

STATISTICAL PHYSICS

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This book is essentially based on the lecture course on “Statistical Physics”, which was taught by the author at the physical faculty of the Ural State University in Ekaterinburg since 1992. This course was intended for all physics students, not especially for those specializing in theoretical physics. In this sense the material presented here contains the necessary minimum of knowledge of statistical physics (which is also often called statistical mechanics), which is in author’s opinion necessary for every person wishing to obtain the general education in the field of physics.

This posed rather difficult problem of the choice of material and compact enough presentation. At the same time it necessarily should contain all the basic principles of statistical physics, as well as its main applications to different physical problems, mainly from the field of the theory of condensed matter. Extended version of these lectures was published in Russian in 2003. For the present English edition much of the material was rewritten and several new sections and paragraphs were added, bringing contents more up to date and adding more discussion on some more difficult cases.

Of course, the author was much influenced by several classical books on statistical physics [1, 2, 3], and this influence is obvious in many parts of the text. However, the choice of material and the form of presentation is essentially his own. Still, most of attention is devoted to rather traditional problems and models of statistical physics. One of few exceptions is an attempt to present an elementary and short introduction to the modern quantum theoretical methods of statistical physics at the end of the book. Also a little bit more attention than usual is given to the problems of nonequilibrium statistical mechanics. Some of more special paragraphs, of more interest to future theorists, are denoted by asterisks or moved to Appendices.

Of course, this book is too short to give the complete presentation of modern statistical physics. After reading it those interested in further developments should address more fundamental monographies and modern physical literature.

M.V. Sadovskii, Ekaterinburg, 2012.

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Chapter 1

BASIC PRINCIPLES OF STATISTICS

We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant, and differing not merely infinitesimally, but it may be so as to embrace every conceivable combination of configuration and velocities. And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time, when the distribution has been given for some one time. The fundamental equation for this inquiry is that which gives the rate of change of the number of systems which fall within any infinitesimal limits of configuration and velocity. Such inquiries have been called by Maxwell statistical. They belong to a branch of mechanics which owes its origin to the desire to explain the laws of thermodynamics on mechanical principles, and which Clausius, Maxwell and Boltzmann are to be regarded as principal founders.

J. Willard Gibbs, 1902 [4]

1.1 Introduction

Traditionally statistical physics (statistical mechanics) deals with systems consisting of the large number of particles, moving according to the laws of classical or quantum mechanics. Historically it evolved by the end of XIX century from the attempts to provide mechanistic derivation of the laws of thermodynamics in the works by J.Maxwell and L.Boltzmann. The formalism of statistical mechanics was practically finalized in the fundamental treatise by J.W.Gibbs [4], which appeared at the beginning of the XX century. Remarkable advantage of Gibbs method, which was created long before the appearance of the modern quantum theory, is its full applicability to the studies of quantum (many-particle) systems. Nowadays, statistical physics has outgrown the initial task of justification of thermodynamics, its methods and ideology penetrate actually all the basic parts of modern theoretical physics. Still being understood mainly as the theory of many (interacting) particle systems, it has deep connections with modern quantum field theory, which is at present the most fundamental theory of matter. At the same time, now it is also clear that even the description of mechanical motion of relatively few particles moving according to the laws of classical mechanics often requires the use of statistical methods, as this motion, in general (nontrivial) cases, is usually extremely complicated (unstable). The ideas and methods of statistical mechanics form the basis of our understanding of physical processes in solids, gases, liquids and plasma, while the modern theory of elementary particles (based on the quantum field theory), from the very beginning is actually the theory of systems with infinite number of degrees of freedom, where statistical methods are at the heart of the problem. Unfortunately, due to the lack of space we will not be able to discuss in detail all of these deep interconnections and just limit ourselves to the studies of more or less traditional models of statistical mechanics [1, 2, 3], which provide the ground for understanding of much more complicated problems.

1.2 Distribution functions.

Consider a system of N identical (for simplicity) interacting particles, moving in a finite but macroscopically large volume V . For simplicity we also assume that these particles do not possess internal degrees of freedom. If we describe the motion of particles by classical mechanics, the state of the motion of the k -th particle is completely characterized by the values of its coordinates \mathbf{q}_k and momentum \mathbf{p}_k , and the state of the system as a whole is determined by the values of all particles coordinates $\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N$ and momenta $\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$. Thus the state of the system may be described by the point in $6N$ -dimensional *phase* space: $(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ — the so called *phase point*. Dynamical evolution (motion) of the system is determined by Hamilton equations of motion:¹

$$\frac{d\mathbf{q}_k}{dt} = \frac{\partial H}{\partial \mathbf{p}_k} \quad \frac{d\mathbf{p}_k}{dt} = -\frac{\partial H}{\partial \mathbf{q}_k}, \quad (1.1)$$

where

$$H = H(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) \equiv H(p, q) \quad (1.2)$$

¹It is interesting to note that Gibbs approach is completely based on the use of Hamilton form of mechanics and not on that of Lagrange.

is the full Hamiltonian of the system.

Consider the simplest case when particles interact with each other via two-particle spherically symmetric potential $U(|\mathbf{q}_i - \mathbf{q}_k|)$, so that the Hamiltonian takes the form:

$$H = \sum_{k=1}^N \frac{\mathbf{p}_k^2}{2m} + \frac{1}{2} \sum_{i \neq k} U(|\mathbf{q}_i - \mathbf{q}_k|) \quad (1.3)$$

The the equations of motion are written as:

$$\dot{\mathbf{q}}_k = \frac{\mathbf{p}_k}{m} \quad \dot{\mathbf{p}}_k = - \sum_{i \neq k} \frac{\partial U(|\mathbf{q}_i - \mathbf{q}_k|)}{\partial \mathbf{q}_k} = \mathbf{F}_k, \quad (1.4)$$

where \mathbf{F}_k is the force acted upon the k -th particle by the rest. It is clear that for any significantly large value of N the complete solution of the system of equations (1.4) is not feasible even numerically. Also such a solution (in improbable case we find it) would be of no real use. The real trajectory of each particle will be most probably quite complicated (chaotic). More so, we have to solve Eqs. (1.4) with appropriate initial conditions and this solution is, as a rule, quite sensitive to the choice of initial velocities and coordinates, which are actually not known precisely in any realistic situation. As the motion of particles is in most cases unstable, the trajectories corresponding even to quite close initial values in rather short time become quite different (and this difference grows exponentially with time), so that they just do not have anything in common. Thus, from such solutions we have almost nothing to learn about *macroscopic* property of the system with large number N of particles, which are of the main interest to us. In fact, these problems due to the instability of mechanical motion appear usually even for systems consisting of rather few particles. This inevitably leads us to use the statistical analysis.

Thus the equations of motion (1.4) determine the trajectory of the phase point in the phase space, defining the mechanical state of the system. This trajectory in phase space is called the *phase trajectory*. For conservative systems with fixed energy we can write:

$$H(q, p) = E \quad (1.5)$$

This means that the phase trajectory belongs to the surface of constant energy in the phase space, defined by Eq.(1.5) — the so called *ergodic surface*².

When a macroscopic system is in (thermodynamic) equilibrium its macroscopic characteristics (temperature, volume, pressure etc.) remain constant in time, though its microscopic state continuously change and we do not know it at all (i.e. where precisely is its phase point on the ergodic surface at the given moment of time). Statistical approach attempts to determine only the *probability* of realization of some set of microstates, corresponding to the given macrostate of our system. In fact, following Gibbs, we shall consider not the fixed system, but an *ensemble* i.e. the set of the large number (in the limit of

²We must stress here the important role of Cauchy theorem on the uniqueness of the solution of the system of usual differential equations. Under rather weak requirements for the r.h.s. of Eqs. (1.4), there exists the unique (at any moment of time) solution, which automatically excludes the possibility of the crossing of two *different* phase trajectories in any regular point of the phase space (except some fixed points, corresponding to the zeroes of the r.h.s. of (1.4)).

$N \rightarrow \infty$ the infinite!) of its copies, all remaining in macroscopically equivalent conditions (states). This is usually called the *Gibbs ensemble*, describing the macroscopic state of the system. Macroscopic equivalence of external conditions (states) means that all the systems within the ensemble are characterized by the same values of appropriate macroscopic parameters (neglecting small fluctuations) and the same types of contacts with surrounding bodies (energy or particle reservoirs, pistons, walls etc.). This leads to certain limitations on coordinates and momenta of particles, which otherwise remain rather arbitrary.

Statistical ensemble is defined by *distribution function* $\rho(p, q, t)$, which has the meaning of probability density of systems in the phase space, so that:

$$dw = \rho(p, q, t) dpdq \quad (1.6)$$

gives the probability to find a system (from the Gibbs ensemble!) at the moment t in the element of phase space $dpdq$ around the point $(p, q) \equiv (\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{q}_1, \dots, \mathbf{q}_N)$. Distribution function must satisfy the obvious normalization condition:

$$\int dpdq \rho(p, q, t) = 1, \quad (1.7)$$

as the sum of the probabilities of all possible states must be unity. Such normalization condition is used e.g. in the famous book by Landau and Lifshitz [1]. However, this is not the only possible form of normalization condition. In fact we understand from the very beginning, that classical statistics is the limiting case of quantum statistics (below we shall see that transition from quantum case to the classical one takes place at high enough temperatures, when quantum effects become negligible) From quantum mechanics we know [5] that the notions of coordinate and momenta of the particles can be introduced only within the limits of quasiclassical approximation. The minimal size of the phase space cell for the one-dimensional motion of the i -th particle in quasiclassical approximation is given by $h = 2\pi\hbar$.³

$$\Delta q_i^x \Delta p_i^x \geq h \quad (1.8)$$

Thus the minimal size of the cell in the phase space of one particle (for three-dimensional motion) is equal to $h^3 = (2\pi\hbar)^3$, and $(2\pi\hbar)^{3N}$ in the phase space of N particles. The value of $(2\pi\hbar)^{3N}$ is the natural volume unit in the phase space. Accordingly, it is often convenient to introduce the distribution function normalized to unity after the integration over the dimensionless phase space $\frac{dpdq}{(2\pi\hbar)^{3N}}$.

For the system consisting of N identical particles we have to take into account the fact that permutations of identical particles does not change the quantum state of the system. The number of permutations of N identical particles is equal to $N!$ and the volume of the phase space cell should be divided by $N!$ if we wish to take into account only physically distinguishable states.

³Quasiclassical quantization condition of Bohr and Sommerfeld in one-dimensional case takes the form: $\oint pdq = (n + \frac{1}{2})h$. The integral here represents an area of the closed orbit in phase space. Dividing this area into cells of area $2\pi\hbar$ we obtain n cells. But n here is the number of quantum state with energy below the given value, corresponding to this orbit. Thus for any quantum state there is a corresponding cell in the phase space with an area $2\pi\hbar$. Introducing the wave vector of a particle as $k = p/\hbar$ we get $\frac{\Delta p \Delta q}{2\pi\hbar} = \frac{\Delta k \Delta q}{2\pi}$, which corresponds to the well known relation for the number of the (eigen)modes of the wave field [6].

Thus it is convenient to define the distribution function by the relation:

$$dw = \rho(p, q, t) \frac{dpdq}{N!(2\pi\hbar)^{3N}}, \quad (1.9)$$

and write normalization condition as:

$$\int d\Gamma \rho(p, q, t) = 1, \quad (1.10)$$

where:

$$d\Gamma = \frac{dpdq}{N!(2\pi\hbar)^{3N}} \quad (1.11)$$

is the *dimensionless* phase space element. Integration in (1.10) corresponds to the summation over all distinguishable quantum states of the system⁴.

Knowing the distribution function $\rho(p, q, t)$ we can, in principle, calculate the average values of arbitrary physical characteristics, which depend on coordinates and momenta of particles forming our system. The average value of any such function of dynamic variables $f(p, q)$ is defined as:

$$\langle f \rangle = \int d\Gamma \rho(p, q, t) f(p, q) \quad (1.12)$$

and is sometimes called the *phase* average (ensemble average). Averaging with distribution function (over the phase space) comes here instead of another possible procedure, when we follow the precise time evolution of $f(p, q)$ and calculate its average behavior in time. This last approach reduces to performing measurements in different moments of time, producing explicit time dependence $f = f(t)$, and calculating its average value as:

$$\tilde{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt f(t) \quad (1.13)$$

i.e. as *time* average.

In general case, the proof of the equivalence of phase and time averaging is very difficult (and still not completely solved) problem of the so called *ergodic* theory, which is a developing branch of modern mathematics [8, 9]. In recent decades significant progress was achieved, but this material is definitely outside the scope of this book. Below we shall only give some brief and elementary discussion of this problem. The physical meaning of Gibbs approach may be qualitatively illustrated as follows. Let us consider a small, but still macroscopic, subsystem within our closed (isolated) system. This subsystem is also described by the laws of classical mechanics, but it is non isolated and influenced by all possible interactions with the rest parts of the (big) system. Under these conditions, the state of our subsystem will change in time in a very complicated and chaotic way. Due to this chaotic motion, during a long enough time interval T the subsystem will many times "visit" all its possible states. Or in more rigorous terms, let us define $\Delta p \Delta q$ some small volume in the phase space of

⁴Remarkably, the necessity to divide the phase space volume by $N!$ for the system of identical particles was stressed by Gibbs long before the discovery of quantum mechanics as a recipe to avoid the so called Gibbs paradox — the growth of entropy during the mixing of *identical* gases at the fixed temperature, volume and pressure [7].

the subsystem. It can be assumed that during the large enough time interval T the complicated (chaotic) phase trajectory of the subsystem will pass this volume many times. Let Δt be that part of time T during which the subsystem is somewhere within this phase space volume $\Delta p \Delta q$. As T grows to infinity, the value of $\Delta t/T$ will tend to some limit:

$$\Delta w = \lim_{T \rightarrow \infty} \frac{\Delta t}{T} \quad (1.14)$$

which can be considered as probability of finding our subsystem within this volume of the phase space at a given moment of time. Now going to the limit of infinitesimally small phase space volume we introduce the distribution function $\rho(p, q, t)$ and by definition of (1.14) statistical (phase) averaging (1.12) seems to be physically equivalent to time averaging (1.13). These simple justification is usually sufficient for physicists. In particular Landau claimed [1] that the importance of ergodic theory is overestimated by mathematicians. Though discussions of this problem are still continuing, from pragmatic point of view the Gibbs approach is in no doubts correct, as all conclusions obtained within statistical mechanics are getting full *experimental* confirmation.

Finally, we shall mention one more qualitative point, which is very important for understanding of the foundations of statistical mechanics. Distribution function of a given subsystem is, in general, independent of initial state of any other part of the same system, as the influence of this initial state during long enough time interval is completely smeared by the influence of many other parts of the system. It is also independent of the initial state of subsystem under consideration itself, as it passes through all possible states during its long time evolution and actually each of these states can be considered as initial (“memory” loss).

1.3 Statistical independence.

Let us consider some simple facts from mathematical statistics, which will be useful in the following. In many cases, the closed macroscopic system can be “divided” into a number of subsystems, which rather weakly interact with each other, and during long enough time intervals behave (approximately) as closed (isolated) systems. We shall call such subsystems quasi closed (or quasi isolated). Statistical independence of such subsystems means that the state of a given subsystem does not influence the probability distributions of other subsystems.

Consider two such subsystems with infinitesimal volume elements of phase spaces $dp^{(1)}dq^{(1)}$ and $dp^{(2)}dq^{(2)}$. If we consider the composite system consisting of both subsystems then, from mathematical point of view, the statistical independence of subsystems means that the probability for composite system to be found in the element of its phase space volume $dp^{(12)}dq^{(12)} = dp^{(1)}dq^{(1)}dp^{(2)}dq^{(2)}$ factorizes into the product of probabilities:

$$\rho_{12} dp^{(12)} dq^{(12)} = \rho_1 dp^{(1)} dq^{(1)} \rho_2 dp^{(2)} dq^{(2)}, \quad (1.15)$$

so that

$$\rho_{12} = \rho_1 \rho_2, \quad (1.16)$$

where ρ_{12} is the distribution function of composite system, while ρ_1 and ρ_2 are distribution functions of subsystems.

The inverse statement is also valid — *factorization* of distribution function means that the system can be decomposed into statistically independent subsystems. If f_1 or f_2 are two physical characteristics of two subsystems, from Eqs. (1.15) and (1.12) it immediately follows that the average value of the product $f_1 f_2$ is equal to the product of the averages:

$$\langle f_1 f_2 \rangle = \langle f_1 \rangle \langle f_2 \rangle. \quad (1.17)$$

Consider some physical quantity f characterizing the macroscopic body or its part. As time evolves it changes (fluctuates) around its average value $\langle f \rangle$. As a measure of these fluctuations we can not take just the difference $\Delta f = f - \langle f \rangle$, as due to possibility of fluctuations of both signs we shall get its average zero: $\langle \Delta f \rangle = 0$. Thus, as a measure of fluctuations it is convenient to take its mean square: $\langle (\Delta f)^2 \rangle$. Then we always obtain $\langle (\Delta f)^2 \rangle \geq 0$, and the average here tends to zero only as $f \rightarrow \langle f \rangle$, i.e. when the deviation of f from $\langle f \rangle$ appear with small probability. The value of

$$\sqrt{\langle (\Delta f)^2 \rangle} = \sqrt{\langle (f - \langle f \rangle)^2 \rangle} \quad (1.18)$$

is called *mean square* fluctuation of f . It is easily seen that:

$$\begin{aligned} \langle (\Delta f)^2 \rangle &= \langle f^2 - 2f \langle f \rangle + \langle f \rangle^2 \rangle \\ &= \langle f^2 \rangle - 2 \langle f \rangle \langle f \rangle + \langle f \rangle^2 = \langle f^2 \rangle - \langle f \rangle^2, \end{aligned} \quad (1.19)$$

so that the mean square fluctuation is determined by the difference between the average square and the square of the average of the physical characteristic under study. The ratio of $\sqrt{\langle (\Delta f)^2 \rangle} / \langle f \rangle$ is called the *relative* fluctuation of f . It can be shown that the relative fluctuations of the typical physical characteristics of macroscopic systems fast drop with the growth of the size (the number of particles) of the body. In fact, most of physical quantities are additive (due to the quasi isolated nature of different parts of the system): the value of such quantity for the whole body (system) is the sum of its values for different parts (subsystems). Let us divide our system into the large number N of more or less similar (or equal) subsystems (often this may be just the number of particles in the system). Then for additive characteristic we can write:

$$f = \sum_{i=1}^N f_i, \quad (1.20)$$

where f_i characterizes the i -th part (subsystem or particle). Obviously, for the average value we get:

$$\langle f \rangle = \sum_{i=1}^N \langle f_i \rangle. \quad (1.21)$$

With the growth of N the value of $\langle f \rangle$ grows approximately proportionally N : $\langle f \rangle \sim N$. Let us calculate the mean square fluctuation of f :

$$\langle (\Delta f)^2 \rangle = \langle \left(\sum_i \Delta f_i \right)^2 \rangle. \quad (1.22)$$

Due to statistical independence of different parts (subsystems) we have:

$$\langle \Delta f_i \Delta f_k \rangle = \langle \Delta f_i \rangle \langle \Delta f_k \rangle = 0 \quad (i \neq k) \quad (1.23)$$

as each $\langle \Delta f_i \rangle = 0$. Then:

$$\langle (\Delta f)^2 \rangle = \sum_{i=1}^N \langle (\Delta f_i)^2 \rangle \quad (1.24)$$

Then it is clear that with the growth of N we also get $\langle (\Delta f)^2 \rangle \sim N$. Then the relative fluctuation is estimated as:

$$\frac{\sqrt{\langle (\Delta f)^2 \rangle}}{\langle f \rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}. \quad (1.25)$$

Now we see that the relative fluctuation of any additive characteristic is inversely proportional to the square root of the number of independent parts of the macroscopic body (e.g. number of particles), so that for large enough value of N (e.g. for $N \sim 10^{22}$ for typical number of particles in the cubic centimeter) the value of f may be considered practically constant and equal to its average value. If N is not big enough, e.g. $N \sim 10^6$, the relative fluctuations become not small and quite observable. Such systems sometimes are called *mesoscopic*.

1.4 Liouville theorem.

Introduction of distribution function for mechanical system as probability density in the phase space is based on the Liouville theorem – purely mechanical statement, which does not contain any statistical assumptions. According to this theorem, for systems with motion described by Hamilton equations:

$$\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k} \quad \frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k} \quad (1.26)$$

the phase volume (of an ensemble) remains constant in time. If at the initial moment of time the phase points (p^0, q^0) of systems forming the Gibbs ensemble continuously fill some region G_0 in the phase space, while at the moment t they fill the region G_t , then the volumes of these regions in the phase space are the same:

$$\int_{G_0} dp^0 dq^0 = \int_{G_t} dp dq \quad (1.27)$$

or, for infinitesimal elements of the phase space:

$$dp^0 dq^0 = dp dq \quad (1.28)$$

In other words, *the motion of phase points representing systems of the ensemble is like that of non compressible liquid*, as it is shown in Fig.1.1 – the “drop”, formed by phase points, representing an ensemble, can deform in rather complicated way in the process of motion, but its volume is conserved.

To prove Liouville theorem we transform the integral in the r.h.s. of Eq. (1.27) by changing integration variables from p, q to p^0, q^0 . Then according to the well known rules for multiple integral we get:

$$\int_{G_t} dp dq = \int_{G_0} \frac{\partial(p, q)}{\partial(p^0, q^0)} dp^0 dq^0, \quad (1.29)$$

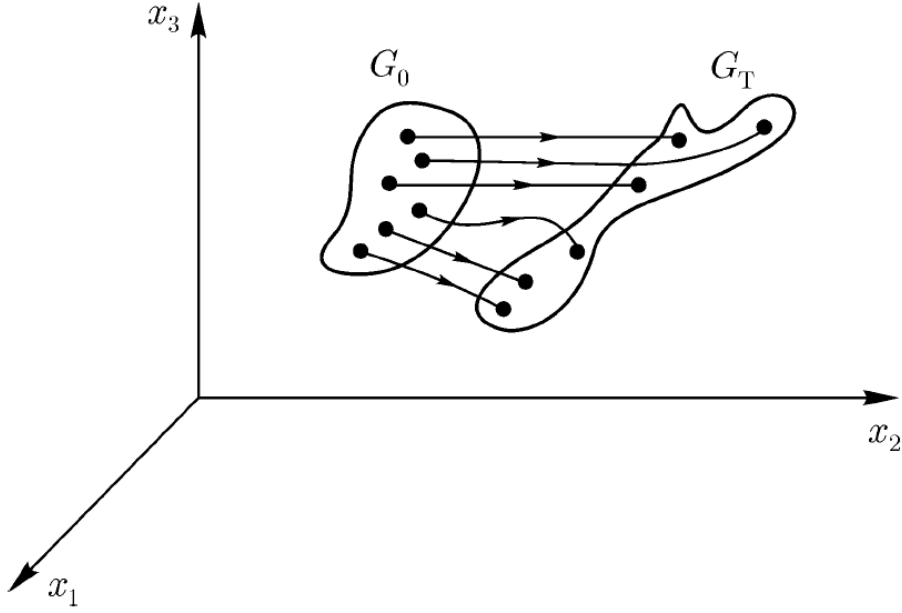


Figure 1.1: The change of initial volume G_0 in the phase space due to the motion of phase points representing an ensemble according to Liouville theorem.

where $\frac{\partial(p,q)}{\partial(p^0,q^0)}$ is the appropriate Jacobian. We remind that the Jacobian is a determinant of the following form (for simplicity we write the explicit expression below for two-dimensional case, generalization for multiple dimensions is direct):

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}. \quad (1.30)$$

The following general properties of Jacobian are:

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} \quad (1.31)$$

$$\frac{\partial(u,y)}{\partial(x,y)} = \frac{\partial u}{\partial x} \quad (1.32)$$

Also it is easy to see that:

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(t,s)} \frac{\partial(t,s)}{\partial(x,y)} \quad (1.33)$$

$$\frac{d}{dt} \frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(\frac{du}{dt}, v)}{\partial(x,y)} + \frac{\partial(u, \frac{dv}{dt})}{\partial(x,y)}. \quad (1.34)$$

Let us show now that the Jacobian in Eq. (1.29) is unity if systems move according to Hamilton equations:

$$\frac{\partial(p,q)}{\partial(p^0,q^0)} = 1. \quad (1.35)$$

To prove this we show that the total time derivative of the Jacobian is equal to zero:

$$\frac{d}{dt} \frac{\partial(p, q)}{\partial(p^0, q^0)} = 0. \quad (1.36)$$

Then it follows that the Jacobian is a constant, more precisely just unity, because it was equal to unity at the initial moment of time.

For simplicity let us write down the proof for the case of two-dimensional phase space, when there is only one coordinate q and one momentum p . According to Eq. (1.34) we can write:

$$\frac{d}{dt} \frac{\partial(p, q)}{\partial(p_0, q_0)} = \frac{\partial(\dot{p}, q)}{\partial(p_0, q_0)} + \frac{\partial(p, \dot{q})}{\partial(p_0, q_0)}. \quad (1.37)$$

Then, according to Eqs. (1.32) and (1.33) we have:

$$\frac{\partial(p, \dot{q})}{\partial(p_0, q_0)} = \frac{\partial(p, \dot{q})}{\partial(p, q)} \frac{\partial(p, q)}{\partial(p_0, q_0)} = \frac{\partial \dot{q}}{\partial q} \frac{\partial(p, q)}{\partial(p_0, q_0)} \quad (1.38)$$

$$\frac{\partial(\dot{p}, q)}{\partial(p_0, q_0)} = \frac{\partial(\dot{p}, q)}{\partial(p, q)} \frac{\partial(p, q)}{\partial(p_0, q_0)} = \frac{\partial \dot{p}}{\partial p} \frac{\partial(p, q)}{\partial(p_0, q_0)} \quad (1.39)$$

$$\frac{d}{dt} \frac{\partial(p, q)}{\partial(p_0, q_0)} = \left(\frac{\partial \dot{p}}{\partial p} + \frac{\partial \dot{q}}{\partial q} \right) \frac{\partial(p, q)}{\partial(p_0, q_0)} \quad (1.40)$$

It is seen that the sum in the r.h.s. is equal to zero due to equations of motion:

$$\dot{q} = \frac{\partial H}{\partial p}; \quad \dot{p} = -\frac{\partial H}{\partial q} \quad (1.41)$$

so that

$$\frac{\partial \dot{q}}{\partial q} = \frac{\partial^2 H}{\partial q \partial p} = -\frac{\partial \dot{p}}{\partial p} \quad (1.42)$$

and accordingly

$$\left(\frac{\partial \dot{p}}{\partial p} + \frac{\partial \dot{q}}{\partial q} \right) = 0 \quad (1.43)$$

which proves everything.

Liouville theorem is a purely mechanical statement and nowhere, up to now, we have used distribution function. However, with the help of distribution function we may give another formulation of Liouville theorem. As the “drop” representing the Gibbs ensemble moves through the phase space (Fig.1.1), the number of phase point in it (the number of systems in the ensemble) obviously does not change and all phase points belonging at the moment t to volume element $dpdq$ move at the moment t' to element $dp'dq'$. Then we can write⁵:

$$\rho(p, q, t) dpdq = \rho(p', q', t') dp'dq', \quad (1.44)$$

and from Liouville theorem we have $dpdq = dp'dq'$, so that:

$$\rho(p, q, t) = \rho(p', q', t') \quad (1.45)$$

⁵Distribution function ρ can be obviously treated just as the density of phase points in the ensemble!

Now we see that distribution function ρ is *constant along phase trajectories* – this is an alternative formulation of Liouville theorem, using the notion of distribution function. But still it is simply a mechanical statement, not using any probability (statistical) considerations.

Using this results, now we can derive the Liouville *equation*, which actually the equation of motion for distribution function. Assuming the moment t to be infinitesimally close to $t' = t + dt$ from Eq. (1.45) we get:

$$\rho(p, q, t) = \rho(p + \dot{p}dt, q + \dot{q}dt, t + dt) \quad (1.46)$$

so that (if ρ is differentiable) we obtain a differential equation:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{k=1}^{3N} \left(\frac{\partial\rho}{\partial p_k} \dot{p}_k + \frac{\partial\rho}{\partial q_k} \dot{q}_k \right) = 0 \quad (1.47)$$

and taking into account the Hamilton equations:

$$\frac{\partial\rho}{\partial t} = \sum_k \left(\frac{\partial H}{\partial q_k} \frac{\partial\rho}{\partial p_k} - \frac{\partial H}{\partial p_k} \frac{\partial\rho}{\partial q_k} \right) \quad (1.48)$$

The sum in the r.h.s. of Eq. (1.48) is the so called *Poisson bracket* [11] for H and ρ :

$$\{H, \rho\} = \sum_k \left(\frac{\partial H}{\partial q_k} \frac{\partial\rho}{\partial p_k} - \frac{\partial H}{\partial p_k} \frac{\partial\rho}{\partial q_k} \right) \quad (1.49)$$

so that the Liouville equation can be written as:

$$\frac{\partial\rho}{\partial t} = \{H, \rho\}. \quad (1.50)$$

This equation is the basic *equation of motion* for distribution function, which remains valid for both equilibrium and non equilibrium problems. In principle, it allows one to calculate ρ at any moment of time t if it is known in an initial moment $t = t_0$. It can also be used, as we shall show later, to find the response of statistical systems to an *external perturbation*.

It is easy to see that Liouville equation can be written as a continuity equation for the phase points moving in the phase space. Consider the motion of phase points in $6N$ -dimensional phase space as the motion of “phase liquid” with density ρ . The velocity of this motion is represented by the vector $(\dot{\mathbf{p}}_1, \dot{\mathbf{p}}_2, \dots, \dot{\mathbf{p}}_N; \dot{\mathbf{q}}_1, \dot{\mathbf{q}}_2, \dots, \dot{\mathbf{q}}_N)$ in this space. Accordingly, the appropriate continuity equation takes the form:

$$\frac{\partial\rho}{\partial t} + \sum_k \left[\frac{\partial}{\partial p_k} (\rho \dot{p}_k) + \frac{\partial}{\partial q_k} (\rho \dot{q}_k) \right] = 0 \quad (1.51)$$

where an expression in parentheses is just the divergence of the appropriate current. Performing differentiations we can write this term as:

$$\sum_k \left[\dot{p}_k \frac{\partial\rho}{\partial p_k} + \dot{q}_k \frac{\partial\rho}{\partial q_k} \right] + \rho \sum_k \left[\frac{\partial\dot{p}_k}{\partial p_k} + \frac{\partial\dot{q}_k}{\partial q_k} \right] \quad (1.52)$$

Because of Hamilton equations the second term in this expression is identically zero, so that Eq.(1.51) reduces to:

$$\frac{\partial \rho}{\partial t} + \sum_k [\dot{p}_k \frac{\partial \rho}{\partial p_k} + \dot{q}_k \frac{\partial \rho}{\partial q_k}] = 0 \quad (1.53)$$

which coincides with Eq.(1.47). From here it follows, in particular, that the motion of “phase liquid” is *incompressible*. For the case of systems in statistical (thermodynamic) equilibrium both ρ and H do not depend *explicitly* on time⁶, so that Eq. (1.50) reduces to:

$$\{H, \rho\} = 0 \quad (1.54)$$

and distribution function becomes ρ becomes an *integral of motion*. As we shall see, this fact alone (based upon an *assumption* of the existence of thermodynamic equilibrium!) immediately leads to radical simplification of the whole analysis of equilibrium statistical ensembles.

1.5 Role of energy, microcanonical distribution.

Thus we convinced ourselves that for the system in thermodynamic equilibrium distribution function should be an integral of motion, i.e. it should be expressed via such combinations of coordinated and momenta p and q , which remain constant in time as (closed) system performs its motion in phase space. The number of independent integrals of motion for the closed (conserved) mechanical system with s degrees of freedom is equal to $2s - 1$ [11]. For the system consisting of N particles moving in three-dimensional space we have $2s = 6N$ (i.e. the number of all components of particle coordinates and momenta), so that the number of integrals of motion is immensely large. However, we can drastically reduce the number of intergrals of motion on which distribution function can actually depend. To do this we shall use *statistical* (not mechanical!) arguments. We have seen above that distribution function ρ_{12} of composite system consisting of two independent (non interacting) subsystems is equal to the product of distribution functions ρ_1 and ρ_2 of these subsystems: $\rho_{12} = \rho_1 \rho_2$. Thus:

$$\ln \rho_{12} = \ln \rho_1 + \ln \rho_2 \quad (1.55)$$

i.e. the logarithm of distribution function is additive. Accordingly, the logarithm of distribution function of the system in equilibrium should be not just be an integral of motion, but an *additive* integral of motion.

In mechanics it is shown [11], that from the whole number of integral of motion of closed (isolated) system only few are in fact additive. These are the integrals of motion connected with basic properties of space and time — homogeneity and isotropy: energy, momentum and angular momentum⁷. Let us denote these integrals of motion for the a -th subsystem as $E_a(p, q)$, $\mathbf{P}_a(p, q)$

⁶In this case there is no explicit time dependence also in appropriate *averages* of any physical characteristics, considered as functions of coordinates and momenta of particles of our system, which is an obvious property of equilibrium state

⁷Additivity of energy follows from its general expression via Lagrange function: $E = \sum_k \dot{q}_k \frac{\partial L}{\partial \dot{q}_k} - L$, and from additivity of Lagrange function itself, which follows from the fact that equations of motion of each of non interacting parts of the system can not contain any

and $\mathbf{M}_a(p, q)$. The only additive combination of these integrals is the linear combination of the following form:

$$\ln \rho_a = \alpha_a + \beta E_a(p, q) + \gamma \mathbf{P}_a(p, q) + \delta \mathbf{M}_a(p, q) \quad (1.56)$$

with constant coefficients $\alpha_a, \beta, \gamma, \delta$, and where β, γ, δ should be the same for all subsystems — only in this case additivity (1.55) is satisfied. The coefficient α_a is just the normalization constant and can be determined from the requirement of $\int d\Gamma_a \rho_a = 1$. The coefficients β, γ and δ can be similarly determined via the constant values of corresponding additive integrals of motion (calculating the appropriate averages with distribution function (1.56)).

Thus we come to most important conclusion: the values of additive integrals of motion — energy, momentum and angular momentum — *completely* determine statistical properties of closed (isolated) system and statistical distributions of its (independent) subsystems, as well as the average values of its arbitrary physical characteristics in the state of thermodynamic (statistical) equilibrium. This seven (taking into account the number of vector components) additive integrals of motion replace the immense number of variables on which distribution function can depend in general (non equilibrium) case and which are necessary for “complete” mechanical description of the many particle system.

The number of relevant integrals of motion diminishes, if from the very beginning we consider systems at rest. Then both full momentum and angular momentum are obviously zero and distribution function of the equilibrium state depends only on *one* variable — total energy of the system:

$$\rho = \rho(E) \quad (1.57)$$

Thus the introduction of the simplest statistical considerations for systems at equilibrium immediately leads to radical reduction of the number of relevant variables on which distribution function depends and opens the way for the formulation of equilibrium statistical mechanics. Let us stress that these radical conclusions are based on the introduction of statistics and are “non derivable” from classical mechanics. Of course, in general case, distribution function can depend on some “external” parameters, which define macroscopic conditions for an ensemble and which are considered the same for all copies of the system within the ensemble (e.g. on volume, number of particles etc.).

Let us now explicitly construct distribution function for *closed* (adiabatically isolated) system in equilibrium⁸. It was first proposed by Gibbs. Consider the statistical ensemble of closed *energetically isolated* systems with a constant volume V , i.e. the ensemble of systems with a constant number of particles N , which are surrounded by *adiabatic* (in thermodynamic sense) boundaries and possessing the same energy E , fixed up to some small uncertainty $\Delta E \ll E$. Following Gibbs we *assume* that distribution function $\rho(p, q)$ for such ensemble is just constant within some layer of the phase space between two isoenergetic

parameters from other parts. Additivity of momentum of many particle system is obvious: $\mathbf{P} = \sum_k m_k \mathbf{v}_k$, and unlike energy momentum is simply the sum of the momenta of different particles, despite the possibility of their interaction. Analogous property is valid also for the angular momentum: $\mathbf{M} = \sum_k [\mathbf{r}_k \mathbf{p}_k]$.

⁸Eq. (1.56) in fact already represents an explicit form of distribution function of an arbitrary *subsystem* weakly interacting with an environment of much larger closed system. We shall return to this case later.

surfaces, corresponding to energies E and $E + \Delta E$ and zero outside this layer:

$$\rho(p, q) = \begin{cases} [\mathcal{W}(E, N, V)]^{-1} & \text{for } E \leq H(p, q) \leq E + \Delta E \\ 0 & \text{outside this layer} \end{cases} \quad (1.58)$$

Such distribution (ensemble) is called *microcanonical*. Distribution function (1.58) expresses the principle of *equal probability* of all microscopic states of a closed system. In fact it is a simplest possible assumption – we suppose that there is no preferable microscopic states, all are equally probable, so that systems of an ensemble, during the motion in phase space, just randomly “visit” all the microscopic states within the energy layer of the width ΔE , to which belong all the phase trajectories. Distribution function (1.58) represent simply the statistics of a “gambling dice” with \mathcal{W} sides. Naturally, this distribution can not apparently be *derived* from purely mechanical considerations, it can be justified only by comparing the results obtained with its help with experiments.

