/2\mu$ for metals and $K = (5n\Lambda T/2mv)(7/2 - \mu/T)$ for semiconductors. These expressions agree with $K = cv\Lambda$ up to some

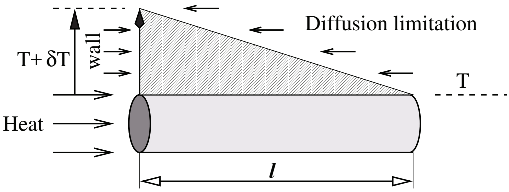

Figure 14.4: Stationary regime.

minor numerical factors.

The heat δE absorbed by the pulse is its internal thermal energy, due to the thermal excitations of the quasiparticles. For instance, it is due to the particle-hole excitations of the electron quasiparticles in a Fermi liquid. Apart from this energy, the electron quasiparticles in a pulse possess also single-particle energy, arising from the change in the chemical potential. Indeed, in order to preserve the charge neutrality of the sample, a change $(\partial f/\partial\mu)\delta\mu$ occurs in the quasiparticle density at the cold end of the sample, such as $(\partial f/\partial T)\delta T + (\partial f/\partial\mu)\delta\mu = 0$; it follows that a voltage drop U appears at the hot end of the sample, with respect to the rest of the sample, such as $-eU = -\delta\mu$, or

$$U = -\frac{1}{e}[(\partial f/\partial T)/(\partial f/\partial\mu)]\delta T = Q\delta T \qquad (14.16)$$

where $-e$ is the electron charge and $Q = -(1/e)[(\partial f/\partial T)/(\partial f/\partial\mu)]$ is the well-known Seebeck thermopower coefficient. One can see easily that Q acquires negative values for electrons. The voltage U has the same spatial dependence as the temperature drop and the quasiparticle density, *i.e.* the gaussian given by equation (14.14). Again, making use of the statistical distribution functions, it is easy to compute the thermopower. For metals $Q = -(\pi^2/6e)(T/\mu)$, while for semiconductors $Q = -(1/e)(3/2 - \mu/T)$. One can see easily that the thermopower coefficient Q is much higher for semiconductors than for metals, as it is well known (typical values for semiconductors are of the order of $200\mu V/K$).

The voltage U corresponds to an electric field $-gradU = -QgradT$, and therefore an electric flow (charge per unit area of the cross section and unit time) occurs inside the pulse, given by $\mathbf{j} = -\sigma QgradT$,

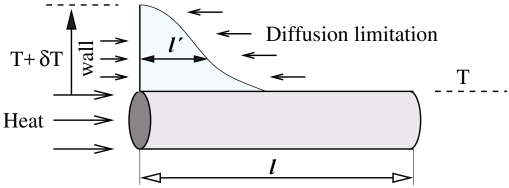

Figure 14.5: A thermoelectric gaussian half-pulse.

where σ denotes the electrical conductivity; this is a well-known basic equation of the thermoelectricity (in the absence of external electric fields). It is worth noting the opposite flow of the electrons with respect to the temperature gradient as well as the high current density for pulses due to $gradT = \delta T/l'$ (not $\delta T/l$; $l' \ll l$).

It is also worth noting that j is the electric flow inside the pulse, as given by the microscopic transport of the charge carriers. It can also be written as

$$j = -ev[\delta n(x) - \delta n(x + \delta x)] = ev\Lambda(\partial f/\partial T)(\partial T/\partial x) \ , \qquad (14.17)$$

hence the electrical conductivity

$$\sigma = -ev\Lambda(\partial f/\partial T)/Q = e^2 v\Lambda(\partial f/\partial \mu) \ . \qquad (14.18)$$

This is a well-known representation for the electrical conductivity, where $\partial f/\partial \mu \sim n/mv^2$. Making use of the statistical distributions given above, we get $\sigma = 3e^2 nv\Lambda/2\mu$ for metals and $\sigma = e^2 nv\Lambda/mv^2$ for semiconductors. Using the thermoconductivities computed above, we can obtain the Lorentz number defined as $L = K/\sigma T$. It is given by $L = \pi^2/3e^2$ for metals and $L = (5/2e^2)(7/2 - \mu/T)$ for semiconductors, as it is well known.

The electric power per unit volume is given by $-gradU \cdot \mathbf{j} = -QgradT \cdot \mathbf{j} = j^2/\sigma$, which is the Joule-Lenz dissipated heat. Indeed, a voltage drop $U = Q\delta T$ implies an electric potential $\varphi = QT$, and therefore a heat flow $\mathbf{q} = QT\mathbf{j}$; this is the Peltier heat, electrically transported (or the electrothermal Peltier heat), which is included in the basic equation (14.12) of the thermoelectricity ($\mathbf{q} = QT\mathbf{j} - KgradT$). From $q = QTj$ one gets easily the dissipated heat per unit volume and unit

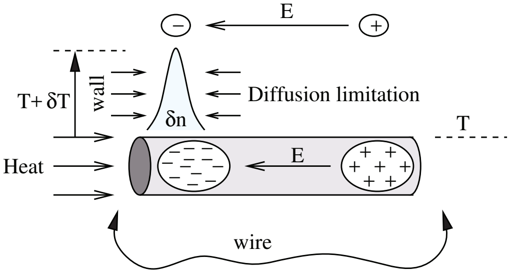

Figure 14.6: Pulse and the thermoelectric "condenser".

time $-\partial q/\partial x = -Qj(\partial T/\partial x) = j^2/\sigma$, *i.e.* the Joule-Lenz dissipated heat. The Peltier heat $q = QTj$ is worth to be noted: if we are going to get high currents in the pulsed transport, we get a high Peltier cooling by reversing the mode of operation.

The electric power of a pulse of extension l' is therefore $j^2/\sigma \cdot l' = Uj = -\sigma Q^2 \delta T(\partial T/\partial x)$ (per unit area of the cross-section). The efficiency quotient of such a thermoelectric pulse is obtained by dividing the electric power $j^2/\sigma \cdot l' = -\sigma Q^2 \delta T(\partial T/\partial x)$ to the sum of this electric power, the Peltier heat QTj and the thermoconducted heat $-K(\partial T/\partial x)$, using $j = -\sigma Q gradT$ and dividing both the numerator and the denominator by $\sigma Q^2 T(\partial T/\partial x)$. The result was obtained above. We get straightforwardly

$$\eta = \frac{j^2/\sigma \cdot l'}{j^2/\sigma \cdot l' + QTj - K(\partial T/\partial x)} = \frac{\eta_c}{\eta_c + 1 + K/Q^2\sigma T} \ , \qquad (14.19)$$

where $\eta_c = \delta T/T$ is the Carnot efficiency quotient and $L = K/\sigma T$ is the Lorenz number.

The efficiency quotient can also be written as $\eta = \eta_c/(\eta_c + 1/ZT)$, where $ZT = Q^2/(L + Q^2)$ is a "figure of merit". This generalized "figure of merit" has been recently discussed in a broader context of thermoelectric transport. One can see that the "figure of merit" introduced here can never exceed unity, and it is related to the usual "figure of merit" $ZT' = Q^2/L$ by $ZT = ZT'/(1 + ZT')$. Since $L = \pi^2/3e^2$ and $Q = -(\pi^2/6e)(T/\mu)$ for the electron quasiparticles in metals, we have $L \gg Q^2$, and ZT reduces to ZT'; as it is well known the efficiency quotient is very low in this case. On the contrary, for electrons in typical semiconductors one obtains $L = (5/2e^2)(7/2 - \mu/T)$ and $Q = -(1/e)(3/2 - \mu/T)$, as noted above, so that L and Q^2 are comparable; for large values of the ratio $-\mu/T$ the "figure of merit" ZT approaches unity, and the efficiency quotient is increased. On the other hand, however, the Joule-Lenz heat is drastically diminished, as a consequence of the low electrical conductivity of the dilute gas of charge carriers in typical semiconductors, as it is also well known.

It is worth noting that the efficiency quotient derived above for pulses is the same as for an ideal stationary thermoelectric transport.

14.6 Thermoelectricity of pulses

The efficiency quotient, as well as the electric flow, the electric power, and the basic equations of the thermoelectricity are derived above for the internal, microscopic transport inside pulses. As expected, they agree (are practically identical) with the corresponding quantities of the classical, stationary transport, where a small, uniform, continuous gradient of temperature and quasiparticle density extends over the whole length of the sample. One can also say that this microscopic transport holds for pulses at rest. It is easy to see however that these equations hold also for the macroscopic pulse-like transport as well, whereby a pulse is viewed as a whole. Indeed, the electric flow of such a pulse is given by

$$j = -e\delta n l'/t' = -ev\Lambda\delta n/l' = -ev\Lambda(\partial f/\partial T)\delta T/l' \ , \tag{14.20}$$

and one can see that it is identical with the electric flow of the microscopic transport as given by equation (14.17). Such an electric pulse dissipates gradually the Joule-Lenz heat $-e\delta n l' Q\delta T$ (per unit area of the cross-section); it is easy to see, by making use of equations (14.16) and (14.18), that the Joule-Lenz heat can also be written as

$$-e\delta n l' Q\delta T = (j^2/\sigma)(l'^3/v\Lambda) \ , \tag{14.21}$$

where the electric flow is given by equation (14.20); hence, making use of equation (14.15), the electric power of the pulse is

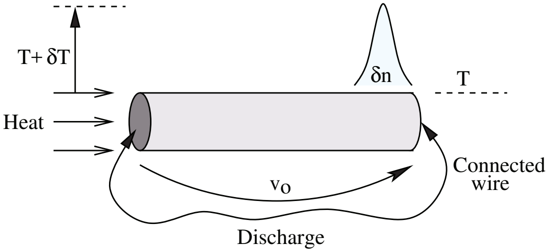

Figure 14.7: Discharge of the "condenser".

$$P = j^2/\sigma \cdot l' \tag{14.22}$$

(per unit area of the cross-section), as for the microscopic transport used in equation (14.19). Similarly, the flow of the Peltier heat is QTj and the flow of the thermoconducted heat is $K\delta T/l' = -K(\partial T/\partial x)$, so the efficiency quotient of the pulse-like transport is the same as that given by equation (14.19) for the microscopic transport, as expected. All these flows, as well as the electric power, last for a time t', *i.e.* the time during which the pulse is built up at the hot end of the sample. In addition, the pulse contains also its internal heat $\delta E = cl'\delta T$. It is worth emphasizing that the electric flow of the pulse-like transport, as given either by equation (14.17) or equation (14.20), can also be written as

$$j = j_s(l/l') \ , \tag{14.23}$$

where j_s corresponds to the electric flow in the stationary transport, *i.e.* to the pulse extending over the whole length of the sample ($l' = l$). One can see that the electric flow is increased in the pulse-like transport by the ratio l/l' of the sample length to the pulse extension, as expected. This increase originates in the concentration of the charge carriers on small spatial extensions of narrow pulses. Similarly, the dissipated Joule-Lenz heat per unit area of the cross-section and per time, *i.e.* the flow of electric power as given by equation (14.22), can be written as

$$P = P_s(l/l') \ , \tag{14.24}$$

i.e. the electric power produced by the pulse transport is higher, by the same factor l/l', than the corresponding electric power delivered in the stationary transport. It is easy to see that the stationary power $P_s = j_s^2/\sigma \cdot l$ (per unit area of the cross-section) can also be written as $P_s = \sigma U^2/l$, which is $P_s = U^2/r$, where r is the internal electric resistance, as expected.

14.7 "Flying" pulses

A thermoelectric sample with a charge pulse built up at the hot end evokes an electric "condenser", and, like any other "condenser", such a "thermoelectric condenser" can be "discharged" by switching on the electric contacts to the external circuit. Under these circumstances the (ideal) sample end-wall does not block anymore the motion of the charge carriers, and the pulse "flies" through the external circuit as a whole, with the transport velocity $v_0 = v$, according to equations (14.13) and (14.14). This is a macroscopic, non-stationary, fast, pulsed-like transport, taking place in the transient regime prior to establishing the extension of the pulse along the whole length of the sample. In order to allow a smooth "fly", the cross-section of the external circuit must be equal to, or greater than, the cross-section of the sample (and, of course, the contacts are assumed to be perfect). The "flying" of the pulse through the external circuit of length l_e takes an on-time $\tau_{on} = l_e/v$. On the other side, the time t' needed to build up a pulse at the hot end of the sample is an off-time, $\tau_{off} = t'$. In addition, it is worth noting that such a "flying" pulse does not obey Ohm's law, as the transport is discontinuous. The electric charge is conserved, so the external (local) electric flow is

$$\begin{aligned} j_e &= -e\delta n l'/(l'/v) = -ev\delta n = \\ &= j(t'/l')v = j(\tau_{off}/\tau_{on})(l_e/l') \ , \end{aligned} \tag{14.25}$$

where equation (14.20) has been used. The energy is conserved, *i.e.* the electric energy $E_{el} = -e\delta n l' Q\delta T$ (per unit area of the cross-section) as given by equation (14.21) is the energy delivered into the external circuit. The (discontinuous) power delivered into the external circuit is $E_{el}/(l'/v) = (\tau_{off}/\tau_{on})(ll_e/l'^2)P_s$, where equation

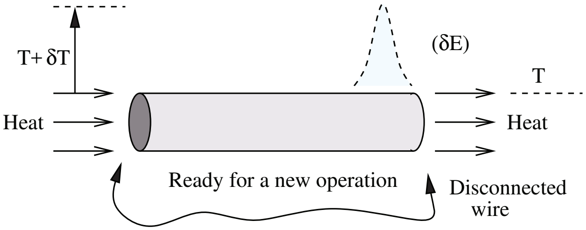

Figure 14.8: Deflating the pulse, ready for another operation.

(14.24) has been used. It is less relevant; less relevant also is the external power averaged over the on-time, $E_{el}/\tau_{on} = (\tau_{off}/\tau_{on})(l/l')P_s$. While "flying" through the external circuit the pulse dissipates gradually the Joule-Lenz heat E_{el}, and gives away the Peltier heat (the Peltier heat is transported from the hot junction to the cold one), until it reaches the cold end of the sample and compensates the positive ionic charges there. After completing its "flight" through the external circuit the pulse is left with its internal heat $\delta E = cl'\delta T$, and it must be "deflated" of this internal energy in order to have a cyclic process. The time needed to extract this amount of heat is $t' = \tau_{off}$, *i.e.* precisely the time during which an identical pulse is built up at the hot end of the sample, such that, after this duration, the thermoelectric sample is ready for another operation. It follows that the thermal contacts should be maintained continuously during the operation of such a pulsed-like transport, while the electric contacts must be switched off once the pulse arrived at the cold end of the sample; otherwise, the pulse would move continuously through the entire circuit and the stationary regime would set up. Therefore, the electric contacts must be switched on and off periodically, with a certain frequency $f = 1/(\tau_{off} + \tau_{on})$, where $\tau_{on} = l_e/v$, and a certain duration of the on- and off- times. The building of the pulse at the hot end is shown in Fig. 14.6, the flying pulse is shown in Fig. 14.7 and the deflation of the pulse at the cold end is shown in Fig. 14.8.

As it was said above, the on-time is the "flight" time $\tau_{on} = l_e/v$ of the pulse through the external circuit, where l_e is the length of the external circuit. The off-time, or the waiting time, is the time $t' = l'^2/v\Lambda$ needed for building up a pulse of length l' at the hot end

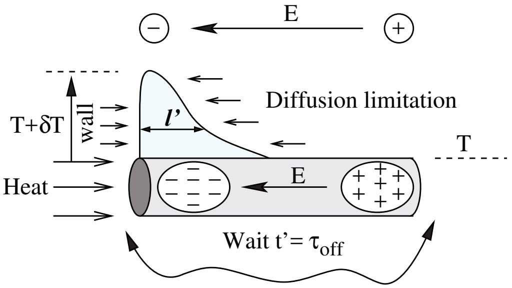

Figure 14.9: Building up a gaussian pulse in a thermoelectric "condenser".

of the sample (and for "deflating" a similar pulse of its internal heat at the cold end of the sample). The operating frequency is therefore $f = 1/(\tau_{on} + \tau_{off}) = v/(l_e + l'^2/\Lambda)$, and it ranges between $f_0 = v/(l_e + \Lambda) \simeq v/l_e$, corresponding to δ-pulses, and $f_1 = v/(l_e + l^2/\Lambda)$, for pulses extending over the whole length l of the sample, where the stationary transport regime begins to set up. For reasonable values of l_e, the ratios $l^2/\Lambda l_e$ and $l'^2/\Lambda l_e$ acquire large values, so that one may write $f = v\Lambda/l'^2 = f_1(l/l')^2$, *i.e.* the operating frequency is quadratic in the ratio l/l' of the sample length l to the pulse extension l'. This corresponds to very short on-times τ_{on} in comparison with the off-times $\tau_{off} = t'$, and to pulses of large extension l'. For $\tau_{on} \geq t'$, *i.e.* $l_e \geq l'^2/\Lambda$ the extension of the pulses starts to become microscopic. It is worth noting that during the on-time the sample is not at local equilibrium, and additional elastic waves may be excited inside the sample, which takes over the heat excess, allowing thus the flowing of heat. In addition, the phonon thermoconduction may be present in the sample, as well as the heat thermoconducted by other elementary excitations, which may tend to establish in fact a small, uniform, continuous gradient of temperature along the sample. However, this local-equilibrium regime bears no relevance upon the pulses of the charge carriers as described herein, because the latter are not at local equilibrium, and are practically decoupled from the rest of the sample.

14.8 Power in external circuit

The Joule-Lenz heat E_{el} as given by equation (14.21) is the total energy (per unit area of the cross-section) dissipated by a pulse during its "flight". Consequently, the average power produced in such a pulsed transport cyclically operated is given by

$$\overline{P} = (j^2/\sigma)(l'^3/v\Lambda) \cdot \frac{1}{\tau_{on} + \tau_{off}} = P_s(l/l') \cdot \frac{1}{1 + \Lambda l_e/l'^2} \ , \qquad (14.26)$$

where equations (14.23) and (14.24) have been used. One can see that for macroscopic pulses, corresponding to short on-times, *i.e.* for $\Lambda l_e/l'^2 \ll 1$, the average power is practically identical with the pulse power given by equation (14.24), $\overline{P} = P = P_s(l/l')$, *i.e.* it is increased by the factor l/l'. In this case, the operating frequency $f = f_1(l/l')^2$ given above is proportional to the square of the electric power, *i.e.* $f \sim P^2$. In the opposite limit however, corresponding to microscopic pulses of extension Λ, the increase factor is controlled by the ratio l/l_e of the sample length to the length of the external circuit (which may be higher than unity very well). In both cases the average power is increased in comparison with the equilibrium-operated thermoelements. The maximum value of the average power is obtained for $l' = \sqrt{\Lambda l_e}$, *i.e.* just for the border between microscopic and macroscopic pulses, as defined before. It is given by

$$\overline{P}^{max} = \frac{1}{2}\frac{l}{\sqrt{\Lambda l_e}} P_s \ ; \qquad (14.27)$$

it corresponds to an optimal $\tau_{off} = l_e/v = \tau_{on}$ (ratio $\tau_{on}/\tau_{off} = 1$) and an optimal frequency $f = v/2l_e$. It is, perhaps, more convenient to refer the power to the maximal power $P_{dc} = U^2/4r = P_s/4$, corresponding to a load electric resistance equal to the internal resistance in a stationary operating regime (drift current). One obtains therefore $\overline{P}^{max} = 2(l/\sqrt{\Lambda l_e})P_{dc}$. The optimal power in the pulsed-operating regime as given by equation (14.27) is much higher than the stationary power.

The external power given by equation (14.26) can also be written as

$$\overline{P} = P_s(l/l') \cdot \frac{\tau_{off}}{\tau_{on} + \tau_{off}} = \frac{l}{\sqrt{v\Lambda}} \sqrt{f(1 - \tau_{on} f)} P_s \ , \qquad (14.28)$$

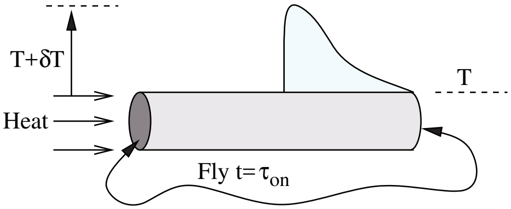

Figure 14.10: Discharging a gaussian pulse in the thermoelectric "condenser".

where $\tau_{on} = l_e/v$ and $(1 + l^2/\Lambda l_e)^{-1} < \tau_{on} f < (1 + \Lambda/l_e)^{-1}$. It has a maximum value at the optimal frequency $f = 1/2\tau_{on}$ given before, and a characteristic frequency dependence. Making use of $\tau_{on} = l_e/v$ equation (14.28) gives also a characteristic dependence of the external power on the load resistance $\sim l_e$.

The pulsed-operating mode of the thermoelectric transport is shown in Figs. 14.9-14.11.

Finally, we give here some numerical estimates. For typical values $n = 10^{22} cm^{-3}$, $\mu = 1eV$ and $v = 10^5 m/s$ in metals, and for room temperature $T = 300K$ and $\delta T = 100K$ one obtains a δ-pulse electric flow $j \simeq 10^7 \mathrm{A/cm}^2$, according to equation (14.20). Indeed, it is easy to see, making use of the Fermi-Dirac distribution, that the variation in the charge density is given by $\delta n = (\pi^2/4)(nT\delta T/\mu^2)$. Making use of a typical mean freepath value $\Lambda = 10^3 \mathring{A}$ one obtains a stationary flow $j_s \simeq 10^3 A/cm^2$ for a sample length $l = 1mm$. The voltage is $U \simeq 4 \times 10^{-4} V$ (thermopower coefficient $Q = -(\pi^2/6e)(T/\mu) \simeq 4 \times 10^{-6} V/K$). The electric power of the pulse is therefore $P \simeq 4kw/cm^2$, in comparison with the stationary power $P_s \simeq 0.4w/cm^2$, which implies a factor 10^4. For an optimal pulse length $l' = l/10$ the current is $\underline{j} = 10^4 A/cm^2$, the power is $P \simeq 4w/cm^2$ and the maximal power is $\overline{P}^{max} \sim 2w/cm^2$ for an operating frequency $f \simeq 500kHz$, with a very short on-time ($\tau_{on} \simeq 10^{-6}s$ and $l_e = 10cm$). This implies an increase factor 5 in comparison with the stationary regime ($P_s \simeq 0.4w/cm^2$).

For electrons in semiconductors we may take $n = 10^{17} cm^{-3}$ and $v = 10^4 m/s$ as an illustrative example; one obtains $\mu/T = -5.7$ ($\mu/T =$

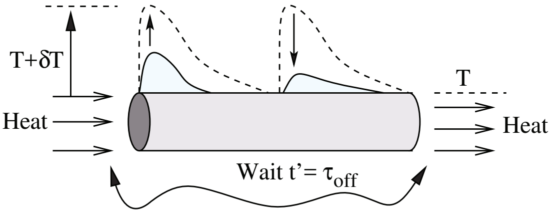

Figure 14.11: Deflating the pulse while building up another.

$\ln[n(2\pi\hbar^2/mT)^{3/2}/2]$ from the Boltzmann distribution,) and an electric flow $j \simeq 4 \cdot 10^4 A/cm^2$ for a δ-pulse ($\delta n = n(3/2 - \mu/T)\delta T/T$, similarly, from the Boltzmann distribution), for the same temperature values as those used above; the voltage is $U \simeq 6 \times 10^{-2} V$ ($Q \simeq 6 \times 10^{-4} V/K$), and the electric power $P \simeq 2.4 kw/cm^2$. For a mean freepath $\Lambda = 100\text{Å}$ one obtains $j_s \simeq 0.4 A/cm^2$ for a sample length $l = 1mm$ and a stationary power $P_s \simeq 2.4 \times 10^{-2} w/cm^2$. The increase factor is 10^5. For a pulse of optimal extension $l' = l/30$, the operating frequency is approximately $f \simeq 50kHz$, the current is $j = 12A/cm^2$, the electric power $P \simeq 0.72 w/cm^2$, and the maximal power is $\overline{P}^{max} \sim 0.36 w/cm^2$; the on-time is $\tau_{on} \simeq 10^{-5} s$ (for $l_e = 10cm$). Comparing $\overline{P}^{max} \sim 0.36 w/cm^2$ with $P_s \simeq 2.4 \times 10^{-2} w/cm^2$ we can see an increase factor 15.

14.9 Conclusions

In conclusion, a mechanism of thermoelectric transport has been described here, which proceeds by pulses of charge carriers. It is a macroscopic, cyclic, non-stationary, fast, transient transport regime, which may diminish the effects of a spatially-extended thermal diffusion. This pulsed-like transport regime is operated by periodically switching on and off the electric contacts, while maintaining continuously the thermal contacts. The operating frequency is determined, as well as the on- and off-times, as functions of the nature of the sample, the extension of the pulses and the length of the external circuit. The electric flow and the power are higher for pulsed-like transport than for stationary, classical transport, as a consequence of concentrating the charge carriers on pulses of small spatial extent. Such a pulsed-like transport may be operated cyclically, with an ideal efficiency quotient equal with the ideal efficiency quotient of the stationary transport. It may open the possibility of a practical realization of a high-power thermoelectric converter. High values of thermopower Q and conductivity σ are desirable, but low values of thermoconductivity K are not critical.

Of course, the pulsed transport described here is an ideal process, intended to illustrate the physical principles of another type of thermoelectric transport. As regards practical purposes, there are several technical issues which must be addressed, in order to get the increasing performance of this type of thermoelectric transport. Among these, we may say that the contacts, both electric and thermal, must be as good as possible, in order to minimize the loss. In this respect, although the ideal efficiency coefficient of the pulsed transport is equal to the ideal efficiency coefficient of the stationary, continuous regime, the technical efficiency may be increased for the former, because the pulsed transport reduces the risk of heat loss due to spatially-extended dissipation along the whole length of the sample. Another important issue related to the pulsed transport is the extraction of the electric energy delivered into the external circuit. At high frequencies, the transport proceeds mainly by impedance, and most of the energy may reside in the electromagnetic field of the reactances, so the usual Joule-Lenz effect is diminished, in fact. Finally, one may also note that the material parameters which usually decrease the efficiency of a classical thermoelement are not critical anymore for a pulsed transport, so we may, therefore, be open to employing new classes of thermoelectric materials in pulsed transport.

15 Liquids

15.1 Introduction

The liquids discussed herein are represented as correlated ensembles of particles, moving around and interacting with strong, short-range forces. A spectrum of local vibrations is introduced for the local, collective movements of particles in such model liquids. The resulting statistics is formally equivalent with that of an ideal gas of bosons in two dimensions, which in turn, as it is well-known, leads to a thermodynamics which is equivalent to that of an ideal gas of fermions in two dimensions. The parameters used for describing the statistics of the model are the cohesion energy per particle, the spacing between the energy levels of local vibrations and a constraining volume. The corresponding thermodynamics is derived, with explicit emphasis on both low- and high-temperature regimes. The condensation occurring in the low-temperature limit is discussed.

15.2 Local vibrations

Let us consider an ensemble of particles moving around and interacting strongly with short-range forces. The motion of the particles is highly correlated over short distances, in the sense that the movement of a particle entails appreciable movements of the neighbouring particles. The local character of the short-range, strong forces and the high correlations involved have special consequences on the particle motion. First, the particle movements are collective, so they may imply comparatively small amounts of energy, in contrast to highly-localized movements. Next, the correlated particle movements are local. In addition, the strong character of the interaction gives rise to a cohesion energy $-\varepsilon_0 < 0$, in the sense that one needs to spend such an amount of energy in order to take a particle out of the ensemble. The role played by the strong interactions and short-range correlations in such ensembles of particles has been previously emphasized.[1]

The short-range correlations reduce the number of available spatial states of particles moving in volume V of the liquid. The motion of each particle is restricted by its neigbouring particles. These short-range correlated configurations of particles are identified by their distinct positions in space. It is convenient to associate a volume b to each of such local particle configurations, such that the total number of available spatial states is V/b and the corresponding density of states can be written as dV/b. In view of the short-range character of these local correlations, the constraining volume b is, typically, of the order of a^3, where a is the mean inter-particle distance.

The energy of an ensemble of interacting particles in equilibrium depends on this mean inter-particle distance a. An energy $\varepsilon(a)$ may, therefore, be assigned to each particle, such as the total energy can be written as $N\varepsilon(a)$, where N is the number of particles. This energy depends on the nature of the liquid, *i.e.* on the forces acting between the particles, on their mass, etc. In order to identify the possible movements of particles, one may allow small deviations δa of the mean inter-particle distance from its equilibrium value a and write down a series expansion of $\varepsilon(a)$ in powers of δa. Such a series expansion reads

$$\varepsilon = -\varepsilon_0 + A(\delta a)^2 + ... \ , \tag{15.1}$$

where A is an expansion coefficient. The first power in δa is missing in equation (15.1), as for an expansion about the equilibrium. Equation (15.1) suggests that the local spectrum of energy in such a model liquid is a spectrum of vibrations with one degree of freedom. Higher-order terms may be included in the expansion (15.1), as corresponding to anharmonic vibrations. The local, short-range correlations make the vibration spectra given by equation (15.1) to be independent for each local particle configuration, in the sense that these vibrations are not coupled to each other for various particle configurations. At the same time, these vibrations do not correspond to individual particles, but to local particle configurations. Correspondingly, they represent collective movements, extended over relatively short distances, and the expansion coefficient in equation (15.1) may correspond to vibration frequencies (and energies) much lower than the frequencies of a highly-localized particle. The dynamics of the present model liquid is therefore represented by local particle configurations, labelled by distinct positions in space, moving around over a restricted number of spatial states and vibrating locally according to the vibration spectrum given by equation (15.1). These particle configurations can be viewed as elementary excitations of the model liquid.

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[1] J. E. Lennard-Jones and A. F. Devonshire, "Critical phenomena in gases. I", Proc. Roy. Soc. (London) **A163** 53 (1937); "Critical phenomena in gases. II. Vapour pressures and boiling points", Proc. Roy. Soc. (London) **A165** 1 (1938); J. de Boer, "Theories of the liquid state", Proc. Roy. Soc. (London) **A215** 4 (1952); "Cell-cluster theory for the liquid state I", Physica **20** 655 (1954); J. G. Kirkwood,"Statistical mechanics of fluid mixtures", J. Chem. Phys. **3** 300 (1935); M. Born and H. S. Green, "A general kinetic theory of liquids I. The molecular distribution functions", Proc. Roy. Soc. (London) **A188** 10 (1946); J. Frenkel, *Kinetic Theory of Liquids*, Dover, NY (1955).

The spectrum given by equation (15.1) corresponds to an isotropic liquid, where local vibrations do not depend on direction. More particular assumptions can be employed. Specifically, the range of the correlations may be extended, or the anisotropies may be taken into account, or anharmonicities may be included, etc; the local vibrations considered here include longitudinal phonons; transverse phonons are present in liquids, for limited wavevectors.[2] The discussion herein is limited to the most simple spectrum as the one described by equation (15.1), corresponding to a set of independent harmonic oscillators with one degree of freedom. The corresponding energy levels are therefore given by[3]

$$\varepsilon = -\varepsilon_0 + \varepsilon_1(n + 1/2) \ , \tag{15.2}$$

where $n = 0, 1, 2, ...$ is the quantum number of vibrations and $\varepsilon_1$is the spacing between the energy levels. Both parameters ε_0 and ε_1 in equation (15.2) depend on a. For a continuum spectrum the dependence of ε_1 on a may be neglected.

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[2] J. Frenkel, *Kinetic Theory of Liquids*, Dover, NY (1955).

[3] M. Apostol, "A model for the thermodynamics of simple liquids", Physica **B403** 3946 (2008).

15.3 Statistics

The next step is to set up the statistics for such a model, in order to establish its thermal properties. The vibration spectrum given by equation (15.2) corresponds to a Bose-Einstein type of statistics. It is associated with each local particle configuration, these configurations being labelled by distinct positions in space. Since these positions are different, and since the vibration spectrum given by equation (15.2) corresponds to a collective motion, it follows that the Bose-Einstein statistics, as defined by the energy spectrum (15.2) and by the motion of the vibrating configurations among distinct positions in space, does not depend on the particular fermionic or bosonic character of the constitutive particles of the liquid. It holds therefore for ensembles of particles, irrespective of the fermionic or bosonic character of the underlying particles in the ensemble. This is a consequence of the assumption of strong interaction and collective and correlated movements. As mentioned above, the quanta of the vibration spectrum given by equation (15.2) associated with the particle configurations moving around through the liquid may be viewed as the elementary excitations of such liquids.

Since the vibration spectrum given by (15.2) associates one degree of freedom to each particle, through the mean inter-particle spacing a, it follows that the mean occupation number of vibrations of each particle configuration is determined by the size of these configurations. Therefore, the Bose-Einstein statistics has a determined chemical potential μ and, for a continuum spectrum of energy with density $d\varepsilon/\varepsilon_1$, the number of particles can be written as

$$N = \frac{V}{b\varepsilon_1}\int_0^\infty d\varepsilon \frac{1}{z\exp(\beta\varepsilon)-1} \ , \tag{15.3}$$

where $\beta = 1/T$ is the inverse of temperature T and $z = \exp[-\beta(\mu + \varepsilon_0)]$ is the inverse of the fugacity. The particle concentration is written as $c = N/V = 1/a^3$. The continuum-spectrum approximation is valid for $T \gg \varepsilon_1$. The degeneracy associated with the energy levels given by equation (15.2), as naturally arising from various particle movements in space, is incorporated in the spatial density of states dV/b.

The statistics given by equation (15.3) corresponds to an ideal gas of bosons in two dimensions. It is well-known that it is equivalent with the statistics of an ideal gas of fermions in two dimensions,[4] as expected from its applicability, irrespective of the fermionic or bosonic character of the constitutive particles, as noted above.