Macroscopic state of microcanonical ensemble is characterized by three extensive parameters E, N, V . The constant $\mathcal{W}(E, N, V)$ is called *statistical weight* and is determined by normalization condition:

$$\int \frac{dpdq}{N!(2\pi\hbar)^{3N}} \rho(p, q) = 1$$

$$\int_{E \leq H(p, q) \leq E + \Delta E} \frac{dpdq}{N!(2\pi\hbar)^{3N}} \frac{1}{\mathcal{W}(E, N, V)} = 1 \quad (1.59)$$

and is in fact the dimensionless phase volume of our energy layer ΔE , i.e. the *number of quantum states* in it (which is just the number of sides of our “gambling dice”):

$$\mathcal{W}(E, N, V) = \frac{1}{N!(2\pi\hbar)^{3N}} \int_{E \leq H(p, q) \leq E + \Delta E} dpdq \quad (1.60)$$

In case of classical statistics we always can perform the limit of $\Delta E \rightarrow 0$ and write:

$$\rho(p, q) = \mathcal{W}^{-1}(E, N, V) \delta(H(p, q) - E) \quad (1.61)$$

where

$$\mathcal{W}(E, N, V) = \frac{1}{N!(2\pi\hbar)^{3N}} \int dpdq \delta(H(p, q) - E) \quad (1.62)$$

Now it is also obvious that \mathcal{W} can be also considered as the density of states on the surface of constant energy in phase space. In quantum case all this is limited by the well known uncertainty relation for time and energy: $\Delta E \Delta t \sim \hbar$. In the following we always, even in the classical limit, use microcanonical distribution in the form (1.58), assuming quasiclassical limit of quantum mechanics.

Hypothesis that microcanonical ensemble describes macroscopic state of a closed (adiabatically isolated) system, i.e. the averages calculated with distribution function (1.58) give experimentally observable values of all physical characteristics of the system, is one of the major postulates of equilibrium statistical mechanics. We already mentioned above that the observable values of arbitrary physical quantity $f(p, q)$ can also be calculated as an average over some observation time, and the problem of justification of our replacements of

time averages by phase averages over the ensemble is called the ergodic problem. From this point of view, the problem of justification of microcanonical distribution reduces to the proof that for the closed (isolated) systems in equilibrium we actually have:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt f(p(t), q(t)) = \frac{1}{N!(2\pi\hbar)^{3N}} \int dpdq \rho(p, q) f(p, q) \quad (1.63)$$

where $\rho(p, q)$ is defined by microcanonical distribution (1.58). This problem is very difficult and, despite some important achievements by mathematicians, is still unsolved. Physically it is usually justified by the so called *ergodic hypothesis* that the phase trajectory of a closed system during rather long time period necessarily passes infinitesimally close to any given point on ergodic surface. In Appendix A we shall present some elementary considerations related to this problem. Rigorous mathematical analysis can be found in Ref. [8], while the modern situation is discussed in Ref. [9]. Here we only briefly note that in recent years the problem of conceptual foundations of statistical mechanics obtained a new developments related to the discovery of stochastic instability (chaotization) of mechanical motion in different more or less simple dynamical systems with pretty *small* number of degrees of freedom [12]. Now it is clear that statistical description is actually necessary even for such systems, which naively appear to be quite “solvable” within classical mechanics. This is also briefly discussed on elementary level in Appendix A. In this sense, from the modern point of view, the requirement of a large number of degrees of freedom to justify the statistical approach is unnecessary and we can not ignore them even in rather “simple” systems, where typically we observe an extreme sensitivity of phase trajectories to initial conditions, which leads to chaotic instability of the motion in phase space. Thus, the notorious Laplace determinism is rather illusory even in classical mechanics of such systems.

1.6 Partial distribution functions*.

The knowledge of the general distribution function (1.6), depending on dynamical variables (coordinates and momenta) of all N particles, allows to determine different macroscopic characteristics of the system. For example, the density of particles at point \mathbf{r} , by definition, is given by:

$$\rho(t, \mathbf{r}) = \int \hat{\rho}(\mathbf{r}) \rho(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{p}_N \quad (1.64)$$

where $\hat{\rho}(\mathbf{r})$ is density operator (here it is convenient to introduce operators of physical quantities even in classical case):

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N m_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (1.65)$$

where m_i is the mass of the i -the particle. Analogously, the current density at point \mathbf{r} is:

$$\mathbf{J}(\mathbf{r}) = \int \hat{\mathbf{J}}(\mathbf{r}) \rho(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{p}_N \quad (1.66)$$

where $\hat{\mathbf{J}}(\mathbf{r})$ is current density operator:

$$\hat{\mathbf{J}}(\mathbf{r}) = \sum_{i=1}^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i). \quad (1.67)$$

The density of kinetic energy at point \mathbf{r} is equal to:

$$E(t, \mathbf{r}) = \int \hat{E}(\mathbf{r}) \rho(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{p}_N \quad (1.68)$$

where $\hat{E}(\mathbf{r})$ is kinetic energy operator:

$$\hat{E}(\mathbf{r}) = \sum_{i=1}^N \frac{p_i^2}{2m_i} \delta(\mathbf{r} - \mathbf{r}_i). \quad (1.69)$$

For charged particles we can introduce the electric current density as:

$$\mathbf{j}(t, \mathbf{r}) = \int \hat{\mathbf{j}}(\mathbf{r}) \rho(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{p}_N \quad (1.70)$$

where $\hat{\mathbf{j}}(\mathbf{r})$ is electric current density operator:

$$\hat{\mathbf{j}}(\mathbf{r}) = \sum_{i=1}^N \frac{e_i}{m_i} \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (1.71)$$

where e_i is the charge of the i -th particle.

Distribution function $\rho(t, \mathbf{r}_1, \dots, \mathbf{p}_N)$ is the function of practically infinite number of variables. However, expressing macrovariables via microscopic characteristics using the general formula:

$$A(t, \mathbf{r}) = \int \hat{A}(\mathbf{r}) \rho(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{p}_N \quad (1.72)$$

we have to take into account that the majority of physical operators of interest to us can be written as:

$$\hat{A}(\mathbf{r}) = \sum_{j=1}^N \hat{A}(\mathbf{r}_j, \mathbf{p}_j) \delta(\mathbf{r} - \mathbf{r}_j), \quad (1.73)$$

that is expressed as the sum of operators acting on dynamical variables of one particle (single particle operators). Examples of such operators are $\hat{\rho}$, $\hat{\mathbf{J}}$, \hat{E} and $\hat{\mathbf{j}}$ introduced above. Much more rarely we are dealing with two particle operators of the form:

$$\hat{A}(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{i \neq j} \hat{A}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{p}_i, \mathbf{p}_j) \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j). \quad (1.74)$$

Example of such an operator is the operator of potential energy of the system of particles interacting via some central potential:

$$\hat{U}(\mathbf{r}', \mathbf{r}'') = \frac{1}{2} \sum_{i \neq j} U(|\mathbf{r}_i - \mathbf{r}_j|) \delta(\mathbf{r}' - \mathbf{r}_i) \delta(\mathbf{r}'' - \mathbf{r}_j). \quad (1.75)$$

Operators consisting of linear combinations of operators acting on dynamical variables of three, four and larger number particles almost never appear in any practical tasks of interest.

Thus, solving majority of problems we actually do not need to know the full N -particle distribution function:

$$F_N(t, \mathbf{r}_1, \dots, \mathbf{p}_N) \equiv \rho(t, \mathbf{r}_1, \dots, \mathbf{p}_N), \quad (1.76)$$

depending on the dynamic variables of the enormous number of particles, it is sufficient to determine somehow only the one particle $F_1(t, \mathbf{r}_i, \mathbf{p}_j)$ and two particle $F_2(t, \mathbf{r}_i, \mathbf{r}_j, \mathbf{p}_i, \mathbf{p}_j)$ distribution functions, which are defined as (V is the volume of the system) [13, 14]:

$$F_1(t, \mathbf{r}_i, \mathbf{p}_i) = \quad (1.77)$$

$$V \int F_N(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_{i-1} d\mathbf{p}_{i+1} \dots d\mathbf{p}_N,$$

$$F_2(t, \mathbf{r}_i, \mathbf{r}_j, \mathbf{p}_i, \mathbf{p}_j) = \quad (1.78)$$

$$V^2 \int F_N(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_{j-1} d\mathbf{r}_{j+1} \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_{i-1} \\ d\mathbf{p}_{i+1} \dots d\mathbf{p}_{j-1} d\mathbf{p}_{j+1} \dots d\mathbf{p}_N.$$

or, in general case, the s -particle distribution function (with $s \ll N$):

$$F_s(t, \mathbf{r}_1, \dots, \mathbf{r}_s, \mathbf{p}_1, \dots, \mathbf{p}_s) = V^s \int F_N(t, \mathbf{r}_1, \dots, \mathbf{p}_N) d\mathbf{r}_{s+1} \dots d\mathbf{r}_N d\mathbf{p}_{s+1} \dots d\mathbf{p}_N. \quad (1.79)$$

From an obvious normalization condition

$$\frac{1}{V^s} \int F_s(t, \mathbf{r}_1, \dots, \mathbf{p}_s) d\mathbf{r}_1 \dots d\mathbf{p}_s = 1 \quad (1.80)$$

it follows that $\frac{1}{V^s} F_s(t, \mathbf{r}_1, \dots, \mathbf{p}_s)$ gives the probability for s particles in the system of N particles to be present at the moment t in the elementary phase space volume $d\mathbf{r}_1 \dots d\mathbf{p}_s$ of $6s$ -dimensional phase space near the point $(\mathbf{r}_1, \dots, \mathbf{p}_s)$. There are following relations between these partial distribution functions, which are directly derived from their definition:

$$F_s(t, \mathbf{r}_1, \dots, \mathbf{p}_s) = \frac{1}{V} \int F_{s+1}(t, \mathbf{r}_1, \dots, \mathbf{p}_{s+1}) d\mathbf{r}_{s+1} d\mathbf{p}_{s+1}. \quad (1.81)$$

The use of these distribution functions allows to calculate the average values of single particle, two particle etc. operators of different physical quantities. For example, for a macrovariable described by operator (1.73) we have:

$$A(t, \mathbf{r}) = \frac{1}{V} \sum_{j=1}^N \int \hat{A}_j(\mathbf{r}, \mathbf{p}_j) F_1(t, \mathbf{r}, \mathbf{p}_j) d\mathbf{p}_j \quad (1.82)$$

If all \hat{A}_j are the same, i.e. $\hat{A}_j = \hat{a}(j = 1, 2, \dots, N)$, we have:

$$A(t, \mathbf{r}) = \frac{N}{V} \int \hat{a}(\mathbf{r}, \mathbf{p}) F_1(t, \mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (1.83)$$

For macrovariables described by two particle operators of the type of (1.74) we get:

$$A(t, \mathbf{r}', \mathbf{r}'') = \frac{1}{2} \sum_{i \neq j} \frac{1}{V^2} \int \hat{A}_{ij}(\mathbf{r}', \mathbf{p}_i, \mathbf{r}'', \mathbf{p}_j) F_2(t, \mathbf{r}', \mathbf{r}'', \mathbf{p}_i, \mathbf{p}_j) d\mathbf{p}_i d\mathbf{p}_j. \quad (1.84)$$

If all \hat{A}_{ij} are the same, i.e. $\hat{A}_{ij} = \hat{a}$, we have:

$$A(t, \mathbf{r}', \mathbf{r}'') = \frac{N(N-1)}{2V^2} \int \hat{a}(\mathbf{r}', \mathbf{p}', \mathbf{r}'', \mathbf{p}'') F_2(t, \mathbf{r}', \mathbf{r}'', \mathbf{p}', \mathbf{p}'') d\mathbf{p}' d\mathbf{p}'' \quad (1.85)$$

where obviously we can take $(N-1) \approx N$.

Thus we obtain the following expressions for the main macroscopic characteristics of systems consisting of identical particles:

$$\rho(t, \mathbf{r}) = m \frac{N}{V} \int F_1(t, \mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (1.86)$$

$$\mathbf{J}(t, \mathbf{r}) = \frac{N}{V} \int \mathbf{p} F_1(t, \mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (1.87)$$

$$E(t, \mathbf{r}) = \frac{1}{2m} \frac{N}{V} \int \mathbf{p}^2 F_1(t, \mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (1.88)$$

$$\mathbf{j}(t, \mathbf{r}) = \frac{e}{m} \frac{N}{V} \int \mathbf{p} F_1(t, \mathbf{r}, \mathbf{p}) d\mathbf{p}. \quad (1.89)$$

The problem now is to find an explicit form of single particle distribution function.

The general approach to find partial distribution functions can be formulated as follows. An arbitrary N -particle distribution function (1.76) satisfies the Liouville equation (1.47), (1.48), (1.50):

$$\frac{\partial F_N}{\partial t} = \{H, F_N\} \quad (1.90)$$

Integrating Eq. (1.90) over phase spaces of $N-s$ particles and taking into account Eq. (1.79) we get:

$$\frac{1}{V^s} \frac{\partial F_s(t, \mathbf{r}_1, \dots, \mathbf{p}_s)}{\partial t} = \int \{H, F_N\} d\mathbf{r}_{s+1} \dots d\mathbf{p}_N. \quad (1.91)$$

For the Hamiltonian of the system of *interacting* particles:

$$H = \frac{1}{2m} \sum_{i=1}^N \mathbf{p}_i^2 + \frac{1}{2} \sum_{i \neq j} U(|\mathbf{r}_i - \mathbf{r}_j|), \quad (1.92)$$

after some direct, but rather tedious calculations [14], we obtain from Eq. (1.91):

$$\frac{\partial F_s}{\partial t} = \{H^{(s)}, F_s\} + \frac{N}{V} \sum_{i=1}^s \int \frac{\partial U(|\mathbf{r}_i - \mathbf{r}_{s+1}|)}{\partial \mathbf{r}_i} \frac{\partial F_{s+1}}{\partial \mathbf{p}_i} d\mathbf{r}_{s+1} d\mathbf{p}_{s+1} \quad (1.93)$$

where $H^{(s)}$ denotes the Hamiltonian of the subsystem consisting of s particles.

The most important property of Eq. (1.93) is that the equation of motion for s -particle distribution function contains the term, describing the interaction

of the subsystem of s particles with the rest of the N -particle system, which depends on $s + 1$ -particle distribution function F_{s+1} . Thus, during the construction of equations of motion for partial distribution functions we necessarily obtain practically infinite system of integro – differential equations, which is usually called *Bogolyubov's chain*. Strictly speaking, now we have to solve this whole chain of equations, which is certainly not easier than solving the general Liouville equation for N -particle distribution function. However, in many cases, using some physical assumptions and models, we can “decouple” this chain, reducing the problem to a finite number of equations, e.g. expressing F_{s+1} via F_s, F_{s-1} etc. Then we remain with the closed system of s equations for F_1, F_2, \dots, F_s . In particular, most interesting is the possibility to obtain the closed equation for single particle distribution function:

$$\frac{\partial F_1}{\partial t} = L(F_1) \quad (1.94)$$

where L is some operator. Construction and solving of this, so called *kinetic*, equation is the central problem of kinetic theory or *physical kinetics* [15]. We shall briefly discuss it in Chapter 10. In most cases, kinetic equations can be derived and solved only by some approximate methods. As a result, we can calculate the behavior of average physical characteristics of our system, including their time dependence in non equilibrium case. The formalism of partial distribution functions can also serve as a ground for constructing the equilibrium statistical mechanics [16, 17], but in the following we shall use more traditional approaches.

1.7 Density matrix.

Up to now we considered the classical statistical mechanics in which the state of a system was described by the point (p, q) in $6N$ -dimensional phase space of coordinates and momenta of all particles and time evolution was determined by Hamilton equations. In quantum mechanics such description becomes impossible as due to uncertainty relations we can not simultaneously measure both coordinate and moment of a quantum particle. It is clear that we have to construct a special formalism of quantum statistical mechanics. However, the remarkable fact is that the main principles of the Gibbs approach remain valid also in quantum case.

1.7.1 Pure ensemble.

In quantum mechanics the state of a many particle system is described by the wave function $\psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t)$, which depends on time and coordinates of the particles $\mathbf{x}_1, \dots, \mathbf{x}_N$ (or on another set of simultaneously measurable variables, e.g. momenta). Time evolution is determined by Schroedinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad (1.95)$$

For example, for the system of N identical particles with mass m , without internal degrees of freedom and interacting with two particle potential $U(|\mathbf{x}|)$,

the Schroedinger equation can be written as:

$$i\hbar \frac{\partial \psi}{\partial t} = \left\{ -\frac{\hbar^2}{2m} \sum_{j=1}^N \nabla_j^2 + \frac{1}{2} \sum_{j \neq k} U(|\mathbf{x}_j - \mathbf{x}_k|) \right\} \psi \quad (1.96)$$

Schroedinger equation fully determines the wave function ψ at the moment t if it was known at some initial moment $t = 0$. For example, for isolated system with time independent H we can write down its formal solution as:

$$\psi(t) = e^{\frac{i}{\hbar} H t} \psi(0) \quad (1.97)$$

Physical characteristics of a system in quantum mechanics are represented by linear Hermitian (self-adjoint) operators acting in a Hilbert space of the wave functions. Eigenvalues of such operators define the possible values of physical observables. The knowledge of quantum state of the system ψ (vector in Hilbert space), in general case, does not lead to the precise knowledge of physical characteristics. It allows only to calculate the average value of a dynamic variable represented an operator A in the state ψ as:

$$\langle A \rangle = (\psi^*, A\psi) \quad (1.98)$$

where, as usual, we assume wave functions to be normalized:

$$(\psi^*, \psi) = 1 \quad (1.99)$$

where parenthesis denote the scalar product of vectors in Hilbert space:

$$(\psi^*, \phi) = \int dx \psi^*(x) \phi(x) \quad (1.100)$$

where for brevity we denote by x the whole set of coordinates $\mathbf{x}_1, \dots, \mathbf{x}_N$. Only in a special case, when ψ is an eigenfunction of operator A , Eq. (1.98) gives the precise value of the physical quantity A in the state ψ .

The state described by the wave function usually is called the *pure* state. Corresponding statistical ensemble, i.e. the large number of non interacting “copies” of the system, belonging to the same quantum state, is called the pure ensemble. Pure state (ensemble) gives the most *complete* description of the system within the quantum mechanics.

Expressions for the averages of physical quantities in pure ensemble can be conveniently written using the notion of projection operator. Let us write down the linear operator A as a matrix in x -representation, defining it by matrix elements:

$$A\psi(x) = \int dx' A(x, x') \psi(x') \quad (1.101)$$

Substituting (1.101) into (1.98) we get⁹:

$$\langle A \rangle = \int dx dx' A(x, x') \mathcal{P}(x', x) = Sp(AP) \quad (1.102)$$

⁹In the following we use the notation of Sp for the sum of the diagonal elements of the matrix (trace), which is traditional in European and Russian literature. In English literature it is usually denoted as Tr .

where:

$$\mathcal{P}(x, x') = \psi(x)\psi^*(x') \quad (1.103)$$

is projection operator on state ψ . It can be said that the pure ensemble is described by the projection operator (1.103), while the averages over this ensemble are calculated according to (1.102). Naturally this description is completely equivalent to the standard formalism of quantum mechanics using the wave function.

The name projection operator is connected with the nature of the action of \mathcal{P} on arbitrary vector φ in Hilbert space – it projects it on the “direction” of the vector ψ :

$$\mathcal{P}\varphi = \int dx' \mathcal{P}(x, x')\varphi(x') = (\psi^*, \varphi)\psi(x) \quad (1.104)$$

Projection operator is Hermitian, it can be seen from its definition (1.103):

$$\mathcal{P}^*(x, x') = \mathcal{P}(x', x) \quad (1.105)$$

It also has the following property:

$$\mathcal{P}^2 = \mathcal{P} \quad (1.106)$$

which follows from (1.104) – after the first projection the following projections on the same “direction” change nothing. We also have:

$$Sp\mathcal{P} = 1 \quad (1.107)$$

which follows from (1.102) after the replacement of A by unity operator or from the definition (1.103) with the account of normalization (1.99).

1.7.2 Mixed ensemble.

Quantum mechanics is inherently statistical theory of pure ensembles, which provide the complete description of quantum reality. Quantum statistical mechanics considers more general *mixed* ensembles, which are based on *incomplete* information about the quantum system. Let us consider the big number of identical non interacting copies of the given system, which can be in different quantum states. In the mixed ensemble we only know the probabilities w_1, w_2, \dots to find a system in its exact quantum states ψ_1, ψ_2, \dots . We do not know precisely in which state the system is in reality, in this sense our knowledge is incomplete, we know only these probabilities. However, in the mixed ensemble we can certainly calculate the average value of an arbitrary physical quantity, represented by an operator A as:

$$\langle A \rangle = \sum_k w_k (\psi_k^*, A\psi_k) \quad (1.108)$$

where

$$\sum_k w_k = 1; \quad w_k \leq 1. \quad (1.109)$$

This relations are, in fact, quite obvious as $(\psi_k^*, A\psi_k)$ represents the quantum mechanical average of an operator A in the state ψ_k . The pure ensemble is just the limiting case of the mixed ensemble, when all probabilities w_k are zero, except the only one, which is equal to unity. Then (1.108) reduces to (1.98).

To study mixed ensembles it is convenient to use the statistical operator introduced first independently by Landau and von Neumann. Let us return to the linear operator A in x -matrix representation (1.101). Substituting (1.101) into (1.108), we get:

$$\langle A \rangle = \int dx dx' A(x, x') \rho(x', x) \quad (1.110)$$

or

$$\langle A \rangle = Sp(\rho A) \quad (1.111)$$

where

$$\rho(x, x') = \sum_k w_k \psi_k(x) \psi_k^*(x') \quad (1.112)$$

is the *statistical operator* in x -matrix representation or the so called *density matrix*.

Density matrix depends on $2N$ variables $\mathbf{x}_1, \dots, \mathbf{x}_N, \mathbf{x}'_1, \dots, \mathbf{x}'_N$ and satisfies normalization condition:

$$Sp\rho = 1, \quad (1.113)$$

which is evident from its definition:

$$Sp\rho = \int dx \rho(x, x) = \sum_k w_k (\psi_k^*, \psi_k) = 1 \quad (1.114)$$

where the last equality follows from $(\psi_k^*, \psi_k) = 1$ and $\sum_k w_k = 1$. Eq. (1.113) is the direct analogue of normalization condition for distribution function in classical statistical mechanics.

The general relation (1.111) is most convenient as the trace of the matrix is invariant with respect to unitary transformations. Thus, Eq. (1.111) is independent of the representation used for operators A and ρ , it is valid for arbitrary representation, not only for x -representation used above. For example in some discrete n -representation we have:

$$\langle A \rangle = \sum_{mn} A_{mn} \rho_{nm} \quad (1.115)$$

where A_{mn} are the matrix elements of operator A in n -representation, ρ_{nm} is the density matrix in n -representation.

Density matrix (statistical operator) is Hermitian:

$$\rho^*(x, x') = \rho(x', x) \quad (1.116)$$

which directly follows from its definition (1.112). Using the projection operator (1.103) we can write the statistical operator (1.112) as:

$$\rho = \sum_k w_k \mathcal{P}_{\psi_k}; \quad \sum_k w_k = 1; \quad w_k \leq 1 \quad (1.117)$$

where \mathcal{P}_{ψ_k} is projection operator on the state ψ_k . In case of all w_k zero, except one, which is unity, statistical operator (1.117) simply coincides with projection operator (1.103).

To conclude this discussion, we show that statistical operator is positive definite, i.e. its eigenvalues are non negative. As ρ is Hermitian, positive definiteness of its eigenvalues is equivalent to:

$$\langle A^2 \rangle = Sp(\rho A^2) \geq 0 \quad (1.118)$$

where A is an arbitrary Hermitian operator. It becomes obvious, if we diagonalize ρ (which is possible due to its Hermiticity) and write Eq. (1.118) as:

$$\sum_{nk} \rho_{nn} A_{nk} A_{kn} = \sum_{nk} \rho_{nn} |A_{nk}|^2 \geq 0, \quad (1.119)$$

which leads to conclusion that $\rho_{nn} \geq 0$. For the density matrix (1.112) the property (1.118) is satisfied as:

$$\langle A^2 \rangle = \sum_k w_k (A^2)_{kk} = \sum_{km} w_k A_{km} A_{mk} = \sum_{km} w_k |A_{km}|^2 \geq 0 \quad (1.120)$$

so that statistical operator is positively definite. It can also be shown that all matrix elements of the density matrix are limited by [3]:

$$Sp \rho^2 = \sum_{mn} |\rho_{mn}|^2 \leq 1. \quad (1.121)$$

1.8 Quantum Liouville equation.

Let us consider time evolution of the density matrix (statistical operator) of an ensemble of systems described by Hamiltonian H , which has no explicit time dependence. At the moment t density matrix (1.112) has the form:

$$\rho(x, x') = \sum_k w_k \psi_k(x, t) \psi_k^*(x', t) \quad (1.122)$$

where all the time dependence is contained in wave functions, while probabilities w_k do not depend on t , as they correspond to distribution of systems in ensemble at $t = 0$. Wave functions $\psi_k(x, t)$ are the solutions of time dependent Schroedinger equation with initial conditions:

$$\psi_k(x, t)|_{t=0} = \psi_k(x) \quad (1.123)$$

where $\psi_k(x)$ is some system of wave functions defining density matrix at $t = 0$:

$$\rho(x, x') = \sum_k w_k \psi_k(x) \psi_k^*(x') \quad (1.124)$$

If at the initial moment the relative number w_k of dynamical systems were at the state $\psi_k(x, 0)$, then at the moment t the same number of systems will be in the state $\psi_k(x, t)$.

Time dependence of $\psi_k(x, t)$ is determined by Schroedinger equation:

$$i\hbar \frac{\partial \psi_k(x, t)}{\partial t} = H \psi_k(x, t) \quad (1.125)$$

or in x -matrix representation:

$$i\hbar \frac{\partial \psi_k(x, t)}{\partial t} = \int dx' H(x, x') \psi_k(x', t) \quad (1.126)$$

Accordingly, the density matrix satisfies the equation:

$$\begin{aligned} i\hbar \frac{\partial \rho(x, x', t)}{\partial t} &= \\ &= \int dx'' \sum_k [H(x, x'') w_k \psi_k(x'', t) \psi_k^*(x', t) - w_k \psi_k(x, t) \psi_k^*(x'', t) H(x'', x')] = \\ &= \int dx'' [H(x, x'') \rho(x'', x', t) - \rho(x, x'', t) H(x'', x')] \end{aligned} \quad (1.127)$$

where we have used the Hermiticity of Hamiltonian $H^*(x, x') = H(x', x)$. Thus we obtain the equation of motion for the density matrix — the so called quantum Liouville equation. In operator form it is written as:

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho] \quad (1.128)$$

where

$$\frac{1}{i\hbar} [H, \rho] = \frac{1}{i\hbar} (H\rho - \rho H) \equiv \{H, \rho\} \quad (1.129)$$

are the quantum Poisson brackets.

For systems in statistical (thermodynamic) equilibrium ρ does not explicitly depend on time and quantum Liouville equation takes the form:

$$[H, \rho] = 0 \quad (1.130)$$

so that ρ commutes with Hamiltonian and is an integral of motion, similarly to the case of classical statistical mechanics. Commutativity of operators ρ and H and their Hermiticity allows them to have the common system of eigenfunctions. Thus, the statistical operator of equilibrium system can be written as:

$$\rho(x, x') = \sum_k w(E_k) \psi_k(x) \psi_k^*(x') \quad (1.131)$$

where the wave functions are eigenfunctions of the Hamiltonian (stationary Schroedinger equation):

$$H\psi_k = E_k \psi_k \quad (1.132)$$

1.9 Microcanonical distribution in quantum statistics.

Main ideas of the Gibbs approach based on the concept of statistical ensembles can be directly generalized from classical case to quantum. In the equilibrium state density matrix can depend only on *additive* integrals of motion, for the same reasons as in classical case (factorization of density matrix for statistically independent systems and additivity of its logarithm). In quantum mechanics

these integrals of motion are the same as in classics: total energy of the system (Hamiltonian H), total momentum \mathbf{P} and total angular momentum \mathbf{M} (corresponding operators acting in the space of wavefunctions). Accordingly, the equilibrium density matrix can be the function of H , \mathbf{P} , \mathbf{M} only:

$$\rho = \rho(H, \mathbf{P}, \mathbf{M}) \quad (1.133)$$

If the number of particles in systems of an ensemble N is not fixed, it has to be taken into account as an additional integral of motion:

$$[N, H] = 0 \quad (1.134)$$

where N is particle number operator with positive integer eigenvalues $0, 1, 2, \dots$. Then:

$$\rho = \rho(H, \mathbf{P}, \mathbf{M}, N) \quad (1.135)$$

For the system at rest we have $\mathbf{P} = \mathbf{M} = 0$ and:

$$\rho = \rho(H) \quad \text{or} \quad \rho = \rho(H, N) \quad (1.136)$$

Besides that, statistical operator can depend on external parameters fixed for all systems in an ensemble, e.g. on volume V .

Microcanonical distribution in quantum statistics can be introduced in the same way as in classical statistics. Consider an ensemble of closed, energetically (adiabatically) isolated systems with constant volume V and total number of particles N , which possess the same energy E up to some small uncertainty $\Delta E \ll E$. Let us suppose that all quantum states in an energy layer $E, E + \Delta E$ are *equally probable*, i.e. we can find a system from an ensemble in either of these states with equal probability. Then:

$$w(E_k) = \begin{cases} [\mathcal{W}(E, N, V)]^{-1} & \text{for } E \leq E_k \leq E + \Delta E \\ 0 & \text{outside this layer} \end{cases} \quad (1.137)$$

and this is just what we call microcanonical distribution of quantum statistics. Here everything is similar to the classical case, though the statistical weight $\mathcal{W}(E, N, V)$ is not equal to the phase volume, but from the very beginning is just the number of quantum states in the energy layer $E, E + \Delta E$, for the system of N particles and volume V . This directly follows from normalization condition $\sum_k w(E_k) = 1$. Microcanonical distribution corresponds to the density matrix of the form:

$$\rho(x, x') = \mathcal{W}^{-1}(E, N, V) \sum_{1 \leq k \leq \mathcal{W}} \psi_k(x) \psi_k^*(x') \quad (1.138)$$

which can be written also in operator form as:

$$\rho = \mathcal{W}^{-1}(E, N, V) \Delta(H - E) \quad (1.139)$$

where $\Delta(x)$ is the function, which is unity on the interval $0 \leq x \leq \Delta E$, and zero otherwise.

Let us stress once again that the assumption of equal probability of quantum states with the same energy for the closed (isolated) system is a simplest one, but not obvious. The justification of this hypothesis is the task of quantum ergodic theory.

1.10 Partial density matrices*.

Similarly to classical case, in practice we do not need the knowledge of the full density matrix of N -particle system. In fact, the most important information about the system can be obtained from the study of statistical operators for (rather small) complexes of particles or so called partial density matrices [18]. Consider again an arbitrary system of N identical particles. Let us denote as x_1, x_2, \dots, x_N the variables of these particles (these may be coordinates, momenta etc.). Wave functions of the whole system are functions of these variables:

$$\psi_n(x, t) = \psi_n(x_1, \dots, x_N, t) \quad (1.140)$$

where n denotes the “number” (the set of quantum numbers) of the given state of the system. Operators of physical quantities are represented by generalized matrices of the following form:

$$\mathcal{A} = \mathcal{A}(x_1, \dots, x_N; x'_1, \dots, x'_N) \quad (1.141)$$

Consider the statistical operator of N -particle system:

$$\rho(x_1, \dots, x_N; x'_1, \dots, x'_N; t) = \sum_n w_n \psi_n(x_1, \dots, x_N, t) \psi_n^*(x'_1, \dots, x'_N, t) \quad (1.142)$$

For the system of Bosons:

$$P\psi_n(x_1, \dots, x_N, t) = \psi_n(x_1, \dots, x_N, t) \quad (1.143)$$

where P is permutation operator of variables x_i ($i = 1, 2, \dots, N$). For the system of Fermions:

$$P\psi_n(x_1, \dots, x_N, t) = (-1)^P \psi_n(x_1, \dots, x_N, t) \quad (1.144)$$

where $(-1)^P = 1$ for even permutations and $(-1)^P = -1$ for odd permutations. Thus, in both cases we have:

$$P\rho = \rho P \quad \text{or} \quad P\rho P^{-1} = \rho. \quad (1.145)$$

While calculating the average values of physical characteristics we usually deal with operators depending on variables of one, two, ..., s -particles:

$$\mathcal{A}_1 = \sum_{1 \leq \mathbf{r} \leq N} \mathcal{A}(\mathbf{r}) \quad (1.146)$$

$$\mathcal{A}_2 = \sum_{1 \leq \mathbf{r}_1 < \mathbf{r}_2 \leq N} \mathcal{A}(\mathbf{r}_1, \mathbf{r}_2) \quad (1.147)$$

$$\mathcal{A}_s = \sum_{1 \leq \mathbf{r}_1 < \mathbf{r}_2 < \dots < \mathbf{r}_s \leq N} \mathcal{A}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_s) \quad (1.148)$$

where \mathbf{r}_i denotes the dependence on coordinates of the i -th particle. The average values of such operators can be calculated with the help of density matrices, obtained from the general ρ , taking the $S\rho$ over the (most) part of independent

variables. Taking into account the symmetry of ρ with respect to particles permutations (1.145), we get:

$$\langle \mathcal{A}_1 \rangle = N S p_1 \{ \mathcal{A}(1) \rho_1(1) \} \quad (1.149)$$

$$\langle \mathcal{A}_2 \rangle = \frac{N(N-1)}{2!} S p_{1,2} \{ \mathcal{A}(1,2) \rho_2(1,2) \} \quad (1.150)$$

.....

$$\langle \mathcal{A}_s \rangle = \frac{N(N-1)\dots(N-s+1)}{s!} S p_{1,2,\dots,s} \{ \mathcal{A}(1,2,\dots,s) \rho_s(1,2,\dots,s) \} \quad (1.151)$$

where we have introduced the notations:

$$\rho_1(1) = S p_{2,\dots,N} \rho(1,2,\dots,N) \quad (1.152)$$

$$\rho_2(1,2) = S p_{3,\dots,N} \rho(1,2,\dots,N) \quad (1.153)$$

.....

$$\rho_s(1,2,\dots,s) = S p_{s+1,\dots,N} \rho(1,2,\dots,s,s+1,\dots,N) \quad (1.154)$$

and for brevity we used the notations $\rho_2(1,2) \equiv \rho_2(x_1, x_2; x'_1, x'_2, t)$, $S p_2 \rho_2(1,2) = S p_{x_2} \rho_2(x_1, x_2; x'_1, x'_2; t)$, etc. Density matrices ρ_s are called statistical operators of complexes of s -particles or s -particle density matrices.

For operators ρ_s , due to (1.145), we have the following relations:

$$P_s \rho_s P_s^{-1} = \rho_s \quad (1.155)$$

where P_s is permutation operator of s particles, and

$$\rho_s(1,2,\dots,s) = S p_{s+1} \rho_{s+1}(1,\dots,s,s+1) \quad (1.156)$$

which gives the expression of s -particle density matrix via $s+1$ -particle density matrix.

Let us use instead of ρ_s operators F_s defined as:

$$F_s(1,\dots,s) = N(N-1)\dots(N-s+1) \rho_s(1,\dots,s) \quad (1.157)$$

From (1.156) we obtain similar relations:

$$F_s(1,\dots,s) = \frac{1}{N-s} S p_{s+1} F_{s+1}(1,\dots,s,s+1) \quad (1.158)$$

In the limit of $N \rightarrow \infty$ and for fixed s , we can neglect s in the denominator, so that:

$$F_s(1,\dots,s) = \frac{1}{N} S p_{s+1} F_{s+1}(1,\dots,s,s+1) \quad (1.159)$$

In analogy with classical case we shall call F_s s -particle distribution functions. Under permutations we obviously have: $P_s F_s P_s^{-1} = F_s$. The averages of physical quantities (1.151) are written now as:

$$\langle \mathcal{A}_s \rangle = \frac{1}{s!} S p_{1,\dots,s} \{ \mathcal{A}(1,\dots,s) F_s(1,\dots,s) \} \quad (1.160)$$

Let us write an operator \mathcal{A}_s in the standard second quantized form:

$$\mathcal{A}_s = \frac{1}{s!} \sum_{\{f,f'\}} A(f_1,\dots,f_s; f'_1,\dots,f'_s) a_{f_1}^+ \dots a_{f_s}^+ a_{f'_s} \dots a_{f'_1} \quad (1.161)$$

where a_f^+, a_f are operators of creation and annihilation of particles in some single particle states, characterized by quantum numbers f , and $A(f_1, \dots, f_s; f'_s, \dots, f'_1)$ is the appropriate matrix element of an operator of dynamical variable A . Then, calculating the ensemble averages we have:

$$\langle \mathcal{A}_s \rangle = \frac{1}{s!} \sum_{\{f, f'\}} A(f_1, \dots, f_s; f'_s, \dots, f'_1) \langle a_{f_1}^+ \dots a_{f_s}^+ a_{f'_s} \dots a_{f'_1} \rangle \quad (1.162)$$

Comparing this expression with Eq. (1.160) we obtain the following general expression for s -particle distribution function in second quantized form:

$$F_s(1, \dots, s) = \langle a_{f_1}^+ \dots a_{f_s}^+ a_{f'_s} \dots a_{f'_1} \rangle \quad (1.163)$$

which is very convenient in practical calculations of quantum statistical mechanics and is widely used in the modern theory of many particle systems¹⁰. In fact, calculation of these averages in different physical situations is the main task of this theory. One of the methods to perform such calculations is to construct the system of coupled equations for such distribution functions (Bogolyubov's chain), similar to the classical case and its approximate solution by some method. This approach is used e.g. during the derivation of quantum kinetic equations (see Chapter 10).

For a number of problems, as well as to discuss the correspondence with classical case, often is convenient to introduce the so called Wigner's distribution function in the "mixed" coordinate – momentum representation. Consider the single particle density matrix $\rho_1(1) = \rho(\mathbf{x}, \mathbf{x}')$, where \mathbf{x} are coordinates of the particle, and define Wigner's distribution function as:

$$f(\mathbf{x}, \mathbf{p}) = \frac{1}{(2\pi)^3} \int d\xi e^{\frac{i}{\hbar} \mathbf{p} \xi} \rho \left(\mathbf{x} + \frac{\xi}{2}, \mathbf{x} - \frac{\xi}{2} \right) \quad (1.164)$$

i.e. via Fourier transform over the difference of coordinates $\xi = \mathbf{x} - \mathbf{x}'$. Integrating this function by \mathbf{x} and \mathbf{p} we obtain diagonal elements of the density matrix in \mathbf{x} and \mathbf{p} representations:

$$\rho(\mathbf{x}, \mathbf{x}) = \int d\mathbf{p} f(\mathbf{x}, \mathbf{p}) \quad \rho(\mathbf{p}, \mathbf{p}) = \int d\mathbf{x} f(\mathbf{x}, \mathbf{p}) \quad (1.165)$$

which is easily obtained from definition of Wigner's function after proper change of variables. Of course, this distribution function $f(\mathbf{x}, \mathbf{p})$ can not be understood as distribution function over coordinates and momenta (because of uncertainty principle!), but its integrals separately define distribution functions over coordinates and momenta. By itself, Wigner's function can even be negative and does not have the meaning of the usual (classical) distribution function.

1.11 Entropy.

1.11.1 Gibbs entropy. Entropy and probability.

Let us return to the case of classical statistical mechanics and consider the logarithm of distribution function (with inverse sign):

$$\eta = -\ln \rho(p, q, t) \quad (1.166)$$

¹⁰Let us stress that angular brackets here denote averaging (taking the trace) with full N -particle density matrix!

This function plays a special role, e.g. above we have already seen that it is additive for factorizing distribution functions of independent subsystems, which is analogous to the additivity of entropy in thermodynamics. The average value of this function is called *Gibbs entropy*:

$$S = \langle \eta \rangle = - \int \frac{dpdq}{(2\pi\hbar)^{3N} N!} \rho(p, q, t) \ln \rho(p, q, t) \quad (1.167)$$

Let us calculate this entropy for microcanonical distribution (1.58) describing a closed system in equilibrium. Substituting into Eq. (1.167) distribution function given by (1.58):

$$\rho(p, q) = \begin{cases} [\mathcal{W}(E, N, V)]^{-1} & \text{for } E \leq H(p, q) \leq E + \Delta E \\ 0 & \text{outside this layer} \end{cases} \quad (1.168)$$

where

$$\mathcal{W}(E, N, V) = \frac{1}{N!(2\pi\hbar)^{3N}} \int_{E \leq H(p, q) \leq E + \Delta E} dpdq \quad (1.169)$$

we obtain:

$$\begin{aligned} S(E, N, V) &= - \int_{E \leq H(p, q) \leq E + \Delta E} \frac{dpdq}{(2\pi\hbar)^{3N} N!} \frac{1}{\mathcal{W}(E, N, V)} \ln[\mathcal{W}(E, N, V)]^{-1} = \\ &= \ln \mathcal{W}(E, N, V) \end{aligned} \quad (1.170)$$

Thus, for microcanonical distribution Gibbs entropy is equal to the logarithm of statistical weight, i.e. to the logarithm of the number of quantum states in the energy layer of the width ΔE , corresponding to given macroscopic state of our system¹¹.

In quantum statistics we may similarly introduce the operator of entropy via logarithm of the density matrix:

$$\eta = - \ln \rho \quad (1.171)$$

We have seen above that statistical operator ρ is Hermitian and positive definite. Accordingly, its logarithm is also Hermitian and entropy operator is positive: if w_1, w_2, \dots are the eigenvalues of operator ρ , the eigenvalues of operator η are correspondingly $-\ln w_1, -\ln w_2, \dots$, as eigenvalues of the function of an operator are equal to the same function of eigenvalues. From $0 \leq w_k \leq 1$ it follows that $-\ln w_k \geq 0$.

Entropy operator is additive: if operator ρ is a direct product of operators $\rho_1 \rho_2$:

$$\rho = \rho_1 \times \rho_2 \quad (1.172)$$

¹¹Statistical weight $\mathcal{W}(E, N, V) = \exp S(E, N, V)$, by definition, is the number of energy levels on the energy interval ΔE , which characterized the energy distribution width. Dividing ΔE by $\mathcal{W}(E, N, V)$ we obviously get the average distance between the energy levels in the spectrum in the vicinity of E . Denoting this distance by $D(E)$ we obtain: $D(E) = \Delta E \exp(-S(E))$. In this sense, the value of entropy $S(E)$ determines the density of states in this energy interval. Due to additivity of entropy we can claim that the average distance between energy levels of macroscopic system is dropping exponentially fast with the growth of the number of particles, so that the spectrum of a macroscopic body is, in fact, continuous [1].

we get

$$\eta = -\ln \rho_1 - \ln \rho_2 = \eta_1 + \eta_2 \quad (1.173)$$

Now we can again introduce Gibbs entropy as average logarithm of the density matrix (with a minus sign):

$$S = \langle \eta \rangle = - \langle \ln \rho \rangle = -S p \rho \ln \rho \quad (1.174)$$

Entropy is positive definite and in some diagonal representation it can be written as:

$$S = - \sum_k w_k \ln w_k \geq 0 \quad (1.175)$$

Only for the special case, when density matrix corresponds to pure state, we have $S = 0$ (one of $w_k = 1$, all others are zero). If ρ describes statistically independent ensembles (1.172), we get $S = S_1 + S_2$, where $S_1 = -S p \rho_1 \ln \rho_1$ and $S_2 = -S p \rho_2 \ln \rho_2$, so that Gibbs entropy is additive (as entropy in thermodynamics).

Let us discuss statistical meaning of entropy. Consider a macroscopic state of the system, which is characterized by E, N, V and some additional macroscopic parameters (x_1, x_2, \dots, x_n) , or just x for brevity. Let the statistical weight of the macroscopic state with the *fixed* values of these parameters be $\mathcal{W}(E, N, V, x)$. Then, the probability of realization of this state (E, N, V, x) due to the equal probability of all states in microcanonical ensemble is simply given by (sum of probabilities!):

$$w(x) = \frac{\mathcal{W}(E, N, V, x)}{\sum_x \mathcal{W}(E, N, V, x)} = C \exp(S(E, N, V, x)) \quad (1.176)$$

where

$$S(E, N, V, x) = \ln \mathcal{W}(E, N, V, x) \quad (1.177)$$

is the entropy of the state (E, N, V, x) .

In many cases the most probable value of x , which we denote by x^* , and the average value $\langle x \rangle$ just coincide, as probability $w(x)$ possesses a sharp peak at $x = x^*$ (for large enough system). The most probable value x^* is determined by the maximum of $w(x)$:

$$S(E, N, V, x) = \text{Max} \quad \text{for} \quad x = x^* \quad (1.178)$$

or

$$\frac{\partial S(E, N, V, x_1^*, \dots, x_n^*)}{\partial x_j^*} = 0 \quad j = 1, 2, \dots, n \quad (1.179)$$

It is easy to conclude that

$$w(\Delta x) = C' \exp\{S(E, N, V, x^* + \Delta x) - S(E, N, V, x^*)\} \quad (1.180)$$

determines the probability of deviations (fluctuations) Δx of parameters x from their most probable (average or equilibrium!) values¹². This property of entropy gives the foundation of its statistical applications (Boltzmann's principle), it is also the foundation for the theory of fluctuations (Einstein, see Chapter 7).

¹²We can write: $w(x^* + \Delta x) = C \exp\{S(x^* + \Delta x)\} = C' \exp\{S(x^* + \Delta x) - S(x^*)\}$, where $C' = C \exp\{S(x^*)\}$ is just the new normalization constant.

1.11.2 The law of entropy growth.

In thermodynamics it is shown that the entropy of an isolated system can only increase or remain constant in the state of thermodynamic equilibrium. For the equilibrium state we shall show below that Gibbs definition of entropy is actually equivalent to thermodynamic entropy. However, for non equilibrium cases, when distribution function $\rho(p, q, t)$ depends on time, situation is much more complicated. In fact, we can easily show that for isolated system Gibbs entropy does not depend on time at all, thus it just can not increase. To see this, let at $t = 0$ distribution function be $\rho(p^0, q^0, 0)$, while at the moment t it is equal to some $\rho(p, q, t)$, where (p, q) belongs to a phase trajectory passing through (p^0, q^0) and moving according to Hamilton equations. According to Liouville theorem we have (1.45):

$$\rho(p^0, q^0, 0) = \rho(p, q, t), \quad (1.181)$$

Then at time moment t Gibbs entropy is equal to:

$$\begin{aligned} S &= - \int \frac{dpdq}{(2\pi\hbar)^{3N} N!} \rho(p, q, t) \ln \rho(p, q, t) = \\ &= - \int \frac{dp^0 dq^0}{(2\pi\hbar)^{3N} N!} \rho(p^0, q^0, 0) \ln \rho(p^0, q^0, 0) \end{aligned} \quad (1.182)$$

as due to Liouville theorem on conservation of the phase volume we have $dpdq = dp^0 dq^0$. Then it is obvious that Gibbs entropy can not serve as the general definition of entropy for the arbitrary non equilibrium state. This is the major paradox directly connected to principal difficulty of justifying the irreversible thermodynamic behavior by time - reversible equations of motion of classical (and also quantum) mechanics, which lead to active discussions already at the initial stages of development of statistical mechanics (Boltzmann, Zermelo, Poincare, Gibbs).

Using some early ideas of Gibbs, further developed by Paul and Tatiana Ehrenfest, the following heuristic picture can illustrate the statistical sense of entropy growth with time evolution of mechanical system. Starting with the idea of inevitable limitations of measurements of coordinates and momenta in the phase space¹³ let us introduce the “coarse grained” distribution function related to “microscopic” distribution $\rho(p, q, t)$ by the following relation:

$$\tilde{\rho}(p, q, t) \equiv \rho_i = \frac{1}{\omega_i} \int_{\omega_i} dpdq \rho(p, q, t) \quad (1.183)$$

where the integration (averaging) is performed over some small fixed “cells” in the phase space ω_i , with size determined by the limitations of measurements mentioned above. Such averaging (“coarse graining”) of distribution function just means that we introduce some “natural” and finite resolution in the phase space – smaller scales are outside the limits of measurements procedures available to us. For example, we have already noted that there exists the absolute lower boundary for any “cell” ω_i in the phase space, which can not be

¹³This may be related to finite resolution of experimental apparatus, sensitivity to initial conditions etc.

smaller than $(2\pi\hbar)^{3N}$ due to uncertainty principle¹⁴. “Coarse grained” distribution function (1.183) is obviously constant inside the appropriate “cell” ω_i , surrounding the point (p, q) . Then, any integral over the whole phase space with our distribution function can be written as:

$$\int dpdq\rho(p, q)\dots = \sum_i \rho_i \omega_i \dots = \sum_i \int_{\omega_i} dpdq\rho(p, q)\dots = \int dpdq\tilde{\rho}(p, q)\dots \quad (1.184)$$

Now we shall see that Gibbs entropy, constructed with the help of “coarse grained” distribution is, in general case, time dependent and can increase with time. Let us compare the values of Gibbs entropy calculated with “coarse grained” distribution function at the moments t and $t = 0$, assuming that at the initial moment microscopic distribution function just coincides with “coarse grained”:

$$\rho(p^0, q^0, 0) = \tilde{\rho}(p^0, q^0, 0) \quad (1.185)$$

We have:

$$\begin{aligned} S_t - S_0 &= \\ &= - \int d\Gamma \tilde{\rho}(p, q, t) \ln \tilde{\rho}(p, q, t) + \int d\Gamma_0 \rho(p^0, q^0, 0) \ln \rho(p^0, q^0, 0) = \\ &= - \int d\Gamma \{ \rho(p, q, t) \ln \tilde{\rho}(p, q, t) - \rho(p, q, t) \ln \rho(p, q, t) \} \quad (1.186) \end{aligned}$$

where we have used Liouville theorem to write $d\Gamma_0 = d\Gamma$ and also (1.181) and removed tilde over distribution function, which is not under the logarithm, which according to (1.184) is always correct under integration¹⁵.

For two arbitrary normalized distribution functions ρ and ρ' , defined in the same phase space, we can prove the following Gibbs inequality¹⁶:

$$\int d\Gamma \rho \ln \left(\frac{\rho}{\rho'} \right) \geq 0 \quad (1.187)$$

where equality is achieved only in the case of $\rho = \rho'$. Then, from Eq. (1.186) (taking $\tilde{\rho} = \rho'$) we immediately obtain:

$$S_t \geq S_0 \quad (1.188)$$

Let $\rho(p^0, q^0, 0)$ be some non equilibrium distribution, then at the moment t :

$$\rho(p, q, t) \neq \tilde{\rho}(p, q, t) \quad (1.189)$$

¹⁴In general, the situation with entropy time dependence in quantum statistical mechanics is quite similar to that in classical statistical mechanics and we shall limit ourselves here to classical case only, referring to the discussions of the quantum case in literature [3].

¹⁵We have: $\int dpdq\tilde{\rho}(p, q) \ln \tilde{\rho}(p, q) = \sum_i \rho_i \omega_i \ln \rho_i = \sum_i \left[\int_{\omega_i} dpdq\rho(p, q) \ln \rho_i \right] = \int dpdq\rho(p, q) \ln \tilde{\rho}(p, q)$, which was used in Eq. (1.186).

¹⁶This inequality follows from $\ln \left(\frac{\rho}{\rho'} \right) \geq 1 - \frac{\rho'}{\rho}$ ($\rho > 0, \rho' > 0$), where equality is valid only for $\rho = \rho'$. It is clear from inequality $\ln x \geq 1 - \frac{1}{x}$, valid for $x > 0$ (equality for $x = 1$), where we put $x = \frac{\rho}{\rho'}$. After multiplication by ρ and integration over the phase space we get: $\int \rho \ln \left(\frac{\rho}{\rho'} \right) d\Gamma \geq \int \rho \left(1 - \frac{\rho'}{\rho} \right) d\Gamma = 0$, where we have used normalization, thus proving Eq. (1.187.)

as though $\rho(p, q, t)$ does not change along phase trajectory, but the “cell”, ω , surrounding an arbitrary point (p, q) will be “visited” by phase points from other “cells” (chaotically coming and going), and these processes, in general case, will not compensate each other. This is called “mixing” of phase points. Taking into account Eq. (1.189) from Eq. (1.188) it follows that:

$$S_t > S_o \quad (1.190)$$

i.e. entropy, defined with “coarse grained” distribution function, grows with time. This conclusion is valid if the motion of phase points is “mixing” in the above mentioned sense. The “mixing” nature of motion in phase space is intimately related to local instability of phase trajectories, which appears (as a rule!) for non trivial physical systems. even with pretty small number of particles [12]. This instability leads to exponential (in time) growth of the distance between phase points on different trajectories initially quite close to each other. In more details, though still on rather elementary level, we shall discuss this situation in Appendix A.

However, the introduction of the “coarse grained” distribution function can not be considered as quite satisfactory solution of the problem. The smaller the scale of “coarse graining” (the size of the “cells” ω) the smaller is the entropy growth, and in the limit of $\omega \rightarrow 0$ it just goes to zero. At the same time, the growth of physical entropy should not depend on the scale of “coarse graining”. For example, we could have taken $\omega \sim \hbar^{3N}$, in agreement with requirements of quantum mechanics, but in this case the growth of the entropy would be controlled by the size of Planck constant \hbar . However, this is obviously not so, there is no such relation at all. There are different point of view with respect to this problem. Some researchers believe [3] that “coarse graining” should be performed within two limiting procedures: first we must go to the usual thermodynamic limit of statistical mechanics with number of particles in the system $N \rightarrow \infty$, system volume $V \rightarrow \infty$, while particle density remains finite $N/V = const$, and *only afterwards* we perform the limit of $\omega \rightarrow 0$. Modern point of view [12] is that thermodynamic limit here is irrelevant and “mixing” of phase points (positive Kolmogorov entropy, see Appendix A) is sufficient to guarantee “correct” physical behavior, even for systems with rather small number of degrees of freedom $N > 2$. An isolated system, irrespective of initial conditions, evolves to the equilibrium state, where it can be (with equal probability) discovered in any of its possible microscopic states (ergodic behavior).

Another, probably more physical approach to defining non equilibrium entropy [1] is based on the unquestionable definition of the entropy of equilibrium state (1.170). Assume that the system is initially in some not completely equilibrium state and start to analyze its evolution during time intervals Δt . Let us separate the system in some smaller (more or less independent) parts, so small that their relaxation times are also small compared with Δt (relaxation times are usually smaller for smaller systems – an empirical fact!). Such subsystems during the time interval Δt can be considered to be in their partial equilibrium states, which are described by their own microcanonical ensembles, when we can use the usual definitions of statistical weight and calculate appropriate (equilibrium) entropies. Then the statistical weight of the complete system is defined as the product $\mathcal{W} = \prod_i \mathcal{W}_i$ of statistical weights of the separate subsystems, and entropy $S = \sum_i S_i$. In such an approach, the entropy characterize only

some average properties of the body during some finite time interval Δt . Then it is clear that for too small time intervals Δt the notion of entropy just loses its meaning and, in particular, we can not speak about its *instant* value.

More formally we can analyze the entropy growth in this approach in the following way. Consider the closed macroscopic system at the time moment t . If we break this system into relatively small parts (subsystems), each will have its own distribution function ρ_i . The entropy S of the whole system at that moment is equal to:

$$S = - \sum_i \langle \ln \rho_i \rangle = - \langle \ln \prod_i \rho_i \rangle \quad (1.191)$$

Considering our subsystems as quasi independent, we can introduce the distribution function of the whole system as:

$$\rho = \prod_i \rho_i \quad (1.192)$$

To obtain distribution function at some later time t' we have to apply to ρ the mechanical equations of motion for the closed system. Then ρ will evolve at the moment t' to some ρ' . To obtain the distribution function of only i -th part of the system at the moment t' we must integrate ρ' over phase volumes of all subsystems, except the i -th. If we denote this distribution function as ρ'_i , then at the moment t' we get:

$$\rho'_i = \int_1 \int_2 \dots \int_{i-1} \int_{i+1} \dots d\Gamma_1 d\Gamma_2 \dots d\Gamma_{i-1} d\Gamma_{i+1} \dots \rho' \quad (1.193)$$

Note that in general case ρ' already can not be written as a product of all ρ'_i . The entropy at the moment t' , according to our definition is:

$$S' = - \sum_i \langle \ln \rho'_i \rangle \quad (1.194)$$

where the averaging $\langle \dots \rangle$ is performed already with distribution function ρ' . Let us use now the inequality $\ln x \leq x - 1$, valid for $x > 0$. Put here $x = \frac{\prod_i \rho'_i}{\rho'}$ to obtain:

$$- \ln \rho' + \sum_i \ln \rho'_i \leq \frac{\prod_i \rho'_i}{\rho'} - 1 \quad (1.195)$$

Averaging both sides of this inequality with distribution function ρ' , we get zero in the r.h.s., as $\int d\Gamma_1 d\Gamma_2 \dots \prod_i \rho'_i = \prod_i \int d\Gamma_i \rho_i = 1$ due to normalization, while the l.h.s. reduces to $\langle - \ln \rho' \rangle + \sum_i \langle \ln \rho'_i \rangle$. Finally we get:

$$- \langle \ln \rho' \rangle - S' \leq 0 \quad (1.196)$$

According to Liouville theorem distribution function ρ does not change under mechanical motion, so the value of $-\langle \ln \rho' \rangle$ remains equal to $-\langle \ln \rho \rangle$, which is the initial entropy S . Thus we obtain:

$$S' \geq S, \quad (1.197)$$

proving the entropy law: *if the closed system is defined by its macroscopic state at some moment of time, the most probable behavior at some later time is the growth of entropy.*

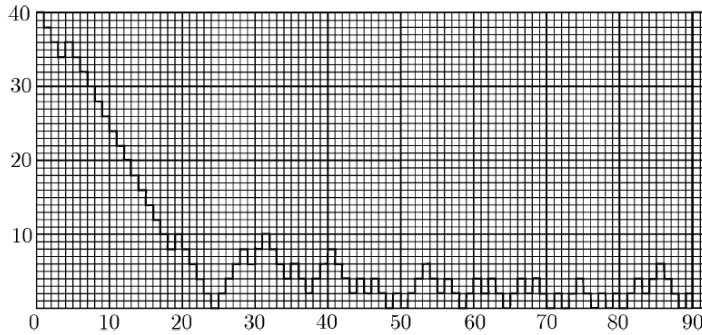


Figure 1.2: Typical realization of Ehrenfest’s “ H -curve”. Ordinate shows the value of $|n_A(s) - n_B(s)| = 2|n_A(s) - R|$.

Mechanical equations of motion are symmetric with respect to the replacement of t by $-t$. If mechanical laws allow some process, e.g. characterized by the growth of entropy, they also must allow just the opposite process, when system passes through precisely the same configurations in inverse order, so that its entropy diminishes. It may seem that we came to a contradiction. However, the formulation of law of the entropy growth used above, does not contradict the time invariance, if we speak only about the *most probable* evolution of some macroscopically defined state. In fact, the above arguments never used explicitly the fact that $t' > t$! Similar discussion will show that $S' \geq S$ also for $t \leq t'$. In other words, the law of the entropy growth means only that given the macroscopic state, of all microscopic states forming this macroscopic state, immensely vast majority will evolve at a later time to the state with larger entropy (or the same entropy in case of equilibrium). Thus the entropy law is primarily a *statistical* statement!

To understand this situation better, we may use a heuristic model discussed first by Paul and Tatiana Ehrenfest. Consider $2R$ balls, numbered from 1 to $2R$, and distributed among two boxes A and B . At some discrete moment of time s random number generator produces some integer from the interval between 1 and $2R$. Then, the ball with this number is just transferred from one box to another and this procedure continues for many times. Actually, this procedure is simple to realize on any modern PC. Intuitively, it is quite clear what happens. Consider, for simplicity, the initial state when all balls are in the box A . Then, on the first step we necessarily transfer one ball from A to B . On the second step we may return to the initial state, but probability of this event is $(2R)^{-1}$ and small if $2R$ is big enough. Actually, with much larger probability $1 - (2R)^{-1}$ another ball is transferred to box B . It is clear that until the number of balls n_A in box A is significantly larger than the number of balls n_B in box B , we “almost always” will observe only transitions from A to B . Or in more detail, let there be $n_A(s)$ balls in box A at the time moment s , while in box B there are $2R - n_A(s)$ balls. At the next moment $s + 1$ probability of emergence of the ball with number belonging to box A is $\frac{n_A}{2R}$, while the probability of emergence of the ball from box B is, naturally, $\frac{2R - n_A}{2R}$. However, until $n_A > 2R - n_A$, the “relative chance” $\frac{n_A}{2R - n_A}$ of ball from A to appear, compared with the similar chance of emergence of the ball from B , is obviously

larger than 1. Thus, more probable is transition $A \rightarrow B$ and the difference of the number of balls in our boxes diminishes with “time”. This tendency persists until we achieve the equality $n_A - (2R - n_A) = 0$, and it becomes weaker as this difference approaches zero. Thus, as the number of balls in both boxes tends to be equal, the probabilities of emergence of balls from either from A or B become closer to each other, and the result (for the further moments of time) becomes less and less clear. The next transfer may lead to further “equalization” of the number of balls in both boxes, but it may also lead to inverse process. Fig.1.2 shows a typical realization of such experiment with 40 balls. It is seen that initially the process seems to be irreversible, but close to the “equilibrium state” the difference of number of balls in our boxes starts to fluctuate, which shows that in fact we are dealing with reversible process¹⁷. We can not say that this difference always diminishes with “time”, but we can be absolutely sure that for large values of the number of balls $2R$ it diminishes “almost always”, while we are far enough from the “equilibrium”. The behavior of entropy in non equilibrium many particle system is precisely the same (with negative sign)!

Ehrenfest’s model allows a simple answer to all objections against the statistical mechanical justification of irreversible behavior. According to the principle of microscopic reversibility of mechanical motion, the process after “time reversal”, when the movement of the balls will precisely go in *reverse* order along the same “ H -curve”, is completely possible. But for large enough values of R such process is absolutely improbable. The probability of all balls to return “some-time” to a single box is not zero, but it is extremely small (say for $R \sim 10^{22}$!). Precisely the same is the meaning of thermodynamic irreversibility and the law of entropy growth¹⁸.

Thus, the common viewpoint is that an evolving isolated system essentially passes through states corresponding to *more and more probable* distributions. This behavior is overwhelming due to the factor $\exp(S)$, where in the exponent we have an additive entropy. Thus, the processes closed in non equilibrium system develop in such a way, that the system continuously go from the states with lower entropy to the states with larger entropy, until the entropy reaches its maximum in the state of statistical equilibrium. Speaking about “most probable” behavior we must take into account that in reality the probability of a transition to a state with larger entropy is immensely larger, than the probability of any significant entropy drop, so that such transitions are practically unobservable (up to small fluctuations). This, purely statistical, interpretation of the entropy growth was first formulated by Boltzmann. “It is doubtful whether the law of increase of entropy thus formulated could be derived on the basis of classical mechanics”[1]¹⁹. In the framework of modern statistical mechanics of

¹⁷On Fig.1.2 these fluctuations are always positive because the ordiante shows the absolute value of the difference in the number of balls in boxes A and B .

¹⁸“What, never? No, never! What, never? Well, hardly ever!” to quote Captain Corcoran of *H.M.S. Pinafore* by W.Gilbert and A.Sullivan (1878). This quotation was used in the context of entropy behavior in Ch. 4 of “Statistical Mechanics” by J.Mayer and M.Goeppert-Mayer, Wiley, NY 1940.

¹⁹Landau made an interesting observation that in quantum mechanics situation probably change. Though Schroedinger equation, by itself, is invariant with respect to time reversal (with simultaneous replacement of ψ by ψ^*), quantum mechanics contains some inequivalence of both directions of time. This inequivalence appears due to the importance of the process of interaction of the quantum object with a classical system (e.g. related to the measurement process). If the quantum object undergoes successively two processes of such interaction, say

non equilibrium systems [3, 16] and physical kinetics [13, 14, 15] it is possible to explicitly demonstrate the entropy growth in a number of concrete statistical models. However, we always need some physical (statistical) assumption to obtain this behavior. We shall return to brief discussion of these problems later.

A and B , the claim that the probability of some outcome of the process B is determined by the result of the process A is justified only if the process A preceded B . Thus it seems that in quantum mechanics there is some physical inequivalence of both directions of time, so that the law of the entropy growth may follow from it. However, in this case there should be some inequality containing \hbar , justifying the validity of this law. There is no evidence at all that this is true. Similarly, we may mention the possibility to explain irreversible thermodynamic behavior by the experimentally known fact of very weak CP -symmetry violation in the modern physics of elementary particles, which inevitably leads to a weak violation of T -invariance in the processes of elementary particles interactions. Up to now there is no accepted interpretations of this kind.

Chapter 2

GIBBS DISTRIBUTION

2.1 Canonical distribution.

Let us consider most important, from practical point of view, task of finding the distribution function of an arbitrary macroscopic body, which is a small part (subsystem) of much larger closed (adiabatically isolated) system. Suppose that we can consider this large system as consisting of two parts: the body (subsystem) of interest to us and the rest of a system (surrounding the body), which we shall call *thermostat* or *bath* (cf. Fig. 2-1). It is assumed that thermostat



Figure 2.1: System (1) in thermostat (bath) (2).

is a system with many degrees of freedom, which can exchange energy with our subsystem, and it is so large that its own state is unchanged during such

interaction¹.

Let us start with quantum statistics. Both parts, our subsystem and bath, can be considered as a single, energetically isolated (closed) system with Hamiltonian:

$$H = H_1 + H_2 \quad (2.1)$$

where H_1 is the Hamiltonian of (sub)system under study and H_2 is the Hamiltonian of bath (thermostat), which is assumed to be much larger than system of interest to us. Interaction between our system and bath is assumed to be very weak, but, strictly speaking, finite, as it is to guarantee the equilibrium state of both parts of the large system (in Hamiltonian (2.1) this interaction is just dropped)². In this case the wave function, corresponding to the Hamiltonian (2.1), is factorized into a product of the wave functions of the bath (system 2) and the body under study (system 1):

$$\psi_{ik}(x, y) = \psi_k(x)\psi_i(y) \quad (2.2)$$

where $\psi_k(x)$ is an eigenfunction of H_1 and $\psi_i(y)$ is an eigenfunction of H_2 , while x and y are sets of coordinates of the system and the bath correspondingly.

Energy levels of the whole (composite) system (neglecting small surface interaction effects) are just sums of energy levels of systems (1) and (2):

$$E_{ik} = E_i + E_k \quad (2.3)$$

where E_k denote energy levels of system (1), and E_i denote energy levels of bath (2).

Statistical operator (density matrix) of the whole (closed!) system is:

$$\rho(xy; x'y') = \sum_{ik} w_{ik} \psi_{ik}(x, y) \psi_{ik}^*(x', y') \quad (2.4)$$

where w_{ik} is defined, according to our basic assumption, by microcanonical distribution (1.58):

$$w(E_{ik}) = \begin{cases} [\mathcal{W}(E)]^{-1} & \text{for } E \leq E_{ik} \leq E + \Delta E \\ 0 & \text{outside this energy layer} \end{cases} \quad (2.5)$$

Density matrix of the system under study (1) can be obtained by taking the trace of the statistical operator of the whole (composite) system over the coordinates (variables) of the bath (subsystem (2))³:

$$\rho(x, x') = Sp_2 \rho(xy; x'y') = \sum_{ik} w_{ik} \int dy \psi_{ik}(x, y) \psi_{ik}^*(x', y) \quad (2.6)$$

From here, using (2.2) and orthonormality of wave functions, we immediately obtain:

$$\rho(x, x') = \sum_k w_k \psi_k(x) \psi_k^*(x') \quad (2.7)$$

¹The following presentation mainly follows Ref. [3]. Some points are explained following Ref. [1].

²For example, the thermal contact of our body with a bath is only through its boundary and can be considered a small surface effect.

³This operation is similar to that we used while obtaining e.g. the single particle density matrix from the two particle one.

where

$$w_k = \sum_i w_{ik} \quad (2.8)$$

Now it is clear that to get the probability distribution of quantum states for system (1) we have simply to sum the probability distribution for the whole system over the states of the bath (thermostat):

$$w(E_k) = \sum_i w(E_i + E_k)|_{E_i+E_k=E} = \frac{1}{\mathcal{W}(E)} \sum_i 1|_{E_i=E-E_k}. \quad (2.9)$$

where for brevity we denoted $E_{ik} = E$. It is clear that (2.9) reduces to:

$$w(E_k) = \frac{\mathcal{W}_2(E - E_k)}{\mathcal{W}(E)} \quad (2.10)$$

where $\mathcal{W}_2(E - E_k)$ is the number of quantum states of the bath with energy $E - E_k$, while $\mathcal{W}(E)$ is the number of states of the whole (composite) system, corresponding to energy E .

Introducing entropy of the bath $S_2(E)$ and entropy of the whole system $S(E)$ via (1.170), we rewrite (2.10) as:

$$w(E_k) = \exp\{S_2(E - E_k) - S(E)\} \quad (2.11)$$

Taking into account that our system (1) is small in comparison with the bath, so that $E_k \ll E$, we can write an expansion:

$$S_2(E - E_k) \approx S_2(E) - \frac{\partial S_2}{\partial E} E_k \quad (2.12)$$

Substituting (2.12) into (2.11) we get:

$$w(E_k) = A \exp\left(-\frac{E_k}{T}\right) \quad (2.13)$$

where we have introduced the *temperature* T (of the bath!) as:

$$\frac{1}{T} = \frac{\partial S_2(E)}{\partial E} = \frac{\partial \ln \mathcal{W}_2(E)}{\partial E} \quad (2.14)$$

This definition of (inverse) temperature coincides with that used in thermodynamics, if we identify our entropy with that of thermodynamics. In Eq. (2.13) $A = \exp\{S_2(E) - S(E)\} = \text{const.}$, is a constant independent of E_k , i.e. independent of the state of our system under study (1), and this constant can be determined just by normalization condition. Equation (2.13) is one of the most important expressions of statistical mechanics, it defines the statistical distribution for an arbitrary macroscopic body, which is a relatively small part of some large closed system (essentially, this is probably the most general case of a problem to be solved in reality – there is always some surrounding media for any system of interest!). Eq. (2.13) is called *canonical* Gibbs distribution.

Normalization constant A is determined from $\sum_k w_k = 1$, and using (2.13) we immediately get:

$$\frac{1}{A} \equiv Z = \sum_k e^{-\frac{E_k}{T}}. \quad (2.15)$$

Here we introduced Z , which is usually called statistical sum or *partition function*. Using this notation we can rewrite the canonical distribution (2.13) in the following standard form⁴:

$$w(E_k) = Z^{-1} \exp\left(-\frac{E_k}{T}\right) \quad (2.16)$$

The average value of an arbitrary physical variable, described by quantum operator f , can be calculated using Gibbs distribution as:

$$\langle f \rangle = \sum_k w_k f_{kk} = \frac{\sum_k f_{kk} e^{-\frac{E_k}{T}}}{\sum_k e^{-\frac{E_k}{T}}} \quad (2.17)$$

where f_{kk} is the diagonal matrix element f calculated with eigenfunctions corresponding to exact energy levels of the system E_k .

In classical statistics we may proceed in a similar way. Let us consider a small part of an isolated classical system (subsystem), so that we can write a volume element $d\Gamma_0$ of the phase space of the whole (isolated) system as $d\Gamma_0 = d\Gamma' d\Gamma$, where $d\Gamma$ is related to our subsystem, while $d\Gamma'$ relates to bath (surrounding media). We are interested in distribution function for the subsystem, and where is the bath in the phase space is of no interest to us, so that we just integrate over its variables (coordinates and momenta). Using the equality of probabilities of all states of microcanonical ensemble (describing the whole closed system, consisting of our subsystem and the bath) we get:

$$dw \sim \mathcal{W}' d\Gamma \quad (2.18)$$

where \mathcal{W}' is the phase space (statistical weight) of the bath. Rewriting this statistical weight via entropy we obtain:

$$\mathcal{W}' \sim \exp\{S'(E_0 - E(p, q))\} \quad (2.19)$$

where E_0 is the energy of the whole closed system, while $E(p, q)$ is the energy of subsystem. The last relation takes into account simply, that the energy of thermostat (bath) is given by: $E' = E_0 - E(p, q)$, because $E_0 = E' + E(p, q)$, if we can neglect interactions between the subsystem and the bath. Now everything is quite easy:

$$dw = \rho(p, q) d\Gamma \sim \exp\{S'(E_0 - E(p, q))\} d\Gamma \quad (2.20)$$

so that

$$\rho(p, q) \sim \exp\{S'(E_0 - E(p, q))\} \quad (2.21)$$

As above we can expand:

$$S'(E_0 - E(p, q)) \approx S'(E_0) - E(p, q) \frac{dS'(E_0)}{dE_0} = S'(E_0) - \frac{E(p, q)}{T} \quad (2.22)$$

where once again we have introduced the temperature of the bath T . Finally we obtain the canonical distribution:

$$\rho(p, q) = Ae^{-\frac{E(p, q)}{T}} \quad (2.23)$$

⁴If we measure the temperature in absolute degrees (K), and not in energy units, as it is done in the whole text, we have to replace $T \rightarrow k_B T$, where k_B is Boltzmann's constant, $k_B = 1.38 \cdot 10^{-16}$ erg/K or $k_B = 1.38 \cdot 10^{-23}$ J/K. In this case we also have to add k_B to our definition of entropy: $S = k_B \ln \mathcal{W}$.

where $E(p, q)$ is the energy of the body under study (subsystem in the bath), as a function of coordinates and momenta of its particles. Normalization constant A is determined by condition:

$$\int d\Gamma \rho(p, q) = A \int d\Gamma e^{-\frac{E(p, q)}{T}} = 1$$

$$Z = A^{-1} = \int d\Gamma e^{-\frac{E(p, q)}{T}} \quad (2.24)$$

where Z is called statistical integral or partition function.