Equation (15.3) requires $z > 1$, *i.e.* $\mu + \varepsilon_0 < 0$. With decreasing temperature the integral in equation (15.3) decreases, so that $\mu + \varepsilon_0$ increases, in order to satisfy this equation. For the limiting value $\mu + \varepsilon_0 = 0$ ($z = 1$) the integral in equation (15.3) has a logarithmic singularity at $\varepsilon = 0$, so it is divergent, in contrast to the three-dimensional case. Consequently, there is no critical temperature corresponding to a Bose-Einstein condensation in two dimensions, as it is well-known. However, a continuous, gradual condensation on the zero-point vibration level occurs in the limit of the low temperatures, as it is shown below.

The integral in equation (15.3) can be performed straightforwardly. We get

$$b\varepsilon_1/a^3T = \sum_{n=1}(nz^n)^{-1} = \ln[z/(z-1)] \ , \tag{15.4}$$

whence $z = (1-e^{-C})^{-1}$ and the chemical potential

$$\mu = -\varepsilon_0 + T\ln(1-e^{-C}) \ , \tag{15.5}$$

where $C = b\varepsilon_1/a^3T = b\varepsilon_1 c/T$.

Similarly, the energy is given by

$$E = -N\varepsilon_0 + \frac{VT^2}{b\varepsilon_1}G(z) \ , \tag{15.6}$$

where

$$G(z) = \sum_{n=1}(n^2z^n)^{-1} = \sum_{n=1}\frac{1}{n^2}(1-e^{-C})^n \ . \tag{15.7}$$

In the low-temperature limit $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$ it amounts to

$$E = -N\varepsilon_0 + \pi^2VT^2/6b\varepsilon_1 \ , \tag{15.8}$$

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[4] M. H. Lee, "Equivalence of ideal gases in two dimensions and Landen's relations", Phys. Rev. **E55** 1518 (1997); R. M. May, "Quantum statistics of ideal gases in two dimensions", Phys. Rev. **135** A1515 (1964); M. Apostol, "Dimensionality effects in the ideal Bose and Fermi gases", Phys. Rev. **E56** 4854 (1997).

and for high temperature $T \gg b\varepsilon_1/a^3$

$$E = -N\varepsilon_0 + NT \ , \tag{15.9}$$

as for a classical ensemble. However, anharmonic corrections in the expansion (15.1) may be important in this limit, which would modify the simple T-law given by equation (15.9).

The entropy for the Bose-Einstein distribution introduced here is given by

$$S = \frac{V}{b\varepsilon_1}\int_0^\infty d\varepsilon[(n+1)\ln(n+1) - n\ln n] \ , \tag{15.10}$$

where $n = (ze^{\beta\varepsilon} - 1)^{-1}$ is the mean occupation number. It leads to

$$S = -N\ln(1 - e^{-C}) + \frac{2VT}{b\varepsilon_1}G(z) \ , \tag{15.11}$$

the free energy

$$F = E - TS = -N\varepsilon_0 + NT\ln(1 - e^{-C}) - \frac{VT^2}{b\varepsilon_1}G(z) \tag{15.12}$$

and the thermodynamic potential

$$\begin{aligned}\Omega = F - \mu N = \tfrac{VT}{b\varepsilon_1}\textstyle\int d\varepsilon\ln(1 - e^{-\beta\varepsilon}/z) = \\ = -(E + N\varepsilon_0) = -\tfrac{VT^2}{b\varepsilon_1}G(z) \ .\end{aligned} \tag{15.13}$$

The pressure $p = -(\partial F/\partial V)_{T,N}$ is given by

$$p = -c^2\varepsilon_0' + \frac{T^2}{b\varepsilon_1}G(z) \ , \tag{15.14}$$

where ε_0' is the derivative of the energy ε_0 with respect to concentration c. This is the equation of state of the present liquid model. The dependence of ε_1 on concentration is neglected. We note that for suitable values of $c^2\varepsilon_0'$ the equilibrium can be reached for low values of pressure.

In the low-temperature limit $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$, the pressure given by equation (15.14) reads $p = -c^2\varepsilon_0' + \pi^2T^2/6b\varepsilon_1$, whence the isothermal compressibility

$$\kappa_T = V^{-1}(\partial V/\partial p)_T = \frac{1}{c\partial(c^2\varepsilon_0')/\partial c} < 0 \ . \tag{15.15}$$

It is worth noting that $c\partial(c^2\varepsilon_0')/\partial c$ must acquire large, negative values for the stability of the ensemble and for ensuring low values of the compressibility, in accordance with the behaviour of such liquids. Similarly, the thermal expansion coefficient at constant pressure is given by

$$\alpha = V^{-1}(\partial V/\partial T)_p = -\frac{\pi^2 T}{3b\varepsilon_1}\kappa_T > 0 \ . \tag{15.16}$$

The entropy given by equation (15.11) at low temperatures reads $S = \pi^2 VT/3b\varepsilon_1$ and the heat capacity at constant volume is $c_V = T(\partial S/\partial T)_V = S$. The heat capacity at constant pressure is given by $c_p = c_V - V\alpha^2 T/\kappa_T > c_V$. Similarly, the adiabatic compressibility is given by $\kappa_S = V^{-1}(\partial V/\partial p)_S = \kappa_T(1 + \pi^2 T^2\kappa_T/3b\varepsilon_1) > \kappa_T$. It is related to the sound velocity u by $u^2 = -1/\rho\kappa_S$, where ρ is the mass density. These quantities may give access to experimental determination of the parameters ε_0 and $b\varepsilon_1$.

In the high-temperature limit $T \gg b\varepsilon_1/a^3$ the present liquid model behaves classically, with the entropy $S = N\ln(e^2a^3T/b\varepsilon_1)$ and pressure $p = -c^2\varepsilon_0' + NT/V$. The compressibilities are given by

$$\begin{gathered} \kappa_T = -\tfrac{1}{c}\cdot\tfrac{1}{T-\partial(c^2\varepsilon_0')/\partial c} \ , \\ \kappa_S = -\tfrac{1}{2c}\cdot\tfrac{1}{T-(1/2)\partial(c^2\varepsilon_0')/\partial c} \ , \end{gathered} \tag{15.17}$$

the coefficient of thermal expansion is

$$\alpha = \frac{1}{T - \partial(c^2\varepsilon_0')/\partial c} \ , \tag{15.18}$$

and the heat capacities are $c_V = N$ and

$$c_p = c_V - VT\alpha^2/\kappa_T = c_V + \frac{NT}{T - \partial(c^2\varepsilon_0')/\partial c} \ . \tag{15.19}$$

The validity of these expressions is restricted to a limited range of temperature and concentration characteristic for such liquids. Their experimental determination gives access only to the parameter ε_0. Also, for high values of T anharmonic corrections have to be included.

15.4 Low temperature

For values of the temperature T comparable with the spacing ε_1 between the energy levels the quantum effects are important and the accuracy of replacing the summation over n in equation (15.2) by the integral given by equation (15.3) must be checked, according to MacLaurin's formula

$$\sum_a^b f(x_n) = \int_{a-1/2}^{b+1/2} f(x)dx - (1/24)f'^{\,b+1/2}_{a-1/2} + ... \ . \tag{15.20}$$

Applying this formula to function $f = [ze^{-\beta\varepsilon_1(n+1/2)} - 1]^{-1}$ we get

$$\begin{aligned} b/a^3 &= \textstyle\sum_{n=0} \frac{1}{z\exp[\beta\varepsilon_1(n+1/2)]-1} = \\ &= \textstyle\int_0 dn \frac{1}{z\exp(\beta\varepsilon_1 n)-1} - \frac{\beta\varepsilon_1}{24}\cdot\frac{z}{(z-1)^2} + ... = \\ &= \textstyle\frac{1}{\beta\varepsilon_1}\ln\frac{z}{z-1} - \frac{\beta\varepsilon_1}{24}\cdot\frac{z}{(z-1)^2} + ... \ , \end{aligned} \tag{15.21}$$

and we can see that the error made in approximating the summation by integral becomes comparable with the integral for large values of $\beta\varepsilon_1$ and $z \to 1$. This error arises from the fact that the integral gives little weight to the value of the function at $n = 0$. Consequently, we single out the term $n = 0$ in equation (15.21), and write

$$b/a^3 = \tfrac{1}{z'-1} + \tfrac{1}{\beta\varepsilon_1}\ln\tfrac{z'e^{\beta\varepsilon_1/2}}{z'e^{\beta\varepsilon_1/2}-1} - \tfrac{\beta\varepsilon_1}{24}\cdot\tfrac{z'e^{\beta\varepsilon_1/2}}{(z'e^{\beta\varepsilon_1/2}-1)^2} + ... \ , \tag{15.22}$$

where $z' = ze^{\beta\varepsilon_1/2}$. In the low temperature limit $\beta\varepsilon_1 \to \infty$ it is the first term in equation (15.22) that brings the main contribution and we have

$$z = (1 + a^3/b)e^{-\beta\varepsilon_1/2} \ , \ \beta\varepsilon_1 \to \infty \ . \tag{15.23}$$

In the high-temperature limit $\beta\varepsilon_1 \to 0$ the main contribution is brought by the ln-term in equation (15.22), and

$$z = \frac{a^3 T}{b\varepsilon_1}e^{-\beta\varepsilon_1/2} \ , \ \beta\varepsilon_1 \to 0 \ . \tag{15.24}$$

A fair interpolation between equations (15.23) and (15.24) gives

$$z = (1 + a^3/b + a^3T/b\varepsilon_1)e^{-\beta\varepsilon_1/2} \tag{15.25}$$

and the chemical potential

$$\mu = -\varepsilon_0 + \varepsilon_1/2 - T\ln(1 + a^3/b + a^3T/b\varepsilon_1) \ . \tag{15.26}$$

As one can see, although there is a condensation on the lowest state of zero-point vibrations in the limit of low temperatures, there is no phase transition, *i.e.* no discontinuity, and z approaches gradually zero (not unity!) for $T \to 0$, in contrast to the Bose-Einstein condensation in the three-dimensional case[5] (a behaviour which may indicate a superfluid transition). The characteristic temperature of this continuous condensation is given by $\beta\varepsilon_1 \sim 1$. For such temperatures, the liquid may undergo, very likely, a phase transition, probably to a solid-like phase. Such a transition is characterized by the increase of the constraining volume b, which becomes of the order of the volume $V = Na^3$, such that the number of the available spatial states for each particle in the ensemble reduces to unity. The ensemble becomes now rigid and it can only move as a whole. At the same time, the vibration spectrum changes correspondingly, from one of local vibrations to global, collective oscillations.

The low-temperature behaviour derived herein has long been introduced in the statistical model of the atomic nuclei.[6] Making use of equations (15.8), (15.11) and (15.12), we get

$$Q = E + N\varepsilon_0 = -(F + N\varepsilon_0) = \pi^2VT^2/6b\varepsilon_1 \ , \tag{15.27}$$

and

$$S = \pi^2VT/3b\varepsilon_1 = \sqrt{2\pi^2VQ/3b\varepsilon_1} \tag{15.28}$$

where Q denotes the excitation energy of the nucleus. The density of states $\rho = d\mathcal{N}/dQ = e^S(dS/dQ)$ gives the spacing between the energy levels

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[5] M. F. M. Osborne, "The Bose-Einstein condensation for thin films", Phys. Rev. **76** 396 (1949).

[6] H. Bethe, "An attempt to calculate the number of energy levels of a heavy nucleus", Phys. Rev. **50** 332 (1936); "Nuclear radius and many-body problem", Phys. Rev. **50** 977 (1936); L. Landau, "On the statistical theory of nuclei", ZhETF **7** 819 (1937) (Phys. Z. Sowjet. **11** 556 (1937)) (in Russian); J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics*, Dover, NY, (1991).

$$\delta\varepsilon = \delta Q = \sqrt{6b\varepsilon_1 Q/\pi^2 V} e^{-\sqrt{2\pi^2 VQ/3b\varepsilon_1}} \; . \tag{15.29}$$

These equations are valid in the low-temperature limit corresponding to $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$, where $T = \sqrt{6b\varepsilon_1 Q/\pi^2 Na^3}$. The distribution of the energy levels among states with different angular momenta changes to some extent the prefactor in equation (15.29), without material consequences for the estimations given here.[7] For heavy nuclei one may take approximately $\delta\varepsilon \sim 5eV$ for $Q \simeq 8MeV$, as derived from experiments of neutron scattering, resonances, or radiative capture. Equation (15.29) gives then $b\varepsilon_1/a^3 \simeq 40MeV$ and temperature $T \simeq 1MeV$ for $N \sim 200$. If volume b is of the order of a^3, this temperature would be much lower than the energy ε_1 as derived from $b\varepsilon_1/a^3 \simeq 40MeV$. It is likely, therefore, that a transition to a solid-like state is expected, *i.e.* the volume b becomes of the order of $b = Na^3$ (the volume of the nucleus is given by $V = Na^3$, where $a = 1.5 \times 10^{-15}m = 1.5fm$). The energy ε_1 acquires then the value $\varepsilon_1 \sim 40MeV/N = 200keV$ for $N = 200$, and it may be viewed as an estimate of the mean separation of the energy levels in the nucleus.

A similar evaluation can be made for classical, common, liquids. A typical value for ε_1 for such liquids might be of the order of $1meV$. The mean inter-particle spacing is a few Ås and this is also the order of magnitude of the molecular size and short-range forces. It follows that each molecule has a number of spatial states of the order of N at its disposal, *i.e.* b is of the order of a^3.

15.5 Summarizing remarks

In conclusion, a liquid model is introduced herein, described as a correlated ensemble of particles, moving around and interacting strongly with short-range forces. The correlations give rise to a constraining volume b, which is one of the parameters of the thermodynamics of such a liquid model. The local, collective movements are described as a set of independent harmonic oscillators with one degree of freedom, corresponding to vibrations of local particle configurations. The other two parameters are the distance ε_1 between the energy levels of these vibrations and the cohesion energy $-\varepsilon_0$ per particle. The statistics derived on this basis is formally equivalent with the statistics of an ideal gas of bosons in two dimensions, which, as it is known, leads to a thermodynamics equivalent with that of an ideal gas of fermions. This thermodynamics is explicitly derived, both in the low- and the high-temperature limits. The limit of temperatures comparable with the distance ε_1 between the energy levels is also discussed, where a continuous, gradual condensation on the lowest energy level occurs, which may be the precursor of a transition towards a solid-like state.

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[7] L. Landau, "On the statistical theory of nuclei", ZhETF **7** 819 (1937) (Phys. Z. Sowjet. **11** 556 (1937)) (in Russian).

15.6 Transport properties

The elementary excitations in liquids consist of quanta ε of local vibrations associated to short-range correlated particle configurations which move around with the spatial density of states dV/b, where V is the volume of the liquid and b is a "constraining " volume. The volume b is of the order of the molecular volume a^3, where a is the mean inter-particle spacing ($b > a^3$). The vibration quanta are governed by the Bose-Einstein distribution n with a non-vanishing chemical potential corresponding to the number N of particles in liquid.

The transport is performed by elementary excitations. Each elementary excitation carries a density of energy $\partial(\varepsilon n/b)/\partial T \cdot \Delta T$ with velocity $v_\parallel$ along a gradient $\partial T/\partial z$ of temperature in the z-direction. Therefore, the energy flux is $\partial(\varepsilon n/b)/\partial T \cdot \Delta T \cdot v_\parallel \tau$, where τ is the lifetime of the elementary excitations. The flow is given by $\partial q/\partial t = \partial(\varepsilon n/b)/\partial T \cdot v_\parallel^2 \tau \cdot \partial T/\partial z$, where $v_\parallel^2 = v^2/3$, v being the velocity of the elementary excitations. The thermoconductivity is defined as

$$K = \int (d\varepsilon/\varepsilon_1)\partial(\varepsilon n/b)/\partial T \cdot v_\parallel^2 \tau \ ; \tag{15.30}$$

it is easy to see that it can be written as

$$K = \frac{1}{3} cv\Lambda \ , \tag{15.31}$$

where c is the heat capacity per volume and $\Lambda = v\tau$ is the mean freepath of the excitations. The heat capacity per volume (at constant volume) is given by $c = \pi^2 T/3b\varepsilon_1$ in the low-temperature limit $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$ and $c = 1/a^3$ in the high-temperature limit $T \gg b\varepsilon_1/a^3$ (according to the calculations described above). The mean freepath is given by $\Lambda = b^{1/3}$. In the low-temperature limit the thermal energy per particle is given by $\pi^2 a^3 T^2/6b\varepsilon_1$, such that a composite of b/a^3 particles carries the energy $\varepsilon_{exc} = \pi^2 T^2/6\varepsilon_1$. It may be taken as the energy of the elementary excitations in the low-temperature limit, and $\tau \sim \hbar/\varepsilon_{exc}$ may be taken as their lifetime (which means that such excitations are rather poorly defined). (Such a procedure exhibits an interesting general potential of being used in estimating the lifetime and mean freepath effects in the vortex-roton-sound quanta in superfluids). The momentum is therefore given by $\hbar/b^{1/3}$, and the velocity $v = \varepsilon_{exc} b^{1/3}/\hbar$. The thermoconductivity becomes

$$K = \frac{\pi^4}{54} \cdot \frac{T^3}{\hbar b^{1/3} \varepsilon_1^2} \tag{15.32}$$

in the low-temperature limit. In the high-temperature limit the energy of the elementary excitations is given by $\varepsilon_{exc} = b\varepsilon_1/a^3$, such that the thermoconductivity becomes

$$K = \frac{b^{5/3}\varepsilon_1}{3\hbar a^6} \tag{15.33}$$

for $T \gg b\varepsilon_1/a^3$.