Let us return to quantum case. Density matrix corresponding to canonical Gibbs distribution can be written as:

$$\rho(x, x') = Z^{-1} \sum_k e^{-\frac{E_k}{T}} \psi_k(x) \psi_k^*(x') \quad (2.25)$$

where x is the coordinate set (and probably also spins) of particles (if we work in coordinate representation), $\psi_k(x)$ are eigenfunctions of Hamiltonian H .

Let us introduce *operator* $\exp\left(-\frac{H}{T}\right)$. Then we can write down the compact operator expression for canonical distribution:

$$\rho = Z^{-1} \exp\left(-\frac{H}{T}\right) \quad (2.26)$$

and partition function:

$$Z = Sp \exp\left(-\frac{H}{T}\right) \quad (2.27)$$

This expression for partition function is very convenient because of the invariance of trace (Sp) with respect to matrix representations it is independent of the choice of wave functions $\psi_k(x)$, which may not necessarily be eigenfunctions of H .

Up to now we have spoken about canonical Gibbs distribution as statistical distribution for a subsystem inside some large closed system. Note that above in Eq. (1.56) we, in fact, already obtained it almost from “nothing”, while discussing the role of energy and other additive integrals of motion. This derivation was absolutely correct, but it was relatively obscure and formal from the physical point of view.

It is necessary to stress that canonical distribution may be successfully applied also to closed systems. In reality, the values of thermodynamic characteristics of the body are independent of whether we consider it as closed system or a system in some (probably imaginary) thermostat (bath). The difference between isolated (closed) and open body is only important, when we analyze relatively unimportant question of fluctuations of the total energy of this body. Canonical distribution produces some finite value of its average fluctuation, which is a real thing for the body in some surrounding media, while it is fictitious for an isolated body, as its energy is constant by definition and is not fluctuating. At the same time, canonical distribution is much more convenient in most calculations, than microcanonical distribution. In fact it is mostly used in practical tasks forming the basis of statistical mechanics mathematical apparatus.

2.2 Maxwell distribution.

As a simplest example of an important application of canonical distribution we consider the derivation of Maxwell's distribution function. In classical case the energy $E(p, q)$ can always be represented as a sum of kinetic and potential energy. Kinetic energy is usually a quadratic form of momenta of atoms of the body, while potential energy is given by some function of their coordinates, depending on the interaction law and external fields if present:

$$E(p, q) = K(p) + U(q) \quad (2.28)$$

so that probability $dw = \rho(p, q)dpdq$ is written as:

$$dw = Ae^{-\frac{K(p)}{T}} e^{-\frac{U(q)}{T}} dpdq \quad (2.29)$$

i.e. is factorized into the product of the function of momenta and function of coordinates. This means that probability distributions for momenta (velocities) and coordinates are independent of each other. Then we can write:

$$dw_p = ae^{-\frac{K(p)}{T}} dp \quad (2.30)$$

$$dw_q = be^{-\frac{U(q)}{T}} dq \quad (2.31)$$

Each of these distribution functions can be normalized to unity, which will define normalization constants a and b .

Let us consider probability distribution for momenta (velocities), which within the classical approach is independent of interactions between particles or an external fields, and is in this sense universal. For an atom with mass m we have⁵:

$$dw_p = a \exp\left(-\frac{1}{2mT}(p_x^2 + p_y^2 + p_z^2)\right) dp_x dp_y dp_z \quad (2.32)$$

from which we see that distributions of momentum components are also independent. Using the famous Poisson-Gauss integral⁶:

$$I = \int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} \quad (2.33)$$

we find:

$$\begin{aligned} a \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \exp\left[-\frac{1}{2mT}(p_x^2 + p_y^2 + p_z^2)\right] &= \\ &= a \left(\int_{-\infty}^{\infty} dp e^{-p^2/2mT}\right)^3 = a(2\pi mT)^{3/2} \end{aligned}$$

so that:

$$a = (2\pi mT)^{-3/2} \quad (2.34)$$

⁵Kinetic energy of the body is the sum of kinetic energies of constituent atoms, so that this probability distribution is also factorized into the product of distributions, each of which depends only on the momenta of one atom

⁶It is easy to see that $I^2 = \int_{-\infty}^{\infty} dx e^{-\alpha x^2} \int_{-\infty}^{\infty} dy e^{-\alpha y^2} = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy e^{-\alpha(x^2+y^2)} = 2\pi \int_0^{\infty} d\rho \rho e^{-\alpha\rho^2} = \pi \int_0^{\infty} dz e^{-\alpha z} = \pi/\alpha$, thus proving Poisson-Gauss expression.

Finally, probability distribution for momenta has the following form:

$$dw_p = \frac{1}{(2\pi mT)^{3/2}} \exp\left(-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}\right) dp_x dp_y dp_z \quad (2.35)$$

Transforming from momenta to velocities, we can write the similar distribution function for velocities:

$$dw_{\mathbf{v}} = \left(\frac{m}{2\pi T}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2T}\right) dv_x dv_y dv_z \quad (2.36)$$

This is the notorious Maxwell's distribution, which one of the first results of classical statistics. In fact it is factorized into the product of three independent factors:

$$dw_{v_x} = \sqrt{\frac{m}{2\pi T}} e^{-\frac{mv_x^2}{2T}} dv_x \dots \quad (2.37)$$

each determining the probability distribution for a separate component of velocity.

Note that Maxwell distribution is valid also for molecules (e.g. in molecular gas), independent of the nature of intra molecular motion of atoms (m in this case is just the molecular mass), it is also valid for Brownian motion of particles in suspensions.

Transforming from cartesian to spherical coordinates, we obtain:

$$dw_{\mathbf{v}} = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-\frac{mv^2}{2T}} v^2 \sin\theta d\theta d\varphi dv \quad (2.38)$$

where v is the absolute value of velocity, while θ and φ are polar and azimuthal angles, determining the direction of velocity vector \mathbf{v} . Integrating over angles we find probability distribution for the absolute values of velocity:

$$dw_v = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} e^{-\frac{mv^2}{2T}} v^2 dv \quad (2.39)$$

As a simple example of application of Maxwell distribution, let us calculate the average value of kinetic energy of an atom. For any of cartesian components of velocity we have⁷:

$$\langle v_x^2 \rangle = \sqrt{\frac{m}{2\pi T}} \int_{-\infty}^{\infty} dv_x v_x^2 e^{-\frac{mv_x^2}{2T}} = \frac{T}{m} \quad (2.40)$$

Thus, the average value of kinetic energy of an atom is equal to $3T/2$, i.e. $3k_B T/2$ if we measure the temperature in absolute degrees. Then the average kinetic energy of all particles of the body in classical statistics is always equal to $3NT/2$, where N is the number of atoms.

⁷For integral of general form $I_n = \int_0^{\infty} dx x^n e^{-\alpha x^2}$ we have: $I_n = \frac{1}{2} \alpha^{-\frac{n+1}{2}} \Gamma\left(\frac{n+1}{2}\right)$, where $\Gamma(x)$ is Γ -function, its values for half-integer values of argument are well known and can be found in handbooks.

2.3 Free energy from Gibbs distribution.

According to Eq. (1.175) the entropy of a body can be calculated as the average value of the logarithm of distribution function:

$$S = - \langle \ln w_k \rangle = - \sum_k w_k \ln w_k \quad (2.41)$$

Substituting here canonical distribution in the form of Eq. (2.16), we obtain: $-\langle \ln w_k \rangle = \ln Z + \frac{1}{T} \sum_k w_k E_k = \ln Z + \frac{\langle E \rangle}{T}$, where $\langle E \rangle = \sum_k w_k E_k$ is the average energy. As this average energy $\langle E \rangle$ is precisely the same thing as energy of the body E in thermodynamics, we can write (2.41) as: $S = \ln Z + \frac{E}{T}$, or using the expression for the free energy in thermodynamics $F = E - TS$:

$$F = -T \ln Z = -T \ln \sum_k e^{-\frac{E_k}{T}} \quad (2.42)$$

This is the basic relation of the equilibrium statistical mechanics giving an expression for the free energy of an arbitrary system via its statistical sum (partition function). In fact, this fundamental result shows that to calculate the free energy of a body, it is sufficient to know its exact *energy spectrum*. We do not have to know e.g. wave functions, and the finding the spectrum of Schroedinger equation is much simpler task, than the solution of the complete quantum mechanical problem, including the determination of the wave functions (eigenvectors).

From Eq. (2.42) we can see that the normalization factor in Gibbs distribution (2.16), in fact, is expressed via free energy: $\frac{1}{Z} = e^{\frac{F}{T}}$, so that Eq. (2.16) can be written as:

$$w_k = \exp\left(\frac{F - E_k}{T}\right) \quad (2.43)$$

It is the most common way to write Gibbs distribution.

Similarly, in classical case, using (1.167), (2.23) and (2.24), we obtain:

$$\rho(p, q) = \exp\left(\frac{F - E(p, q)}{T}\right) \quad (2.44)$$

where

$$F = -T \ln \int d\Gamma \exp\left(-\frac{E(p, q)}{T}\right) \quad (2.45)$$

and $d\Gamma = \frac{dpdq}{(2\pi\hbar)^{3N} N!}$. Thus, in classical approach the statistical sum is just replaced by statistical integral. Taking into account that $E(p, q)$ here can be always represented by the sum of kinetic $K(p)$ and potential U energies, and kinetic energy is always a quadratic form of momenta, we can perform momentum integration in statistical integral in its general form (cf. discussion of Maxwell distribution above!). Thus, the problem of calculation of statistical integral is reduced to integration over all coordinates in $e^{-\frac{U(q)}{T}}$, which is of course impossible to do exactly.

2.4 Gibbs distribution for systems with varying number of particles.

Up to now we implicitly assumed that the number of particles in the system is some predetermined constant. In reality, different subsystems of a large system can exchange particles between them. The number of particles N in a subsystem fluctuates around its average value. In this case distribution function depends not only on energy of the quantum state, but also on the number of particles N of the body, in fact, energy levels E_{kN} themselves are different for different values of N . Let us denote as w_{kN} the probability for the body to be in k -th state and contain N particles. This probability distribution can be obtained in the same way, as we derived probability w_k above.

Consider the closed (isolated) system with energy $E^{(0)}$ and number of particles $N^{(0)}$, consisting of two weakly interacting subsystems with energies E' (bath) and E_{kN} (small subsystem) and respective numbers of particles N' (bath) and N (subsystem):

$$E^{(0)} = E_{kN} + E' \quad N^{(0)} = N + N' \quad (2.46)$$

We assume that subsystem of interest to us is small in comparison to bath (particle reservoir), so that:

$$E_{kN} \ll E' \quad N \ll N' \quad (2.47)$$

As we assume the full composite system to be isolated, it can again be described by microcanonical distribution. Similarly to the derivation of canonical distribution above, we can find probability distribution for small subsystem w_{kN} by summing microcanonical distribution for the whole system over all states of the bath. In complete analogy with Eq. (2.10) we get:

$$w_{kN} = \frac{\mathcal{W}'(E^{(0)} - E_{kN}, N^{(0)} - N)}{\mathcal{W}^{(0)}(E^{(0)}, N^{(0)})} \quad (2.48)$$

where \mathcal{W}' is statistical weight of the bath, while $\mathcal{W}^{(0)}$ is statistical weight of the full (closed) system. Using the definition of entropy we immediately obtain:

$$w_{kN} = Const \exp \left\{ S'(E^{(0)} - E_{kN}, N^{(0)} - N) \right\} \quad (2.49)$$

Now we again can expand S' in powers of E_{kN} and N , limiting ourselves by linear terms only:

$$S'(E^{(0)} - E_{kN}, N^{(0)} - N) \approx S'(E^{(0)}, N^{(0)}) - \left(\frac{\partial S'}{\partial E} \right)_{V, N} E_{kN} - \left(\frac{\partial S'}{\partial N} \right)_{E, V} N + \dots \quad (2.50)$$

Then, remembering the thermodynamic relations for the system with variable number of particles [1]:

$$dE = TdS - PdV + \mu dN; \quad \mu = \left(\frac{\partial E}{\partial N} \right)_{S, V} \quad (2.51)$$

or

$$dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN, \quad (2.52)$$

we obtain:

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \quad (2.53)$$

Then we can rewrite the expansion (2.50) as:

$$S'(E^{(0)} - E_{kN}, N^{(0)} - N) \approx S'(E^{(0)}, N^{(0)}) - \frac{E_{kN}}{T} + \frac{\mu N}{T} \quad (2.54)$$

Notice that both the chemical potential μ and temperature T of the body (subsystem) and the bath (thermostat) just coincide due to the standard conditions of thermodynamic equilibrium.

Finally, we obtain the distribution function:

$$w_{kN} = A \exp\left(\frac{\mu N - E_{kN}}{T}\right) \quad (2.55)$$

Normalization constant A can again be expressed via thermodynamic variables. To see this let us calculate the entropy of the body:

$$S = -\langle \ln w_{kN} \rangle = -\ln A - \frac{\mu}{T} \langle N \rangle + \frac{1}{T} \langle E \rangle \quad (2.56)$$

or

$$T \ln A = \langle E \rangle - TS - \mu \langle N \rangle. \quad (2.57)$$

Identifying $\langle E \rangle$ with energy of the body E in thermodynamics, and $\langle N \rangle$ with the particle number N in thermodynamics, taking into account thermodynamic relation $E - TS = F$, and introducing thermodynamic potential Ω as $\Omega = F - \mu N$ [1], we have: $T \ln A = \Omega$, so that Eq. (2.55) can be rewritten as:

$$w_{kN} = \exp\left(\frac{\Omega + \mu N - E_{kN}}{T}\right) \quad (2.58)$$

This is the final form of Gibbs distribution for the system with variable number of particles, which is called *grand canonical* distribution.

The usual normalization condition for (2.58) is:

$$\sum_N \sum_k w_{kN} = e^{\frac{\Omega}{T}} \sum_N \left(e^{\frac{\mu N}{T}} \sum_k e^{-\frac{E_{kN}}{T}} \right) = 1 \quad (2.59)$$

From here we obtain the general expression for thermodynamic potential Ω in statistical mechanics:

$$\Omega = -T \ln \sum_N \left(e^{\frac{\mu N}{T}} \sum_k e^{-\frac{E_{kN}}{T}} \right) \quad (2.60)$$

where the expression in the right hand side can be called grand partition function.

The average number of particles $\langle N \rangle$ in our system is determined by the relation:

$$\langle N \rangle = \sum_N \sum_k N w_{kN} = e^{\frac{\Omega}{T}} \sum_N \left(N e^{\frac{\mu N}{T}} \sum_k e^{-\frac{E_{kN}}{T}} \right) \quad (2.61)$$

which can be considered as a kind of additional “normalization” condition. Actually, this equation implicitly determines the chemical potential μ as function of temperature and *fixed* average particle number $\langle N \rangle$, which is equivalent to the number of particles N in thermodynamics. This is the general recipe to determine μ , which will be often used in future calculations.

Expressions (2.42) and (2.60) determine thermodynamic characteristics for arbitrary systems in equilibrium. Free energy F is determined as a function of T , N and V , while thermodynamic potential Ω is determined by (2.60) as a function of T , μ and V .

Similarly to previous analysis, in classical statistics the grand canonical distribution is written as:

$$dw_N = \exp\left(\frac{\Omega + \mu N - E_N(p, q)}{T}\right) \frac{dp^{(N)} dq^{(N)}}{(2\pi\hbar)^{3N} N!} \equiv \rho_N d\Gamma_N \quad (2.62)$$

The variable N is written here as an index of distribution function and also of the phase space volume element, to stress that there is a different phase space for each value of N (with its own dimensions $6N$). Expression for potential Ω is now:

$$\Omega = -T \ln \left\{ \sum_N e^{\frac{\mu N}{T}} \int d\Gamma_N \exp\left(-\frac{E_N(p, q)}{T}\right) \right\} \quad (2.63)$$

It is clear that in calculations of all statistical (thermodynamic) properties of the body, except fluctuations of the total number of particles, both canonical and grand canonical Gibbs distributions are equivalent. Neglecting fluctuations of particle number N we have $\Omega + \mu N = F$ and these distributions just coincide.

The use of one or another distribution in most practical tasks is mostly the question of convenience of calculations. In practice, microcanonical distribution is most inconvenient, while the most convenient is often the grand canonical distribution.

2.5 Thermodynamic relations from Gibbs distribution.

Let us complete statistical justification of thermodynamics by derivation of its main relations from Gibbs distribution. Already during our discussion of the role of additive integrals of motion and derivation of Eq. (1.56), which is essentially the canonical distribution itself, we noted that the factor β before the energy in Eq. (1.56) is the same for all subsystems of the given closed system. Taking into account that in canonical distribution we have $\beta = -1/T$, we come to the conclusion that this is equivalent to the usual thermodynamic condition of equality of temperatures for all parts of the system being in the state of thermodynamic equilibrium⁸. It is easy to see that temperature $T > 0$, otherwise there appear divergence in normalization sum $\sum_k w_k$, because energy levels E_k may be arbitrarily big. All these properties just coincide with the basic properties of temperature in thermodynamics.

⁸Eq. (1.56) coincides with canonical distribution (2.43), if we also take $\alpha = F/T$ and consider system at rest.

Basic thermodynamic relations may be derived in different ways. Let us write down the canonical distribution in operator form as:

$$\rho = e^{-\frac{F-H}{T}} \quad (2.64)$$

Normalization condition $Sp\rho = 1$ can be rewritten as:

$$e^{-\frac{F}{T}} = Sp\left(e^{-\frac{H}{T}}\right) \quad (2.65)$$

which is in essence the definition of free energy. Differentiating this expression by T we get:

$$\left(\frac{F}{T^2} - \frac{1}{T} \frac{\partial F}{\partial T}\right) e^{-\frac{F}{T}} = \frac{1}{T^2} Sp\left(He^{-\frac{H}{T}}\right) \quad (2.66)$$

Multiplying this relation by $T^2 e^{\frac{F}{T}}$ and taking into account that $\langle H \rangle = E$, we obtain the basic Gibbs–Helmholtz relation of classical thermodynamics:

$$F = E + T \frac{\partial F}{\partial T} \quad (2.67)$$

Comparing this expression with definition of free energy $F = E - TS$, we get:

$$S = -\frac{\partial F}{\partial T} = -\frac{1}{T}(F - \langle H \rangle) \quad (2.68)$$

According to Eq. (1.174) we can write down entropy in operator form as:

$$S = -Sp\rho \ln \rho \quad (2.69)$$

The identity of this expression for S with the previous one can be easily seen — according to Eq. (2.64) we have $\ln \rho = \frac{1}{T}(F - H)$, the rest is obvious.

Another way to obtain basic thermodynamic relations is to consider the normalization condition for Gibbs distribution:

$$\sum_k e^{-\frac{F-E_k}{T}} = 1 \quad (2.70)$$

and differentiate it, considering the left hand side as a function of T and some variables $\lambda_1, \lambda_2, \dots$, which characterize external conditions for the body under study. These variables may, for example, determine the geometrical form and size of its volume, define external fields etc. Energy levels of the system E_k parametrically depend on $\lambda_1, \lambda_2, \dots$. After differentiation we obtain (for brevity we write explicitly only one parameter λ)⁹:

$$\sum_k \frac{w_k}{T} \left[dF - \frac{\partial E_k}{\partial \lambda} d\lambda - \frac{F - E_k}{T} dT \right] = 0 \quad (2.71)$$

Then we have:

$$dF \sum_k w_k = d\lambda \sum_k w_k \frac{\partial E_k}{\partial \lambda} + \frac{dT}{T} (F - \sum_k w_k E_k) \quad (2.72)$$

⁹More precisely we write down the full differential of the left hand side of Eq. (2.70): $d \sum_k e^{-\frac{F-E_k}{T}} = \sum_k w_k d \left(\frac{F-E_k}{T} \right) = 0$, which gives us Eq. (2.71)

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Taking into account $\sum_k w_k = 1$, $\sum_k w_k E_k = \langle E \rangle = E$ and $\sum_k w_k \frac{\partial E_k}{\partial \lambda} = \frac{\partial \langle E_k \rangle}{\partial \lambda}$, as well as $F - E = -TS$ and the relation¹⁰:

$$\frac{\partial \langle E_k \rangle}{\partial \lambda} = \frac{\partial \langle H \rangle}{\partial \lambda} \quad (2.73)$$

we finally obtain:

$$dF = -SdT + \frac{\partial \langle H \rangle}{\partial \lambda} d\lambda = -SdT + \frac{\partial E}{\partial \lambda} d\lambda \quad (2.74)$$

which represents the general form of the differential of free energy in thermodynamics.

Similarly, from normalization condition for grand canonical distribution¹¹ (2.59) we can obtain the general form of the differential of thermodynamic potential Ω :

$$d\Omega = -SdT - Nd\mu + \frac{\partial \langle H \rangle}{\partial \lambda} d\lambda \quad (2.75)$$

We assumed above that external parameters $\lambda_1, \lambda_2, \dots$ characterize macroscopic state of the system in equilibrium. These may be the volume (form) of a vessel, the values of external electric or magnetic fields etc. Parameters $\lambda_1, \lambda_2, \dots$ are also assumed to change very slowly in time, so that during the time of the order of relaxation time for the system to evolve to equilibrium, these parameters can be considered as practically constant. Then we can suppose that at any moment of time the system is in some equilibrium state, despite the fact that external parameters change. Such slow process of change of external parameters may be called quasistatic. If we consider parameters $\lambda_1, \lambda_2, \dots$ as generalized coordinates, corresponding generalized forces can be introduced as:

$$\Lambda_i = -\frac{\partial H}{\partial \lambda_i} \quad (2.76)$$

For quasistatic process the observed values of generalized forces can be obtained by the averaging over the equilibrium statistical ensemble as:

$$\langle \Lambda_i \rangle = Sp(\rho \Lambda_i) = -\frac{\partial \langle H \rangle}{\partial \lambda_i} \quad (2.77)$$

Let us consider some typical examples. If we choose as an external parameter the volume of the system V , the generalized force is pressure:

$$P = -\frac{\partial \langle H \rangle}{\partial V} = -\frac{\partial E}{\partial V} \quad (2.78)$$

Then Eq. (2.74) takes the well known form:

$$dF = -SdT - PdV \quad (2.79)$$

¹⁰If the Hamiltonian H and its eigenvalues E_k depend of parameter λ , we have: $\frac{\partial E_k}{\partial \lambda} = \left(\frac{\partial H}{\partial \lambda} \right)_{kk}$, so that after the averaging we obtain (2.73).

¹¹Note that grand canonical distribution can also be derived with arguments used in derivation of Eq. (1.56), if we consider the number of particles as N as an additive integral (constant) of motion. Then, for system at rest we can write: $\ln w_{kN} = \alpha + \beta E_{kN} + \gamma N$, where γ and β are to be the same for all parts of the system at equilibrium. Putting here $\alpha = \Omega/T$, $\beta = -1/T$ and $\gamma = \mu/T$ we obtain the grand canonical distribution. By the way, here we obtained the well known condition of equality of chemical potentials of subsystems at equilibrium with each other.

If we choose as a parameter an external electric field \mathbf{E} , the generalized force is polarization (electric dipole moment of the body) \mathbf{P} and:

$$dF = -SdT - \mathbf{P}d\mathbf{E}; \quad \mathbf{P} = -\frac{\partial \langle H \rangle}{\partial \mathbf{E}} \quad (2.80)$$

For the case of an external magnetic field \mathbf{H} the generalized force is magnetization (magnetic moment) of the body \mathbf{M} and:

$$dF = -SdT - \mathbf{M}d\mathbf{H}; \quad \mathbf{M} = -\frac{\partial \langle H \rangle}{\partial \mathbf{H}} \quad (2.81)$$

Thus, we succeeded in construction of the complete statistical derivation of all basic relations of thermodynamics. Historically, the development of statistical mechanics was directly related with this task.

The last problem to be discussed with relation to justification of the laws of thermodynamics is Nernst theorem, sometimes called the third law of thermodynamics. We note from the very beginning that in contrast to the first and the second laws, which directly follow from Gibbs approach, the similar (in generality) proof of Nernst theorem is absent, though for all “reasonable” models of statistical mechanics it is valid. Let us analyze the limiting behavior of Gibbs distribution

$$w_k = e^{\frac{F - E_k}{T}} \quad (2.82)$$

for temperatures $T \rightarrow 0$. Using the expression for entropy:

$$S = \frac{1}{T}(\langle H \rangle - F), \quad (2.83)$$

we can write $w_k = \exp\{-S + \frac{1}{T}(\langle H \rangle - E_k)\}$, or:

$$w_k = \exp\left\{-S + \frac{\langle H \rangle - E_0}{T} + \frac{E_0 - E_k}{T}\right\} \quad (2.84)$$

where E_0 is the energy of the ground state of the system, so that $E_k > E_0$ for all $k \neq 0$. Calculating the limit of (2.84) for $T \rightarrow 0$, we obtain:

$$\lim_{T \rightarrow 0} w_k = w_k(0) = \exp\{-S(0) + C_V(0)\} \delta_{E_k - E_0} \quad (2.85)$$

where

$$\delta_{E_k - E_0} = \begin{cases} 1 & \text{for } E_k = E_0 \\ 0 & \text{for } E_k \neq E_0 \end{cases} \quad (2.86)$$

In Eq. (2.85) $C_V(0) = \left(\frac{\partial \langle H \rangle}{\partial T}\right)_{T=0}$ denotes the specific heat of the body at $T = 0$ and for constant volume. However, from Eq. (2.83) it follows (using l'Hôpital's rule) that for $T \rightarrow 0$:

$$S(0) = \left(\frac{\partial \langle H \rangle}{\partial T} - \frac{\partial F}{\partial T}\right)_{T \rightarrow 0} = C_V(0) + S(0) \quad (2.87)$$

so that $C_V(0) = 0$ (Nernst theorem). Accordingly Eq. (2.85) reduces to:

$$w_k(0) = \exp\{-S(0)\} \delta_{E_k - E_0} \quad (2.88)$$

which is, in fact, just the microcanonical distribution:

$$w_k(0) = \frac{1}{\mathcal{W}_0} \delta_{E_k - E_0} \quad (2.89)$$

where \mathcal{W}_0 is the degeneracy of the ground state. Then the entropy in the ground state at $T = 0$:

$$S(0) = \ln \mathcal{W}_0 \quad (2.90)$$

For the majority of physical systems (like crystals, quantum gases and liquids etc.) the ground state is non degenerate, so that $\mathcal{W}_0 = 1$, and thus the entropy tends to zero as $T \rightarrow 0$. Even for the case of $\mathcal{W}_0 \gg 1$, but for $\lim_{N \rightarrow \infty} \frac{1}{N} \ln \mathcal{W}_0 = 0$ (entropy per single particle) we may assume $S(0) = 0$, which is, in fact, the general formulation of Nernst theorem¹².

Unfortunately, the situation here is not so simple and the physical behavior of systems, described by Nernst theorem, is not directly related to non degeneracy of the ground state. Actually it reflects the behavior of an effective behavior of excitation spectra of macroscopic bodies at small energies, and Nernst theorem manifests itself for temperatures T , which are much larger than the energy difference between the first excited state of the system and its ground state. Above we have already seen that the energy spectrum of a macroscopic body can be considered as practically continuous, so this energy difference is, in fact, unobservable. It follows even from the simplest estimates. Consider an ideal gas of atoms with mass m , moving in the volume $V = L^3$. Then we can estimate:

$$E_1 - E_0 \sim \frac{\hbar^2}{2m} k_{min}^2 = \frac{h^2}{2mV^{2/3}} \quad \text{where} \quad k_{min} = \frac{2\pi}{L} \quad (2.91)$$

and the volume $V \rightarrow \infty$. Experimentally, for an ideal gas manifestations of Nernst theorem become observable for finite temperatures of the order or below the so called degeneracy temperature $T_0 \sim \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{2/3}$.

To give the general proof of Nernst theorem, we have to understand the distribution of energy levels E_k close to the ground state, i.e. to find the general behavior of statistical weight $\mathcal{W}(E, N, V)$ close to $E = E_0$. Up to now such behavior was only studied only for some specific models. The behavior necessary to reproduce Nernst theorem in all cases, when the weak (low energy) excitations of the system can be represented by an ideal gas of *quasiparticles*. Below we shall consider only such systems, and the concept of quasiparticles will be of central importance.

This concludes our presentation of the basics of Gibbs approach to statistical mechanics. The rest of the book will be devoted to applications of this formalism to different concrete problems of the physics of many particle systems.

¹²Note that Nernst theorem is inapplicable for amorphous solids (glasses) or disordered alloys, which are not, in fact, in the state of complete thermodynamic equilibrium, but can be “frozen” (at $T \rightarrow 0$) in some of many possible metastable states with quite large or even practically infinite relaxation time.

Chapter 3

CLASSICAL IDEAL GAS

3.1 Boltzmann distribution.

The simplest model to illustrate the applications of general principles of statistical mechanics is an ideal gas of noninteracting atoms or molecules¹. This model played an important role at the early stages of development of statistical physics².

The absence of interaction between atoms (molecules) of an ideal gas allows us to reduce the quantum mechanical problem of finding the energy levels E_n of a gas as a whole to the problem of finding the energy levels of an isolated atom (molecule). We shall denote these levels as ε_k , where k is the set of quantum numbers, determining the state of an atom (molecule). Because of the absence of interactions the energy levels E_n are just the sums of energies of each of the atoms (molecules). Let us denote as n_k the number of gas particles occupying the quantum state k and calculate its average value $\langle n_k \rangle$ for the important limit of:

$$\langle n_k \rangle \ll 1. \quad (3.1)$$

Physically, this limit corresponds to strongly diluted gas. Let us apply canonical Gibbs distribution to gas molecules, considering a single molecule as a subsystem in the bath (of the rest of the molecules). Then it is clear that the probability for the molecule to be in the k -th state, and also the average number $\langle n_k \rangle$ of molecules in this state, will be $\sim e^{-\frac{\varepsilon_k}{T}}$, so that

$$\langle n_k \rangle = a e^{-\frac{\varepsilon_k}{T}} \quad (3.2)$$

where the coefficient a can be determined by normalization condition:

$$\sum_k \langle n_k \rangle = N \quad (3.3)$$

where N is the total number of particles in a gas. Distribution function given by Eq. (3.2) is called Boltzmann's distribution.

¹Surely, the existence of some weak interaction (e.g. rare collisions) between atoms or molecules is necessary to reach the equilibrium state. However, during the calculations of equilibrium thermodynamic properties of an ideal gas we can neglect it from the very beginning.

²Below we basically follow the presentation of Ref. [1].

Let us give another derivation of Boltzmann distribution, which is based on application of grand canonical Gibbs distribution to all particles of the gas occupying the same quantum state, which is considered as a subsystem in the bath (of all other particles). In the general expression for grand canonical distribution (2.58) we have now to put $E = n_k \varepsilon_k$ and $N = n_k$. Adding an index k also to thermodynamic potential Ω , we obtain:

$$w_{n_k} = e^{\frac{\Omega_k + n_k(\mu - \varepsilon_k)}{T}} \quad (3.4)$$

In particular, $w_0 = e^{\frac{\Omega_k}{T}}$ is simply the probability of an absence of any particle in this given state. In the limit of interest to us, when $\langle n_k \rangle \ll 1$, the probability $w_0 = e^{\frac{\Omega_k}{T}} \approx 1$, and from Eq. (3.4) we obtain:

$$w_1 = e^{\frac{\mu - \varepsilon_k}{T}} \quad (3.5)$$

As to probabilities of the values of $n_k > 1$, in this approximation they are just zeroes. Thus, in the sum determining $\langle n_k \rangle$, remains only one term:

$$\langle n_k \rangle = \sum_{n_k} w_{n_k} n_k = w_1, \quad (3.6)$$

and we get:

$$\langle n_k \rangle = e^{\frac{\mu - \varepsilon_k}{T}} \quad (3.7)$$

We see that the coefficient in Eq. (3.2) is expressed via the chemical potential of the gas, which is implicitly defined by normalization condition for the total number of particles (3.3).

3.2 Boltzmann distribution and classical statistics.

Previous analysis was based on quantum approach. Let us consider the same problem in classical statistics. Let dN denote the average number of molecules belonging to an element of the phase space of the molecule $dpdq = dp_1 \dots dp_r dq_1 \dots dq_r$ (r is the number of degrees of freedom of the molecule). We can write it as:

$$dN = n(p, q) d\tau \quad d\tau = \frac{dpdq}{(2\pi\hbar)^r} \quad (3.8)$$

where $n(p, q)$ is probability density in the phase space. Then:

$$n(p, q) = e^{\frac{\mu - \varepsilon(p, q)}{T}} \quad (3.9)$$

where $\varepsilon(p, q)$ is the energy of the molecule as a function of coordinates and momenta of its atoms.

For a gas in the absence of any kind of external field this distributions reduces to Maxwell distribution³:

$$dN_p = \frac{N}{V(2\pi mT)^{3/2}} e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}} dp_x dp_y dp_z \quad (3.10)$$

³In difference with the form of Maxwell distribution discussed above, here we introduced an additional factor N/V , which is related to normalization to particle density used here.

$$dN_v = \frac{N}{V} \left(\frac{m}{2\pi T} \right)^{3/2} e^{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2T}} dv_x dv_y dv_z \quad (3.11)$$

where m is the mass of a molecule. Comparing (3.10) and (3.9) we obtain $e^{\frac{\mu}{T}} = \frac{N}{V} (2\pi)^{3/2} \hbar^3 (mT)^{-3/2}$, so that the chemical potential of Boltzmann gas is:

$$\mu = T \ln \left(\frac{N}{V} \frac{(2\pi)^{3/2} \hbar^3}{(mT)^{3/2}} \right) \quad (3.12)$$

This result can also be obtained directly from normalization (3.9) to the total number of particles in unit volume (density) given by Eq. (3.3). In classical approximation $\varepsilon_k = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$, so that (3.3) can be written as:

$$\sum_k e^{\frac{\mu - \varepsilon_k}{T}} = N \quad \text{or} \quad e^{\frac{\mu}{T}} \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}} = \frac{N}{V} \quad (3.13)$$

which gives (3.12) after calculation of an elementary Gaussian integral:

$$\mu = T \ln \left\{ \frac{N}{V} \left(\int \frac{d^3p}{(2\pi\hbar)^3} e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}} \right)^{-1} \right\} = T \ln \left(\frac{N}{V} \frac{(2\pi)^{3/2} \hbar^3}{(mT)^{3/2}} \right) \quad (3.14)$$

Thus, the chemical potential of the gas is completely determined by density of the particles and temperature.

Consider now the gas in an external field, when the potential energy of a molecule depends on coordinates of its center of mass: $U = U(x, y, z)$. Typical example is the gas in gravitational field. Maxwell distribution for velocities remains, as was noted above, valid, while distribution for center of mass coordinates is given by:

$$dN_r = n_0 e^{-\frac{U(x,y,z)}{T}} dV \quad (3.15)$$

which gives the number of molecules in volume element $dV = dx dy dz$. Obviously

$$n(\mathbf{r}) = n_0 e^{-\frac{U(\mathbf{r})}{T}} \quad (3.16)$$

gives the density of particles at the point \mathbf{r} . Here n_0 is the density at points, where $U = 0$. Eq. (3.16) is sometimes called Boltzmann's law.

As an example, consider a gas in homogeneous gravitational field (e.g. on Earth's surface) directed along z -axis, so that $U = mgz$ (g is the free fall acceleration) and for density distribution of a gas we obtain:

$$n(z) = n_0 e^{-\frac{mgz}{T}} \quad (3.17)$$

where n_0 is density at $z = 0$ (at the sealevel).

3.3 Non-equilibrium ideal gas.

Consider an ideal gas in an arbitrary (in general non equilibrium) state. Let us assume that all quantum states of a single particle of the gas can be classified into certain groups of levels with energies close to each other, and the number of levels in each group, as well as the number of particles on these levels, are large

enough⁴. Let us enumerate these groups of levels by numbers $j = 1, 2, \dots$ and let G_j be the number of levels in j -th group, while N_j is the number of particles in these states. The set of numbers N_j completely determines the macroscopic state of the gas, while their arbitrariness, in fact means that we are dealing with an arbitrary, in general, non equilibrium state of the system.

To calculate the entropy of this macroscopic state we have to determine its statistical weight \mathcal{W} , i.e. the number of microscopic distributions of particles over the levels, which realize such state. Considering each group of N_j particles as an independent subsystem and denoting its statistical weight by \mathcal{W}_j , we can write:

$$\mathcal{W} = \prod_j \mathcal{W}_j \quad (3.18)$$

Now we have to calculate \mathcal{W}_j . In Boltzmann's statistics the average occupation numbers of all quantum states are small in comparison to unity. This means that $N_j \ll G_j$, though N_j are still very large. The smallness of occupation numbers leads to the conclusion that all particles are distributed over different states independent of each other. Placing each of N_j particles in one of G_j states we obtain in all $G_j^{N_j}$ possible distributions, including physically equivalent, which differ only due to permutations of identical particles. Accordingly we have to divide the total number of possible distributions (configurations) by $N_j!$, so that:

$$\mathcal{W}_j = \frac{G_j^{N_j}}{N_j!} \quad (3.19)$$

Then the entropy is calculated as:

$$S = \ln \mathcal{W} = \sum_j \ln \mathcal{W}_j = \sum_j (N_j \ln G_j - \ln N_j!) \quad (3.20)$$

Using Stirling asymptotics, which is valid for $N \gg 1$ ⁵:

$$\ln N! \approx N \ln \left(\frac{N}{e} \right) \quad (3.21)$$

we get:

$$S = \sum_j N_j \ln \frac{e G_j}{N_j} \quad (3.22)$$

This expression determines the entropy of an ideal gas in arbitrary macroscopic state, defined by the set of numbers N_j . Let us rewrite it introducing the average numbers $\langle n_j \rangle$ of particles in j -th group of quantum levels $\langle n_j \rangle = N_j / G_j$. Then:

$$S = \sum_j G_j \langle n_j \rangle \ln \frac{e}{\langle n_j \rangle} \quad (3.23)$$

Describing particles in quasiclassic approximation, we can introduce distribution function in phase space. Dividing the phase space into small elementary volumes $\Delta p^{(j)} \Delta q^{(j)}$, which still contain large enough number of particles, we can write

⁴This assumption is made just to simplify our analysis and does not restrict its generality.

⁵For $N \gg 1$ the sum $\ln N! = \ln 1 + \ln 2 + \dots + \ln N$ is approximately expressed as $\int_0^N dx \ln x$, which immediately gives Eq. (3.21).

down the number of quantum states in such volume as (r is the number of degrees of freedom of a gas molecule, for one-atom gas $r = 3$):

$$G_j = \frac{\Delta p^{(j)} \Delta q^{(j)}}{(2\pi\hbar)^r} = \Delta\tau^{(j)}, \quad (3.24)$$

The number of particles in these states can be written as $N_j = n(p, q)\Delta\tau^{(j)}$. Substituting these expressions into Eq. (3.23), we obtain:

$$S = \int d\tau n(p, q) \ln \frac{e}{n(p, q)} \quad (3.25)$$

This is the so called Boltzmann's entropy of an ideal gas in arbitrary (non equilibrium) state, defined by *single particle* distribution function $n(p, q)$ ⁶.

What is the connection of Boltzmann entropy (3.25) with Gibbs entropy defined in (1.167)? In the expression for Gibbs entropy:

$$S = - \int \frac{dpdq}{(2\pi\hbar)^{3N} N!} \rho(p, q, t) \ln \rho(p, q, t) \quad (3.26)$$

$\rho(p, q)$ denotes the full N -particle distribution function, depending on coordinates and momenta of all N molecules of gas. For an ideal gas of noninteracting particles this distribution function is obviously factorized (statistical independence – absence of interactions!) into the product of single particle distribution functions for all particles:

$$\rho(p, q) = \frac{N!}{N^N} \prod_{i=1}^N n(p_i, q_i) \quad (3.27)$$

where single particle distribution functions $n(p_i, q_i)$ are normalized as (for one-atom gas, i.e. $r = 3$):

$$\int \frac{dp_1 dq_1}{(2\pi\hbar)^3} n(p_1, q_1) = N \quad (3.28)$$

The factor of $N!/N^N$ in (3.27) is introduced here to guarantee agreement between this normalization with that used above for $\rho(p, q)$:

$$\int d\Gamma \rho(p, q) = \left\{ \frac{1}{N} \int \frac{dp_1 dq_1}{(2\pi\hbar)^3} n(p_1, q_1) \right\}^N = 1 \quad d\Gamma = \frac{dpdq}{(2\pi\hbar)^{3N} N!} \quad (3.29)$$

Then, using (3.27), (3.21) in (3.26) we get:

$$S = - \int \frac{dp_1 dq_1}{(2\pi\hbar)^3} n(p_1, q_1) \ln \frac{n(p_1, q_1)}{e} \quad (3.30)$$

which coincides with (3.25).

In equilibrium state the entropy is to be maximal. This can be used to find the equilibrium distribution function. Let us find $\langle n_j \rangle$, which gives the

⁶Distribution function $n(p, q)$ can depend on time and this time dependence can be calculated using Boltzmann's *kinetic equation*. For this entropy (3.25) the famous Boltzmann's *H-theorem*, is proved in classical kinetics, describing the time growth of (3.25).

maximal value of the sum (3.23), with additional demands of the fixed (average) number of particles and average energy of the system:

$$\sum_j N_j = \sum_j G_j \langle n_j \rangle = N \quad (3.31)$$

$$\sum_j \varepsilon_j N_j = \sum_j \varepsilon_j G_j \langle n_j \rangle = E \quad (3.32)$$

Using the method of Lagrange multipliers we demand:

$$\frac{\partial}{\partial n_j} (S + \alpha N + \beta E) = 0 \quad (3.33)$$

where α and β are some constants. After differentiation we get:

$$G_j (-\ln \langle n_j \rangle + \alpha + \beta \varepsilon_j) = 0 \quad (3.34)$$

leading to $\ln \langle n_j \rangle = \alpha + \beta \varepsilon_j$, or

$$\langle n_j \rangle = \exp(\alpha + \beta \varepsilon_j) \quad (3.35)$$

We obtained Boltzmann distribution, where the constants α and β are related to T and μ : $\alpha = \mu/T$, $\beta = -1/T$. This is clear, in particular, from the possibility to write (3.33) as a relation between differentials: $dS + \alpha dN + \beta dE = 0$, which is to coincide with the well known thermodynamic relation for differential of energy (for fixed volume): $dE = TdS + \mu dN$.

3.4 Free energy of Boltzmann gas.

Let us apply the basic relation of statistical mechanics:

$$F = -T \ln Z = -T \ln \sum_n e^{-\frac{E_n}{T}} \quad (3.36)$$

to calculation of the free energy of an ideal gas, described by Boltzmann statistics. Energy levels E_n of the whole system (gas) are simple the sums of energies of isolated molecules ε_k , which in Boltzmann case are all different (because in each quantum state of a gas there is no more than one molecule). Then we can write down $e^{-\frac{E_n}{T}}$ as a product of factors $e^{-\frac{\varepsilon_k}{T}}$ for each molecule and summing over all states of each molecule, which leads to the following expression for the partition function of the gas⁷:

$$Z \sim \left(\sum_k e^{-\frac{\varepsilon_k}{T}} \right)^N \quad (3.37)$$

This expression is also to be divided by $N!$, taking into account the number of permutations of identical particles (molecules), leading to physically equivalent states (configurations). Then we have:

$$Z = \sum_n e^{-\frac{E_n}{T}} = \frac{1}{N!} \left(\sum_k e^{-\frac{\varepsilon_k}{T}} \right)^N \quad (3.38)$$

⁷We have $e^{-\frac{E_n}{T}} = e^{-\frac{\varepsilon_{k_1}}{T}} e^{-\frac{\varepsilon_{k_2}}{T}} \dots e^{-\frac{\varepsilon_{k_N}}{T}}$, with N factors at all, with all k_L ($L = 1, 2, \dots, N$) different. Calculating now $\sum_{k_1} \sum_{k_2} \dots \sum_{k_N} \rightarrow (\sum_k)^N$, we get Eq. (3.37)

Substituting this expression into (3.36), we get:

$$F = -TN \ln \sum_k e^{-\frac{\varepsilon_k}{T}} + T \ln N! \quad (3.39)$$

or, using once again $\ln N! \approx N \ln N/e$, we obtain:

$$F = -NT \ln \left\{ \frac{e}{N} \sum_k e^{-\frac{\varepsilon_k}{T}} \right\} \quad (3.40)$$

In classical statistics we can immediately write:

$$F = -NT \ln \left[\frac{e}{N} \int d\tau e^{-\frac{\varepsilon(p,q)}{T}} \right] \quad d\tau = \frac{d^r p d^r q}{(2\pi\hbar)^r} \quad (3.41)$$

where r is again the number of degrees of freedom of a gas molecule.

3.5 Equation of state of Boltzmann gas.

Energy of a gas molecule can be written as:

$$\varepsilon_k(p_x, p_y, p_z) = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \varepsilon'_k \quad (3.42)$$

where the first term is kinetic energy of molecular motion, while ε'_k denote internal energy levels of the molecule (corresponding e.g. to rotation of the molecule, atomic oscillations near equilibrium positions, energy levels of atoms etc.). Here it is important to note that ε'_k do not depend on momenta (velocities) and coordinates of the center of mass of the molecule. Then, the sum under \ln in Eq. (3.40) is equal to⁸:

$$\begin{aligned} \sum_k \frac{1}{(2\pi\hbar)^3} e^{-\frac{\varepsilon'_k}{T}} \int_V dV \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2mT}} = \\ = V \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \sum_k e^{-\frac{\varepsilon'_k}{T}} \end{aligned} \quad (3.43)$$

Then the free energy of the gas is written as:

$$F = -NT \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} \sum_k e^{-\frac{\varepsilon'_k}{T}} \right] = -NT \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} Z' \right] \quad (3.44)$$

where we have introduced an “internal” partition function of a molecule $Z' = \sum_k e^{-\frac{\varepsilon'_k}{T}}$. This some can not be calculated in general form, it depends on the values of internal energy levels of molecules, i.e. on the type of gas. However, it is important to note that it is some function of temperature only, so that Eq. (3.44) gives the complete dependence of the free energy on volume. This volume dependence can be written explicitly by rewriting Eq. (3.44) as:

$$F = -NT \ln \frac{eV}{N} + Nf(T); \quad f(T) = -T \ln \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} Z' \quad (3.45)$$

⁸Integral over dV here is related to integration over coordinates of the center of mass of the molecule and reduces to the total volume occupied by gas V .

Then for the gas pressure we immediately obtain:

$$P = -\frac{\partial F}{\partial V} = \frac{NT}{V} \quad \text{or} \quad PV = NT \quad (3.46)$$

i.e. an equation of state of an ideal gas. If we measure the temperature in absolute degrees, we have to write:

$$PV = Nk_B T = RT \quad (3.47)$$

For gramm-molecule (mole) of gas $N = 6.023 \cdot 10^{23}$ (Avogadro number), $R = 8.314 \cdot 10^7 \text{erg/K}$, $k_B = 1.3804 \cdot 10^{-16} \text{erg/K}$.

From F we can find other thermodynamic potential. For example, Gibbs thermodynamic potential:

$$\Phi = F + PV = E - TS + PV = W - TS = -NT \ln \frac{eV}{N} + Nf(T) + PV \quad (3.48)$$

where W is enthalpy. Expressing V via P and T using equation of state (3.46), to rewrite Φ as a function of P and T (remember that $d\Phi = -SdT + VdP$) and introducing new function of temperature as: $\chi(T) = f(T) - T \ln T$, we obtain:

$$\Phi = NT \ln P + N\chi(T) \quad (3.49)$$

Entropy of gas (remember that $dF = -SdT - PdV$):

$$S = -\frac{\partial F}{\partial T} = N \ln \frac{eV}{N} - Nf'(T) \quad (3.50)$$

or, as a function of P and T :

$$S = -\frac{\partial \Phi}{\partial T} = -N \ln P - N\chi'(T) \quad (3.51)$$

Internal energy of gas:

$$E = F + TS = Nf(T) - NTf'(T) \quad (3.52)$$

and is a function of temperature only, the same is valid for enthalpy $W = E + PV = E + NT$. The physical reason is simple – molecules of an ideal gas do not interact, so that the change of average intermolecular distance during the change of volume does not influence energy. Due to this behavior of E and W , both types of specific heat $C_v = \left(\frac{\partial E}{\partial T}\right)_V$ and $C_p = \left(\frac{\partial W}{\partial T}\right)_P$ also depend only on T . Writing specific heat per molecule we introduce $C_v = Nc_v$ and $C_p = Nc_p$. For an ideal gas $W - E = NT$, so that the difference $c_p - c_v$ is universal:

$$c_p - c_v = 1 \quad \text{or} \quad c_p - c_v = k_B \quad (3.53)$$

or $C_p - C_v = R$ per mole.

3.6 Ideal gas with constant specific heat.

From experiments it is known that in a wide interval of high enough temperatures specific heat of gases is a constant independent of T . Physical reasons

for such behavior will become clear later, while now we shall show that, under the assumption of temperature independence of specific heat, thermodynamic characteristics of a gas can be calculated in general form. More precisely, in this case we can determine the general form of unknown function of temperature $f(T)$, introduced above in Eq. (3.45), expressing it via constants to be determined from experiments. In this case we just do not have to calculate the “internal” partition function Z' . Simply differentiating Eq. (3.52) for internal energy by temperature we find:

$$c_v = -Tf''(T) \quad (3.54)$$

Assuming specific heat to be a constant defined by experiments, we can integrate Eq. (3.54) twice to obtain:

$$f(T) = -c_v T \ln T - \zeta T + \varepsilon_0 \quad (3.55)$$

where ζ and ε_0 are two constants of integration. Then, from Eq. (3.45) we get the free energy in the form:

$$F = N\varepsilon_0 - NT \ln \frac{eV}{N} - Nc_v T \ln T - N\zeta T \quad (3.56)$$

The constant ζ is called the chemical constant of a gas, for any concrete gas it is to be determined experimentally. Now using Eq. (3.52) we obtain internal energy as a linear function of temperature:

$$E = N\varepsilon_0 + Nc_v T \quad (3.57)$$

Gibbs thermodynamic potential is obtained by adding $PV = NT$ to Eq. (3.56), and we have to express the volume of gas via pressure and temperature. Thus we obtain:

$$\Phi = N\varepsilon_0 + NT \ln P - Nc_p T \ln T - N\zeta T \quad (3.58)$$

Enthalpy $W = E + PV$ is equal to:

$$W = N\varepsilon_0 + Nc_p T \quad (3.59)$$

Differentiating (3.56) and (3.58) by T , we obtain entropy expressed via T and V or T and P respectively:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = -N \ln \frac{eV}{N} + Nc_v \ln T + (\zeta + c_v)N \quad (3.60)$$

$$S = - \left(\frac{\partial \Phi}{\partial T} \right)_P = -N \ln P + Nc_p \ln T + (\zeta + c_p)N \quad (3.61)$$

From these expressions we can obtain the relation between the volume, temperature and pressure of an ideal gas (with constant specific heat) during its adiabatic expansion or compression. During adiabatic process the entropy remains constant and from Eq. (3.61) we have: $-N \ln P + Nc_p \ln T = \text{const}$, so that $T^{c_p}/P = \text{const}$, or using $c_p - c_v = 1$:

$$T^\gamma P^{1-\gamma} = \text{const} \quad (3.62)$$

where $\gamma = c_p/c_v$. Using equation of state $PV = NT$, we obtain the relations between T and V and also between P and V :

$$TV^{\gamma-1} = \text{const} \quad PV^\gamma = \text{const} \quad (3.63)$$

3.7 Equipartition theorem.

Let us consider the problem of calculation of thermodynamic properties of gases from the point of view of classical statistical mechanics. Gas molecule is essentially some configuration of atoms, performing small oscillations near respective equilibrium positions, corresponding to the minimum of potential energy. Obviously, this potential energy can be represented as some quadratic form of atomic coordinates:

$$U = \varepsilon_0 + \sum_{i,k=1}^{r_{osc}} a_{ik} q_i q_k \quad (3.64)$$

where ε_0 is the potential energy of atoms at equilibrium positions, r_{osc} is the number of vibrational degrees of freedom.

The number r_{osc} can be determined from very simple analysis, starting with the number of atoms in the molecule n . We know that n -atomic molecule possess $3n$ degrees of freedom at all. Three of these correspond to free translations of the molecule in space as a whole, and another three – to its rotations as a whole. The rest of the degrees of freedom correspond to atomic oscillations, so that $r_{osc} = 3n - 6$. If all atoms are placed along a straight line (like e.g. in two-atomic molecule), we have only two rotational degrees of freedom. In this case $r_{osc} = 3n - 5$. For one-atom gas $n = 1$ and there are no oscillations (and rotations) at all, one atom can move only along three directions in space, we have only translational degrees of freedom.

The full energy $\varepsilon(p, q)$ of a molecule is the sum of potential and kinetic energies. Kinetic energy is always a quadratic function of all momenta, the number of these momenta is equal to the total number of degrees of freedom $3n$. Thus this energy can be written as $\varepsilon(p, q) = \varepsilon_0 + f_{II}(p, q)$, where $f_{II}(p, q)$ is some quadratic function of both coordinates and momenta, and the total number of variables in this function is $l = 6n - 6$ (for the general three-dimensional molecule) or $l = 6n - 5$ for linear molecule. For one-atom gas $l = 3$ and coordinates simply do not enter the expression for energy.

As a result for the free energy of a gas, from Eq. (3.41) we have:

$$F = -NT \ln \frac{e e^{-\frac{\varepsilon_0}{T}}}{N} \int d\tau e^{-\frac{f_{II}(p, q)}{T}} \quad (3.65)$$

Let us make here transformation $p = p' \sqrt{T}$, $q = q' \sqrt{T}$ for all l variables of $f_{II}(p, q)$. Due to quadratic nature of $f_{II}(p, q)$ we obtain:

$$f_{II}(p, q) = T f_{II}(p', q') \quad (3.66)$$

and T in the exponent under the integral just disappear. Similar transformation in differentials entering $d\tau$ produces the factor $T^{l/2}$, which is moved outside the integral. Integration over coordinates of oscillators q is done over the possible values of atomic oscillations within the molecule. However, due to fast convergence (quadratic function in the exponent) integration over p' and q' can be extended to infinite interval from $-\infty$ to ∞ , so that our integral is reduced to some constant independent of temperature. Taking into account that integration over the coordinates of the center of mass of the molecule gives simply the total volume V of the gas, we obtain for the free energy the following expression:

$$F = -NT \ln \frac{AV e^{-\frac{\varepsilon_0}{T}} T^{l/2}}{N} \quad A = const \quad (3.67)$$

Then:

$$F = N\varepsilon_0 - NT \ln \frac{eV}{N} - N \frac{l}{2} T \ln T - NT \ln A \quad (3.68)$$

which coincides with Eq. (3.56) if we put:

$$c_v = \frac{l}{2} \quad (3.69)$$

and $\zeta = \ln A$. Accordingly:

$$c_p = c_v + 1 = \frac{l+2}{2} \quad (3.70)$$

Thus the specific heat of a classical ideal gas is constant, and for each degree of freedom of a molecule $\varepsilon(p, q)$ we get the same contribution of $1/2$ in specific heat c_v (or $k_B/2$ in standard units). It corresponds to the similar $T/2$ ($k_B T/2$ if we measure T in absolute degrees) contribution to gas energy. This rule is called *equipartition* law or theorem and is quite general statement of classical statistical mechanics. In particular it is easily generalized also for the case of condensed matter⁹. Taking into account that each of translational and rotational degrees of freedom enter $\varepsilon(p, q)$ only through respective momenta, we can say that each of these degrees of freedom gives to specific heat a contribution of $1/2$. For each of oscillator we have a contribution of two degrees of freedom into $\varepsilon(p, q)$ (coordinate and momentum) and its contribution to specific heat is 1.

3.8 One-atom ideal gas.

Let us consider an ideal gas of single atoms (not molecules). Complete knowledge of the free energy of such gas requires calculation of an “internal” partition function Z' introduced in Eq. (3.44):

$$Z' = \sum_k e^{-\frac{\varepsilon_k}{T}} \quad (3.71)$$

where ε_k are internal energy levels of an atom. These levels may be degenerate, in this case the respective term enters the sum g_k times, where g_k is degeneracy of corresponding level. Then:

$$Z' = \sum_k g_k e^{-\frac{\varepsilon_k}{T}} \quad (3.72)$$

Free energy of the gas, according to Eq. (3.44), is given by:

$$F = -NT \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{3/2} Z' \right] \quad (3.73)$$

From quantum mechanics it is known that in atoms the ground state level and first excited level (neglecting superfine splitting) are separated by an energy of

⁹As temperature lowers, significant deviations from this law are observed in the experiments. It is obvious that constancy of specific heat contradicts nernst theorem. Historically, the breaking of equipartition law was one of the first indications for the inadequacy of classical treatment, which lead to the discovery of quantum mechanics.

the order of ionization energy (potential) I_{ion} , which for most atoms lie in the interval of $I_{ion}/k_B \sim 5 - 28 \cdot 10^4 K$. Thus, for temperatures $T \ll I_{ion}$, which are of main interest to us, gas does not contain significant number of ionized or even excited atoms. All atoms can be assumed to be in their ground states.

Consider the simplest case of atoms with orbital or spin momentum in the ground state ($L = S = 0$), for example noble gases¹⁰. In this case the ground state is non degenerate and “internal” partition function consists of one term: $Z' = e^{-\frac{\epsilon_0}{T}}$. Then from Eq. (3.73) we immediately obtain an expression for the free energy similar to (3.56), with constant specific heat:

$$c_v = 3/2 \quad (3.74)$$

and chemical constant:

$$\zeta = \frac{3}{2} \ln \frac{m}{2\pi\hbar^2} \quad (3.75)$$

The last expression is called Sakura-Tetrode formula.

These expressions allow to find the criterion of applicability of Boltzmann statistics. Previously we obtained Boltzmann distribution assuming the smallness of average occupation numbers:

$$\langle n_k \rangle = e^{\frac{\mu - \epsilon_k}{T}} \ll 1. \quad (3.76)$$

Obviously, instead it is sufficient to require that:

$$e^{\frac{\mu}{T}} \ll 1, \quad (3.77)$$

From this expression it is clear that the chemical potential of Boltzmann gas is always negative and large in absolute value. Let us find the chemical potential from its thermodynamic definition $\mu = \Phi/N$, using the expression of Gibbs thermodynamic potential (3.58), substituting $c_p = c_v + 1 = 5/2$ and ζ from Eq. (3.75). We obtain:

$$\mu = T \ln \left[\frac{P}{T^{5/2}} \left(\frac{2\pi\hbar^2}{m} \right)^{3/2} \right] = T \ln \left[\frac{N}{V} \left(\frac{2\pi\hbar^2}{mT} \right)^{3/2} \right] \quad (3.78)$$

which obviously coincide with Eq. (3.12), determined in another way (from normalization to fixed average number of particles). Then from (3.77) and (3.78) we obtain the criterion of validity of Boltzmann statistics in the following form:

$$\frac{N}{V} \left(\frac{\hbar^2}{mT} \right)^{3/2} \ll 1 \quad \text{or} \quad T \gg \frac{\hbar^2}{m} \left(\frac{N}{V} \right)^{2/3}. \quad (3.79)$$

Boltzmann statistics is valid if gas is sufficiently diluted and temperature is high enough. Characteristic temperature (energy) from the right hand side of Eq. (3.79) is called the temperature (energy) of degeneracy. It grows with the growth of gas density. Its physical meaning is easily understood from simple estimates. The average distance between atoms of the gas $a \sim (V/N)^{1/3}$. Quantum indeterminacy of energy of an atom corresponding its localization on this length scale is of order of $E_0 \sim \frac{\hbar^2}{ma^2} \sim \frac{\hbar^2}{m} (N/V)^{2/3}$. Condition $T \gg E_0$ in Eq. (3.79)

¹⁰Detailed discussion of more complicated cases, as well as molecular gases, can be found in Refs. [1, 2]

means that we can neglect quantum effects. On the contrary, for $T < E_0$ quantum effects become important and we have to move from Boltzmann statistics to quantum statistics of ideal gases¹¹.

¹¹Expressions for thermodynamic characteristic of gases obtained above are obviously unsatisfactory and contradicting Nernst theorem, neither entropy nor specific heat tend to zero as $T \rightarrow 0$.

Chapter 4

QUANTUM IDEAL GASES

4.1 Fermi distribution.

We have seen above that as temperature of an ideal gas lowers (at fixed density), Boltzmann statistics becomes invalid due to emergence of quantum effects (Cf. Eq. (3.79)). It is clear that to describe low temperature (or high density) behavior we need another statistics, appropriate for the cases when the average occupation numbers of different quantum states are not assumed to be small¹. This statistics is different depending of the nature (type) of the gas particles. Most fundamental classification of particles in modern quantum theory, based on most general theorems of quantum field theory, is classification into either Fermions (particles with half-integer spins) and Bosons (particles with integer spin). Wave functions of the system of N identical Fermions are antisymmetric with respect to permutations of particles, while those of Bosons – symmetric.

For the system of particles described by antisymmetric wave functions (Fermions) Pauli exclusion principle applies and the corresponding statistics is called Fermi (or Fermi-Dirac) statistics. Similarly to derivation of Boltzmann statistics from grand canonical ensemble given above (Cf. (3.4)–(3.7)), let us apply Gibbs distribution to a set of particles, occupying the given quantum state (subsystem in the bath). Let us denote as Ω_k thermodynamic potential of this set of particles. From Eq. (2.60), taking into account that for the gas of noninteracting particles $E_{n_k} = n_k \varepsilon_k$, we obtain:

$$\Omega_k = -T \ln \sum_{n_k} \left(e^{\frac{\mu - \varepsilon_k}{T}} \right)^{n_k} \quad (4.1)$$

where n_k is the number of particles in k -th quantum state. According to Pauli principle, in case of Fermions, this number can be either 0 or 1. Then, in the sum over n_k in (4.1) only two terms remain and we get:

$$\Omega_k = -T \ln \left(1 + e^{\frac{\mu - \varepsilon_k}{T}} \right) \quad (4.2)$$

¹Below we follow the analysis of Ref. [1].

The average number of particles in the system is equal to minus derivative of potential Ω_k over chemical potential μ , so that:

$$\langle n_k \rangle = -\frac{\partial \Omega_k}{\partial \mu} = \frac{e^{\frac{\mu - \varepsilon_k}{T}}}{1 + e^{\frac{\mu - \varepsilon_k}{T}}} \quad (4.3)$$

or:

$$\langle n_k \rangle = \frac{1}{e^{\frac{\varepsilon_k - \mu}{T}} + 1} \quad (4.4)$$

This is called Fermi distribution. It is easy to see that we always have $\langle n_k \rangle \leq 1$, and for $e^{\frac{\varepsilon_k - \mu}{T}} \gg 1$ Eq. (4.4) reduces to Boltzmann distribution².

Normalization condition for Fermi distribution can be written as:

$$\sum_k \frac{1}{e^{\frac{\varepsilon_k - \mu}{T}} + 1} = N \quad (4.5)$$

where N is the total number of particles of the gas. This relation gives an implicit equation determining the chemical potential μ , as a function of T and N .

Thermodynamic potential Ω for the gas as a whole is obviously obtained from Ω_k (4.2) summing it over all quantum states:

$$\Omega = -T \sum_k \ln \left(1 + e^{\frac{\mu - \varepsilon_k}{T}} \right). \quad (4.6)$$

4.2 Bose distribution.

Consider now statistics of an ideal gas of particles with integer spin (Bosons), described by symmetric wave functions, which is called Bose (or Bose-Einstein) statistics.

Occupation numbers of quantum states for Bosons can be arbitrary (unlimited). Similarly to (4.1) we have:

$$\Omega_k = -T \ln \sum_{n_k} \left(e^{\frac{\mu - \varepsilon_k}{T}} \right)^{n_k} \quad (4.7)$$

The series entering here is just a geometric progression, which converges if $e^{\frac{\mu - \varepsilon_k}{T}} < 1$. This condition should be satisfied for arbitrary ε_k , so that

$$\mu < 0 \quad (4.8)$$

i.e. the chemical potential of a Bose gas is always negative. Previously we have seen that for Boltzmann gas $\mu < 0$ and is large in absolute value. Below we shall see that for Fermi gas μ may be of either sign.

Summing the progression in (4.7) we get:

$$\Omega_k = T \ln \left(1 - e^{\frac{\mu - \varepsilon_k}{T}} \right) \quad (4.9)$$

²If we require the validity of this inequality for arbitrary ε_k , it reduces to $e^{\mu/T} \ll 1$, coinciding with criterion of validity of Boltzmann statistics given in Eq. (3.77).

Now for $\langle n_k \rangle = -\frac{\partial \Omega_k}{\partial \mu}$ we obtain:

$$\langle n_k \rangle = \frac{1}{e^{\frac{\varepsilon_k - \mu}{T}} - 1} \quad (4.10)$$

which is called Bose distribution. Again, in case of $e^{\frac{\varepsilon_k - \mu}{T}} \gg 1$ it reduces to Boltzmann distribution.

Normalization condition is again written as:

$$N = \sum_k \frac{1}{e^{\frac{\varepsilon_k - \mu}{T}} - 1} \quad (4.11)$$

and implicitly defines chemical potential.

Thermodynamic potential Ω for the whole gas, similarly to (4.6), is given by:

$$\Omega = T \sum_k \ln \left(1 - e^{\frac{\mu - \varepsilon_k}{T}} \right). \quad (4.12)$$

4.3 Non-equilibrium Fermi and Bose gases.

Let us consider the entropy of Fermi and Bose (ideal) gases in general (non equilibrium) states. Equilibrium Bose and Fermi distributions will be obtained requiring the maximal value of entropy in equilibrium. This analysis can be performed similarly to the case of Boltzmann gas. Again we can consider groups of levels close in energy numbered by $j = 1, 2, \dots$. Let G_j be the number of states in j -th group and N_j – the number of particles in these states. The set of numbers N_j completely characterizes the microscopic state of a gas.

In case of Fermi statistics only one particle can occupy each quantum state, but numbers N_j are not small, but of the order of G_j . The number of possible distributions of N_j identical particles over G_j states, with no more than one particle in each state, is equal to the number of ways to choose N_j of G_j states, i.e. the number of combinations of G_j elements by N_j :

$$\mathcal{W}_j = \frac{G_j!}{N_j!(G_j - N_j)!}. \quad (4.13)$$

Taking the logarithm and using for all three factorials in (4.13) Stirling's asymptotics $\ln N! \approx N \ln(N/e)$, we find entropy as:

$$S = \sum_j \{G_j \ln G_j - N_j \ln N_j - (G_j - N_j) \ln(G_j - N_j)\}. \quad (4.14)$$

Introducing again the average occupation numbers $\langle n_j \rangle = N_j/G_j$ we obtain the following expression for the entropy of non equilibrium Fermi gas:

$$S = - \sum_j G_j [\langle n_j \rangle \ln \langle n_j \rangle + (1 - \langle n_j \rangle) \ln(1 - \langle n_j \rangle)] \quad (4.15)$$

Requiring its maximum with additional conditions:

$$\sum_j N_j = \sum_j G_j \langle n_j \rangle = N; \quad \sum_j \varepsilon_j G_j \langle n_j \rangle = E \quad (4.16)$$

i.e. using the method of Lagrange multipliers, from:

$$\frac{\partial}{\partial \langle n_j \rangle} [S + \alpha N + \beta E] = 0 \quad (4.17)$$

we immediately obtain Fermi distribution as $\langle n_j \rangle = [e^{\alpha + \beta \varepsilon_j} + 1]^{-1}$, where $\alpha = -\mu/T$, $\beta = 1/T$.

In case of Bose statistics in each quantum state we can place an arbitrary number of particles, so that statistical weight \mathcal{W}_j represents the number of all ways to distribute N_j over G_j states:

$$\mathcal{W}_j = \frac{(G_j + N_j - 1)!}{(G_j - 1)! N_j!} \quad (4.18)$$

To understand this expression we note that here we are speaking about e.g. the number of ways to distribute N_j identical balls over G_j boxes. Let us denote balls by N_j points, while boxes can be numbered and their borders can be visualized by $G_j - 1$ vertical strokes. In total there are $G_j + N_j - 1$ point and strokes. The number we seek is given by the number of ways to choose $G_j - 1$ places for strokes, i.e. the number of combinations of $N_j + G_j - 1$ elements by $G_j - 1$, which gives us Eq. (4.18).

Taking logarithm and neglecting unity in comparison with large numbers $G_j + N_j$ and G_j , we get:

$$S = \sum_j \{(G_j + N_j) \ln(G_j + N_j) - N_j \ln N_j - G_j \ln G_j\} \quad (4.19)$$

Introducing $\langle n_j \rangle$ we can write down the entropy of non equilibrium Bose gas as:

$$S = \sum_j G_j [(1 + \langle n_j \rangle) \ln(1 + \langle n_j \rangle) - \langle n_j \rangle \ln \langle n_j \rangle]. \quad (4.20)$$

Equilibrium Bose distribution follows from the requirement of maximum of this expression, similarly to the case of Fermi statistics.

For $N_j \ll G_j$ (4.15), (4.20) naturally reduce to Boltzmann expression (3.23):

$$S = \sum_j G_j \langle n_j \rangle \ln \frac{e}{\langle n_j \rangle} = \sum_j G_j [\langle n_j \rangle (1 - \ln \langle n_j \rangle)]; \quad \langle n_j \rangle \ll 1. \quad (4.21)$$

In the inverse limit of $N_j \gg G_j$, i.e. $\langle n_j \rangle \gg 1$, the entropy of Bose gas (4.20) reduces to:

$$S = \sum_j G_j \ln \frac{e N_j}{G_j}, \quad (4.22)$$

and statistical weight (4.18) $\mathcal{W}_j = \frac{N_j^{G_j - 1}}{(G_j - 1)!}$.

4.4 General properties of Fermi and Bose gases.

Many physical characteristics of Fermi and Bose gases can be written and calculated in general form. In all expressions below the upper plus corresponds to Fermi statistics, while the lower minus – to Bose statistics.

Energy of a free (non relativistic) particle can be written as:

$$\varepsilon_p = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = \frac{\mathbf{p}^2}{2m}. \quad (4.23)$$

For a given value of momentum, the state of a particle is defined also by its spin projection. The number of particles in an element of phase space $dp_x dp_y dp_z dV$ can be obtained by multiplication of Fermi (Bose) distribution by the number of states in this phase space volume:

$$gd\tau = g \frac{dp_x dp_y dp_z dV}{(2\pi\hbar)^3} \quad g = 2s + 1 \quad (4.24)$$

where s is the spin of the particle. Thus we obtain:

$$dN_p = \frac{gd\tau}{e^{\frac{\varepsilon_p - \mu}{T}} \pm 1}. \quad (4.25)$$

Integrating over dV we get the total volume of the gas V . Then, transforming to spherical coordinates in momentum space ($dp_x dp_y dp_z \rightarrow 4\pi p^2 dp$), we obtain the momentum distribution as:

$$dN_p = \frac{gV p^2 dp}{2\pi^2 \hbar^3 \left(e^{\frac{\varepsilon_p - \mu}{T}} \pm 1 \right)} \quad (4.26)$$

or distribution over energies:

$$dN_\varepsilon = \frac{gV m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\frac{\varepsilon - \mu}{T}} \pm 1} = \frac{\mathcal{N}(\varepsilon) d\varepsilon}{e^{\frac{\varepsilon - \mu}{T}} \pm 1} \quad (4.27)$$

where we have introduced rather useful function:

$$\mathcal{N}(\varepsilon) = \frac{gV m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \sqrt{\varepsilon} = gV \frac{m p_\varepsilon}{2\pi^2 \hbar^3}; \quad p_\varepsilon = \sqrt{2m\varepsilon} \quad (4.28)$$

which is called the density of states of a particle in the energy interval $\varepsilon, \varepsilon + d\varepsilon$. These expressions replace Maxwell distribution for quantum gases.

Integrating (4.27) over $d\varepsilon$, we obtain:

$$N = \int_0^\infty d\varepsilon \frac{\mathcal{N}(\varepsilon)}{e^{\frac{\varepsilon - \mu}{T}} \pm 1} = \frac{gV m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{e^{\frac{\varepsilon - \mu}{T}} \pm 1} \quad (4.29)$$

Introducing dimensionless variable $\varepsilon/T = z$ we can write:

$$\frac{N}{V} = \frac{g(mT)^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty dz \frac{\sqrt{z}}{e^{z - \frac{\mu}{T}} \pm 1} \quad (4.30)$$

which gives an implicit equation for chemical potential μ as a function of T and particle density N/V .