As it is well-known, the fluctuations are governed by the probability $\sim e^S$, where S is the entropy (actually, the probability is given by $\exp[(T\Delta S - \Delta E - p\Delta V)/T]$, as for non-equilibrium; the variations, given by the second derivatives, are those pertaining to ΔE; they are equivalent with those given in the main text; equally well, from $dE = -pdV + TdS$, we get $(\Delta T\Delta S - \Delta p\Delta V)/T$ for the exponent of the probability (with minus sign)). For instance, the fluctuations δV^2 in volume are given by $\left|\partial^2 S/\partial V^2\right| = |(\partial p/\partial V)/T| = 1/|VT\kappa_T|$, where κ_T is the isothermal compressibility, so the fluctuations in volume per particle are given by $\delta v \sim \sqrt{|vT\kappa_T|}$, and the fluctuations in the mean inter-particle distance are $\delta a \sim \sqrt{|T\kappa_T|/a}$. The compressibilities of the liquid are given below. In the low temperature limit the fluctuations δa go like $\sqrt{T}$, while in the high-temperature limit they go like $\delta a \sim a$.

Similarly, the fluctuations δE in energy are given by $\left|\partial^2 S/\partial E^2\right| = \left|(\partial T/\partial E)/T^2\right|$, and the fluctuations in energy per particle are therefore given by $\delta\varepsilon \sim T\sqrt{\partial e/\partial T}$, where e is the energy per particle. The energy per particle for a liquid is given by

$$e = -\varepsilon_0 + \pi^2 a^3 T^2/6b\varepsilon_1 \tag{15.34}$$

in the low-temperature limit, and by $e = -\varepsilon_0 + T$ in the high-temperature limit. Therefore, we get

$$\delta\varepsilon \sim T(\pi^2 T a^3/3b\varepsilon_1)^{1/2} \ , \ T \to 0 \ , \tag{15.35}$$

and $\delta\varepsilon \sim T$ for $T \to \infty$.

We can check the series of inequalities $\varepsilon_{eq} > T > \delta\varepsilon_f > \delta\varepsilon_{ex} \gg \delta\varepsilon_q > \delta\varepsilon_{obs}$, where ε_{eq} is the scale energy for statistical equilibrium (cohesion energy per particle ε_0), $\delta\varepsilon_f$ is the fluctuation energy per particle derived above, $\delta\varepsilon_{ex}$ is the uncertainty in the energy of the elementary excitations (related to their lifetime, herein ε_{ex}), $\delta\varepsilon_q$ is the separation between the quantum-mechanical energy levels (ε_1), and, finally, $\delta\varepsilon_{obs}$ is the measured (observed) energy per particle. According to the results given above, in the low-temperature regime $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$ these inequalities read

$$T > T(\pi^2 T a^3/3b\varepsilon_1)^{1/2} > \pi^2 T^2/6\varepsilon_1 \gg \varepsilon_1 \ \ , \tag{15.36}$$

and one can see that they are fulfilled. Therefore, the equilibrium is attained in this regime, and the excitations are well-defined. In the high-temperature regime $T \gg b\varepsilon_1/a^3$ the above inequalities become

$$T > \delta\varepsilon_f > b\varepsilon_1/a^3 \gg \varepsilon_1 \ \ , \tag{15.37}$$

and one can see that they are again fulfilled; $\delta\varepsilon_f$ is actually lower than its asymptotic T-value given above.

The fluctuations give an additional pressure δp related to the velocity fluctuations through $\delta p \sim \eta(\delta v/\delta a) \sim \eta/\tau_f \sim \eta\delta\varepsilon/n\hbar$, where η is the viscosity and n is an undefined quantum-mechanical number depending on the nature of the fluid, the process, etc. The fluctuations in pressure are given by $\left|\partial^2 S/\partial p^2\right| = \left|(\partial V/\partial p)_S/T\right| = \left|V\kappa_S/T\right|$, such that $\delta p \sim \sqrt{\left|T/v\kappa_S\right|}$, where κ_S is the adiabatic compressibility (similarly, we get the fluctuations in temperature from $\left|\partial^2 S/\partial T^2\right|$, which leads to $\delta T \sim T/\sqrt{c_V}$, where c_V is the heat capacity per particle at constant volume). Therefore, we get

$$\eta = \sqrt{T/a^3\,|\kappa_S|} \cdot \frac{n\hbar}{\delta\varepsilon} \ , \tag{15.38}$$

such that $\eta \sim 1/T$ in the low-temperature limit and $\eta \sim \sqrt{T(T+c)}/T$ in the high-temperature limit, where c is a constant (see below). For classical ideal gases we get $\eta = n\hbar/a^3$, which suggests a quantum $\hbar$ for viscosity ηa^3.[8]

The pressure of the liquid is given by

$$p = -c^2\varepsilon_0' + \pi^2 T^2/6b\varepsilon_1 \tag{15.39}$$

in the low-temperature limit and by

$$p = -c^2\varepsilon_0' + cT \tag{15.40}$$

in the high-temperature limit, where $-\varepsilon_0(c) < 0$ is the cohesion energy per particle (here $c = 1/a^3$ is the concentration). The isothermal compressibility (given above) reads

$$\kappa_T = \frac{1}{c\partial(c^2\varepsilon_0')/\partial c} < 0 \tag{15.41}$$

in the low-temperature limit and

$$\kappa_T = -\frac{1}{c} \cdot \frac{1}{T - \partial(c^2\varepsilon_0')/\partial c} \tag{15.42}$$

in the high-temperature limit. Similarly, the isentropic compressibilities are given by

$$\kappa_S = \kappa_T(1 + \pi^2 T^2 \kappa_T/3b\varepsilon_1) \tag{15.43}$$

in the low-temperature limit and

$$\kappa_S = -\frac{1}{2c} \cdot \frac{1}{T - (1/2)\partial(c^2\varepsilon_0')/\partial c} \tag{15.44}$$

in the high-temperature limit. The diffusion coefficient is defined as $D \sim (\delta a)^2/\tau_f$, and we get $D \sim T^{5/2}$ in the low-temperature limit and $D \sim a^2 T/n\hbar$ in the high-temperature limit. In the latter case one may check the validity of the hydrodynamic representation $D \sim T/a\eta$.

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[8] M. Apostol, "Quanta of viscosity", J. Theor. Phys. **62** (2001).

15.7 Non-equilibrium

The liquid state provides an opportunity to discuss the main problem of Statistical Physics, which is the derivation of the statistical equilibrium from mechanical motion. This is so, because the liquids exhibit a more correlated motion of their molecular components, which, hopefully, will make easier the solution. On the other hand, the classical liquids may set the problem in more intuitive terms. The procedure consists in the Liouville equation for the distribution function of n particles, which connects this function to higher-order distribution functions of $n+1$, $n+2$, etc particles; it is known as the BBGKY hierarchy.[9] It is a generalization of the Boltzmann equation. The interaction between particles gives the collision integral. The hope is to describe the approach to equilibrium. This equation hierarchy illustrates a mechanical motion of many particles, which is not integrable; various approximations are not warranted. Close to equilibrium these equations may describe, at most, the compatibility of the statistical motion with the mechanical motion. For transport, the equations at local equilibrium are solved by using non-mechanical concepts like lifetime and mean freepath. The approach to equilibrium is not mechanical, it is statistical; it is embodied in the statistical principle.

Along similar lines, the direct and indirect two-particle correlation functions are related through the Ornstein-Zernike integral equation[10] and Percus-Yevick closure relation (approximation) or hypernetted-chain approximation.[11] These procedures aim at deriving the properties of correlated ensembles (like liquids, including the approach to equilibrium) from their internal interactions.[12] However, it is worth noting that the statistical behaviour of matter is irrelevantly related to the internal interaction. "To solve such a problem is not only impossible, but it is not even needed" (Landau, approximate quote).

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[9] J. Yvon, "La th*é*orie statistique des fluides et l'*é*quation d'*é*tat", Actual. Sci. & Indust. **203**, Paris, Hermann (1935); J. G. Kirkwood, "The statistical mechanical theory of transport processes I. General theory", J. Chem. Phys. **14** 180 (1946); "The statistical mechanical theory of transport processes II. Transport in gases", J. Chem. Phys. **15** 72 (1947); M. Born and H. S. Green, "A general kinetic theory of liquids I. The molecular distribution functions", Proc. Roy. Soc. **A188** 10 (1946); N. N. Bogoliubov, "Kinetic equations", ZhETF **16** 691 (1946) (in Russian) (J. Phys. USSR **10** 265 (1946); N. N. Bogoliubov and K. P. Gurov, "Kinetic equations in quantum mechanics", ZhETF **17** 614 (1947) (in Russian).

[10] L. S. Ornstein and F. Zernike, "Accidental deviations of density and opalescence at the critical point of a single substance", Proc. Roy. Netherlands Acad. Arts and Sciences (KNAW) **17** 793 (1914).

[11] J. K. Percus and G. J. Yevick, "Analysis of classical statistical mechanics by means of collective coordinates", Phys. Rev. **110** 1 (1958).

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[12] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, NY (1940).

16 Density Oscillations in Water

16.1 Introduction

We suggest here that the dynamics of liquid water has a component consisting of O^{-2z} (oxygen) anions and H^{+z} (hydrogen) cations, where z is a (small) reduced effective electron charge. Such a model may apply to other similar liquids. The eigenmodes of density oscillations are derived for such a two-species ionic plasma, including the sound waves, and the dielectric function is calculated. It is shown that the sound anomaly in water can be understood on the basis of this model. The results are generalized to an asymmetric short-range interaction between the ionic species as well as to a multi-component plasma, and the structure factor is calculated.[1]

As simple as it may appear, water is still a complex liquid involving various interactions as well as kinematic and dynamic correlations. It is widely agreed that the water molecule in liquid water preserves to some extent its integrity, especially the directionality of the sp^3-oxygen orbitals, though it may be affected substantially by hydrogen bonds.[2] As such, it is conceived that water has a molecular electric moment, an intrinsic polarizability and hindered rotations (librations) which may affect its orientational polarizability. We examine herein another possible component of the dynamics of the liquid water, as resulting from the dissociation of water molecule.

Water molecule H_2O has two $H-O$ (hydrogen-oxygen) bonds which make an angle of about 109° in accordance with the tetragonal symmetry of the four hybridized sp^3-oxygen orbitals. The "spherical" diameter of water molecule is approximately 2.75Å and the intermolecular spacing in liquid water under normal conditions is $a \sim 3$Å. This suggests that water molecule in liquid water, while preserving the directionality of the oxygen electronic orbitals, might be dissociated to a great extent. Dissociation models which assume $OH^- - H^+$ or $OH^- - H_3O^+$ pairs are well-known for water. This indicates a certain mobility of hydrogens (and oxygens) in water. We analyze herein the hypothesis that water may consist of O^{-2z} anions of mass $M = 16amu$ and density n and H^{+z} cations (protons) of mass $m = 1amu$ and density $2n$, where z is a small reduced effective electron charge (the atomic mass unit is $1amu \simeq 1.7 \times 10^{-24}g.$). We shall see that such a hypothesis adds another dimension to the dynamics of water. Such a model may be used for other similar liquids.

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[1] M. Apostol and E. Preoteasa, "Density oscillations in a model of water and other similar liquids", Phys. Chem. Liq. **46** 653 (2008).

[2] L. Pauling, *General Chemistry*, Dover, NY (1982).

Due to their large mass the ions have a classical dynamics. Herein, we limit ourselves to considering the ions motion in water under the action of the Coulomb potentials $\varphi_{OO} = 4z^2e^2/r$, $\varphi_{HH} = z^2e^2/r$ and $\varphi_{OH} = -2z^2e^2/r$, where $-e$ ($\simeq -4.8 \times 10^{-10}esu$) is the electron charge and r denotes the distance between the ions. For stability, it is also necessary to introduce a short-range repulsive (hard-core) potential χ.[3] It is shown that in the limit $z \to 0$ water may exhibit an anomalous sound-like mode besides both the ordinary (hydrodynamic) one and the non-equilibrium sound-like excitations governed by short-range interactions. We compute the density oscillations for this model, the dielectric function, the structure factor, and extend the model to a multicomponent plasma, including an asymmetric short-range interaction between ion species.

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[3] See also in this respect E. Teller, "On the stability of molecules in the Thomas-Fermi theory", Revs. Mod. Phys. **34** 627 (1962)l; E. H. Lieb and B. Simon, "Thomas-Fermi theory revisited", Phys. Rev. Lett. **31** 681 (1973); "The Thomas-Fermi theory of atoms, molecules and solids", Adv. Math. **23** 22 (1977); L. Spruch, "Pedagogic notes on Thomas-Fermi theory (and on some improvements); atoms, stars, and the stability of bulk matter", Revs. Mod. Phys. **63** 151 (1991). As it is well-known, a classical (jellium) plasma with Coulomb interaction is unstable.

16.2 Plasmons

Let us consider one species of charged particles, with charge $-ze$, continuously distributed with density n in a neutralising rigid continuous background of positive charge. This is the well-known jellium model.[4] The Coulomb interaction reads

$$U = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \varphi(\mathbf{r} - \mathbf{r}') \delta n(\mathbf{r}) \delta n(\mathbf{r}') \ , \tag{16.1}$$

where $\delta n(\mathbf{r})$ denotes a small disturbance of density (which preserves the global neutrality). We introduce the Fourier representation

$$\delta n(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \delta n(\mathbf{q}) e^{i\mathbf{qr}} \ , \ \delta n(\mathbf{q}) = \frac{n}{\sqrt{N}} \int d\mathbf{r} \delta n(\mathbf{r}) e^{-i\mathbf{qr}} \ , \tag{16.2}$$

where $N = nV$ is the total number of particles in volume V. Similarly,

$$\varphi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} \varphi(\mathbf{q}) e^{i\mathbf{qr}} \ , \ \varphi(\mathbf{q}) = \int d\mathbf{r} \varphi(\mathbf{r}) e^{-i\mathbf{qr}} \ , \tag{16.3}$$

where $\varphi(\mathbf{q}) = 4\pi z^2 e^2 / q^2$ is the Fourier transform of the Coulomb potential (interaction). The Coulomb interaction given by equation (16.1) becomes

$$U = \frac{1}{2n} \sum_{\mathbf{q}} \varphi(q) \delta n(\mathbf{q}) \delta n(-\mathbf{q}) \tag{16.4}$$

(where the $q = 0$-term is excluded by the positive background).

The small variations $\delta n(\mathbf{r})$ in density can be represented as $\delta n = -n div \mathbf{u}$, where $\mathbf{u}$ is a displacement vector. We emphasize that such a representation holds for $\mathbf{qu}(\mathbf{r}) \ll 1$. It follows $\delta n(\mathbf{q}) = -in\mathbf{qu}(\mathbf{q})$, and one can see that the Coulomb interaction involves only longitudinal components of the displacement vector $\mathbf{u}(\mathbf{q})$ along the wavevector $\mathbf{q}$. Therefore, we may write $\mathbf{u}(\mathbf{q}) = (\mathbf{q}/q) u(\mathbf{q})$, with $\delta n^*(-\mathbf{q}) = \delta n(\mathbf{q})$, $\mathbf{u}^*(-\mathbf{q})=\mathbf{u}(\mathbf{q})$ and $u^*(-\mathbf{q}) = -u(\mathbf{q})$. The Coulomb interaction given by equation (16.4) becomes

$$U = -\frac{n}{2} \sum_{\mathbf{q}} q^2 \varphi(q) u(\mathbf{q}) u(-\mathbf{q}) \ . \tag{16.5}$$

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[4] D. Pines, *Elementary Excitations in Solids*, Benjamin, NY (1963).

The kinetic energy associated with the coordinates $u(\mathbf{q})$ is given by

$$T = \frac{1}{2}\int d\mathbf{r}nm\dot{\mathbf{u}}^2 = -\frac{1}{2}m\sum_{\mathbf{q}}\dot{u}(\mathbf{q})\dot{u}(-\mathbf{q}) \ , \tag{16.6}$$

where m denotes the particle mass. The equations of motion obtained from the Lagrange function $L = T - U$ are

$$m\ddot{u}(\mathbf{q}) + nq^2\varphi(q)u(\mathbf{q}) = 0 \ , \tag{16.7}$$

which leads to the well-known plasma oscillations with frequency given by $\omega_p^2 = 4\pi nz^2e^2/m$.

16.3 Two ionic species

We apply the above model to the two species of ions O^{-2z} and H^{+z}. The change in density is associated with a displacement vector $\mathbf{v}$ in the former and a displacement vector $\mathbf{u}$ in the latter. First we note that the Fourier transforms of the Coulomb potentials are given by $\varphi_{OO} = 4\varphi(q)$, $\varphi_{HH} = \varphi(q)$ and $\varphi_{OH} = -2\varphi(q)$, where $\varphi(q) = 4\pi z^2e^2/q^2$. Therefore, the interactions can be written as

$$\begin{aligned} U_{OO} &= -\tfrac{n}{2}\textstyle\sum_{\mathbf{q}} q^2\left[4\varphi(q)+\chi(q)\right]v(\mathbf{q})v(-\mathbf{q}) \ , \\ U_{HH} &= -2n\textstyle\sum_{\mathbf{q}} q^2\left[\varphi(q)+\chi(q)\right]u(\mathbf{q})u(-\mathbf{q}) \ , \\ U_{OH} &= n\textstyle\sum_{\mathbf{q}} q^2[2\varphi(q)-\chi]u(\mathbf{q})v(-\mathbf{q}) \ , \end{aligned} \tag{16.8}$$

where $n = N/V$ is the density of water molecules and the Fourier transform χ of a hard-core potential has been introduced (the same for both species). The kinetic energy is given by

$$T = -\frac{1}{2}M\sum_{\mathbf{q}}\dot{v}(\mathbf{q})\dot{v}(-\mathbf{q}) - m\sum_{\mathbf{q}}\dot{u}(\mathbf{q})\dot{u}(-\mathbf{q}) \tag{16.9}$$

and the equations of motion read

$$\begin{aligned} m\ddot{u} + 2nq^2(\varphi+\chi)u - nq^2(2\varphi-\chi)v &= 0 \ , \\ M\ddot{v} + nq^2(4\varphi+\chi)v - 2nq^2(2\varphi-\chi)u &= 0 \ , \end{aligned} \tag{16.10}$$

where we have dropped out the argument $\mathbf{q}$.

The solutions of these equations can be obtained straightforwardly. In the long wavelength limit $\mathbf{q} \to 0$ there are two branches of eigenfrequencies, one given by

$$\omega_p^2 = \frac{16\pi n z^2 e^2}{\mu} \tag{16.11}$$

corresponding to plasma oscillations and another given by

$$\omega_s^2 = \frac{9n\chi}{M + 2m} q^2 = v_s^2 q^2 \tag{16.12}$$

corresponding to sound-like waves propagating with velocity v_s given by equation (16.12). $\mu = 2mM/(2m + M)$ is the reduced mass. The plasma oscillations are associated with antiphase oscillations of the relative coordinate $(2mu + Mv = 0)$, while the sound waves are associated with in-phase oscillations of the center-of-mass coordinate $(u - v = 0)$.

16.4 Polarization

An external electric field arising from a potential $\phi(\mathbf{r})$ gives an additional energy

$$U_i = q_i \int d\mathbf{r} \phi(\mathbf{r}) \delta n_i(\mathbf{r}) = -i(n_i q_i / n) \sum_{\mathbf{q}} q \phi(\mathbf{q}) u_i(-\mathbf{q}) \tag{16.13}$$

for a species of ions labelled by i, with electric charge q_i and density n_i. We apply this formula to the two-species ionic plasma, and get

$$U_H = -2ize \sum_{\mathbf{q}} q\phi(\mathbf{q}) u(-\mathbf{q}) \ , \ U_O = 2ize \sum_{\mathbf{q}} q\phi(\mathbf{q}) v(-\mathbf{q}) \ . \tag{16.14}$$

Adding these two terms to the lagrangian, the equations of motion (16.10) become

$$\begin{aligned} m\ddot{u} + 2nq^2(\varphi + \chi)u - nq^2(2\varphi - \chi)v &= -izeq\phi \ , \\ M\ddot{v} + nq^2(4\varphi + \chi)v - 2nq^2(2\varphi - \chi)u &= 2izeq\phi \ , \end{aligned} \tag{16.15}$$

where we have dropped out the argument $\mathbf{q}$. This is a system of coupled harmonic oscillators under the action of an external force. In the limit of long wavelengths its solutions are given by

$$\begin{aligned} u &= \frac{izeq}{m}\phi\frac{\omega^2-\frac{2m}{3\mu}\omega_s^2}{(\omega^2-\omega_p^2)(\omega^2-\omega_s^2)} \ , \\ v &= -\frac{2izeq}{M}\phi\frac{\omega^2-\frac{2M}{3\mu}\omega_s^2}{(\omega^2-\omega_p^2)(\omega^2-\omega_s^2)} \ . \end{aligned} \tag{16.16}$$

On the other hand, equation $n_i div \mathbf{u}_i = -\delta n_i$ is, in fact, the Maxwell equation $div \mathbf{E}_i = 4\pi q_i \delta n_i$, where the electric field is given by $\mathbf{E}_i = -4\pi n q_i \mathbf{u}_i$. We have therefore the internal electric fields $E_u = -8\pi nzeu$ and $E_v = 8\pi nzev$. The polarization $P = -(E_u + E_v)/4\pi$ is given by

$$P(\mathbf{q}) = 2nze\left[u(\mathbf{q}) - v(\mathbf{q})\right] = \frac{iq}{4\pi}\phi(\mathbf{q})\frac{\omega_p^2}{\omega^2-\omega_p^2} \ . \tag{16.17}$$

The external field is related to the external potential through $D(\mathbf{q}) = -iq\phi(\mathbf{q})$ and the dielectric function ε is given by $D = \varepsilon E = \varepsilon(D + E_{int})$, where $E_{int} = E_u + E_v$ is the internal field. We get the dielectric function

$$\varepsilon = 1 - \omega_p^2/\omega^2 \ , \tag{16.18}$$

as expected (we disregard here the intrinsic and orientational polarizabilities). As it is well-known, its zero gives the longitudinal mode of plasma oscillations.

The ω_p in the nominator of equation (16.18) defines also the plasma edge: for frequencies lower than ω_p the electromagnetic waves are absorbed (the refractive index is given by $n^2 = \varepsilon$). It is well-known that water exhibits indeed a strong absorption in the gigahertz-terrahertz region. On the other hand, neutron scattering on heavy water, as well as inelastic X-ray scattering, revealed the existence of a dispersionless mode $\simeq 4 - 5meV$ ($\simeq 10^{13}s^{-1}$) in the structure factor, which may be taken tentatively as the ω_p-plasmonic mode given by equation (16.11). Making use of this equation we get $\omega_p \simeq 3 \times 10^{14} zs^{-1}$($n = 1/a^3$, $a = 3\text{Å}$), so we may estimate the reduced effective charge $z \simeq 3\times 10^{-2}$.

16.5 Dielectric function

The dielectric function given by equation (16.18) has a singularity for $\omega = 0$, as arising from the exact cancellation in the static limit of the external field by the internal field. It is plausible to assume that residual polarization fields are still present in this static limit, like, for instance, the intrinsic polarizability. In this case, equation (16.18) is modified, and the dielectric function is of the type

$$\varepsilon = \frac{\omega^2 - \omega_p^2}{\omega^2 + \omega_0^2} \ , \tag{16.19}$$

where ω_0 is a plasma frequency associated with the intrinsic, molecular polarizability. As such, it is a very high frequency, and equation (16.19) gives a small, negative contribution to the dielectric function in the static limit ($\omega \rightarrow 0$).

A static field D produces an electric dipole $p = q_e x$, where q_e is the electric charge and x is a small displacement subjected to the equation of motion $m_e \ddot{x} + m_e \omega_p^2 x = q_e D$, where m_e is the mass of the electronic cloud. According to the plasma model suggested here, we assume that the electronic cloud in the $H-O$ bonds has the same eigenfrequency ω_p as the $H-O$ ensemble. In the static limit $x = q_e D/m_e \omega_p^2$ (polarizability $\alpha = q_e^2/m_e \omega_p^2$ in $p = \alpha D$), and we get a polarization $P = p/a_0^3 = q_e^2 D/m_e a_0^3 \omega_p^2$, where a_0 is of the order of the atomic size. We get an internal field $E_{int} = -4\pi P = -\left(4\pi q_e^2/m_e a_0^3\right) D/\omega_p^2 = -\left(\omega_0^2/\omega_p^2\right) D$, where ω_0 is a frequency of the order of atomic frequencies. Consequently, the dielectric function ε in equation $D = \varepsilon E = \varepsilon(D + E_{int})$ is given by $\varepsilon \simeq -\omega_p^2/\omega_0^2$ ($\omega_p^2/\omega_0^2 \ll 1$), which is precisely the static dielectric function given by equation (16.19).

The dielectric properties of water are still a matter of debate. It is agreed that the permitivity dispersion of water is described to some extent by a Debye model of the form $\varepsilon = a + b/(1 - i\omega\tau)$, where a and b are semi-empirical parameters and $\tau \sim \eta a^3/T$ is a relaxation time; η denotes the viscosity and T is the temperature.[5] This Debye model assumes mainly an orientational polarizability of electric dipoles, which, due to the preservation of the directional character of the $O-H$ bonds, is compatible with the plasma model suggested here for water. Therefore, the contribution given by equation (16.19) should be added to the above Debye formula for the dielectric function, which becomes

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[5] H. Frohlich, *Theory of Dielectrics*, Oxford (1958); P. Debye, *Polar Molecules*, Dover, NY (1945).

$$\varepsilon = a + \frac{b}{1-i\omega\tau} + \frac{\omega^2-\omega_p^2}{\omega^2+\omega_0^2} \ . \tag{16.20}$$

Parameters a and b in equation (16.20) are related to the static permitivity ε_0 and high-frequency permitivity ε_∞ through

$$\varepsilon_0 = a + b - \omega_p^2/\omega_0^2 \ , \ \varepsilon_\infty = a + 1 \ . \tag{16.21}$$

We may neglect ω_p^2/ω_0^2 here because it is too small, and we may also take $\varepsilon_\infty = 1 (a = 0)$. The static permitivity $\varepsilon_0 = b$ is given mainly by the electric dipoles. Let $\mathbf{p}$ be such an electric dipole. Its energy in an electric field $\mathbf{D}$ is $-pD\cos\theta$, where θ is the angle between $\mathbf{p}$ and $\mathbf{D}$. The thermal distribution of such dipoles is $dw \sim \exp(-pD\cos\theta/T)d(\cos\theta)$, where T denotes the temperature. We get easily the thermal average $\langle\cos\theta\rangle = -L(pD/T)$, where $L(x) = \coth x - 1/x$ is the well-known Langevin's function.

We take $p = 2ez_e(a/2) = ez_ea$, where $a \sim 3\text{Å}$ and z_e is a delocalized reduced charge associated with the $H-O$ dipole. We estimate the argument pD/T of the Langevin's function. At room temperature, we find $pD/T \simeq 3\times10^{-4}Dz_e$. For $pD/T = 1$ this corresponds to an external field $D = \frac{1}{3z_e}\times10^4 esu$, or $D = 10^8/z_eV/m$ $(1esu = 3\times10^4V/m)$. This is an extremely high field, so we are justified to take $pD/T \ll 1$, and $L(pD/T) \simeq pD/3T$. We get therefore a polarization $P = -np\langle\cos\theta\rangle = np^2D/3T$, an internal field $E_{int} = -4\pi P = -4\pi np^2D/3T$, and a permitivity

$$\varepsilon_0 = b = \frac{1}{1-4\pi np^2/3T} \tag{16.22}$$

from $D = \varepsilon E = \varepsilon(D+E_{int})$. This is the well-known Kirkwood formula. For the empirical value $\varepsilon_0 = 80$, we get (at room temperature) a reduced charge $z_e \simeq 10^{-2}$. This is in good agreement with the $H^{+z}-O^{-2z}$ plasma charge z estimated above.

16.6 Cohesion and thermodynamics

In "Liquids" chapter a model of liquid has been introduced, based on an excitation spectrum (per particle) of the form $\varepsilon_n = -\varepsilon_0 + \varepsilon_1(n + 1/2)$, where ε_0 is a cohesion energy and ε_1 is the quanta of energy of a harmonic oscillator with one degree of freedom; n represents here the quantum number. The model includes also the kinematic correlations (spatial restrictions) of the movement of the liquid molecules. This model leads to a consistent thermodynamics for liquids, arising from a statistics which is equivalent with the statistics of bosons in two dimensions.

For water, the cohesion energy per particle ε_0 can be estimated from the vaporization heat ($\simeq 40kJ/mol$). It gives $\varepsilon_0 \sim 10^3K$. On the other hand, it was shown[6] that the transition temperature between a gas and a liquid of identical particles is approximately given by

$$T_t = \frac{4}{3}\frac{\varepsilon_0}{\ln(\varepsilon_0/T_0)} \ , \tag{16.23}$$

where $T_0 = \hbar^2 n^{2/3}/m$ is a characteristic temperature of the gas. We can apply this formula to water dissociation, taking n as the density of hydrogen atoms, m as the mass of two hydrogen atoms and $T_t = 383K$ (at normal pressure; ε_0 depends on the inter-particle spacing). We may neglect the oxygen, as it is too heavy in comparison with the hydrogen atoms. We get $T_0 \simeq 2K$ and the above formula gives $\varepsilon_0 \simeq 2000K \simeq 200meV$ for the cohesion energy of water per molecule, which is consistent with the above estimate ($1eV \simeq 11.6 \times 10^3K$; $n \simeq 1/a^3$ with $a = 3\text{Å}$ and $\hbar \simeq 10^{-27}erg \cdot s$; Bohr radius $a_H = \hbar^2/m_e e^2 \simeq 0.53\text{Å}$, $e^2/a_H \simeq 27.2eV$, where m_e is the electron mass). It is worth noting that the mechanism of vaporization assumed here implies the dissociation of the water molecule.

The plasma oscillations obtained above can be quantized and the energy levels of the plasma read

$$E_n = \sum_{\mathbf{q}} \hbar\omega_p(n + 1/2) = \frac{V}{(2\pi)^3}\frac{4\pi}{3}q_c^3 \cdot \hbar\omega_p(n + 1/2) \ , \tag{16.24}$$

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[6] M. Apostol, "The condensation of matter-a model of phase transition of the first kind", Mod. Phys. Let. **B21** 893 (2007).

where q_c is a cutoff wavevector. The prefactor in equation (16.24) is $Vq_c^3/6\pi^2 \simeq N(aq_c/4)^3$, so the energy levels given above can be written as

$$E_n = N\varepsilon_1(n+1/2) \ , \tag{16.25}$$

where $\varepsilon_1 = (aq_c/4)\hbar\omega_p$. These energy levels correspond to a harmonic oscillator with one degree of freedom. It follows that the present description of water as a two-species of highly dissociated ionic plasma provides a further support for the liquid model mentioned above. If we take $q_c \simeq 1/a$, the energy quantum $\varepsilon_1 = (aq_c/4)^3\hbar\omega_p =\simeq 3zmeV$ represents the ε_1 parameter in the spectrum of the liquid. (The plasma frequency given by equation (16.11) is $\omega_p \simeq 200zmeV$).

16.7 Debye screening

As it is well-known the plasma excitations described above represent collective oscillations of the density in the long wavelength limit. At the same time, they induce correlations in the ionic movements. For a classical plasma these correlations are associated with a screening length given by the Debye-Huckel theory as

$$\kappa^{-1} = \left(T/24\pi nz^2e^2\right)^{1/2} \tag{16.26}$$

for our case ($\kappa^{-1} = \left(T/4\pi e^2\sum_i n_iz_i^2\right)^{-1}$where i labels the ionic species with density n_i and charge ez_i). The formula is valid for the Coulomb energy z^2e^2/a much lower than the temperature T. In the present case we have $z^2e^2/a \simeq 45K$ (for $z \simeq 3\times10^{-2}$), which shows that the above condition is fulfilled. From equation (16.26) we get $\kappa^{-1} \sim 1\text{Å}$ (at room temperature), in agreement with the present molecular-dissociation model. The correlation energy per particle is given by

$$\varepsilon_{corr} = -\frac{e^2}{a}\sqrt{\frac{\pi e^2}{Ta}}(6z^2)^{3/2} \tag{16.27}$$

($\varepsilon_{corr} = -(e^2/a)\sqrt{\pi e^2/Ta}(\sum_i n_iz_i^2)^{3/2}$). The estimation of this energy gives $\varepsilon_{corr} \sim 10^2K$ (at room temperature). It contributes to the cohesion energy.