Making similar transformation from summation over quantum states to energy integration if Eqs. (4.6), (4.12) we get:

$$\Omega = \mp \frac{gVTm^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\infty d\varepsilon \sqrt{\varepsilon} \ln \left(1 \pm e^{\frac{\mu - \varepsilon}{T}} \right) \quad (4.31)$$

After partial integration we obtain:

$$\Omega = -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\frac{\varepsilon-\mu}{T}} \pm 1} \quad (4.32)$$

This expression coincides, up to a factor of $-2/3$, with total energy of the gas given by:

$$E = \int_0^\infty \varepsilon dN_\varepsilon = \frac{gVm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\frac{\varepsilon-\mu}{T}} \pm 1}. \quad (4.33)$$

From thermodynamics it is known that $\Omega = -PV$, so that Eqs. (4.32), (4.33) give the generalized equation of state for ideal quantum gases:

$$PV = \frac{2}{3}E \quad (4.34)$$

In the limit of Boltzmann statistics we have $E = 3NT/2$ (equipartition law) and (4.34) reduces to classical result: $PV = NT$.

Rewriting (4.32) as (Cf. (4.30)):

$$P = \frac{g\sqrt{2}m^{3/2}T^{5/2}}{3\pi^2\hbar^3} \int_0^\infty dz \frac{z^{3/2}}{e^{z-\frac{\mu}{T}} \pm 1} \quad (4.35)$$

we obtain the equation of state in parametric form (parameter μ !), i.e. the relation between P , V and T for a given value of μ .

Consider small corrections to classical equation of state. We shall use inequality $e^{\mu/T} \ll 1$ (Boltzmann limit) and expand the integrand in (4.35) in powers of $e^{(\mu/T)-z}$, limiting ourselves to first two terms in the expansion. Then:

$$\int_0^\infty dz \frac{z^{3/2}}{e^{\frac{\varepsilon-\mu}{T}} \pm 1} \approx \int_0^\infty dz z^{3/2} e^{\frac{\mu}{T}-z} \left(1 \mp e^{\frac{\mu}{T}-z}\right) = \frac{3\sqrt{\pi}}{4} e^{\frac{\mu}{T}} \left(1 \mp \frac{1}{2^{5/2}} e^{\frac{\mu}{T}}\right). \quad (4.36)$$

and (4.35) can be rewritten as:

$$\Omega = -PV = -\frac{gVm^{3/2}T^{5/2}}{(2\pi\hbar^2)^{3/2}} e^{\frac{\mu}{T}} \left(1 \mp \frac{1}{2^{5/2}} e^{\frac{\mu}{T}}\right) \quad (4.37)$$

This expression in fact reduces to:

$$\Omega = \Omega_{Boltz} \pm \frac{gVm^{3/2}T^{5/2}}{16\pi^{3/2}\hbar^3} e^{\frac{2\mu}{T}}. \quad (4.38)$$

Small corrections to thermodynamic potentials, expressed via appropriate variables, are equal. Thus, rewriting correction to Ω_{Boltz} via T and V using corresponding classical (Boltzmann) expressions (we drop technical details), we can write down the free energy of the gas as:

$$F = F_{Boltz} \pm \frac{\pi^{3/2}}{2g} \frac{N^2\hbar^3}{VT^{1/2}m^{3/2}}. \quad (4.39)$$

From here it is easy to find:

$$PV = NT \left\{ 1 \pm \frac{\pi^{3/2}}{2g} \frac{N\hbar^3}{V(mT)^{3/2}} \right\} \quad (4.40)$$

We can see that quantum corrections (tending to zero as $\hbar \rightarrow 0$) lead to additional growth of pressure in Fermi gas and to the opposite effect in Bose gas. This reflects the natural tendency of Fermions to “avoid” each other (Pauli exclusion principle!), while for Bosons we have just the opposite behavior.

4.5 Degenerate gas of electrons.

Quantum effects in general become important in low temperature limit (in practice these temperatures may be high enough!). Of prime importance are the low temperature properties of Fermi gas. Keeping in mind most important applications, below we shall discuss mainly the gas of free electrons, and we put $g = 2$ ($s = 1/2$).

Let us start from the analysis of situation at $T = 0$. This is the case of so called completely degenerate Fermi gas. Each quantum state in Fermi gas can be occupied by no more than one electron, thus in fact at $T = 0$ they just fill all states with energies from zero (ground state) up to some maximal energy (which is called *Fermi energy*), with value determined simply by the number of particles (density) in gas.

The number of quantum states of electrons moving in the volume V , with absolute values of momenta in the interval $p, p + dp$, is equal to:

$$2 \frac{4\pi p^2 dp V}{(2\pi\hbar)^3}. \quad (4.41)$$

Electrons fill all states with momenta from zero to a maximum momentum $p = p_F$ (*Fermi momentum*). The total number of electrons in these states is determined by³:

$$N = \frac{V}{\pi^2 \hbar^3} \int_0^{p_F} p^2 dp = \frac{V p_F^3}{3\pi^2 \hbar^3}. \quad (4.42)$$

Then for Fermi momentum we obtain:

$$p_F = (3\pi^2)^{1/3} \left(\frac{N}{V} \right)^{1/3} \hbar \quad (4.43)$$

and it grows with the growth of electron density. It is clear that from Eq. (4.43) follows a simple estimate $p_F \sim \hbar/a$, where a is an average distance between electrons.

Correspondingly, Fermi energy is defined as⁴:

$$\varepsilon_F = \frac{p_F^2}{2m} = (3\pi^2)^{2/3} \frac{\hbar^2}{2m} \left(\frac{N}{V} \right)^{2/3} \sim \frac{\hbar^2}{ma^2} \quad (4.44)$$

Naturally it also grows with density of the gas $\sim (N/V)^{2/3}$.

Fermi distribution:

$$n_p = \frac{1}{e^{\frac{\varepsilon_p - \mu}{T}} + 1} \quad (4.45)$$

³In fact, here we simply calculate the volume of the *Fermi sphere* $V_F = \frac{4\pi p_F^3}{3}$, while the number of electrons is determined by the number of available states "inside" this sphere as $N = 2V \frac{V_F}{(2\pi\hbar)^3}$, which gives (4.42). The surface of Fermi sphere is called *Fermi surface*. In metals, where the energy spectrum of electrons may be quite different from that of free electrons, Fermi surface may be also quite different from simple spherical form. Geometry and topology of Fermi surfaces plays very important role in the theory of metals [19]. The simple estimates presented here, strictly speaking, are applicable only for simple metals (like e.g. Na and K).

⁴Note that the value of Fermi energy is practically the same as the degeneracy temperature (energy) of the gas introduced above (3.79).

for $T \rightarrow 0$ becomes a “Fermi step” function:

$$n_p = \begin{cases} 1 & \text{for } p \leq p_F \\ 0 & \text{for } p > p_F \end{cases} \quad (4.46)$$

or

$$n_\varepsilon = \begin{cases} 1 & \text{for } \varepsilon \leq \mu = \varepsilon_F \\ 0 & \text{for } \varepsilon > \mu = \varepsilon_F \end{cases} \quad (4.47)$$

Chemical potential of Fermi gas at $T = 0$ coincides with Fermi energy:

$$\mu = \varepsilon_F \quad (T = 0) \quad (4.48)$$

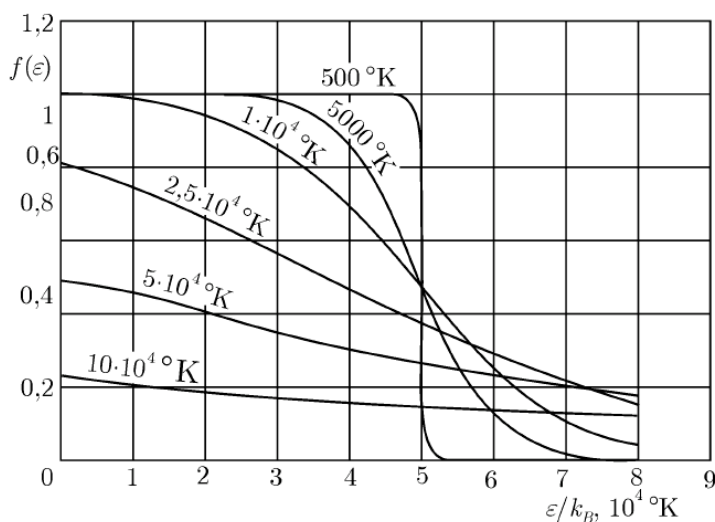


Figure 4.1: Fermi distribution function for different temperatures for $\varepsilon_F/k_B = 50000K$.

At finite temperatures $T \ll \varepsilon_F$ (strongly degenerate gas) Fermi step is “smeared” in energy interval $\sim T$ around Fermi energy (Cf. Fig.4-1). It is easy to see that with the growth of temperature, for $T \gg \varepsilon_F$ Fermi distribution transforms into Boltzmann distribution. Accordingly, with the growth of temperature the chemical potential starts to diminish from a positive value of the order of ε_F and becomes negative in Boltzmann region where $T \gg \varepsilon_F$.

Total energy of the gas at $T = 0$ is obtained by multiplying (4.41) by $p^2/2m$ and integration over all momenta up to $p = p_F$:

$$E = \frac{V}{2m\pi^2\hbar^3} \int_0^{p_F} dp p^4 = \frac{V p_F^5}{10m\pi^2\hbar^3} \quad (4.49)$$

or, taking into account (4.43)

$$E = \frac{3(3\pi^2)^{2/3}}{10} \frac{\hbar^2}{m} \left(\frac{N}{V} \right)^{2/3} N \quad (4.50)$$

Using the general expression (4.34) we can find the equation of state of completely degenerate gas:

$$P = \frac{(3\pi^2)^{2/3} \hbar^2}{5} \frac{1}{m} \left(\frac{N}{V} \right)^{5/3} \quad (4.51)$$

so that at $T = 0$ the pressure of Fermi gas is $\sim (N/V)^{5/3}$.

In fact all the previous expressions are applicable also for finite but low enough temperatures $T \ll \varepsilon_F$. Corresponding temperature corrections are of the order of $(T/\varepsilon_F)^2$. Fermi temperature (degeneracy temperature) $T_F \approx \varepsilon_F$ for the gas of electrons with density $N/V \sim 10^{22} \text{cm}^{-3}$, typical for metals, and mass $m \sim m_e$, where m_e is the mass of a free electron⁵, can be estimated to be in the interval of $10^4 - 10^5 K$. Thus, electron gas in metals under normal conditions is always strongly degenerate. In semiconductors, where electron density may change in rather wide limits, it is not generally so. Quite often the statistics of current carriers these may be Boltzmannian.

To conclude this paragraph, let us make some remarks on the role of interelectron interactions. Degenerate electron gas becomes more “ideal” with the growth of its density. Characteristic kinetic energy of electrons is of the order of Fermi energy: $\varepsilon_F \sim \frac{\hbar^2}{m} (N/V)^{2/3} \sim \frac{\hbar^2}{ma^2}$, where a is interelectron distance (in metals it is practically the same as interatomic distance). At the same time characteristic Coulomb repulsion energy $U \sim \frac{e^2}{a}$. Then the dimensionless parameter of perturbation theory over interaction is given by the ratio $\frac{U}{\varepsilon_F} \sim \frac{e^2}{\hbar} \frac{ma}{\hbar} \sim \frac{e^2}{\hbar} \frac{m}{p_F} = \frac{e^2}{\hbar v_F}$, where we have introduced the velocity of electrons on the Fermi surface (Fermi level) $v_F = p_F/m$. Now we see that the smaller is a (i.e. for higher densities or Fermi velocity) the smaller is this parameter and interaction effects become weaker. Remember now, that the fine structure constant $\frac{e^2}{\hbar c} \approx \frac{1}{137} \sim 10^{-2}$, where $c \approx 3 \cdot 10^{10} \text{cm/sec}$ is velocity of light in vacuum. In metals (for typical electron densities) it is easy to estimate that $v_F \sim 10^8 \text{cm/sec}$. Thus, in real metals perturbation theory parameter is not small: $\frac{e^2}{\hbar v_F} \sim 1!$ Only for electron densities much larger than typical densities in metals electron gas can be considered as nearly free (ideal) gas. So the question arises — why the nearly free electrons picture is so good to describe many of electronic properties of metals? The complete solution of this problem is achieved only within the *Fermi-liquid* theory, which will be briefly discussed later.

4.6 Relativistic degenerate electron gas*

Compression of electron gas leads to the growth of the average electron energy (and Fermi energy ε_F) and sooner or later it becomes comparable to the rest energy mc^2 and even higher. In this situation relativistic effects become important. Let us consider the degenerate ultra relativistic gas with particle energies much greater than mc^2 . In this case energy spectrum of electrons can be written as:

$$\varepsilon_p = \sqrt{c^2 p^2 + m^2 c^4} \approx cp. \quad (4.52)$$

⁵Note that in real metals the mass of an electron is not necessarily equal to the mass of free electron in vacuum.

For the number of quantum states and Fermi momentum the previous expression remain valid:

$$2 \frac{4\pi p^2 dp V}{(2\pi\hbar)^3}. \quad (4.53)$$

$$N = \frac{V}{\pi^2 \hbar^3} \int_0^{p_F} p^2 dp = \frac{V p_F^3}{3\pi^2 \hbar^3}. \quad (4.54)$$

$$p_F = (3\pi^2)^{1/3} \left(\frac{N}{V} \right)^{1/3} \quad (4.55)$$

However, for Fermi energy we have quite new expression:

$$\varepsilon_F = cp_F = (3\pi^2)^{1/3} \hbar c \left(\frac{N}{V} \right)^{1/3} \quad (4.56)$$

Correspondingly, the total energy of the gas is:

$$E = \frac{cV}{\pi^2 \hbar^3} \int_0^{p_F} dp p^3 = V \frac{c p_F^4}{4\pi^2 \hbar^3} \quad (4.57)$$

or

$$E = \frac{3(3\pi^2)^{1/3}}{4} \hbar c N \left(\frac{N}{V} \right)^{1/3} \quad (4.58)$$

Pressure is obtained by differentiation this expression over volume:

$$P = \frac{E}{3V} = \frac{(3\pi^2)^{1/3}}{4} \hbar c \left(\frac{N}{V} \right)^{4/3} \quad (4.59)$$

and is proportional to power 4/3 of density.

The relation

$$PV = \frac{E}{3} \quad (4.60)$$

is valid for ultra relativistic gas not only at absolute zero $T = 0$, but for arbitrary temperatures. This can be seen as follows. Using $\varepsilon_p = cp$ in Eq. (4.6), and going from summation over momenta to integration over energy, we get:

$$\Omega = -\frac{TV}{\pi^2 c^3 \hbar^3} \int_0^\infty d\varepsilon \ln \left(1 + e^{\frac{\mu - \varepsilon}{T}} \right) \quad (4.61)$$

and after partial integration:

$$\Omega = -PV = -\frac{V}{3\pi^2 c^3 \hbar^3} \int_0^\infty d\varepsilon \frac{\varepsilon^3}{e^{\frac{\varepsilon - \mu}{T}} + 1} \quad (4.62)$$

which reduces to finite temperature variant of Eq. (4.60) Note that the pressure obtained from Eq. (4.60) is in fact the highest pressure, which can exist in any macroscopic system [6].

4.7 Specific heat of degenerate electron gas.

At finite temperatures “Fermi step” is smeared in the interval of the order of $\sim T$. All expressions derived above for $T = 0$ are zeroth order terms of expansion in powers of small (at low temperatures) parameter T/ε_F . Let us find corresponding first order corrections. Thermodynamic potential of electron gas, according to (4.32), can be written as:

$$\Omega = -\frac{4}{3} \frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\frac{\varepsilon-\mu}{T}} + 1} \quad (4.63)$$

Consider the general integral containing Fermi distribution function:

$$I = \int_0^\infty d\varepsilon \frac{f(\varepsilon)}{e^{\frac{\varepsilon-\mu}{T}} + 1} \quad (4.64)$$

where $f(\varepsilon)$ is some function (the only limitation is that the integral converges). Eq.(4.63) is the specific case of $f(\varepsilon) = \varepsilon^{3/2}$. For the integral (4.64) the following expansion can be derived [1, 2]:

$$I \approx \int_0^\mu d\varepsilon f(\varepsilon) + \frac{\pi^2}{6} T^2 f'(\mu) + \frac{7\pi^4}{360} T^4 f'''(\mu) + \dots \quad (4.65)$$

which in fact determines the expansion of all physical characteristics of the form of Eq. (4.63) in powers of the small parameter T/ε_F .

Taking here $f(\varepsilon) = \varepsilon^{3/2}$ we write (4.63) as:

$$\Omega = \Omega_0 - VT^2 \frac{\sqrt{2\mu}m^{3/2}}{6\hbar^3} \quad (4.66)$$

where the first term gives the $T = 0$ contribution. Considering the second term as a small correction to Ω_0 and expressing μ via N and V using the zero-order approximation (4.48) $\mu = \varepsilon_F = (3\pi^2)^{2/3} \frac{\hbar^2}{2m} (N/V)^{2/3}$, we can write directly the expression for the free energy⁶:

$$F = F_0 - \frac{B}{2} NT^2 \left(\frac{V}{N} \right)^{2/3} \quad (4.67)$$

where we have introduced the notation $B = (\pi/3)^{2/3} m/\hbar^2$. From this we find the entropy:

$$S = BNT \left(\frac{V}{N} \right)^{2/3} \quad (4.68)$$

and specific heat:

$$C = T \frac{\partial S}{\partial T} = BNT \left(\frac{V}{N} \right)^{2/3}, \quad (4.69)$$

We see that specific heat of degenerate Fermi gas at low temperatures is linear function of temperature (Pauli specific heat). Using the expression for the density of states (4.28) with $g = 2$ (for electrons), we can easily see that Eq. (4.69) can be rewritten as:

$$C = \frac{\pi^2}{3} \nu_F T \quad (4.70)$$

⁶Here we use once again the theorem on small corrections to thermodynamic potentials: $(\delta\Omega)_{T,V,\mu} = (\delta F)_{T,V,N} = (\delta\Phi)_{T,P,N} = (\delta E)_{S,V,N} = (\delta W)_{S,P,N}$

where we have introduced the density of electronic states at the Fermi surface:

$$\nu_F = \mathcal{N}(\varepsilon = \varepsilon_F) = \frac{mp_F}{\pi^2 \hbar^3} V \quad (4.71)$$

This is not a simple coincidence. Eq. (4.71) is rather simply interpreted in the following way. We have seen that in degenerate Fermi gas finite temperatures disturb only a narrow energy layer $\sim T$ around the Fermi level. The number of electrons in this layer $\delta N \sim \nu_F T$. Rising temperature by δT leads to the change of the energy of each of these electrons by $\sim \delta T$. Then the total energy change of the gas is $\delta E \sim \nu_F T \delta T$, and specific heat is $C = \delta E / \delta T = \nu_F T$. This elementary interpretation solves the problem of contradiction of classical equipartition law and Nernst theorem. For $T \rightarrow 0$ not all electrons participate in thermal processes, but only those belonging to a narrow energy layer $\sim T$ close to Fermi level, and the number of such electron tends to zero as $T \rightarrow 0$. The final result (4.70) for specific heat is very important. In fact it provides one of experimental methods of determination of the density of states at the Fermi level of metals from measurements of electron contribution to specific heat. In the simplest case of metals with spherical Fermi surface, when Eq. (4.71) is valid, this allows also experimental determination of the mass of conduction electrons in metal, which in general case does not coincide with that of free electron.

For completeness, let us write down an expression for the total energy of degenerate Fermi gas:

$$E = E_0 + \frac{B}{2} NT^2 \left(\frac{V}{N} \right)^{2/3} = E_0 \left[1 + 0.18 \left(\frac{mT}{\hbar^2} \right)^2 \left(\frac{V}{N} \right)^{4/3} \right] \quad (4.72)$$

where E_0 is given by Eq. (4.49). From this expression it is easily seen that the relative temperature correction to energy is small by parameter $(T/\varepsilon_F)^2$. Specific heat calculated from $C = \frac{\partial E}{\partial T}$ obviously gives the previous result (4.69).

4.8 Magnetism of electron gas in weak fields.

Magnetization of electron gas in weak (external) magnetic fields consists of two contributions: *paramagnetic* magnetization, connected with spin magnetic moment of an electron (Pauli) and *diamagnetic* magnetization, connected with quantization of orbital motion of an electron in magnetic field (Landau).

Below we shall analyze only the case of degenerate electron gas: $T \ll \varepsilon_F$. Magnetic field is considered as weak if $\mu_B H \ll T$, where $\mu_B = \frac{|e|\hbar}{2mc}$ is Bohr magneton.

Calculations can be conveniently done using thermodynamic potential Ω , depending on variables T, V, μ . Then the magnetic moment of the system is defined as:

$$\mathbf{M} = - \left(\frac{\partial \Omega}{\partial \mathbf{H}} \right)_{T, V, \mu} \quad (4.73)$$

Let us start with paramagnetic part of magnetization. Additional energy of electron due to spin interaction with magnetic field is given by $\pm \mu_B H$, for two spin projections $\mp 1/2$. Accordingly, in external field electron energy $\varepsilon_p = p^2/2m$ is replaced by $\varepsilon_{p\mp} = p^2/2m \pm \mu_B H$. As ε always enters Fermi distribution

function in combination $\varepsilon - \mu$, the statement equivalent to the previous one is that we have just to make the replacement $\mu \rightarrow \mu \mp \mu_B H$ in all expressions. Thus, for thermodynamic potential Ω in magnetic field we can write:

$$\Omega(\mu) = \frac{1}{2}\Omega_0(\mu + \mu_B H) + \frac{1}{2}\Omega_0(\mu - \mu_B H) \quad (4.74)$$

where $\Omega_0(\mu)$ is thermodynamic potential in the absence of magnetic field. The factor of $1/2$ is introduced here to account for the change of the number of quantum states for fixed spin projection.

Expanding (4.74) in powers of H we obtain (terms of the first order, obviously cancel each other):

$$\Omega(\mu) = \Omega_0(\mu) + \frac{1}{2}\mu_B^2 H^2 \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2} \quad (4.75)$$

Now we get the magnetic moment (4.73) as:

$$\mathbf{M} = -\mu_B^2 \mathbf{H} \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2} \quad (4.76)$$

Taking into account that $\frac{\partial \Omega_0}{\partial \mu} = -N$ we get paramagnetic susceptibility (per volume of the gas):

$$\chi_p = -\frac{\mu_B^2}{V} \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2} = \frac{\mu_B^2}{V} \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \quad (4.77)$$

Neglecting small (for $T \ll \varepsilon_F$) temperature effects, i.e. considering gas as completely degenerate, we have $\mu = \varepsilon_F = (3\pi^2)^{2/3} \frac{\hbar^2}{2m} (N/V)^{2/3}$, and:

$$N = V \frac{(2m\mu)^{3/2}}{3\pi^2 \hbar^3} \quad (4.78)$$

which after differentiation in (4.77) reduces to:

$$\chi_p = \frac{\mu_B^2 (2m)^{3/2} \sqrt{\mu}}{2\pi^2 \hbar^3} = \frac{\mu_B^2 m p_F}{\pi^2 \hbar^3} \equiv \mu_B^2 \nu_F \quad (4.79)$$

which is called Pauli paramagnetic susceptibility. Thus, paramagnetic susceptibility of degenerate electron gas is independent of temperature (for $T \ll \varepsilon_F$) and is proportional to electron density of states at the Fermi level. This due to a simple fact – external magnetic field leads to difference between the numbers of electrons with spin oriented along and opposite to the direction of magnetic field: $N_\uparrow - N_\downarrow \sim \nu_F \mu_B H$, which leads to the appearance of magnetization along the field $M = \mu_B (N_\uparrow - N_\downarrow) \sim \mu_B^2 \nu_F H$, which gives the susceptibility (4.79)⁷.

Let us turn now to calculations of diamagnetic part of susceptibility connected with orbital motion of electrons. Energy of orbital motion of an electron in magnetic field is determined by Landau levels [5]:

$$\varepsilon_{n,p_z} = \hbar\omega_c \left(n + \frac{1}{2} \right) + \frac{p_z^2}{2m} = (2n+1)\mu_B H + \frac{p_z^2}{2m} \quad (4.80)$$

⁷There are experimental methods allowing direct measurements of only paramagnetic part of magnetization (susceptibility) in metals (e.g. Knight shift measurements in NMR), providing information on the value of the density of states, alongside with measurements of electron contribution to specific heat.

where $\omega_c = \frac{|e|H}{mc}$ is cyclotron frequency, $n = 0, 1, 2, \dots$, p_z is momentum projection on magnetic field direction. The number of states in the interval dp_z at fixed n is given by [5]:

$$2 \frac{V|e|H}{(2\pi\hbar)^2 c} dp_z \quad (4.81)$$

Then, from Eq. (4.6) we get:

$$\Omega = -T \sum_{n=0}^{\infty} 2 \frac{V|e|H}{(2\pi\hbar)^2 c} \int_{-\infty}^{\infty} dp_z \ln \left[1 + \exp \left(\frac{\mu - (n + 1/2)\hbar\omega_c - p_z^2/2m}{T} \right) \right] \quad (4.82)$$

or

$$\Omega = 2\mu_B H \sum_{n=0}^{\infty} f[\mu - (2n + 1)\mu_B H] \quad (4.83)$$

where

$$f(\mu) = -\frac{TmV}{2\pi\hbar^3} \int_{-\infty}^{\infty} dp_z \ln \left[1 + \exp \left(\frac{\mu}{T} - \frac{p_z^2}{2m} \right) \right] \quad (4.84)$$

Summation over n can be performed using the following formula [1, 2]:

$$\sum_{n=0}^{\infty} F(n + \frac{1}{2}) \approx \int_0^{\infty} dx F(x) + \frac{1}{24} F'(0) \quad (4.85)$$

This expression is valid in case of small relative change of F during the single step $n \rightarrow n + 1$. In our case this condition reduces to $\mu_B H \ll T$.

Applying (4.85) to (4.83) and (4.84) we obtain:

$$\begin{aligned} \Omega &= 2\mu_B H \int_0^{\infty} dx f(\mu - 2\mu_B Hx) + \frac{2\mu_B H}{24} \frac{\partial f(\mu - 2n\mu_B H)}{\partial n} \Big|_{n=0} = \\ &= \int_{-\infty}^{\mu} dx f(x) - \frac{(2\mu_B H)^2}{24} \frac{\partial f(\mu)}{\partial \mu} \end{aligned} \quad (4.86)$$

The first term here does not contain H and reduces to $\Omega_0(\mu)$ in the absence of magnetic field. Thus:

$$\Omega = \Omega_0(\mu) - \frac{1}{6} \mu_B^2 H^2 \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2} \quad (4.87)$$

and similarly to paramagnetic case we find diamagnetic susceptibility as:

$$\chi_d = \frac{\mu_B^2}{3V} \frac{\partial^2 \Omega_0(\mu)}{\partial \mu^2} = -\frac{1}{3} \chi_p \quad (4.88)$$

where the last equality was obtained by comparison with (4.77). We see that diamagnetic susceptibility (Landau diamagnetism) of electron gas is equal to 1/3 of paramagnetic susceptibility (Pauli paramagnetism) and opposite in sign. The sum of both contributions is positive, so that electron gas is paramagnetic and its total magnetic susceptibility is equal to:

$$\chi = \chi_p + \chi_d = \frac{2}{3} \chi_p. \quad (4.89)$$

However, it should be noted that these relations between χ_p and χ_d are valid only for the simplest model of free electrons. In real metals the form of electron spectrum may be quite different from that of free electrons, so that these relations may be significantly changed. Due to this problem, during the discussion of real experiments on magnetic susceptibility of metals, we are always dealing with complicated problem of separation of paramagnetic and diamagnetic contributions.

Obviously, the total susceptibility can be calculated directly from the single expression, writing the energy levels as $\varepsilon_{n,p_z,\pm} = (2n+1)\mu_B H + p_z^2/2m \mp \mu_B H$, i.e. including spin splitting into Landau spectrum. This set of levels can be rewritten as: $\varepsilon_{n,p_z} = 2n\mu_B H + p_z^2/2m$ ($n = 0, 1, 2, \dots$), where each value of $n \neq 0$ enters twice, while $n = 0$ enters only once. Similarly to the previous analysis we can easily obtain:

$$\Omega = 2\mu_B H \left\{ \frac{1}{2}f(\mu) + \sum_{n=1}^{\infty} f(\mu - 2\mu_B H n) \right\} \quad (4.90)$$

and perform summation using [1, 2]:

$$\frac{1}{2}F(0) + \sum_{n=1}^{\infty} F(n) = \int_0^{\infty} dx F(x) - \frac{1}{12}F'(0) \quad (4.91)$$

Direct calculations lead to the total susceptibility given by Eq. (4.89).

4.9 Magnetism of electron gas in high fields*.

Consider now the case of so called quantizing magnetic field when

$$T < \mu_B H = \hbar\omega_c \ll \varepsilon_F = \mu \quad (4.92)$$

Under these conditions it is important to take into account the discrete nature of Landau levels, corresponding to electron motion in the plane orthogonal to magnetic field⁸. Now we can not separate orbital and spin effects so that during the calculations it is more convenient to use the general expression (4.90). As will be shown below, for $\hbar\omega_c = \mu_B H > T$ magnetization of electron gas contains *oscillating* (as a function of H) part, and the amplitude of these oscillations is not small. We shall drop some details of calculations, which can be found in Refs. [1, 2].

While calculating (4.90) under conditions of (4.92), we can not use simple summation formulas like (4.91), as the function summed may change rather sharply during the transition from n to $n+1$. Standard approach here is to use

⁸In classical approximation this motion is a simple cyclotron rotation of an electron around the field direction with angular frequency ω_c . In quantum case this rotation is described as quantum oscillator with the same frequency, which leads to the appearance of the first (oscillator like) term in Landau spectrum (4.80). The second term in (4.80) corresponds to free electron motion along field direction.

Poisson summation formula⁹:

$$\frac{1}{2}F(0) + \sum_{n=1}^{\infty} F(n) = \int_0^{\infty} dx F(x) + 2\text{Re} \sum_{k=1}^{\infty} \int_0^{\infty} dx e^{2\pi i k x} F(x) \quad (4.93)$$

Then (4.91) can be written as:

$$\Omega = \Omega_0(\mu) + \frac{TmV}{\pi^2 \hbar^3} \text{Re} \sum_{k=1}^{\infty} I_k \quad (4.94)$$

where

$$I_k = -2\mu_B H \int_{-\infty}^{\infty} dp_z \int_0^{\infty} dx e^{2\pi i k x} \ln \left[1 + \exp \left(\frac{\mu}{T} - \frac{p_z^2}{2mT} - \frac{2x\mu_B H}{T} \right) \right] \quad (4.95)$$

We are only interested in oscillating (with the change of magnetic field) part of integrals, which will be denoted as \tilde{I}_k . After appropriate change of variables in (4.95) we obtain:

$$\tilde{I}_k = - \int_{-\infty}^{\infty} dp_z \int_0^{\infty} d\varepsilon \ln \left[1 + \exp \left(\frac{\mu - \varepsilon}{T} \right) \right] \exp \left(\frac{i\pi k \varepsilon}{\mu_B H} \right) \exp \left(-\frac{i\pi k p_z}{2m\mu_B H} \right). \quad (4.96)$$

Integral over p_z can be calculated explicitly [1, 2], so that:

$$\tilde{I}_k = -e^{-i\frac{\pi}{4}} \sqrt{\frac{2m\mu_B H}{k}} \int_0^{\infty} d\varepsilon e^{\frac{i\pi k \varepsilon}{\mu_B H}} \ln \left[1 + e^{\frac{\mu - \varepsilon}{T}} \right]. \quad (4.97)$$

Here we can twice perform partial integration and transform to variable $\xi = (\varepsilon - \mu)/T$. Dropping non oscillating part, we can write [1, 2]:

$$\tilde{I}_k = \frac{\sqrt{2m}(\mu_B H)^{5/2}}{T\pi^2 k^{5/2}} \exp \left(\frac{i\pi k \mu}{\mu_B H} - \frac{i\pi}{4} \right) \int_{-\infty}^{\infty} d\xi \frac{e^{\xi}}{(e^{\xi} + 1)^2} \exp \left(\frac{i\pi k T}{\mu_B H} \xi \right). \quad (4.98)$$

For $\mu_B H > T$ the main contribution to the remaining integral comes from the region of $\xi \sim 1$, i.e. the vicinity of the Fermi level $\varepsilon - \mu \sim T$, which allows to extend integration to infinity. Practically, the integral is calculated using the formula [1, 2]:

$$\int_{-\infty}^{\infty} d\xi e^{i\alpha \xi} \frac{e^{\xi}}{(e^{\xi} + 1)^2} = \frac{\pi \alpha}{sh(\pi \alpha)}. \quad (4.99)$$

Finally we obtain for oscillating part of Ω potential:

$$\tilde{\Omega} = \frac{\sqrt{2}(m\mu_B H)^{3/2}TV}{\pi^2 \hbar^3} \sum_{k=1}^{\infty} \frac{\cos \left(\frac{\pi \mu}{\mu_B H} k - \frac{\pi}{4} \right)}{k^{3/2} sh \left(\frac{\pi^2 k T}{\mu_B H} \right)}. \quad (4.100)$$

⁹Poisson formula is obtained from the equality: $\sum_{n=-\infty}^{\infty} \delta(x-n) = \sum_{k=-\infty}^{\infty} e^{2\pi i k x}$. The sum of δ -functions in the left hand side is periodic function with period 1, while the sum in the right hand side is Fourier expansion of this function. Multiplying this equality by arbitrary function $F(x)$ and integrating over x from 0 to ∞ , we obtain Poisson formula. We only have to take into account that the term of the sum, corresponding to $n = 0$, is equal to $\int_0^{\infty} dx F(x) \delta(x) = F(0)/2$.

Calculating the magnetic moment as derivative of (4.100) by magnetic field, we have to differentiate only most oscillating factors of cos in numerators of the terms of the sum. This gives Landau result:

$$\tilde{M} = -\frac{\sqrt{2\mu_B}m^{3/2}\mu TV}{\pi\hbar^3\sqrt{H}} \sum_{k=1}^{\infty} \frac{\sin\left(\frac{\pi\mu}{\mu_B H}k - \frac{\pi}{4}\right)}{\sqrt{k}sh\left(\frac{\pi^2 k T}{\mu_B H}\right)}. \quad (4.101)$$

This expression is oscillating with periodicity in inverse magnetic field $1/H$. Period over $1/H$ is given by:

$$\Delta\left(\frac{1}{H}\right) = \frac{2\mu_B}{\mu} \quad (4.102)$$

and is independent of temperature. Here we have $\Delta(1/H)H \sim \mu_B H/\mu \ll 1$, so that oscillations are of high “frequency”. Such oscillations of magnetic moment in external magnetic field are observed in metals at low enough temperatures and “clean” enough samples, and are called de Haas–van Alphen effect. For $\mu_B H \sim T$ the amplitude of oscillating magnetic moment is given by $\tilde{M} \sim V\mu H^{1/2}(m\mu_B)^{3/2}\hbar^{-3}$. Monotonous part of magnetization M is determined by susceptibility (4.89) calculated above, so that $M \sim V\mu^{1/2}Hm^{3/2}\mu_B^2\hbar^{-3}$. Then $\tilde{M}/M \sim (\mu/\mu_B H)^{1/2} \gg 1$ and the amplitude of oscillating part is *large* in comparison to monotonous part. For $\mu_B H \ll T$ this amplitude drops exponentially as $\exp(-\pi^2 T/\mu_B H)$ and becomes negligible.

Expression (4.102) for the period of oscillations can be rewritten as:

$$\Delta\left(\frac{1}{H}\right) = \frac{|e|\hbar}{mc} \frac{1}{\varepsilon_F} = \frac{2|e|\hbar}{c} \frac{\pi}{\pi p_F^2} = \frac{2\pi|e|\hbar}{cS_F} \quad (4.103)$$

where $S_F = \pi p_F^2$ is an area of the maximal “crosssection” of the spherical Fermi surface of free electrons. It turns out that this last expression is also valid for metals with arbitrary Fermi surfaces if S_F is understood as an area of any extremal crosssection of Fermi surface with complicated topology [19]. In real case there may be several such crosssections, so that there appear several periods of de Haas — van Alphen oscillations. Experimental study of these oscillations allows to determine extremal crosssections of the Fermi surface of a real metal, which helps in determining its form and topology.

De Haas — van Alphen effect is first of the number of oscillatory effects in metals in quantizing magnetic fields at low temperatures, e.g. there are similar oscillations of electrical resistivity (Shubnikov — de Haas effect). All of these effects are related to Landau quantization of electron spectrum in magnetic field (4.80), and “passing” of discrete Landau levels (of transverse motion of electrons) through the Fermi level with the change of external magnetic field [19]. Experimental observation of these effects is the powerful method to study the geometry of Fermi surfaces in real metals.