16.8 Sound anomaly

The sound-like branch $\omega_2 \simeq \omega_s = v_s q$, where $v_s = \sqrt{9n\chi/(M+2m)}$ according to equation (16.12), is distinct from the ordinary hydrodynamic sound whose velocity is given by the well-known formula $v_0 = 1/\sqrt{\kappa n m}$ for a one-component fluid, where κ is the adiabatic compressibility. For the present two-component fluid ($H^{+z} - O^{-2z}$ plasma), the velocity of the ordinary sound is given by $v_0 = 1/\sqrt{\kappa n(M+2m)}$. The former represents a non-equilibrium elementary excitation, whose velocity v_s does not depend on temperature, while the latter proceeds by thermodynamic, equilibrium, adiabatic processes, and its velocity v_0 depends on temperature through the adiabatic compressibility κ. In order to distinguish them from the hydrodynamic sound we propose to call the sound-like excitations derived here density "kinetic" modes or "densitons". The distinction between the two sounds is made by a threshold wavevector q_t in the following manner. Suppose that there is a finite lifetime τ for the sound-like excitations ω_s propagating with a velocity v_s and a corresponding mean freepath $\Lambda = v_s\tau$. If the sound-like wavelength λ is much longer than the mean freepath, $\lambda \gg \Lambda$, then we are in the collision-like regime ($\omega_s\tau \ll 1$), and the collisions may restore the thermodynamic equilibrium. In this case the hydrodynamic sound propagates, and the sound-like excitations do not. This condition defines the threshold wavevector $q_t = 1/v_s\tau$. In the opposite case, $q \gg q_t$ (collisionless regime), it is the sound-like excitations that propagate, and not the hydrodynamic sound. The finite lifetime τ originates in the residual interactions between the collective modes and the underlying motion of the individual particles. It is easy to estimate this residual interaction. It is given by $\sqrt{\varepsilon T}$, where ε is the mean energy per particle corresponding to the motion of the individual particles. We get therefore $\tau \simeq \hbar/\sqrt{\varepsilon T}$ and the threshold wavevector $q_t = \sqrt{\varepsilon T}/\hbar v_s$. It is difficult to have a reliable estimation of the mean energy ε; for a resonable value $\varepsilon = 10meV$ we get $q_t \simeq 0.1\mathring{A}^{-1}$ at room temperature for $v = 3000m/s$, which is in good agreement with experimental data.

Indeed, the phenomenon of two-sound anomaly in water is well-documented. Neutron, X-ray, Brillouin or ultraviolet light scattering on water revealed the existence of a hydrodynamic sound propagating with velocity $v_0 \simeq 1500m/s$ for smaller wavevectors and an additional sound propagating with velocity $\simeq 3000m/s$ for larger wavevectors. In addition, though both sound velocities do exhibit an isotopic effect, their ratio does not. According to the above discussion, we assign this additional, faster sound to the sound-like excitations derived here. We can see that both v_0 and v_s given above exhibit a weak isotopic effect, while their ratio $v_s/v_0 = 3n\sqrt{\kappa\chi}$ does not. From $v_s = \sqrt{9n\chi/(M+2m)} = 3000m/s$ we get the short-range interaction $\chi \simeq 7eV \cdot \mathring{A}^3$. Similar results are obtained for other forms of dissociation of the water molecule, like $OH^- - H^+$ or $OH^- - H_3O^+$, so the $H^{+z} - O^{-2z}$ plasma model employed here can be viewed as an effective model for various plasma components that may exist in water.

16.9 Another sound

It is worth calculating the spectrum given by equations of motion (16.10) without neglecting higher-order contributions in q^2. The result of this calculation is given by

$$\omega_{1,2}^2 = \frac{1}{2}\omega_p^2\left[1 + Ax^2 \pm \sqrt{1 + 2Bx^2 + A^2x^4}\right] \ , \tag{16.28}$$

where

$$A = \frac{1}{9\alpha}(2 + 5\alpha + 2\alpha^2) \ , \ B = \frac{1}{9\alpha}(2 - 13\alpha + 2\alpha^2) \ , \tag{16.29}$$

$\alpha = m/M$ and $x = v_s q/\omega_p$. It is shown in Fig. 16.1.

Frequency ω_2 in equation (16.28) represents the sound-like branch, which goes like $\omega_2 \simeq \omega_s = v_s q$ in the long wavelength limit and approaches the horizontal asymptote $\omega_2 = \omega_p/\sqrt{A} \simeq \omega_p\sqrt{m/2M}$ for shorter wavelengths. Frequency ω_1 in equation (16.28) represents the plasmonic branch ($\omega_1 \simeq \omega_p$ for $q \to 0$). In the long wavelength limit it goes like

$$\omega_1 \simeq \omega_p + \frac{(M-m)^2}{9mM}v_s^2 q^2/\omega_p \ , \ q \to 0 \ . \tag{16.30}$$

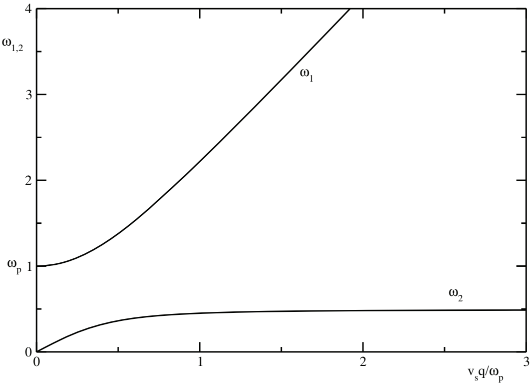

Figure 16.1: The spectrum of the density oscillations given by equation (16.28) for the $H^{+z} - O^{-2z}$ plasma with the same short-range interaction between ionic species.

Due to the large disparity between the two masses m and M we can see that the plasma frequency has an abrupt increase towards the short-wavelength oblique asymptote given by

$$\omega_a \simeq \sqrt{A} v_s q \simeq \sqrt{2M/9m + 5/9} v_s q \ . \qquad (16.31)$$

For small values of ω_p (vanishing Coulomb coupling, $z \to 0$) this asymptotic frequency may look like an anomalous sound propagating with velocity

$$v_a \simeq \sqrt{2M/9m + 5/9} v_s \ . \qquad (16.32)$$

For water, we get $v_a \simeq 2v_s$ from this formula. However, the ratios v_a/v_s or v_a/v_0 exhibit a rather strong isotopic effect, which is not supported by experimental data.

16.10 Multi-component plasma

The model presented herein might be generalized to a multi-component plasma consisting of several ionic species labelled by i, each with a number of particles N_i, density n_i, charge $z_i e$ and mass m_i, such that $\sum_i z_i n_i = 0$.

The lagrangian of the density oscillations is given by

$$\begin{gathered} L = -\tfrac{1}{2n} \sum_{i\mathbf{q}} m_i n_i \dot{u}_i(\mathbf{q}) \dot{u}_i(-\mathbf{q}) + \\ + \tfrac{1}{2n} \sum_{ij\mathbf{q}} n_i n_j q^2 \left[\varphi_{ij}(q) + \chi(q)\right] u_i(\mathbf{q}) u_j(-\mathbf{q}) + \\ + i\tfrac{e}{n} \sum_{i\mathbf{q}} n_i z_i q \phi(\mathbf{q}) u_i(-\mathbf{q}) \ , \end{gathered} \tag{16.33}$$

where $\varphi_{ij}(q) = 4\pi z_i z_j e^2/q^2$. The equations of motion are given by

$$m_i \ddot{u}_i + 4\pi e^2 z_i \sum_j z_j n_j u_j + q^2 \chi \sum_j n_j u_j = -iqez_i\phi \ . \tag{16.34}$$

Making use of the notations

$$S_1 = \sum_i z_i^2 n_i/m_i \ , \ S_2 = \sum_i n_i/m_i \ , \ S_3 = \sum_i z_i n_i/m_i \ , \tag{16.35}$$

the eigenfrequencies $\omega_{1,2}$ of the system of equations (16.34) in the long wavelength limit are given by

$$\omega_1^2 \simeq \omega_p^2 = 4\pi e^2 S_1 = \sum_i \frac{4\pi e^2 z_i^2 n_i}{m_i} \ , \tag{16.36}$$

which represents the plasma branch of the spectrum, and

$$\omega_2^2 \simeq \omega_s^2 = \left(S_2 - S_3^2/S_1\right) \chi q^2 = v_s^2 q^2 \ , \tag{16.37}$$

which represents the sound-like excitations (the sound velocity given by equation (16.37) is always a real quantity, as a consequence of the Schwarz-Cauchy inequality.). The plasma branch of the spectrum has an oblique asymptote given by $\omega_1 \simeq \omega_a = \sqrt{\chi S_2} q$, which may be taken as an anomalous sound propagating with velocity $v_a = \sqrt{\chi S_2}$ for small values of ω_p. The ratio of the two sound velocities is given by

$$v_a/v_s = \frac{1}{\sqrt{1 - S_3^2/S_1 S_2}} \ , \tag{16.38}$$

which is always higher than unity. The sound branch of the spectrum has an horizontal asymptote given by $\omega_2 \simeq \sqrt{1 - S_3^2/S_1S_2}\omega_p$. For the $H^{+z} - O^{-2z}$ plasma we can check from equation (16.38) that $v_a/v_s \simeq (2M/9m + 5/9)^{1/2} \simeq 2$, and $\omega_2 \simeq 3\sqrt{m/2M}\omega_p$, as obtained above. As we have discussed above this ratio exhibits a rather strong isotopic effect, which is not in accord with experimental data. We assign therefore the additional sound to sound-like excitations propagating with velocity v_s given by equation (16.37). The ordinary, hydrodynamic sound in a multi-component mixture has the velocity $v_0 = 1/\sqrt{\kappa \sum_i n_i m_i}$. It can be shown that $v_s^2/v_0^2 \geq n^2\kappa\chi$ for a neutral multi-component mixture.

The internal field is given by

$$E_{int} = -4\pi e \sum_i z_i n_i u_i \ ; \tag{16.39}$$

we get easily from equations (16.34)

$$E_{int} = -iq\phi \frac{\omega_p^2}{\omega^2 - \omega_p^2} \tag{16.40}$$

and the dielectric function $\varepsilon = 1 - \omega_p^2/\omega^2$, as expected.

16.11 Structure factor

The structure factor is defined by

$$\begin{aligned} S(q,\omega) &= \tfrac{1}{2\pi}\int d\mathbf{r}d\mathbf{r'}dt \, \langle \delta n(\mathbf{r},t)\delta n(\mathbf{r'},0)\rangle \, e^{i\mathbf{q}(\mathbf{r}-\mathbf{r'})-i\omega t} = \\ &= \tfrac{N}{2\pi n^2}\int dt \, \langle \delta n(\mathbf{q},t)\delta n(-\mathbf{q},0)\rangle \, e^{-i\omega t} \ , \end{aligned} \tag{16.41}$$

where the brackets stand for the thermal average (we leave aside the central peak). Since

$$\delta n(\mathbf{q},t) = -iq \sum_i n_i u_i(\mathbf{q},t) \ , \tag{16.42}$$

it becomes

$$S(q,\omega) = \frac{Nq^2}{2\pi n^2}\int dt \sum_{ij} n_i n_j \, \langle u_i(t)u_j(0)\rangle \, e^{-i\omega t} \ , \tag{16.43}$$

where we dropped out the argument $\mathbf{q}$.

In order to calculate the thermal averages we turn back to the system of equations (16.34) without the external electric field. This system can be written as

$$\begin{aligned}&(-\omega^2 + aS_1)x + bS_3 y = 0 \ , \\ &aS_3 x + (-\omega^2 + bS_2)y = 0 \ ,\end{aligned} \tag{16.44}$$

where $a = 4\pi e^2$, $b = \chi q^2$, $S_{1,2,3}$ are given by equation (16.35) and

$$x = \frac{1}{n}\sum_i z_i n_i u_i \ , \ y = \frac{1}{n}\sum_i n_i u_i \ . \tag{16.45}$$

In addition,

$$u_i = \frac{anz_i}{m_i\omega^2}x + \frac{bn}{m_i\omega^2}y \ . \tag{16.46}$$

The system of equations (16.44) has two eigenfrequencies $\omega_{1,2}$ as given by equations (16.36) and (16.37). The corresponding eigenvectors are given by

$$x_1 \sim S_1 \ , \ y_1 \sim S_3 \ ; \ x_2 \sim bS_3 \ , \ y_2 \sim -aS_1 \tag{16.47}$$

in the long wavelength limit. According to equation (16.46) the coordinates u_i can be written as

$$u_i^{(1,2)} = \frac{anz_i}{m_i\omega_{1,2}^2}x_{1,2}e^{i\omega_{1,2}t} + \frac{bn}{m_i\omega_{1,2}^2}y_{1,2}e^{i\omega_{1,2}t} \ , \tag{16.48}$$

and one can see that they are coordinates of linear harmonic oscillators with frequencies $\omega_{1,2}$ and potential energies $m_i\omega_{1,2}^2\left[u_i^{(1,2)}\right]^2/2$. The thermal distribution of the coordinate u for such an oscillator is given by $dw = \sqrt{m\omega^2/2\pi T}\exp\left(-m\omega^2u^2/2T\right)du$ in the classical limit, where T denotes the temperature ($T \gg \hbar\omega$). It follows

$$\left\langle u_i^{(1,2)}u_j^{(1,2)}\right\rangle = \frac{T}{m_i\omega_{1,2}^2}\delta_{ij} \ . \tag{16.49}$$

Writing

$$u_i = u_i^{(1)}e^{i\omega_1 t} + u_i^{(2)}e^{i\omega_2 t} \tag{16.50}$$

and making use of equation (16.49) the structure factor given by equation (16.43) becomes

$$\begin{aligned} S(q,\omega) = NTq^2 \left(\textstyle\sum_i n_i^2/n^2 m_i\right) \cdot \\ \cdot \left[\tfrac{1}{\omega_1^2}\delta(\omega-\omega_1) + \tfrac{1}{\omega_2^2}\delta(\omega-\omega_2)\right] \ . \end{aligned} \tag{16.51}$$

We can see from this equation that the relevant sound contributions are given by

$$S(q,\omega) \simeq \frac{NT}{v_{s,a}^2}\left(\sum_i n_i^2/n^2 m_i\right)\delta(\omega - v_{s,a}q) \ . \tag{16.52}$$

The relaxation and damping effects can be included in the above expressions of the structure factor. As it is well-known, they amount to representing the δ-functions by lorentzians.

16.12 Asymmetric interaction

Up to now, the short-range interaction was assumed to be the same for all ionic species. In general, we may introduce a short-range interaction χ_{ij} depending on the nature of the ionic species. If this interaction is separable, the solution given above for a multi-component plasma holds with minor modifications. For a non-separable short-range interaction, appreciable changes may appear in the spectrum, which may exhibit multiple branches. Such a spectrum may serve to identify the nature (mass, charge) of various molecular aggregates in a multi-component plasma. It is worth noting that a range of frequencies $10^{10}s^{-1} - 10^{12}s^{-1}$ is documented in living cells by microwave, Raman and optical spectroscopies and by cell-biology studies, upon which the theory of coherence domains in living matter is built.[7]

We consider here again the $H^{+z} - O^{-2z}$ plasma with different short-range interaction $\chi_{HH} = \chi_1\, , \chi_{OO} = \chi_2\, , \chi_{OH} = \chi_3$; it still exhibits two branches of frequencies, a plasmonic one (ω_1) and a sound-like one (ω_2), but the spectrum may have certain peculiarities (the dielectric constant is not affected by this modification). Equations of motion (16.15) become now

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[7] H. Frohlich, "Bose condensation of strongly excited longitudinal electric modes", Phys. Lett. **A26** 402 (1968); H. Frohlich, "Long-range coherence and energy storage in biological systems", Int. J. Quant. Chem. **2** 641 (1968); G. Preparata, *QED Coherence in Matter*, World Sci. (1995).

$$\begin{aligned} &m\ddot{u} + 2nq^2(\varphi+\chi_1)u - nq^2(2\varphi-\chi_3)v = -izeq\phi \ , \\ &M\ddot{v} + nq^2(4\varphi+\chi_2)v - 2nq^2(2\varphi-\chi_3)u = 2izeq\phi \ . \end{aligned} \tag{16.53}$$

We introduce the notations

$$a = 2nq^2\varphi/m = 8\pi ne^2z^2/m \ , \ \ b_{1,2,3} = n\chi_{1,2,3}/m \ . \tag{16.54}$$

The dispersion relations can be computed straightforwardly. In the long wavelength limit ($q \to 0$) we get the plasmonic branch

$$\omega_1^2 \simeq (1+2\alpha)a + \frac{2b_1+\alpha^2b_2-4\alpha b_3}{1+2\alpha}q^2 \ , \tag{16.55}$$

where $(1+2\alpha)a = 16\pi ne^2z^2/\mu$ is the plasma frequency, and the sound-like branch

$$\omega_2^2 \simeq \frac{\alpha(4b_1+b_2+4b_3)}{1+2\alpha}q^2 = v_s^2q^2 \ ; \tag{16.56}$$

one can see that the sound velocity v_s is always a real quantity.

The sound-like branch exhibits an asymptote in the short-wavelength limit given by

$$\omega_2^2 \sim \frac{1}{2}\left[2b_1+\alpha b_2 - \sqrt{(2b_1-\alpha b_2)^2+8\alpha b_3^2}\right]q^2 \ , \tag{16.57}$$

whose slope may have either sign or vanish. It is easy to see that this slope is positive for $b_3^2 < b_1b_2$, negative for $b_3^2 > b_1b_2$ (when the sound-like branch has a maximum value) and it vanishes for $b_3^2 = b_1b_2$ (when the sound-like branch has an horizontal asymptote). In the case of a negative slope the sound velocity may exhibit a negative velocity and the sound may suffer a strong absorption for moderate values of the wavevector, which may indicate an anomalous or unphysical situation.