4.10 Degenerate Bose gas.

At low temperatures the properties of Bose gas are radically different from the properties of Fermi gas. At $T = 0$ *all* particles of Bose gas occupy the state

with lowest energy (ground state) $\varepsilon = 0$, there is no limitations due to Pauli exclusion principle. Let us consider the equation for total number of particles, determining the chemical potential (4.30) for Bose case:

$$\frac{N}{V} = \frac{g(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty dz \frac{\sqrt{z}}{e^{z-\frac{\mu}{T}} - 1} \quad (4.104)$$

If for fixed density N/V of the gas we start lowering the temperature Eq. (4.104) immediately shows, that chemical potential μ drops in absolute value, remaining negative (in accordance with general requirements of Bose statistics). However, μ can become zero at some *finite* temperature, which is defined by the relation:

$$\frac{N}{V} = \frac{g(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty dz \frac{\sqrt{z}}{e^z - 1} \quad (4.105)$$

The integral here is just a dimensionless constant ≈ 2.315 . Then, solving Eq. (4.105) with respect to T , we obtain characteristic temperature T_0 ¹⁰:

$$T_0 = \frac{3.31}{g^{2/3}} \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{2/3} \quad (4.106)$$

which is called the temperature of *Bose condensation*. The physical meaning of this term, as well as of physical effects appearing below this temperature can be understood from the following arguments. For $T < T_0$ Eq. (4.105) does not give negative solutions for μ , while in Bose statistics chemical potential must be, as was shown above, negative for all temperatures. This contradiction appears because under this conditions we can not use the standard transformation from summation over quantum states in Eq. (4.11) to integration over continuous variable (energy) in Eqs. (4.30), (4.104). In fact, during such transformation the first term in the sum over k in Eq. (4.11), corresponding to energy level $\varepsilon_k = 0$, is multiplied by $\sqrt{\varepsilon} = 0$ (Cf. expression for the density of states (4.28)) and just drops out. But in reality, at T Bose particles will tend to occupy precisely this lowest energy state, until $T = 0$, when all of them will “condense” in this ground state.

Thus, in reality the physical behavior at temperatures $T < T_0$ is as follows. Particles with energy $\varepsilon > 0$ are distributed according to ($\mu = 0!$):

$$dN_\varepsilon = \frac{gm^{3/2}V}{\sqrt{2}\pi^2\hbar^3} \frac{\sqrt{\varepsilon}d\varepsilon}{e^{\frac{\varepsilon}{T}} - 1} \quad (4.107)$$

Accordingly, the total number of particles with energies $\varepsilon > 0$ is equal to:

$$N_{\varepsilon>0} = \int dN_\varepsilon = \frac{gV(mT)^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty dz \frac{\sqrt{z}}{e^z - 1} = N \left(\frac{T}{T_0}\right)^{3/2} \quad (4.108)$$

The remaining

$$N_{\varepsilon=0} = N \left[1 - \left(\frac{T}{T_0}\right)^{3/2} \right] \quad (4.109)$$

¹⁰Note that, similarly to Fermi temperature, this expression is of the order of temperature of gas degeneracy (3.79).

particles are already in the state with lowest energy $\varepsilon = 0$. This effect of *macroscopic* number of particles being “condensed” in the ground state is called *Bose condensation*. Let us stress that we are speaking here about “condensation” of particles in momentum space (at $p = 0$), which has nothing to do with the usual gas condensation in real (coordinate) space. Particles in Bose condensate form a macroscopic quantum state with very peculiar properties.

The total energy of the gas at $T < T_0$ is determined by particles with $\varepsilon > 0$ (Cf. Eq. (4.33) written for $\mu = 0$):

$$E = \frac{gV(mT)^{3/2}T}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty dz \frac{z^{3/2}}{e^z - 1} \approx 0.770NT \left(\frac{T}{T_0}\right)^{3/2} = 0.128g \frac{m^{3/2}T^{5/2}}{\hbar^3} V \quad (4.110)$$

Then we obtain specific heat as:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = \frac{5E}{2T} \sim T^{3/2} \quad (4.111)$$

Integrating specific heat we find entropy:

$$S = \int_0^T \frac{C_v}{T} dT = \frac{5E}{3T} \quad (4.112)$$

and free energy $F = E - TS$:

$$F = -\frac{2}{3}E \quad (4.113)$$

For gas pressure we obtain:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \approx 0.0851g \frac{m^{3/2}T^{5/2}}{\hbar^3} \quad (4.114)$$

At $T = T_0$ all physical characteristics discussed here are continuous, but it can be shown that the derivative of specific heat over T has a finite discontinuity (jump) jumps at this point [1, 2]. In this sense, the point of Bose condensation, in fact, is a point of some kind of phase transition. Note however, that the properties of this transition essentially depend on interaction between particles of the gas, which is neglected here.

During many years the phenomenon of Bose condensation in gases remained just a theoretical result, though its importance was clearly understood, and Bose condensation was in fact observed in such phenomena as superfluidity and superconductivity in condensed matter (where interactions are of prime importance). These will be discussed later, but in recent years Bose condensation was directly observed in unique experiments with ultra cold gases of alkali metals (at temperatures $\sim 10^{-7}K$ in special magnetic traps). These systems apparently are well described by the model of nearly free (ideal) Bose gas, though interactions there are also quite important for the explanation of numerous effects. These studies are at present at the center of interests of modern physics of many particle systems [20].

4.11 Statistics of photons.

Most important physical object to study with Bose statistics is electromagnetic radiation at thermodynamic equilibrium (for historic reasons called also “black

body” radiation), i.e. gas of photons. Linearity of equations of electrodynamics leads to validity of superposition principle, i.e. the absence of interactions between photons — they form an ideal gas! Spin of photons $s = 1$, so this is the Bose gas. In fact, to achieve thermodynamic equilibrium we have always to assume the existence of some small interaction of photons with matter. The mechanism of this interaction consists of absorption and emission of photons by matter¹¹. This leads to an important peculiarity of photon gas: the number of particles (photons) N is not conserved and should be determined from conditions of thermodynamic equilibrium. Requiring the minimum of free energy (at fixed T and V), we obtain the condition: $(\frac{\partial F}{\partial N})_{T,V} = \mu = 0$, so that the chemical potential of photon gas is zero:

$$\mu = 0. \quad (4.115)$$

Distribution function of photons over the states with definite momenta $\hbar\mathbf{k}$ and energy $\hbar\omega = \hbar ck$ (and definite polarizations – spin projections of photons) is given by Bose distribution with $\mu = 0$:

$$n_k = \frac{1}{e^{\frac{\hbar\omega}{T}} - 1} \quad (4.116)$$

which is called Planck distribution.

Assuming the volume V to be big enough, we can as usual transform from discrete to continuous distribution of photon eigenstates. The number of field oscillators with components of wave vector \mathbf{k} in intervals $d^3k = dk_x dk_y dk_z$ is equal to $V \frac{d^3k}{(2\pi)^3}$ [6]. Then, the number of oscillators with absolute value of wave vector in interval $k, k + dk$ is given by:

$$\frac{V}{(2\pi)^3} 4\pi k^2 dk. \quad (4.117)$$

Using $\omega = ck$ and multiplying by 2 (there are two independent directions of polarization), we obtain the number of quantum states of photons with frequencies in the interval $\omega, \omega + d\omega$ as:

$$\frac{V\omega^2 d\omega}{\pi^2 c^3}. \quad (4.118)$$

then the number of photons in this frequency interval is:

$$dN_\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2 d\omega}{e^{\frac{\hbar\omega}{T}} - 1} \quad (4.119)$$

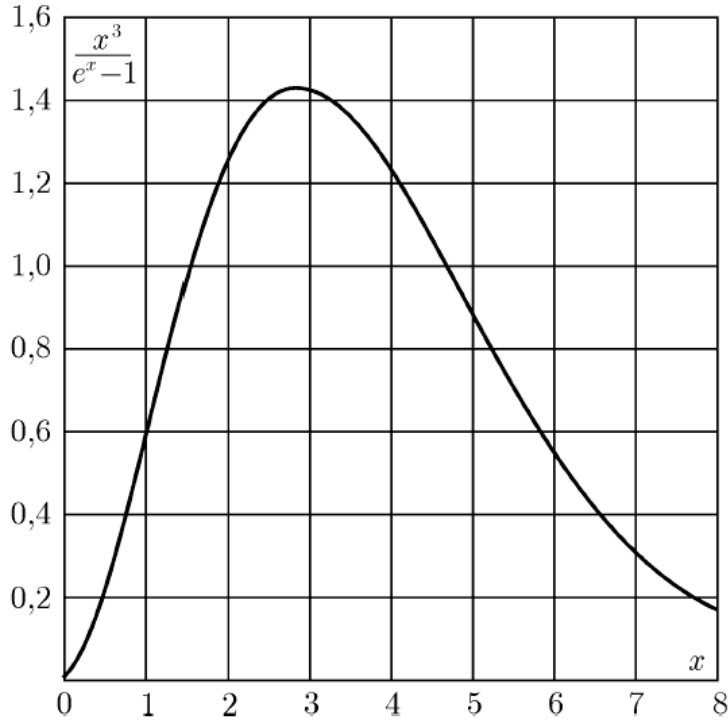
Multiplying by $\hbar\omega$ we obtain energy contained in this part of the spectrum:

$$dE_\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\frac{\hbar\omega}{T}} - 1} \quad (4.120)$$

which is Planck law. Corresponding graph is presented in Fig.4-2. Expressing everything via wavelength $\lambda = \frac{2\pi c}{\omega}$, we have:

$$dE_\lambda = \frac{16\pi^2 \hbar c V}{\lambda^5} \frac{d\lambda}{e^{\frac{2\pi\hbar c}{T\lambda}} - 1}. \quad (4.121)$$

¹¹Good example of such a system is the so called “relict” radiation in the Universe, remaining since the “Big Bang” all over the Space.

Figure 4.2: Planck function $\frac{x^3}{e^x-1}$; $x = \frac{\hbar\omega}{T}$.

For small frequencies $\hbar\omega \ll T$ from (4.120) we obtain Rayleigh – Jeans law:

$$dE_\omega = V \frac{T}{\pi^2 c^3} \omega^2 d\omega \quad (4.122)$$

Here is no dependence on \hbar , as this is a classical limit, and this result can be obtained by multiplying (4.118) by T , i.e. applying equipartition law to each of the field oscillators¹². In the inverse limit of $\hbar\omega \gg T$ (quantum limit) from (4.120) we get Wien’s formula:

$$dE_\omega = V \frac{\hbar}{\pi^2 c^3} \omega^3 e^{-\frac{\hbar\omega}{T}} d\omega \quad (4.123)$$

Spectral density of energy distribution of photon gas $dE_\omega/d\omega$ has a maximum at $\omega = \omega_m$, defined by condition:

$$\frac{\hbar\omega_m}{T} \approx 2.822 \quad (4.124)$$

Thus, increase of temperature leads to the shift of the maximum of energy distribution to higher energies (frequencies) proportionally to T (Wien’s displacement law)¹³.

¹²It is easy to see that the integral (4.122) over all possible frequencies diverges, so that the energy of photon gas becomes infinite. This is so called “ultraviolet catastrophe”, which historically was one of the strong indications of shortcomings of classical theory, leading Planck to introduction of the quanta. Note that Planck suggested his formula (4.120) as a simplest interpolation between (4.122) and experimentally discovered law (4.123).

¹³For cosmological “relict” radiation this maximum corresponds to $T \approx 3K$.

Let us calculate thermodynamic properties of photon gas. For $\mu = 0$ the free energy $F = \Phi - PV = N\mu + \Omega$. Then, putting $\mu = 0$ and transforming from summation over k to integration over ω in (4.12), we obtain:

$$F = T \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \omega^2 \ln \left(1 - e^{-\frac{\hbar\omega}{T}} \right) \quad (4.125)$$

Introducing $x = \hbar\omega/T$ and performing partial integration, we get:

$$F = -V \frac{T^4}{3\pi^2 \hbar^3 c^3} \int_0^\infty dx \frac{x^3}{e^x - 1}. \quad (4.126)$$

The integral here is equal to $\pi^4/15$ [1, 2], so that:

$$F = -V \frac{\pi^2 T^4}{45(\hbar c)^3} = -\frac{4\sigma}{3c} VT^4 \quad (4.127)$$

where the coefficient σ (Stefan – Boltzmann constant) is equal to:

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} \quad (4.128)$$

if we measure the temperature T in absolute degrees. The entropy of photon gas:

$$S = -\frac{\partial F}{\partial T} = \frac{16\sigma}{3c} VT^3. \quad (4.129)$$

The total energy of radiation:

$$E = F + TS = \frac{4\sigma}{c} VT^4 = -3F \quad (4.130)$$

which is Boltzmann's law. Specific heat of photon gas:

$$C_v = \left(\frac{\partial E}{\partial T} \right)_V = \frac{16\sigma}{c} T^3 \sim T^3. \quad (4.131)$$

Radiation pressure¹⁴:

$$P = -\left(\frac{\partial F}{\partial V} \right)_T = \frac{4\sigma}{3c} T^4 \quad (4.132)$$

so that the “equation of state” is:

$$PV = \frac{E}{3} \quad (4.133)$$

characteristic for (ultra) relativistic gas with $\omega = ck$. The total (average) number of photons at given temperature is given by:

$$N = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^2}{e^{\frac{\hbar\omega}{T}} - 1} = \frac{VT^3}{\pi^2 c^3 \hbar^3} \int_0^\infty dx \frac{x^2}{e^x - 1} \approx 0.244 \left(\frac{T}{\hbar c} \right)^3 V. \quad (4.134)$$

¹⁴This pressure is very low at normal conditions, but it may become enormous for high enough temperature, e.g. in astrophysics. Actually, speaking about “practical” applications of this theoretical expression, we note that radiation pressure of photon gas is one of the main driving forces in thermonuclear weapons.

Chapter 5

CONDENSED MATTER

5.1 Solid state at low temperature.

In crystalline solids atoms oscillate around equilibrium positions, which for a regular crystal lattice. At low temperatures these oscillations are small and can be considered harmonic. Similar situations is characteristic for amorphous solids, where equilibrium positions are disordered in space ¹.

Let N denote the number of molecules (atoms) forming a solid, ν – the number of atoms in molecule ($\nu = 1$ if a solid consists of atoms). Then the total number of atoms is equal to $N\nu$. Of total $3N\nu$ degrees of freedom, three correspond to translational and another three to rotational motions of the solid as a whole. The rest $3N\nu - 6$ degrees of freedom correspond to oscillations. Taking into account that $3N\nu$ is an enormous number, we can safely neglect 6 and assume that the number of vibrational degrees of freedom is given by $3N\nu$.

Below we do not take into account electronic degrees of freedom, so that our presentation is related, strictly speaking, only to dielectric solids. In simplest approximations we can assume that in metals electrons just additively contribute to all thermodynamic quantities.

From mechanical point of view the system with $3N\nu$ vibrational degrees of freedom can be considered as the set of $3N\nu$ independent oscillators, each corresponding (in harmonic approximation) to a separate *normal oscillator* [11]. From quantum mechanics it is known [5] that the energy of harmonic oscillator is given by:

$$\varepsilon_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (5.1)$$

where $\hbar\omega$ is quantum of oscillation, $n = 0, 1, 2, \dots$ is oscillator quantum number. Then the statistical sum of a single oscillator is determined as:

$$Z_{osc} = \sum_{n=0}^{\infty} e^{-\frac{\hbar\omega}{T}(n+1/2)}. \quad (5.2)$$

Let us place the zero of energy at the lowest ($n = 0$) oscillator level, i.e. include the zero-point oscillator energy into a constant ε_0 , defining the origin of an

¹Most of the material in this Chapter is based on presentation of Refs. [1, 2].

energy scale. Then:

$$Z_{osc} = \sum_{n=0}^{\infty} e^{-\frac{\hbar\omega}{T}n} = \frac{1}{1 - e^{-\frac{\hbar\omega}{T}}}, \quad (5.3)$$

and corresponding free energy of a single oscillator is given by:

$$F_{osc} = T \ln \left(1 - e^{-\frac{\hbar\omega}{T}} \right). \quad (5.4)$$

Then the free energy of a solid can be written as:

$$F = N\varepsilon_0 + T \sum_{\alpha} \ln \left(1 - e^{-\frac{\hbar\omega_{\alpha}}{T}} \right), \quad (5.5)$$

where summation is performed over all $3N\nu$ normal oscillators, which are numbered by index α . Here $N\varepsilon_0$ is energy of zero-point oscillations, obviously proportional to the number of the molecules in solid, while ε_0 is zero energy of a molecule at $T = 0$.

Consider the limit of low temperatures. At small T in sum over α only terms with small $\hbar\omega \sim T$ are relevant. Small frequency vibrations in solids are the usual sound waves. Wavelength of sound wave is given by $\lambda = u/\omega$, where u is speed of sound. This wavelength is large compared with lattice constant of a typical crystal (or the average interatomic distance in amorphous solid): $\lambda \gg a$. Corresponding frequencies $\omega \ll u/a$. To consider the relevant vibrations as sound waves, we have to restrict temperatures to:

$$T \ll \hbar \frac{u}{a}. \quad (5.6)$$

Let us assume that our solid is isotropic (this is always valid for amorphous solids). In this case we have to deal with either longitudinal (with velocity u_l) or transversal (with velocity u_t) sound waves, as both can propagate in such a solid. Their frequencies are given by:

$$\omega = u_l k \quad \text{and} \quad \omega = u_t k \quad (5.7)$$

where $k = |\mathbf{k}|$ is the absolute value of the wave vector.

The number of vibrational modes corresponding to sound waves with absolute value of the wave vector in the interval from k to $k + dk$ and with fixed polarization is given by:

$$V \frac{4\pi k^2 dk}{(2\pi)^3}. \quad (5.8)$$

For longitudinal polarization we have $k = \omega/u_l$, while for two transversal – $k = \omega/u_t$, so that in the frequency interval from ω to $\omega + d\omega$ we have the following number of vibrational modes:

$$V \frac{\omega^2 d\omega}{2\pi^2} \left(\frac{1}{u_l^3} + \frac{2}{u_t^3} \right). \quad (5.9)$$

Let us introduce the average speed of sound u via the following relation:

$$\frac{3}{u^3} = \frac{2}{u_t^3} + \frac{1}{u_l^3} \quad (5.10)$$

Then Eq. (5.9) can be written as:

$$V \frac{3\omega^2 d\omega}{2\pi^2 u^3}. \quad (5.11)$$

In this form Eq. (5.11) is applicable not only to amorphous solid, but also to crystals, if we assume that u is certain average speed of sound in a crystal of given symmetry. Then, using (5.11) we can transform summation over α in Eq. (5.5) into integration over ω and obtain:

$$F = N\varepsilon_0 + \frac{3VT}{2\pi^2 u^3} \int_0^\infty d\omega \omega^2 \ln \left(1 - e^{-\frac{\hbar\omega}{T}} \right) \quad (5.12)$$

where integration can be extended to infinity due to fast convergence of integral at small T . Dropping $N\varepsilon_0$ contribution, we can see that the rest of this expression differs from Eq. (4.125) for the free energy of photon gas only by the replacement of the light speed c by the speed of sound and the factor of 3/2, related to three polarizations of the sound waves, as opposed to two polarizations of photons. Now we can conclude that thermodynamics of a solid is determined by the quanta of sound waves (lattice vibrations), which we shall call *phonons*. Here for the first time we meet the situation when theoretical description of a many – particle system of (interacting!) atoms (molecules) is reduced to a model of an ideal (noninteracting!) gas of *quasiparticles*.

Now we can just use the obtained above expressions for photon gas with similar replacements. However, we shall repeat explicit derivation. We can once again introduce the dimensionless variable $x = \hbar\omega/T$ and perform partial integration in (5.12) to get:

$$F = N\varepsilon_0 - V \frac{T^4}{2\pi^2 \hbar^3 u^3} \int_0^\infty dx \frac{x^3}{e^x - 1} = N\varepsilon_0 - V \frac{\pi^2 T^4}{30(\hbar u)^3}. \quad (5.13)$$

Entropy of the system is given by:

$$S = -\frac{\partial F}{\partial T} = V \frac{2\pi^2 T^3}{15(\hbar u)^3}. \quad (5.14)$$

and energy $E = F + TS$ is:

$$E = N\varepsilon_0 + V \frac{\pi^2 T^4}{10(\hbar u)^3}. \quad (5.15)$$

Specific heat of a solid in this approximation (low temperatures!), is equal to:

$$C = \left(\frac{\partial E}{\partial T} \right) = \frac{2\pi^2}{5(\hbar u)^3} VT^3 \sim T^3. \quad (5.16)$$

Here we can neglect any difference between C_p and C_v as their difference at low temperatures $C_p - C_v \sim T^7$, i.e. is much smaller than specific heat itself [1, 2].

5.2 Solid state at high temperature.

Let us consider now the opposite limit of high temperatures $T \gg \hbar u/a$. In this case we can write:

$$1 - e^{-\frac{\hbar\omega_\alpha}{T}} \approx \frac{\hbar\omega_\alpha}{T} \quad (5.17)$$

so that from Eq. (5.5) we obtain:

$$F = N\varepsilon_0 + T \sum_{\alpha} \ln \frac{\hbar\omega_{\alpha}}{T} = N\varepsilon_0 - 3N\nu T \ln T + 3N\nu T \ln \hbar \langle \omega \rangle \quad (5.18)$$

where we have introduced the mean logarithmic frequency of vibrations (phonons) $\langle \omega \rangle$ as:

$$\ln \langle \omega \rangle = \frac{1}{3N\nu} \sum_{\alpha} \ln \omega_{\alpha} \quad (5.19)$$

From Eq. (5.18) we find energy $E = F - T \frac{\partial F}{\partial T}$:

$$E = N\varepsilon_0 + 3N\nu T. \quad (5.20)$$

The case of high temperatures corresponds to the classical analysis of atomic vibrations and Eq. (5.20) corresponds to equipartition theorem – each of $3N\nu$ vibrational degrees of freedom contributes the energy T . Specific heat now is given by:

$$C = Nc = 3N\nu, \quad (5.21)$$

where $c = 3\nu$ is specific heat per one molecule². Thus, at high enough temperatures specific heat of solids is a constant independent of temperature and dependent only on the number of atoms. In particular, for all elements ($\nu = 1$) atomic high temperature specific heat is the same and equal to 3 (or $3k_B$ in usual units) – Dulong – Petit's law. At normal temperatures this law agrees well with experiments³.

Using (5.21) we can write free energy as:

$$F = N\varepsilon_0 - NcT \ln T + NcT \ln \hbar \langle \omega \rangle \quad (5.22)$$

$$E = N\varepsilon_0 + NcT. \quad (5.23)$$

Then the entropy of a solid is:

$$S = -\frac{\partial F}{\partial T} = Nc \ln T - Nc \ln \frac{\hbar \langle \omega \rangle}{e} \quad (5.24)$$

Clearly Eq. (5.18) can be directly derived using classical statistics starting from the general expression for the free energy:

$$F = -T \ln \int d\Gamma e^{-\frac{E(p,q)}{T}}. \quad (5.25)$$

Substituting here oscillator energy:

$$E(p, q) = \frac{1}{2} \sum_{\alpha} (p_{\alpha}^2 + \omega_{\alpha}^2 q_{\alpha}^2) \quad (5.26)$$

and taking into account $d\Gamma = \frac{1}{(2\pi\hbar)^{3N\nu}} \prod_{\alpha} dp_{\alpha} dq_{\alpha}$, we can see that integral here is factorized into a product of $3N\nu$ identical integrals of the following form:

$$\int_{-\infty}^{\infty} dp_{\alpha} \int_{-\infty}^{\infty} dq_{\alpha} \exp\left(-\frac{p_{\alpha}^2 + \omega_{\alpha}^2 q_{\alpha}^2}{2T}\right) = \frac{2\pi T}{\omega_{\alpha}} \quad (5.27)$$

²Again we write here simply C , as for solids the difference of C_p and C_v is negligible [1, 2]

³For composite compounds ($\nu > 1$) Dulong – Petit's limit is practically never achieved due melting or chemical decomposition at rather low temperatures.

so that finally we obtain (5.18). Note that the limits of integration here can be extended to infinity due to fast convergence of integrals, though in reality atoms perform only small oscillations around lattice sites. Accordingly, all areas of integration correspond in fact to physically different microscopic states and there is no need to introduce an additional factor of $N!$ in the denominator of the phase volume.

5.3 Debye theory.

Debye proposed a simple, but very effective, interpolation for specific heat which can be used for arbitrary temperatures. Let us consider a model of a solid, where all vibrational frequencies are distributed according to Eq. (5.11), though in reality this expression is valid only for small (sound) frequencies. In fact, phonon spectrum should be limited from the above as vibrational frequency in solid can not be larger than some maximal frequency, which can be determined from the condition that the total number of vibrations is equal to the total number of vibrational degrees of freedom $3N\nu$:

$$\frac{3V}{2\pi^2 u^3} \int_0^{\omega_D} d\omega \omega^2 = \frac{V\omega_D^3}{2\pi^2 u^3} = 3N\nu \quad (5.28)$$

Thus defined *Debye frequency* ω_D is equal to⁴:

$$\omega_D = u \left(\frac{6\pi^2 N\nu}{V} \right)^{1/3} \sim u/a \quad (5.29)$$

Accordingly, frequency distribution or phonon density of states in Debye model is given by:

$$\rho(\omega) = \begin{cases} 9N\nu \frac{\omega^2}{\omega_D^3} & \text{for } \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} \quad (5.30)$$

where we have expressed u via ω_D using (5.29).

Surely, since Debye work, there was an enormous progress of solid state physics and nowadays the real phonon density of states is directly measured e.g. by inelastic scattering of neutrons. However, at small frequencies it always reduces to Debye (sound) dependence $\sim \omega^2$, though at higher frequencies it may become rather complicated (see e.g. Fig.5-1.). The limiting frequency always exists, but Eq. (5.29) defines it only by the order of magnitude. However, in most cases Debye model produces rather satisfactory description of specific heat of real solids. Debye frequency is usually considered just as a fitting parameter, characterizing the concrete solid, to be determined from experiments.

Replacing again summation in Eq. (5.12) by frequency integration we obtain the free energy of a solid as:

$$F = N\varepsilon_0 + T \frac{9N\nu}{\omega_D^3} \int_0^{\omega_D} d\omega \omega^2 \ln \left(1 - e^{-\frac{\hbar\omega}{T}} \right) \quad (5.31)$$

⁴The existence of such limiting frequency is crucial for phonon statistics and is the major difference with statistics of photons. For photons there is no such maximal frequency – electromagnetic field is the system with infinite number of degrees of freedom and in Minkowski space - time no minimal length (similar to lattice constant a) exists (at least at the present level of our knowledge).

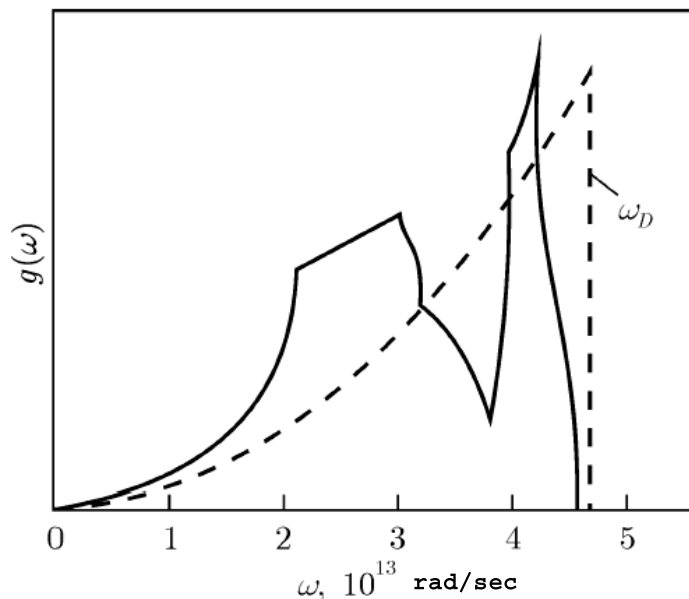


Figure 5.1: Phonon density of states in copper determined from neutron scattering experiments. Dashed line corresponds to Debye model which is fixed by the demand of equality of areas under this line and experimental density of states. Debye temperature $\theta_D = 340K$.

Let us introduce now *Debye temperature* as:

$$\theta_D = \hbar\omega_D \quad (5.32)$$

Then:

$$F = N\varepsilon_0 + 9N\nu T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} dz z^2 \ln(1 - e^{-z}) \quad (5.33)$$

where we have introduced the dimensionless variable $z = \frac{\hbar\omega}{T}$. Performing partial integration and introducing Debye function:

$$D(x) = \frac{3}{x^3} \int_0^x dz \frac{z^3}{e^z - 1} \quad (5.34)$$

we can write (5.33) as:

$$F = N\varepsilon_0 + N\nu T \left\{ 3 \ln \left(1 - e^{-\frac{\theta_D}{T}}\right) - D\left(\frac{\theta_D}{T}\right) \right\}. \quad (5.35)$$

Then energy $E = F - T \frac{\partial F}{\partial T}$ is given by:

$$E = N\varepsilon_0 + 3N\nu T D\left(\frac{\theta_D}{T}\right) \quad (5.36)$$

and specific heat is:

$$C = 3N\nu \left\{ D\left(\frac{\theta_D}{T}\right) - \frac{\theta_D}{T} D'\left(\frac{\theta_D}{T}\right) \right\} \quad (5.37)$$

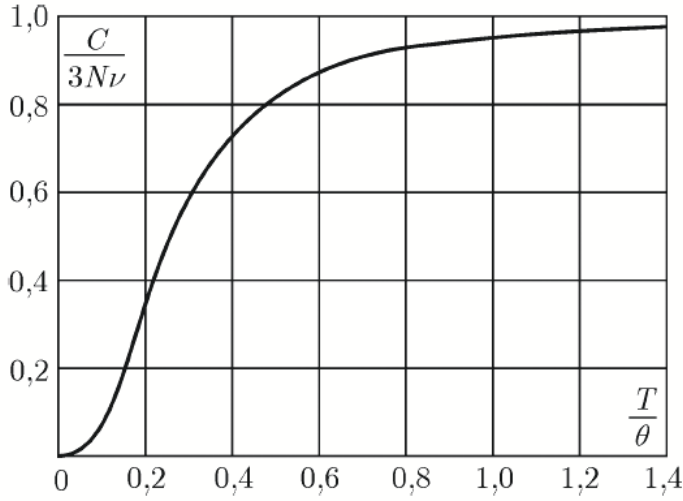


Figure 5.2: Temperature dependence of specific heat in Debye model.

In Fig.5-2 we show the dependence of $\frac{C}{3N\nu}$ on $\frac{T}{\theta_D}$.

For $T \ll \theta_D$ we have $\frac{\theta_D}{T} \gg 1$, so we can replace the upper limit of integration by infinity and the integral is equal to $\frac{\pi^4}{15}$ and

$$D(x) \approx \frac{\pi^4}{5x^3}. \quad (5.38)$$

Then, from Eq. (5.37) we get:

$$C \approx \frac{12N\nu\pi^4}{5} \left(\frac{T}{\theta_D}\right)^3 \quad (5.39)$$

which coincides with (5.16).

For $T \gg \theta_D$ we have $x \ll 1$ and in first approximation we can put $D(x) \approx 1$, so that Eq. (5.37) gives $C = 3N\nu$, i.e. Dulong – Petit law.

Note that the actual form of Debye function $D(x)$ shows that the border between different temperature limit is defined by the comparison of T and $\theta_D/4$ – specific heat is approximately constant for $T \gg \theta_D/4$ and it behaves as $\sim T^3$ for $T \ll \theta_D/4$. In metals, for temperatures $T \ll \theta_D/4$ becomes also observable the linear in T contribution to specific heat from free electrons given by Eq. (4.70), which is rather small and is rapidly “masked” by lattice contribution at higher temperatures. To separate electronic and lattice contributions to specific heat it is convenient to plot experimental data for specific heat of metals at low temperatures as dependence of the ratio C/T on T^2 . In metal we have at low temperatures $C = \gamma T + \beta T^3$, so that $\frac{C}{T} = \gamma + \beta T^2$, and the value of C/T at $T \rightarrow 0$ actually determines the coefficient γ , which in fact gives us (according to Eq. (4.70)) the value of electron density of states at the Fermi level⁵.

⁵Note that in amorphous (insulating) glasses a linear in T specific heat is also sometimes observed due to the contribution of so called tunneling states (two - level systems). However, we shall not discuss it here as this material is outside the scope of our presentation.

Table 5.1: Debye temperatures for some real systems (K).

<i>Pb</i>	<i>Na</i>	<i>KBr</i>	<i>Ag</i>	<i>NaCl</i>	<i>Ga</i>	<i>Cu</i>	<i>Al</i>	<i>Mo</i>	<i>SiO₂</i>	<i>Si</i>	<i>LiF</i>
105	158	180	225	280	320	340	430	450	470	645	732

In Table 5-1 we present the values of Debye temperatures, determined experimentally for a number of real solids. Excluding special cases like diamond (where $\theta_D \sim 2000K$), Debye temperatures for majority of solids are of the order of $10^2 K$.

5.4 Quantum Bose liquid.

In general case, interaction between atoms (molecules) in liquids is strong, and calculations of thermodynamic characteristics becomes very complicated task (as opposed to gases or solids, where interactions or atomic vibrations are small, allowing analytical approach). However, theoretical analysis simplifies in case of so called quantum liquids, which are close to the ground state at nearly zero temperatures. In reality, there is only one such liquid, which does not crystallize up to the absolute zero — that is liquid Helium. Most important quantum liquid is also formed by conduction electrons in metals. There are some other more exotic examples of quantum liquids, e.g. nuclear matter, neutron stars etc. Many properties of these systems are quite unusual, including such spectacular phenomena as superfluidity and superconductivity. Theory of quantum liquids is of principal importance and is one of the major areas of modern theory of many - particle systems.

We have seen that calculation of thermodynamic properties requires the knowledge of energy spectrum (levels) of the body. In case of the system of strongly interacting particles, such as a quantum liquid, we have to deal with energy levels of a liquid as a whole, not of separate atoms forming a liquid. At low temperatures, while calculating the partition function, it is sufficient to take into account only lowest energy levels (excitations) just above the ground state, which leads to great simplifications.

The basic idea of Landau is that lowest energy levels of a quantum liquid can be reduced to some kind of elementary excitations or *quasiparticles*, with well defined energy spectrum. In spatially homogeneous (translational invariant) liquid these excitations can be characterized by momentum (or quasi-momentum in a crystal). Until the number of quasiparticles is low enough (at low temperatures) we can neglect their interactions and assume that, in first approximation, these excitations form an ideal gas⁶.

One of possible types of energy spectrum of weak excitations of a quantum liquid is the Bose - like spectrum, when elementary excitations can appear and disappear one by one. The angular momentum of any quantum system (in our case quantum liquid) can change only by integers (in units of \hbar). Thus, elemen-

⁶Let us stress that the concept of quasiparticles is quite nontrivial. Its final justification appeared only within the modern theory of many - particle systems, based on Green's functions and quantum field theory approach (see Chapter 11 below). Only within this approach we can derive precise criteria of existence of quasiparticles in concrete systems. In some cases (e.g. in so called strongly correlated systems) quasiparticle concept breaks down and much more complicated description is required.

tary excitations appearing one by one necessarily can possess only an integer angular momentum (spin) and obey Bose statistics. The liquid, consisting of Bose particles must have an energy spectrum of this kind. Typical example is liquid He^4 (while He^3 forms Fermi liquid).

Major characteristic of quasiparticles is dispersion (spectrum), i.e. the dependence of their energy on momentum. In Bose liquid elementary excitations with small momenta \mathbf{p} (large wavelengths \hbar/p) correspond to the usual sound waves with dispersion:

$$\varepsilon(p) = up \quad (5.40)$$

where u is the speed of sound. These excitations (quasiparticles) are called phonons. The knowledge of the spectrum $\varepsilon(p)$ at small p allows us to calculate thermodynamic characteristics of a liquid at very small temperatures T , when practically all elementary excitations are phonons. Appropriate expressions can be written immediately using the results obtained above for thermodynamics of a solid at low temperatures. The only difference is that instead of three independent polarizations (two transverse and one longitudinal) in a solid, we have only one (longitudinal) in a liquid, so that all expressions should be divided by 3. For example, the free energy of a liquid from Eq. (5.13) we obtain:

$$F = F_0 - V \frac{\pi^2 T^4}{90(\hbar u)^3} \quad (5.41)$$

where F_0 is free energy of a liquid at $T = 0$. The energy is given by:

$$E = E_0 + V \frac{\pi^2 T^4}{30(\hbar u)^3} \quad (5.42)$$

and specific heat:

$$C = V \frac{2\pi^2 T^3}{15(\hbar u)^3} \sim T^3 \quad (5.43)$$

With the growth of quasiparticle momentum $\varepsilon(p)$ dependence deviates from simple linear and its behavior becomes dependent on interactions. At large enough momenta $\varepsilon(p)$ dependence ceases to exist, as elementary excitations with large momenta are unstable towards decay into several excitations with smaller momenta.