We return now to the plasmon branch given by equation (16.55), and write it as

$$\omega_1^2 = \omega_p^2 + b_2\frac{2x^2-4\alpha\lambda x+\alpha^2}{1+2\alpha}q^2 \ , \tag{16.58}$$

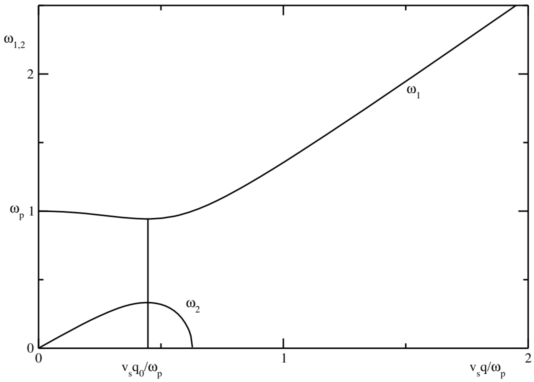

Figure 16.2: Excitation spectrum given by equation (16.59) for the $H^{+z} - O^{-2z}$ plasma with short-range potentials $\chi_{OO} = \chi_{HH} = 0$ and $\chi_{OH} = \chi \neq 0$.

where $\lambda^2 = b_3^2/b_1 b_2$ and $x = \sqrt{b_1/b_2}$. It is easy to see that for $\lambda^2 > 1$ the plasmonic spectrum exhibits a dip around a certain value q_0 of the wavevector q for $\left(\lambda - \sqrt{\lambda^2 - 1/2}\right)\alpha < \sqrt{b_1/b_2} < \left(\lambda + \sqrt{\lambda^2 - 1/2}\right)\alpha$; it approaches an asymptote with a positive slope for $q \to \infty$, which may define again an anomalous sound for small values of ω_p.

We illustrate these anomalies for a particular case of short-range interaction $\chi_{1,2} = 0$ and $\chi_3 = \chi$ $(b_3 = n\chi/m)$. The dispersion relations of the system of equations (16.53) become

$$\omega_{1,2}^2 = \frac{1}{2}\omega_p^2 \left[1 \pm \sqrt{1 - 4v_s^2 q^2/\omega_p^2 + \frac{(1+2\alpha)^2}{2\alpha} v_s^4 q^4/\omega_p^4} \right] . \qquad (16.59)$$

The plasmonic branch has a minimum value for $q_0 \simeq 2\sqrt{m/M}\omega_p/v_s$, where the sound-like branch has a maximum value ($\simeq \sqrt{2m/M}\omega_p$). The spectrum is shown in Fig. 16.2. Using $\omega_p \simeq 10^{13}s^{-1}$ estimated above and the sound velocity $v_s \simeq 3000 m/s$ in water we get $q_0^{-1} \simeq 6$Å. We may expand ω_1 in series of $(q - q_0)^2$ about its minimum value at q_0 and get $\omega_1 \simeq \omega_p + (M/4m + 1)(v_s^4 q_0^2/\omega_p^3)(q - q_0)^2 = \omega_p + (1 + 4m/M)v_s^2(q - q_0)^2/\omega_p$. This is similar with the rotons-like dispersion relation discussed in connection with the coherence domains in water.

Although this might be an interesting suggestion, it is inconsequential here, because ω_p is too small in comparison with the temperatures at which water exists and, therefore, this "dip" feature has no effect for the water thermodynamics.

16.13 Summarizing remarks

We summarize the main features of the model suggested here for liquid water. First, we assume, as it is generally accepted, the four, directional sp^3-oxygen electronic orbitals. The electron delocalization along two such orbitals together with a corresponding delocalization of the hydrogen electronic charge lead to the water cohesion. It is represented by the cohesion energy ε_0 discussed here. Within such a picture, we can still visualize the oxygen and the hydrogen as neutral atoms, moving around almost freely (as a consequence of the uniformity of the environment). This gives a noteworthy support to the "hydrogen bonds" concept. The point of view taken in this paper is that the hydrogen bonds in water are introduced in order to account for the uniformity of the environment of a water molecule in liquid water. As such, it helps understand the cohesion. However, a consistent upholding of the hydrogen-bonds concept would mean a vanishing dipole momentum of liqud water. Pauling,[8] who introduced originally this concept, qualifies it by admitting an asymmetry in the four hydrogen bonds around an oxygen ion, arising from the two-out-of-four occupied orbitals. We suggest that the uniformity of the environment makes the hydrogen atoms (ions) moving as independent entities, while the asymmetry induces a small charge z, so the ion motion is subjected to Coulomb (and short-range interactions). The electric moment is ascribed to the directional character of the sp^3-oxygen electronic orbitals and the charge transfer between oxygen and hydrogen. Thereby, the hydrogen-bond concept is employed here through its two features, directionality and uniformity, with a slight asymmetry, all viewed as independent qualitative ingredients. To this picture the present model adds another component, arising from a very small charge transfer between hydrogen and oxygen atoms, leading to a $H^{+z}-O^{-2z}$ plasma, with the reduced charge z. It may originate in the weak asymmetry of the two occupied sp^3-oxygen electronic orbitals with respect to the other two unoccupied orbitals. Under these circumstances, the hydrogen and the oxygen ions interact, both by Coulomb and short-range potentials. This interaction gives the plasma frequency and the sound-like excitations frequency. The plasmons contribute to the excitations which give rise to a consistent thermodynamics for liquids. In addition, the ionic plasma oscillations entail oscillations of the delocalized electronic cloud, with the same eigenfrequency. Subject to an external field, these electronic oscillations produce an intrinsic polarizability which removes the $\omega = 0$ singularity in the plasma dielectric function (the ω_0 frequency). In addition, the magnitude of the electric moment $\mathbf{p}$ which is responsible for the orientational, static dielectric function is in satisfactory agreement with the plasma charge z derived herein.

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[8] L. Pauling, *General Chemistry*, Dover, NY (1982).

On the basis of this model we are able to understand to some extent, both qualitatively and in some places even quantitatively, the sound anomaly, the dielectric function (permitivity dispersion), the structure factor, cohesion and thermodynamics of water. The model is extended to a multi-component classical plasma, including an asymmetric short-range interaction between the components, which might be relevant for more complex structural aggregates like those in biological matter.

16.14 Molecular mixtures

We compute here the excitation spectrum of the density collective oscillations for multi-component molecular mixtures both with Coulomb and (repulsive) short-range interactions. Distinct sound-like excitations appear, governed by the short-range interaction, which differ from the ordinary hydrodynamic sound. The dielectric function and the structure factor are also calculated. The "two-sounds phenomenon" can be understood by means of the predictions of this model.[9]

The "two-sounds anomaly" is persistently reported over the years in water, either in normal conditions or undercooled, as well as in other liquid molecular mixtures. Inelastic neutron, X-ray, Brillouin and, more recently, ultraviolet scattering, either in ordinary or in heavy water, seem to indicate an additional, faster, higher-frequency sound, propagating with velocity $\simeq 3000 m/s$ up to intermediate wavevectors (mean inter-molecular distance in water is $\simeq 3$Å), besides the ordinary hydrodynamic sound propagating with velocity $\simeq 1500 m/s$. A dispersionless mode ($\simeq 10^{13} s^{-1}$) was also reported sometimes (as well as no additional sound). The phenomenon is also documented both by simulations of molecular dynamics and experimental data in binary mixtures with large mass difference (metallic alloys, rare-gas mixtures).

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[9] M. Apostol, "Dynamics of collective density modes in multi-component molecular mixtures", Phys. Chem. Liq. **47** 35 (2009).

We show herein that such a "two-sounds anomaly" may appear in interacting molecular systems with (repulsive) short-range interaction. Such a model could reasonably be related to liquid water (or other physical systems as those indicated above). The velocity of the sound-like excitations is independent of temperature, in contrast with the velocity of the hydrodynamic sound which is governed by the adiabatic compressibility, and thus temperature-dependent. In addition, the plasma-like branch of the spectrum due to the Coulomb interaction may appear as another sound-like mode for shorter wavelengths and weak Coulomb coupling. We report here also the computation of the dielectric function and the structure factor within such a model.

We start with the well-known representation of the particle density

$$n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) = \frac{1}{V} \sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \sum_i e^{-i\mathbf{q}\mathbf{r}_i} \tag{16.60}$$

for a collection of N particles enclosed in volume V, where $\mathbf{r}_i$ denotes the position of the i-th particle. We consider a small displacement $\mathbf{r}_i \rightarrow \mathbf{r}_i + \mathbf{u}(\mathbf{r}_i)$ in these positions, as given by a displacement field $\mathbf{u}(\mathbf{r}_i)$, such that the particle density becomes

$$\begin{aligned} \widetilde{n}(\mathbf{r}) = \tfrac{1}{V} \textstyle\sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \sum_i e^{-i\mathbf{q}[\mathbf{r}_i + \mathbf{u}(\mathbf{r}_i)]} = \\ = \tfrac{1}{V} \textstyle\sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \sum_i e^{-i\mathbf{q}\mathbf{r}_i} \left[1 - i\mathbf{q}\mathbf{u}(\mathbf{r}_i) + ...\right] \end{aligned} \tag{16.61}$$

for $\mathbf{qu}(\mathbf{r}_i) \ll 1$. Now we employ a Fourier representation

$$\mathbf{u}(\mathbf{r}_i) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \mathbf{u}(\mathbf{q}) e^{i\mathbf{q}\mathbf{r}_i} \tag{16.62}$$

as well as the well-known random-phase approximation

$$\sum_i e^{i(\mathbf{q}-\mathbf{q}')\mathbf{r_i}} = N\delta_{\mathbf{q},\mathbf{q}'} \tag{16.63}$$

to get

$$\widetilde{n}(\mathbf{r}) = n - in\frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} \mathbf{qu}(\mathbf{q}) \ , \tag{16.64}$$

where $n = N/V$ is the particle density. By comparing equations (16.60) and (16.64), we can see that the small change in the density can be represented as

$$\widetilde{n}(\mathbf{r}) - n = \delta n(\mathbf{r}) = -ndiv\mathbf{u}(\mathbf{r}) \ , \tag{16.65}$$

and its Fourier transform $\delta n(\mathbf{q}) = -in\mathbf{qu}(\mathbf{q})$.

We apply this displacement-field approach to a multi-component molecular mixture consisting of several species labelled by i, each with N_i particles in volume V, mass m_i and electric charge ez_i, where $-e$ is the electron charge and z_i is a reduced effective charge, interacting through Coulomb potentials φ_{ij} and short range potentials χ_{ij}. The mixture is subjected to the neutrality condition $\sum_i n_i z_i = 0$, where $n_i = N_i/V$ is the particle density of the i-th species. We consider elementary excitations of the particle density, whose interaction energy is given by

$$U = \frac{1}{2} \sum_{ij} \int d\mathbf{r} d\mathbf{r}' \left[\varphi_{ij}(\mathbf{r}-\mathbf{r}') + \chi_{ij}(\mathbf{r}-\mathbf{r}')\right] \delta n_i(\mathbf{r}) \delta n_j(\mathbf{r}') \ , \tag{16.66}$$

where $\varphi_{ij} = e^2 z_i z_j / |\mathbf{r}-\mathbf{r}'|$ and $\delta n_i(\mathbf{r})$ denotes a small density disturbance which preserves the neutrality. According to equation (16.65) it can be represented as $\delta n_i = -n_i div\mathbf{u}_i$, where $\mathbf{u}_i$ is the displacement field. We use the Fourier transforms

$$\delta n_i(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} \delta n_i(\mathbf{q}) e^{i\mathbf{q}\mathbf{r}} \ , \ \varphi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{q}} \varphi(\mathbf{q}) e^{i\mathbf{q}\mathbf{r}} \ , \tag{16.67}$$

where $N = \sum_i N_i$ is the total number of particles, $\varphi(\mathbf{r}) = e^2/r$ and $\varphi(\mathbf{q}) = \varphi(q) = 4\pi e^2/q^2$. A similar Fourier transform is employed for the displacement field $\mathbf{u}_i$, which leads to $\delta n_i(\mathbf{q}) = -in_i\mathbf{q}\mathbf{u}_i(\mathbf{q})$. We can see that only the longitudinal components $u_i(\mathbf{q})$ of the displacement field are relevant, so we may write $\mathbf{u}_i(\mathbf{q}) = (\mathbf{q}/q)u_i(\mathbf{q})$, $\delta n_i(\mathbf{q}) = -iqu_i(\mathbf{q})$, with $\delta n_i^*(-\mathbf{q}){=}\delta n_i(\mathbf{q})$, $\mathbf{u}_i^*(-\mathbf{q}) = \mathbf{u}_i(\mathbf{q})$ and $u_i^*(-\mathbf{q}) = -u_i(\mathbf{q})$. Making use of the Fourier transforms introduced above, the interaction U given by equation (16.66) can be written as

$$U = -\frac{1}{2n}\sum_{ij\mathbf{q}} n_i n_j q^2 \left[\varphi_{ij}(q) + \chi_{ij}(q)\right] u_i(\mathbf{q})u_j(-\mathbf{q}) \ , \tag{16.68}$$

where $\varphi_{ij}(q) = z_i z_j \varphi(q)$ and $n = N/V$ is the total density of particles. We assume a weak q-dependence of $\chi_{ij}(q)$, as for short-range potentials.

Similarly, the kinetic energy associated with the coordinates u_i is given by

$$T = -\frac{1}{2n}\sum_{i\mathbf{q}} m_i n_i \dot{u}_i(\mathbf{q})\dot{u}_i(-\mathbf{q}) \ . \tag{16.69}$$

In addition, we introduce an external field $\phi(\mathbf{r})$, coupled to the electrical charges, which gives rise to the interaction

$$V = -i\frac{e}{n}\sum_{i\mathbf{q}} n_i z_i q\phi(\mathbf{q})u_i(-\mathbf{q}) \ . \tag{16.70}$$

The equations of motion corresponding to the lagrangian $L = T - U - V$ are given by

$$m_i\ddot{u}_i + 4\pi e^2 z_i \sum_j z_j n_j u_j + q^2\sum_j \chi_{ij} n_j u_j = -iqez_i\phi \ , \tag{16.71}$$

where we dropped out the argument $\mathbf{q}$ in $u_i(\mathbf{q})$ and $\phi(\mathbf{q})$ and neglect the weak q-dependence of $\chi_{ij}(q) = \chi_{ij}$. In order to simplify these equations we take the same (repulsive) short-range potentials for all species, $\chi_{ij} = \chi > 0$, and analyze first the homogeneous system of equations (16.71). We introduce the notations $a = 4\pi e^2$, $b = q^2\chi$,

$$S_1 = \sum_i \frac{z_i^2 n_i}{m_i} \ , \ S_2 = \sum_i \frac{n_i}{m_i} \ , \ S_3 = \sum_i \frac{z_i n_i}{m_i} \ , \tag{16.72}$$

and

$$x=\frac{1}{n}\sum_i z_i n_i u_i\ ,\ y=\frac{1}{n}\sum_i n_i u_i\ . \tag{16.73}$$

Making use of these notations, the homogeneous system of equations (16.71) can be written as

$$\begin{aligned}&\left(-\omega^2+aS_1\right)x+bS_3y=0\ ,\\&aS_3x+\left(-\omega^2+bS_2\right)y=0\ .\end{aligned} \tag{16.74}$$

In addition, we have

$$\omega^2 u_i=\frac{anz_i}{m_i}x+\frac{bn}{m_i}y\ . \tag{16.75}$$

The spectrum of frequencies ω of the system of equations (16.74) can be obtained straightforwardly. It is given by

$$\omega_{1,2}^2=\frac{1}{2}\left[aS_1+bS_2\pm\sqrt{a^2S_1^2+2ab\left(2S_3^2-S_1S_2\right)+b^2S_2^2}\right]\ . \tag{16.76}$$

The ω_1-branch in equation (16.76) (corresponding to the plus sign) represents the plasmonic excitations. In the long wavelength limit it reads

$$\omega_1^2=aS_1+bS_3^2/S_1=\omega_p^2+bS_3^2/S_1\ \ ,\ \ q\to 0\ \ , \tag{16.77}$$

where ω_p, given by

$$\omega_p^2=aS_1=4\pi e^2\sum_i\frac{z_i^2n_i}{m_i}\ \ , \tag{16.78}$$

is the plasma frequency. For shorter wavelengths the ω_1-branch approaches an asymptote given by

$$\omega_1^2\simeq bS_2+aS_3^2/S_2\ \ ,\ \ q\to\infty. \tag{16.79}$$

The ω_2-branch in equation (16.76) (corresponding to the minus sign) represents sound-like excitations. In the long wavelength limit it is given by

$$\omega_2^2=\left(S_2-S_3^2/S_1\right)b=v_s^2q^2\ \ ,\ \ q\to 0\ \ , \tag{16.80}$$

where

$$v_s = \sqrt{(S_2 - S_3^2/S_1)\,\chi} \tag{16.81}$$

is the corresponding sound velocity. We can see easily, by applying the Schwarz-Cauchy inequality to the vectors $a_i = \sqrt{n_i/m_i}$ and $b_i = z_i\sqrt{n_i/m_i}$, that v_s^2 is always positive ($(S_2 - S_3^2/S_1) \geq 0$). For shorter wavelengths the ω_2-branch of the spectrum approaches an horizontal asymptote given by

$$\omega_2^2 \simeq \left(1 - S_3^2/S_1S_2\right)\omega_p^2 \ , \ \ q \to \infty \ . \tag{16.82}$$

In the limit of vanishing Coulomb coupling ($a \to 0$) the sound-branch of the spectrum becomes $\omega_2^2 = bS_2 = v_s^2q^2$, where

$$v_s^2 = \chi S_2 = \chi \sum_i (n_i/m_i) \ , \tag{16.83}$$

an expression which holds also for the same mass $m_i = m$ for all particles (one component), due to the neutrality condition ($S_3 = 0$).

The above elementary excitations, which are governed by interaction, are non-equilibrium collective modes which might be termed density "kinetic" modes. The sound-like excitations (ω_2-branch in equation (16.76)) may be called "densitons", in order to distinguish them from plasmons (ω_1-branch in equation (16.76)) and from the ordinary sound. They may correspond to the density collective modes suggested by Zwanzig for classical liquids.[10] We emphasize that these sound-like excitations are distinct from the ordinary hydrodynamic sound. It is also worth noting that the densitons have the same origin as the superfluid sound modes.

Indeed, the interaction corresponding to the latter can be written as

$$U = \frac{1}{2\kappa}\int d\mathbf{r}\,[div\mathbf{u}(\mathbf{r})]^2 = -\frac{1}{2\kappa n}\sum_{\mathbf{q}} q^2u(\mathbf{q})u(-\mathbf{q}) \ , \tag{16.84}$$

where $\kappa = -(1/V)(\partial V/\partial p)_S$ is the adiabatic compressibility (p denotes the pressure and S stands for entropy). The above equation is derived by making use of the change $\delta V = -V(\delta n/n) = V div\mathbf{u}$ in volume. We emphasize that for thermodynamic equilibrium we have only one displacement field $\mathbf{u}(\mathbf{r})$. Equation (16.84) together with the kinetic energy given by equation (16.69) for $u_i(\mathbf{q}) = u(\mathbf{q})$ lead to the sound branch $\omega_0^2 = v_0^2 q^2$, corresponding to the ordinary sound propagating with a velocity v_0 given by

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[10] R. Zwanzig, "Elementary excitations in classical liquids", Phys. Rev. **156** 190 (1967).

$$v_0^2 = \left(\kappa \sum_i n_i m_i\right)^{-1} . \tag{16.85}$$

For $m_i = m$ (one component) the above equation gives the well-known velocity $v_0 = 1/\sqrt{\kappa n m}$ of the ordinary sound. As it is well-known, it has a slight temperature dependence, through the compressibility, in contrast with the velocity v_s given above for the sound-like excitations. For an electrically neutral multi-component mixture it can be shown easily that $v_s^2/v_0^2 \geq n^2\chi\kappa$.

If we apply equations (16.83) and (16.85) to both ordinary and heavy water (one component, neutral molecule), and assume that interaction χ and the compressibility κ are the same for the two kinds of water, we can see that the two sound velocities v_s and v_0 exhibit a slight isotopic effect, while their ratio $v_s/v_0 = n\sqrt{\chi\kappa}$ does not exhibit such an isotopic effect, in agreement with experimental data. In this case we may take $v_0 = 1500m/s$ and $v_s = 3000m/s$ from experimental data and get the interaction parameter $\chi \simeq 60eV \cdot \mathring{A}^3$ (for a mean inter-molecular spacing $\simeq 3\mathring{A}$) . A similar picture, given by equations (16.83) and (16.85), may apply to rare-gas mixtures, while for metallic alloys the Coulomb coupling must be taken into account (and equation (16.81) employed).

If we assume the existence of a dispersionless mode in water, then we may consider that water molecule is dissociated to some extent, and its components have an electric charge, such that the plasmonic mode given by equation (16.78) can be identified with such a dispersionless mode. Various models of dissociation of the water molecule are known, like $OH^- - H^+$ or $OH^- - H_3O^+$. In all cases a certain mobility of the H^+ (hydrogen) cations and O^- (oxygen) anions is implied. We assume here that the dynamics of liquid water has a plasma-like component consisting of H^{+z} cations with density $2n$ and mass

m (proton mass) and O^{-2z} anions with density n and mass $M = 16m$, where n is the density of water. The excitation spectrum given by equations (16.76) for such an $O^{-2z} - H^{+z}$ plasma is shown in Fig. 16.1. Taking $\omega = 10^{13}s^{-1}(\simeq 5meV)$ of the dispersionless mode as the plasma frequency ω_p given by $\omega_p^2 = 16\pi ne^2z^2/\mu$ (equation (16.78)), where $\mu = 2mM/(M+2m)$ is the reduced mass, we get $z \simeq 3 \times 10^{-2}$. The velocity of the hydrodynamic sound is given by $v_0 = 1/\sqrt{\kappa n(M+2m)}$ according to equation (16.85) and the velocity of the sound-like excitations is given by $v_s = \sqrt{9n\chi/(M+2m)}$ from equation (16.81). We can see that both velocities exhibit an isotopic effect, but their ratio $v_s/v_0 = 3n\sqrt{\chi\kappa}$ does not, in agreement with the experimental data. From $v_s = 3000m/s$ we derive the interaction $\chi \simeq 7eV \cdot \mathring{A}^3$. Similar results are obtained for other forms of dissociation, like $OH^- - H^+$ or $OH^- - H_3O^+$. In this respect, the $O^{-2z} - H^{+z}$ plasma model can be viewed as an average, effective model for various plasma components that may exist in water.

According to equation (16.79), for shorter wavelengths the ω_1-branch approaches an asymptote given by $\omega_1^2 \sim bS_2 + aS_3^2/S_2$. In the limit of weak Coulomb coupling this ω_1-branch may appear as an "anomalous" sound given by

$$\omega_a = \sqrt{bS_2} = v_a q \ , \tag{16.86}$$

propagating with velocity

$$v_a = \sqrt{S_2\chi} = \frac{1}{\sqrt{1 - S_3^2/S_1S_2}} v_s \tag{16.87}$$

(which is always a positive quantity). This additional, anomalous sound is always faster than the sound-like excitations propagating with velocity v_s, since

$$\frac{v_a}{v_s} = \frac{1}{\sqrt{1 - S_3^2/S_1S_2}} > 1 \ . \tag{16.88}$$

It is worth noting that the molecular dynamics studies which originally predicted such a fast, anomalous sound[11] employed, indeed, a

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[11] A. Rahman and F. H. Stillinger, "Propagation of sound in water. A molecular-dynamics study", Phys. Rev. **A10** 368 (1974).

Coulomb interaction and a short-range one. We note, however, that the velocity v_a as given by equation (16.87) does not depend on the Coulomb coupling. In the plasma model for water discussed above the ratio v_a/v_0 is approximately 2 ($\simeq \sqrt{2M/9m+5/9}$), but it exhibits an isotopic effect, which does not seem to be supported by the experimental data.

It is easy to derive the dielectric function in the limit of long wavelengths from equation (16.71). Indeed, for charged particles equation $\delta n_i = -n_i div\mathbf{u}_i$ is equivalent with Maxwell equation $div\mathbf{E}_i = 4\pi q_i \delta n_i$, where the electric field is given by $\mathbf{E}_i = -4\pi q_i n_i \mathbf{u}_i$ and $q_i = ez_i$ is the electric charge of the i-th species. It follows that the internal field is given by

$$E_{int} = -4\pi e \sum_i z_i n_i u_i \ . \tag{16.89}$$

We get easily this field from equations (16.71),

$$E_{int} = -iq\phi \frac{\omega_p^2}{\omega^2 - \omega_p^2} \tag{16.90}$$

in the long wavelength limit (it is proportional to x given by equation (16.73)). The dielectric function is defined by $D = \varepsilon E = \varepsilon(D + E_{int})$, where $D = -iq\phi$ is the external field (electric displacement). We get the plasma dielectric function

$$\varepsilon = 1 - \omega_p^2/\omega^2 \ , \tag{16.91}$$

as expected. It exhibits an absorption edge (ω_p) for very low frequencies. In the static limit it is reasonable to admit the existence of an additional internal field of intrinsic polarizability which removes the $\omega = 0$ singularity.

We pass now to the calculation of the structure factor. From equation (16.75) we can see that the displacement u_i is a superposition of the two eigenvectors of the system of equations (16.74), which oscillate with eigenfrequencies $\omega_{1,2}$. It follows that these coordinates are those of linear harmonic oscillators with the potential energy of the form $m_i\omega^2 u_i^2/2$. The statistical distribution of the coordinates u_i in the classical limit is given by $dw \sim \exp(-m_i\omega^2 u_i^2/2T)du_i$, where T

denotes the temperature. We get the thermal averages

$$\langle u_i u_j \rangle = \frac{T}{m_i \omega^2} \delta_{ij} \ . \tag{16.92}$$

On the other hand the structure factor defined by

$$\begin{aligned} S(q,\omega) &= \tfrac{1}{2\pi} \int d\mathbf{r} d\mathbf{r}' dt \, \langle \delta n(\mathbf{r},t) \delta n(\mathbf{r}',0) \rangle \, e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')-i\omega t} = \\ &= \tfrac{N}{2\pi n^2} \int dt \, \langle \delta n(\mathbf{q},t) \delta n(-\mathbf{q},0) \rangle \, e^{-i\omega t} \end{aligned} \tag{16.93}$$

(we leave aside the central peak) can be written as

$$S(q,\omega) = \frac{Nq^2}{2\pi n^2} \int dt \sum_{ij} n_i n_j \, \langle u_i(t) u_j(0) \rangle \, e^{-i\omega t} \ . \tag{16.94}$$

Writing

$$u_i = u_i^{(1)} e^{i\omega_1 t} + u_i^{(2)} e^{i\omega_2 t} \tag{16.95}$$

and making use of equation (16.92) we get the structure factor

$$\begin{aligned} S(q,\omega) &= NTq^2 \left(\textstyle\sum_i n_i^2 / n^2 m_i \right) \cdot \\ &\cdot \left[\tfrac{1}{\omega_1^2} \delta(\omega - \omega_1) + \tfrac{1}{\omega_2^2} \delta(\omega - \omega_2) \right] \ . \end{aligned} \tag{16.96}$$

We can see that the relevant sound contributions read

$$S(q,\omega) \simeq \frac{NT}{v_{s,a}^2} \left(\sum_i n_i^2 / n^2 m_i \right) \delta(\omega - v_{s,a} q) \ . \tag{16.97}$$

The relaxation and damping effects can be included in the above expressions of the structure factor. As it is well-known, they amount to representing the δ-functions by lorentzians.

The short-range interaction χ can be generalized to an interaction matrix χ_{ij} with distinct elements for each pair of species. In this case, the excitation spectrum of the density oscillations may exhibit, in general, multiple branches, for a multi-component mixture. In addition, it may have special features, like a dip in the plasmonic branch, or negative velocity for the sound-like excitations, which may indicate either an anomalous behaviour or unphysical situations, depending on the mutual magnitudes of the short-range potentials χ_{ij}.

Now it is worthwhile commenting upon the validity of the approach presented above. If we keep higher-order terms in the expansion given by equation (16.61) (*i.e.* for moderate values of $\mathbf{qu}_i$), then additional interactions appear in equation (16.68), which lead to finite lifetimes for the density excitations. This means that for larger wavevectors $\mathbf{q}$ these excitations are not anymore well-defined excitations, as expected. Making use of equation (16.92) we can estimate the mean product qu_i for the sound-like branch as $qu_i \sim \sqrt{T/m_i v_s^2}$, where the velocity v_s is given by equation (16.81). This gives rather small values for qu_i. For instance, for water we get $qu \sim 0.5$ (at room temperature), which shows that the wavevector q may take reasonable large values providing the displacement u is sufficiently small. For the plasmonic branch, the condition $qu_i \ll 1$ gives a cutoff wavevector $q_c^i \simeq \sqrt{m_i \omega_p^2/T}$ for large ω_p; for small values of the plasma frequency the condition becomes $qu_i \sim \sqrt{T/m_i v_a^2} \ll 1$.

Another source of finite lifetime for the density excitations arises from the kinetic term. Indeed, under the displacement $\mathbf{r}_{ik} \to \mathbf{r}_{ik} + \mathbf{u}_i(\mathbf{r}_{ik})$, where $\mathbf{r}_{ik}$ is the position of the k-th particle in the i-th species, a mixed term

$$H_{int} = \sum_{ik} m_i \mathbf{v}_{ik} \dot{\mathbf{u}}_i(\mathbf{r}_{ik}) \tag{16.98}$$

appears in the kinetic term, where $\mathbf{v}_{ik} = \dot{\mathbf{r}}_{ik}$ is the velocity of the ik-particle. It is easy to get an upper bound for this term, by using the Schwarz-Cauchy inequality. It is given by $N \left\langle m_i v_{ik}^2 \right\rangle^{1/2} \left\langle m_i \dot{u}_i^2 \right\rangle^{1/2}$ or, by making use of equation (16.92), $\sqrt{\varepsilon T}$ per particle, where ε represents the mean kinetic energy (which depends on temperature, in principle). This estimation can be taken as an uncertainty in energy, leading to a lifetime $\tau \simeq \hbar/\sqrt{\varepsilon T}$ and a corresponding mean freepath $\Lambda = v_s \tau$ for the sound-like excitations. For wavelengths λ much longer than the mean freepath, *i.e.* for wavevectors q such as $q \ll 1/v_s \tau$ we are in the collision-like regime ($\omega_2 \tau \ll 1$), and the collisions can establish the thermodynamic equilibrium (hydrodynamic regime). In this case the ordinary sound can be propagated (with velocity v_0). For $q \gg 1/v_s \tau$ we are in the collisionless regime, the ordinary sound is absorbed, and the non-equilibrium sound-like excitations ("densitons") can be propagated (with velocity v_s). Unfortunately, it is difficult to have a reliable estimation of the energy ε, and so of the threshold wavevector $q_t = 1/v_s\tau = \sqrt{\varepsilon T}/\hbar v_s$. For $\varepsilon = 10meV$ (and $v_s = 3000m/s$, $T = 300K$) we get $q_t \simeq 0.1\mathring{A}^{-1}$, which is in a reasonable order-of-magnitude agreement with the experimental data. It is interesting to note that if we apply this estimation to weakly-interacting gases, where we may take $\varepsilon \sim T$, we get a high value of the threshold wavevector $q_t \sim T/\hbar v_s$, since v_s is very small (the short-range interaction is weak). We may say that in gases there is very unlikely to exist sound-like excitations; it is only the ordinary sound that exists. On the contrary, the collision-like regime is quite unlikely in ordinary solids, so we have there sound-like excitations and to a much lesser extent ordinary sound.

Finally, we note that the collective excitations derived above contribute to the thermodynamics of liquids. Indeed, the free energy can be written as

$$\begin{aligned} F = F_0 + F_1 + F_2 = F_0 + T\sum\nolimits_{\mathbf{q}} \ln\left(1 - e^{-\hbar\omega_1/T}\right) + \\ + T\sum\nolimits_{\mathbf{q}} \ln\left(1 - e^{-\hbar\omega_2/T}\right) \quad , \end{aligned} \tag{16.99}$$

where F_0 is the free energy associated with the particle movements and $\omega_{1,2}$ are given by equation (16.76). The evaluation of integrals in equation (16.99) depends on the particular magnitude of the excitation spectrum, but usually the integrals are rapidly convergent and their contribution to the thermodynamic properties of the liquid is small. For instance, the sound-like contribution is approximately given by $F_2 \simeq -\pi^2 VT(T/\hbar v_s)^3/90$, which is indeed a small correction to F_0 (the latter being governed mainly by the liquid cohesion).

In conclusion, we have shown that sound-like excitations may appear in interacting molecular systems, controlled by short-range interactions, distinct from the ordinary hydrodynamic sound. The former are non-equilibrium excitations, while the latter appear through equilibrium, adiabatic processes. The velocity v_s of the sound-like excitations is independent of temperature, while the velocity v_0 of the ordinary sound depends on temperature, through the adiabatic compressibility. In order to distinguish them we propose to call the former "kinetic" modes of particle density, or "densitons". In addition, in the presence of Coulomb interaction, the well-known plasmonic branch is present in the spectrum of the density excitations, which, for shorter wavelengths and weak Coulomb coupling may look like another, anomalous, fast sound. We have shown that the "two-sounds anomaly" reported in liquids like water, rare-gas mixtures, metallic alloys, etc, and documented by molecular dynamics studies, can be understood on this basis.

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