After a thorough studies of experimental data on liquid He^4 Landau has postulated the spectrum of elementary excitations for this system, as shown in Fig.5-3. We can see characteristic minimum at $p = p_0$ and close to it $\varepsilon(p)$ can be written as:

$$\varepsilon(p) = \Delta + \frac{(p - p_0)^2}{2\tilde{\mu}} \quad (5.44)$$

Quasiparticles from this part of the spectrum are usually called rotons⁷. Now this form of the spectrum is well confirmed by direct experiments on inelastic neutron scattering. Experimental values of constants for roton part of the spectrum are:

$$\Delta = 8.5K; \quad \frac{p_0}{\hbar} = 1.9 \cdot 10^8 \text{ cm}^{-1}; \quad \tilde{\mu} = 0.16m_{He} \quad (5.45)$$

⁷This name is of purely historic origin. In early works Landau assumed the existence of two separate types of quasiparticles in He^4 – phonons and rotons, i.e. the existence of two independent branches of the spectrum. Later it was discovered that there is single branch of the spectrum with phonon and roton parts. Contrary to the initial opinion of Landau it was also discovered that this form of the spectrum is directly related to Bose condensation in He^4 .

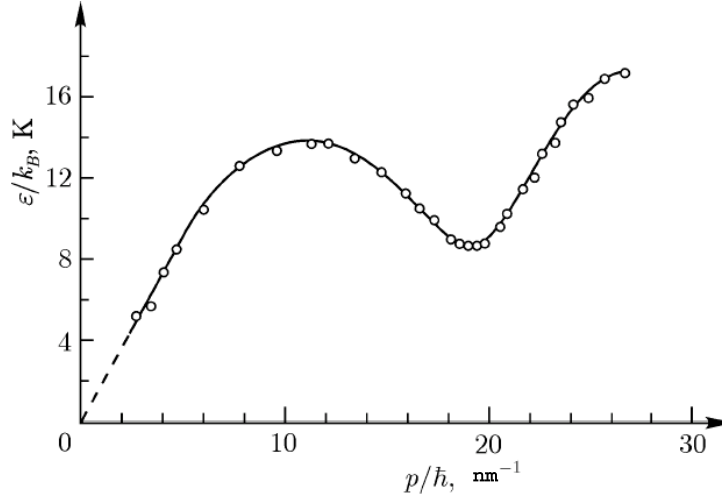


Figure 5.3: Spectrum of elementary excitations in liquid He^4 . Points represent experimental data obtained from inelastic neutron scattering.

Note that $p_0 \sim \hbar a^{-1}$, where a is an average interatomic distance in liquid.

As roton energy has a “gap” Δ , at low enough temperatures $T < \Delta$ we are dealing with dilute gas of rotons, which can be described by Boltzmann’s statistics. Then, to calculate “roton” part of free energy of He^4 we can use Eq. (3.41). Substituting $\varepsilon(p)$, which is independent of coordinates, we immediately obtain:

$$F = -NT \ln \left[\frac{eV}{N} \int \frac{d^3p}{(2\pi\hbar)^3} e^{-\frac{\varepsilon(p)}{T}} \right] \quad (5.46)$$

The number of particles N in roton gas is not fixed and is determined from the requirement of the minimum of F . From the condition of $\frac{\partial F}{\partial N} = \mu = 0$ we find the number of rotons as:

$$N_r = \frac{V}{(2\pi\hbar)^3} \int d^3p e^{-\frac{\varepsilon(p)}{T}} \quad (5.47)$$

where in the integrand we have just the Boltzmann’s distribution with $\mu = 0$. Substituting $N = N_r$ from Eq. (5.47) into Eq. (5.46), we get:

$$F_r = -N_r T \ln e = -TN_r = -\frac{VT}{(2\pi\hbar)^3} \int d^3p e^{-\frac{\varepsilon(p)}{T}} \quad (5.48)$$

Taking into account the explicit form of roton spectrum (5.44) in Eqs. (5.47) and (5.48), due to $p_0^2 \gg \tilde{\mu}T$ we may take $p^2 \approx p_0^2$ outside integral and perform integration within infinite limits. Then we obtain:

$$N_r = \frac{2(\tilde{\mu}T)^{1/2} p_0^2 V}{(2\pi)^{3/2} \hbar^3} e^{-\frac{\Delta}{T}}; \quad F_r = -TN_r \quad (5.49)$$

Accordingly, the contribution of rotons to the entropy and specific heat is:

$$S_r = N_r \left(\frac{3}{2} + \frac{\Delta}{T} \right) \quad C_r = N_r \left[\frac{3}{4} + \frac{\Delta}{T} + \left(\frac{\Delta}{T} \right)^2 \right] \quad (5.50)$$

so that the temperature dependence is exponential and for $T < \Delta$ these contributions are small in comparison to phonon parts determined above. For $T > \Delta$ roton contributions to thermodynamic values may overcome those from phonons, which actually takes place with the rise of temperature.

5.5 Superfluidity.

Liquid Helium at temperatures, below the so called λ -point $T_\lambda = 2.18K$, acquires the remarkable property of superfluidity — the liquid flows through narrow tubes and channels without friction (viscosity). Superfluidity was discovered by Kapitza in 1938, its theoretical interpretation was given few years later by Landau.

Consider first the case of $T = 0$. Assume that the liquid flows in tube with a constant velocity \mathbf{v} . In the presence of viscosity friction of liquid and tube walls, as well as within liquid itself, will induce different processes of dissipation of kinetic energy of the flow, so that the flow slows down and finally stops. It is convenient to consider liquid in coordinate system moving together with the flow. In this system Helium is at rest in the ground state, while the tube walls move with velocity $(-\mathbf{v})$. In the presence of viscosity (friction) Helium initially at rest should start to move. From microscopic point of view it is clear that the appearance of this motion should start from some excitation of internal motions within the liquid, i.e. from the appearance of some elementary excitations (quasiparticles).

Consider the situation with the appearance of only one elementary excitation with momentum \mathbf{p} and energy $\varepsilon(p)$. Then the energy of the liquid E_0 becomes equal to the energy of this excitation $\varepsilon(p)$, while its momentum \mathbf{P}_0 becomes equal to \mathbf{p} . Let us return to the laboratory coordinate system in which the tube is at rest. Using the well known Galilean transformations of classical mechanics [11] we obtain for energy E and momentum \mathbf{P} of the liquid in laboratory system:

$$\mathbf{P} = \mathbf{P}_0 + M\mathbf{v} \quad E = E_0 + \mathbf{P}_0\mathbf{v} + \frac{Mv^2}{2} \quad (5.51)$$

where M is the mass of moving liquid. Substituting now for E_0 and \mathbf{P}_0 the values $\varepsilon(p)$ and \mathbf{p} we have:

$$E = \varepsilon(p) + \mathbf{p}\mathbf{v} + \frac{Mv^2}{2} \quad (5.52)$$

The term $\frac{1}{2}Mv^2$ here represents the initial kinetic energy of liquid flow, while $\varepsilon(p) + \mathbf{p}\mathbf{v}$ is now the *change of the liquid energy due to the appearance of a single elementary excitation*. This change should be negative to diminish the flow energy:

$$\varepsilon(p) + \mathbf{p}\mathbf{v} < 0. \quad (5.53)$$

For a given value of \mathbf{p} the left hand side of Eq. (5.53) is minimal for antiparallel \mathbf{p} and \mathbf{v} , thus in any case we should have $\varepsilon(p) - pv < 0$, so that:

$$v > \frac{\varepsilon(p)}{p} \quad (5.54)$$

This inequality is to be satisfied at least for some values of the momentum p of elementary excitation. Thus, to find the final condition of appearance

of elementary excitations in a moving liquid we have to find the *minimum* of $\varepsilon(p)/p$:

$$v_c = \text{Min} \frac{\varepsilon(p)}{p} \quad (5.55)$$

Geometrically the ratio $\varepsilon(p)/p$ is determined by the slope of a straight line drawn from the origin of coordinate system in (ε, p) – plane to some point of the curve $\varepsilon = \varepsilon(p)$. Its minimal value is determined by the point, where this line is tangent to $\varepsilon(p)$ curve. If this minimum is nonzero, then for velocities of the liquid below v_c , determined by Eq. (5.55), *no elementary excitations can appear*, so that the flow will be dissipationless (no friction!). This is precisely the case of superfluidity and Eq. (5.55) represents Landau's criterion of superfluidity. The value of v_c is called the critical velocity, its existence is confirmed by experiments.

It is easy to see that Landau's spectrum of elementary excitations for He^4 satisfies the criterion of superfluidity. Similarly, this criterion is satisfied by the energy spectrum with a "gap" at $p = 0$. At the same time, the free particle spectrum $\varepsilon(p) = p^2/2m$ obviously does not satisfy this criterion. In essence, it is necessary for the curve $\varepsilon(p)$ not to be tangent to the abscissa at the origin. Thus, superfluidity will appear for almost any spectrum with phonon – like behavior in the long wavelength limit or gap at $p = 0$.

For finite temperatures $T > 0$ liquid is not in the ground state and there is a number of elementary excitations present. Kinematic arguments given above are still valid, and the motion of liquid through the tube with velocities satisfying Landau's criterion still does not produce additional excitations. However, we have clarify the role of excitations already present due to finite temperatures.

Consider the gas of quasiparticles moving as a whole relative to the liquid with velocity \mathbf{v} . Distribution function for the gas moving as a whole is obtained from the distribution function $n(\varepsilon)$ at rest by the substitution $\varepsilon \rightarrow \varepsilon - \mathbf{p}\mathbf{v}$, where \mathbf{p} is the momentum of a quasiparticle⁸. Then the total momentum of the unit volume of the gas is given by:

$$\mathbf{P} = \int \frac{d^3p}{(2\pi\hbar)^3} \mathbf{p} n(\varepsilon - \mathbf{p}\mathbf{v}) \quad (5.56)$$

Let the velocity \mathbf{v} be small, so that we can expand the integrand in powers of $\mathbf{p}\mathbf{v} = pv \cos \theta$. The zero - order term disappears after the integration over directions of the vector \mathbf{p} (θ angle) and we can write:

$$\mathbf{P} = - \int \frac{d^3p}{(2\pi\hbar)^3} \mathbf{p}(\mathbf{p}\mathbf{v}) \frac{dn(\varepsilon)}{d\varepsilon}. \quad (5.57)$$

Integrating here again over the directions of the vector \mathbf{p} we get:

$$\mathbf{P} = -\mathbf{v} \frac{4\pi}{3} \frac{1}{(2\pi\hbar)^3} \int dp p^4 \frac{dn(\varepsilon)}{d\varepsilon}. \quad (5.58)$$

⁸Consider gas of excitations with respect to the liquid with velocity \mathbf{v} . In coordinate system where the gas is at rest the liquid moves with velocity $-\mathbf{v}$. Then the energy E of liquid in this coordinates is connected with energy E_0 in coordinate system, where liquid is at rest, by: $E = E_0 - \mathbf{P}_0\mathbf{v} + \frac{Mv^2}{2}$. Consider an excitation with energy $\varepsilon(p)$, appearing in the rest system of the liquid. Then the additional energy in the rest system of the gas will be given by $\varepsilon - \mathbf{p}\mathbf{v}$, which proves our statement.

Substituting here the spectrum of phonons $\varepsilon = up$ and integrating by parts we have:

$$\mathbf{P} = -\mathbf{v} \frac{1}{(2\pi\hbar)^3} \frac{4\pi}{3u} \int_0^\infty dp p^4 \frac{dn(p)}{dp} = \mathbf{v} \frac{16\pi}{3u} \frac{1}{(2\pi\hbar)^3} \int_0^\infty dp p^3 n(p). \quad (5.59)$$

Here the integral

$$\frac{1}{(2\pi\hbar)^3} \int_0^\infty dp 4\pi p^2 u p n(p) = \int \frac{d^3p}{(2\pi\hbar)^3} \varepsilon n(\varepsilon) \quad (5.60)$$

reduces to the energy E_{ph} of the unit volume of phonon gas, so that:

$$\mathbf{P} = \mathbf{v} \frac{4E_{ph}}{3u^2} \quad (5.61)$$

Coefficient before \mathbf{v} here defines the mass density of the liquid transported by the flow of quasiparticle gas. Nothing can prevent these moving quasiparticles to be scattered by the walls of the tube and exchange momenta as in the usual gas flow. It is clear that this part of the liquid mass will behave as a normal liquid moving with friction. However, this is not the whole mass of the liquid, the rest behaves as a superfluid! In fact, after we substitute into Eq. (5.61) the expression (5.42) for the energy of phonon gas, we obtain for the phonon part of *normal* density ρ_n :

$$(\rho_n)_{ph} = \frac{2\pi^2 T^4}{45\hbar^3 u^5}, \quad (5.62)$$

which goes to zero for $T \rightarrow 0$, when the whole mass of the liquid becomes superfluid. Now we can say that the total density ρ of He^4 at $T > 0$ consists of normal and superfluid parts (components): $\rho = \rho_n + \rho_s$, though certainly it does not mean that there is any kind of real separation of the liquid into two components. It is important to note that there is no momentum transfer (friction!) between these two parts of the liquid: we have obtained this physical picture at the state of statistical equilibrium in a gas moving with fixed velocity. But any motion in the state of thermodynamic equilibrium is in fact dissipationless.

Above we determined the phonon contribution to ρ_n , to find the roton part we note that rotons can be described by Boltzmann statistics, so that $\frac{\partial n}{\partial \varepsilon} = -\frac{n}{T}$ and from Eq. (5.58) we get:

$$\begin{aligned} (\rho_n)_r &= \frac{4\pi}{3T(2\pi\hbar)^3} \int dp p^4 n(p) = \frac{1}{3T} \int \frac{d^3p}{(2\pi\hbar)^3} p^2 n(p) \approx \\ &\approx \frac{p_0^2}{3T} \frac{N_r}{V} = \frac{2\tilde{\mu}^{1/2} p_0^4}{3(2\pi)^{3/2} T^{1/2} \hbar^3} e^{-\frac{\tilde{\mu}}{T}} \end{aligned} \quad (5.63)$$

where p_0 is the momentum corresponding to roton minimum. If we take into account the experimental values of parameters, determining the spectrum of excitations in He^4 , it turns out that the roton contribution to ρ_n matches the phonon part at $T \sim 0.6K$ and overcomes it at higher temperatures.

As temperature T grows more and more of the liquid becomes normal and $\rho_n \rightarrow \rho$ (where ρ is the total density of He^4) for $T \rightarrow T_\lambda$ from below. Superfluid density $\rho_s \rightarrow 0$ for $T \rightarrow T_\lambda$ and $\rho_s = 0$ for $T > T_\lambda$. The value of ρ_n close to λ -point can not be calculated precisely, but the approximate estimate of T_λ can

be obtained from the condition of $(\rho_n)_r \approx \rho$. Using here Eq. (5.63) we can obtain $T_\lambda \approx 2.8K$ in relatively good agreement with experiments.

Superfluid transition in He^4 is a typical second order phase transition. Such transition is always connected with the appearance (or disappearance) of some qualitative property (long-range order!). In case of λ -transition in He^4 this is the appearance (disappearance) of superfluid component of the liquid. From microscopic point we can speak about certain properties of *single-particle* density matrix of our system:

$$\rho(\mathbf{r}, \mathbf{r}') = \int dq \Psi^*(\mathbf{r}, q) \Psi(\mathbf{r}', q) \quad (5.64)$$

where $\Psi(\mathbf{r}, q)$ is the wave function of the system as a whole, where \mathbf{r} are coordinates of a single particle, while q is the set of all coordinates of other particles, which are integrated out. For isotropic medium (liquid) this density matrix depends only on $|\mathbf{r} - \mathbf{r}'|$. In normal (non superfluid) state $\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0$ for $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$. This is not so in superfluid phase.

Consider the Fourier components of the density matrix:

$$\int d^3(\mathbf{r} - \mathbf{r}') e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} \rho(\mathbf{r}, \mathbf{r}'), \quad (5.65)$$

which, up to a constant, coincide with:

$$\int dq \left| \int dV e^{i\mathbf{k}\mathbf{r}} \Psi(\mathbf{r}, q) \right|^2 \quad (5.66)$$

i.e. determine the probability distribution of different values of momentum of a particle $\mathbf{p} = \hbar\mathbf{k}$. If $\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0$ for $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$, probability density in \mathbf{p} -space for $\mathbf{p} \rightarrow 0$ remains finite. However, if $\rho(\mathbf{r}, \mathbf{r}')$ tends to a finite value $\rho_\infty > 0$ at infinity⁹, the integral in (5.65) is equal to $(2\pi)^3 \delta(\mathbf{k}) \rho_\infty$. This corresponds to a finite probability for a particle to have the zero momentum. Thus, in the superfluid state (opposite to the case of normal liquid) the *finite* number (fraction) of particles possess the zero momentum. This clearly relates the superfluidity to Bose condensation. Let us stress that this set of particles should not be identified with superfluid component of the liquid, discussed above. This is obviously will be wrong, as at $T = 0$ all mass of the liquid is superfluid, though not all particles of the *interacting* system possess the zero momentum (cf. below the case of weakly interacting Bose gas).

5.6 Phonons in Bose liquid*.

Let us consider in more details the origin of the spectrum of elementary excitations of liquid He^4 , shown in Fig. 5-3. Energy of the liquid can be written as a functional of its (mass) density and hydrodynamic velocity:

$$E[\rho(\mathbf{r}), \mathbf{v}(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \mathbf{v}^2(\mathbf{r}) + E^{(1)}[\rho(\mathbf{r})] \quad (5.67)$$

where $E^{(1)}$ is the part of energy independent of velocity. Consider small oscillations of density:

$$\rho(\mathbf{r}) = \rho + \delta\rho(\mathbf{r}) \quad (5.68)$$

⁹This is called off-diagonal long-range order (ODLRO).

where ρ is liquid density at equilibrium, while $\delta\rho(\mathbf{r})$ and $\mathbf{v}(\mathbf{r})$ are small deviations, describing oscillations. By definition:

$$\rho = \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r}) \quad \int d\mathbf{r} \delta\rho(\mathbf{r}) = 0 \quad (5.69)$$

Limiting ourselves to terms of the second order in $\delta\rho$ and v we can replace $\rho(\mathbf{r})$ in the first term in Eq. (5.67) by its average value ρ . With the same accuracy $E^{(1)}$ is written as:

$$E^{(1)}[\rho(\mathbf{r})] = E^{(1)}(\rho) + \int d\mathbf{r} \psi(\mathbf{r}) \delta\rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \varphi(\mathbf{r}, \mathbf{r}') \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \quad (5.70)$$

Functions $\psi(\mathbf{r})$ and $\varphi(\mathbf{r}, \mathbf{r}')$ are determined only by properties of unperturbed liquid, which is homogeneous and isotropic, so that $\psi(\mathbf{r}) = \psi = \text{const}$, while $\varphi(\mathbf{r}, \mathbf{r}')$ depends only on distance $|\mathbf{r} - \mathbf{r}'|$: $\varphi(\mathbf{r}, \mathbf{r}') = \varphi(|\mathbf{r} - \mathbf{r}'|)$. Then the first order term in the expansion of $E^{(1)}$ given by Eq. (5.70) is proportional to $\int dV \delta\rho(\mathbf{r}) = 0$, and finally we obtain:

$$E^{(1)}[\rho(\mathbf{r})] = E^{(1)}(\rho) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \varphi(|\mathbf{r} - \mathbf{r}'|) \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}') \quad (5.71)$$

Velocity \mathbf{v} is related to density oscillations by continuity equation:

$$\dot{\rho} + \text{div}(\rho\mathbf{v}) = 0, \quad (5.72)$$

which can be written up to first order terms in $\delta\rho$ and \mathbf{v} as:

$$\dot{\delta\rho} + \rho \text{div}\mathbf{v} = 0. \quad (5.73)$$

Performing Fourier transformation:

$$\delta\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{p}} \rho_{\mathbf{p}} e^{i\mathbf{p}\mathbf{r}} \quad \mathbf{v}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{p}} \mathbf{v}_{\mathbf{p}} e^{i\mathbf{p}\mathbf{r}} \quad (5.74)$$

$$\varphi(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{p}} \varphi_{\mathbf{p}} e^{i\mathbf{p}\mathbf{r}} \quad (5.75)$$

and taking into account the longitudinal nature of liquid oscillations, so that velocity $\mathbf{v}_{\mathbf{p}}$ in a wave with wave vector \mathbf{p} is directed along \mathbf{p} , we can write:

$$\mathbf{v}_{\mathbf{p}} = a_{\mathbf{p}} \mathbf{p} \quad (5.76)$$

Substituting these expressions into continuity equation we immediately obtain:

$$\mathbf{v}_{\mathbf{p}} = i\dot{\rho}_{\mathbf{p}} \frac{1}{\rho} \frac{\mathbf{p}}{p^2} \quad (5.77)$$

so that Eq. (5.71) is rewritten as:

$$E = E^{(1)}(\rho) + \frac{1}{V} \sum_{\mathbf{p}} \left(\frac{|\dot{\rho}_{\mathbf{p}}|^2}{2\rho p^2} + \frac{1}{2} \varphi_{\mathbf{p}} |\rho_{\mathbf{p}}|^2 \right). \quad (5.78)$$

The first term in Eq. (5.78) represents an energy of unperturbed liquid, the second one reduces to the sum of terms, each having the form of harmonic oscillator energy with frequency ω_p :

$$\omega_p^2 = \rho p^2 \varphi_p \quad (5.79)$$

where we have taken into account that in isotropic liquid $\varphi_{\mathbf{p}} = \varphi_p$, i.e. depends only on the absolute value of $|\mathbf{p}|$. In quantum case the energy of such oscillator is¹⁰:

$$\varepsilon(p) = \omega_p \left(n + \frac{1}{2} \right) \quad n = 0, 1, 2, \dots \quad (5.80)$$

Thus, the spectrum of our system (liquid) is in fact determined by the spectrum of these oscillators, i.e. by relations (5.79) and (5.80).

To obtain the final solution we have to express φ_p via characteristics of liquid. In quantum case the ground state energy does not coincide with $E^{(1)}(\rho)$ (as in classics), we have take into account the zero point oscillator energy $\omega_p/2$. Then the ground state energy of quantum Bose liquid becomes equal to:

$$E_0 = E^{(1)}(\rho) + \sum_p \frac{1}{2} \omega_p \quad (5.81)$$

or, with the account of Eq. (5.78):

$$V \frac{\omega_p}{2} = \frac{1}{2\rho p^2} \langle |\rho_p^2| \rangle + \frac{1}{2} \varphi_p \langle |\rho_p|^2 \rangle = \varphi_p \langle |\rho_p|^2 \rangle \quad (5.82)$$

where the angular brackets denote the averaging over the ground state, and we used the well known result that for quantum oscillator the average (over the ground state) kinetic energy equals the average potential energy. Then, expressing in Eq. (5.79) φ_p via (5.82), we obtain:

$$\varepsilon(p) = \omega_p = V \rho \frac{p^2}{2 \langle |\rho_p|^2 \rangle} \quad (5.83)$$

or

$$\varepsilon(p) = \frac{p^2}{2mS(p)} \quad (5.84)$$

where we have introduced:

$$S(p) = \frac{\langle |\rho_p|^2 \rangle}{Vm\rho} \quad (5.85)$$

– the so called structure factor of the liquid, which is determined by the Fourier transformation of density – density correlation function:

$$S(\mathbf{r} - \mathbf{r}') = \frac{1}{n} \langle [n(\mathbf{r}) - n][n(\mathbf{r}') - n] \rangle \quad (5.86)$$

where $n(\mathbf{r}) = \rho(\mathbf{r})/m$ is (volume) density of particles at point \mathbf{r} , while n is the average density of particles in liquid.

Eq. (5.84) was first derived by Feynman, derivation given above belongs to Pitaevskii. This formula expresses excitation spectrum vis structure factor of the liquid. The value of $S(p)$ in general case can not be derived analytically, but in real liquids it is directly measured in neutron and X-ray scattering experiments.

For small momenta excitation spectrum of liquid He^4 is linear over momentum: $\varepsilon(p) \approx up$, accordingly we have $S(p) \approx p/2mu$. For very large momenta

¹⁰Here we use for brevity the system of units, often used by theorists, where $\hbar = 1$ and do not discern momentum and wave vector.

much exceeding the inverse interatomic distance, $p \gg a^{-1}$, we have $S(p) = 1$, which corresponds to $S(r) = \delta(r)$ at small distances. In intermediate region $p \sim a^{-1}$ structure factor $S(p)$ is determined from experiments and for majority of liquids (not only for He^4) it demonstrates characteristic maximum at $p \sim a^{-1}$ (see Fig.5-4). The presence of this maximum is in fact related to the conserva-

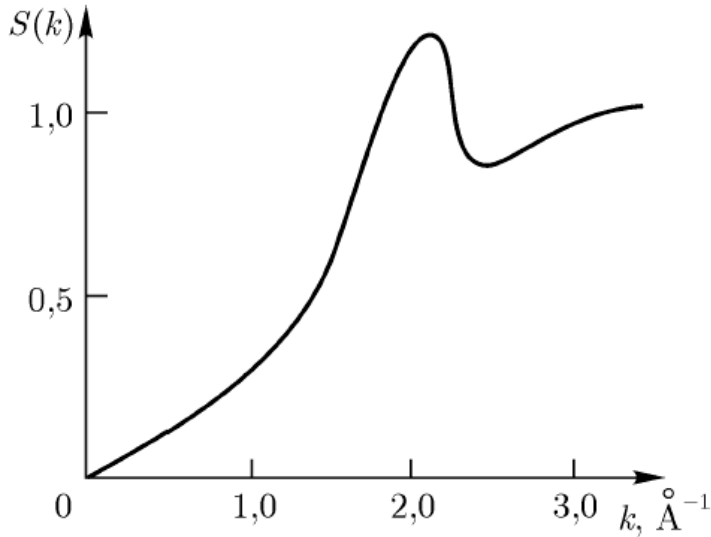


Figure 5.4: Characteristic form of the structure factor of liquid He^4 .

tion of rather strong correlations between atom positions in liquid (short range order).

From Feynman's expression (5.84) becomes clear that for large momenta $p \gg a^{-1}$ excitation spectrum reduces to the spectrum of free particles: $\varepsilon(p) = p^2/2m$. In intermediate region of $p \sim a^{-1}$ the presence of the maximum in $S(p)$ leads to the appearance of roton minimum.

Strictly speaking, this "hydrodynamic" derivation of Feynman's formula is valid only for momenta $p < 1/a$, i.e. when the liquid may be considered as a continuous medium. However, this expression also gives the correct answer for $p \gg 1/a$, i.e. in the free particle limit. It can be considered as a good interpolation also for the region of $p \sim 1/a$, giving a qualitative explanation of Landau spectrum of He^4 .

Note, that the spectrum of density oscillation in usual (classical) liquids has qualitatively similar form, but with rather strong damping of oscillations in the region of wave vectors $p \sim 1/a$. The existence of "roton" minimum in classical liquids is also directly related to the maximum of structure factor.

5.7 Degenerate interacting Bose gas.

Let us consider now the system of interacting Bosons from microscopic point of view. We shall limit ourselves to the analysis of weakly interacting Bose gas, which can be described using rather rigorous approach first proposed by Bogolyubov.

Consider the simple model of Bose gas with point-like repulsion between particles and limit ourselves to the case of $T = 0$. Hamiltonian of the system in second quantization representation can be written as:

$$H = \sum_{\mathbf{p}} \frac{\mathbf{p}^2}{2m} a_{\mathbf{p}}^+ a_{\mathbf{p}} + \frac{v_0}{2V} \sum_{\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}'_1 + \mathbf{p}'_2} a_{\mathbf{p}'_1}^+ a_{\mathbf{p}'_2}^+ a_{\mathbf{p}_2} a_{\mathbf{p}_1} \quad (5.87)$$

where $v_0 > 0$ is the coupling constant of repulsive interaction, creation and annihilation operators of Bosons satisfy commutation relations:

$$\begin{aligned} a_{\mathbf{p}} a_{\mathbf{p}'}^+ - a_{\mathbf{p}'}^+ a_{\mathbf{p}} &= \delta_{\mathbf{p}\mathbf{p}'} \\ a_{\mathbf{p}} a_{\mathbf{p}'} - a_{\mathbf{p}'} a_{\mathbf{p}} &= 0 \quad a_{\mathbf{p}}^+ a_{\mathbf{p}'}^+ - a_{\mathbf{p}'}^+ a_{\mathbf{p}}^+ = 0 \end{aligned} \quad (5.88)$$

In the ground state of an ideal Bose gas all particles are in Bose *condensate*, i.e. in the state with zero momentum and energy. In terms of occupation numbers $N_{\mathbf{p}=0} = N_0 = N$, where N is the total number of particles in gas. Accordingly $N_{\mathbf{p} \neq 0} = 0$. In weakly interacting Bose gas in the ground state and also in weakly excited states $N_{\mathbf{p} \neq 0} \neq 0$, but these occupation numbers are very small compared with *macroscopic* value of N_0 . The fact that $a_0^+ a_0 = N_0 \approx N \gg 1$ means that the expression for commutator of creation and annihilation operators of condensate particles $a_0 a_0^+ - a_0^+ a_0 = 1$ is small in comparison with a_0 and a_0^+ , so that we can neglect unity in the right hand side and consider these operators as the usual *c*-numbers¹¹:

$$a_0 = a_0^+ = \sqrt{N_0} \quad (5.89)$$

Then we can accurately separate in Hamiltonian (5.87) all terms, containing condensate operators and replace them by (5.89). After that we can build a kind of perturbation theory in powers of “small” operators $a_{\mathbf{p}}, a_{\mathbf{p}}^+$ with $\mathbf{p} \neq 0$. The main contribution comes from scattering processes (interactions) of condensate particles and particles excited from the condensate (i.e. transitions of particles to and from condensate), while scattering processes between particles excited “above” condensate can be just neglected (in first approximation).

The zero order term in interaction Hamiltonian contains:

$$\frac{v_0}{2V} a_0^+ a_0^+ a_0 a_0 = \frac{v_0}{2V} a_0^4 = \frac{v_0}{2V} N_0^2 \quad (5.90)$$

The terms of first order in $a_{\mathbf{p}}, a_{\mathbf{p}}^+$ with $\mathbf{p} \neq 0$ are absent as these can not satisfy the momentum conservation, shown explicitly in Eq. (5.87). The second order terms have the form:

$$\frac{v_0}{2V} a_0^2 \sum_{p>0} (a_{\mathbf{p}} a_{-\mathbf{p}} + a_{\mathbf{p}}^+ a_{-\mathbf{p}}^+ + 2a_{\mathbf{p}}^+ a_{\mathbf{p}} + 2a_{-\mathbf{p}}^+ a_{-\mathbf{p}}) \quad (5.91)$$

¹¹More rigorously it is equivalent to an assumption that in the ground state the average values of these operators $\langle a_0 \rangle$ and $\langle a_0^+ \rangle$ are nonzero and equal to $\sqrt{N_0} e^{\pm i\phi}$ (where ϕ is an arbitrary phase of a complex number, which can be assumed here to be just a zero), i.e. there is a *finite* amplitude of creation and annihilation of particles in condensate. Then the number of particles in condensate is not conserved, in this sense the ground state of interacting Bose gas breaks the particle conservation law. Thus, the symmetry of the ground state is *lower* than the symmetry of the Hamiltonian (5.87), which conserves the particle number. This is the first time when we meet the phenomenon of *spontaneous symmetry breaking* and the appearance of *anomalous* averages, breaking the symmetry of Hamiltonian.

Limiting ourselves to second order terms we can replace here $a_0^2 = N_0$ by the total particle number N . However, in term (5.90) we have to take into account more accurate relation:

$$a_0^2 + \sum_{p>0} a_{\mathbf{p}}^+ a_{\mathbf{p}} = N \quad (5.92)$$

and express N_0 via N and $\sum_{\mathbf{p}} a_{\mathbf{p}}^+ a_{\mathbf{p}}$. After explicit calculations, combining (5.90) and (5.91), we obtain:

$$\frac{N^2}{2V} v_0 + \frac{N}{V} v_0 \sum_{p>0} (a_{\mathbf{p}} a_{-\mathbf{p}} + a_{\mathbf{p}}^+ a_{-\mathbf{p}}^+ + a_{\mathbf{p}}^+ a_{\mathbf{p}} + a_{-\mathbf{p}}^+ a_{-\mathbf{p}}) \quad (5.93)$$

Thus we can rewrite Hamiltonian (5.87) with given accuracy as:

$$H = \frac{N^2}{2V} v_0 + \sum_{p>0} \left(\frac{N}{V} v_0 + \frac{\mathbf{p}^2}{2m} \right) (a_{\mathbf{p}}^+ a_{\mathbf{p}} + a_{-\mathbf{p}}^+ a_{-\mathbf{p}}) + \frac{N}{V} v_0 \sum_{p>0} (a_{\mathbf{p}} a_{-\mathbf{p}} + a_{\mathbf{p}}^+ a_{-\mathbf{p}}^+) \quad (5.94)$$

This Hamiltonian is quadratic in operators $a_{\mathbf{p}}$ and $a_{\mathbf{p}}^+$ and can be *diagonalized* by so called $u - v$ - transformation, first introduced by Bogolyubov. Let us transform to new creation and annihilation operators of Bosons $\alpha_{\mathbf{p}}^+$ and $\alpha_{\mathbf{p}}$, related to $a_{\mathbf{p}}^+$ and $a_{\mathbf{p}}$ by linear transformation:

$$\begin{aligned} a_{\mathbf{p}} &= u_p \alpha_{\mathbf{p}} + v_p \alpha_{\mathbf{p}}^+ \\ a_{\mathbf{p}}^+ &= u_p \alpha_{\mathbf{p}}^+ + v_p \alpha_{\mathbf{p}} \end{aligned} \quad (5.95)$$

New operators should satisfy the usual Bose commutation relations like (5.89), it is guaranteed if coefficients u_p and v_p satisfy the condition:

$$u_p^2 - v_p^2 = 1. \quad (5.96)$$

Substituting $a_{\mathbf{p}}^+$ and $a_{\mathbf{p}}$ in the form of (5.95) into Hamiltonian (5.94) we obtain:

$$\begin{aligned} H &= \sum_{p>0} \left\{ \left(\frac{\mathbf{p}^2}{2m} + \frac{Nv_0}{V} \right) (u_p^2 + v_p^2) + 2 \frac{Nv_0}{V} u_p v_p \right\} (\alpha_{\mathbf{p}}^+ \alpha_{\mathbf{p}} + \alpha_{-\mathbf{p}}^+ \alpha_{-\mathbf{p}}) + \\ &+ \sum_{p>0} \left\{ \left(\frac{\mathbf{p}^2}{2m} + \frac{Nv_0}{V} \right) 2u_p v_p + \frac{Nv_0}{V} (u_p^2 + v_p^2) \right\} (\alpha_{\mathbf{p}}^+ \alpha_{-\mathbf{p}}^+ + \alpha_{\mathbf{p}} \alpha_{-\mathbf{p}}) + \\ &+ \sum_{p>0} \left\{ 2 \left(\frac{\mathbf{p}^2}{2m} + \frac{Nv_0}{V} \right) v_p^2 + 2 \frac{Nv_0}{V} u_p v_p \right\} + \frac{N^2 v_0}{2V} \end{aligned} \quad (5.97)$$

To diagonalize this Hamiltonian we have to exclude terms like $\alpha_{\mathbf{p}}^+ \alpha_{-\mathbf{p}}^+$ and $\alpha_{\mathbf{p}} \alpha_{-\mathbf{p}}$, which can be achieved by the requirement:

$$\left(\frac{\mathbf{p}^2}{2m} + \frac{Nv_0}{V} \right) 2u_p v_p + \frac{Nv_0}{V} (u_p^2 + v_p^2) = 0 \quad (5.98)$$

which gives the second relation fixing the coefficients u_p and v_p . Solving equations (5.96) and (5.98) we get:

$$u_p = \frac{1}{\sqrt{1 - A_p^2}} \quad v_p = \frac{A_p}{\sqrt{1 - A_p^2}} \quad (5.99)$$

where

$$A_p = \frac{V}{Nv_0} \left\{ \varepsilon(p) - \frac{p^2}{2m} - \frac{Nv_0}{V} \right\} \quad (5.100)$$

$$\varepsilon(p) = \sqrt{\frac{N}{V} \frac{p^2 v_0}{m} + \frac{p^4}{4m^2}} \quad (5.101)$$

Substituting these coefficients to (5.97) we obtain diagonalized Hamiltonian, having the form of the Hamiltonian of new *noninteracting* quasiparticles, corresponding to operators $\alpha_{\mathbf{p}}^+$ and $\alpha_{\mathbf{p}}$:

$$H = E_0 + \sum_{\mathbf{p} \neq 0} \varepsilon(p) \alpha_{\mathbf{p}}^+ \alpha_{\mathbf{p}} \quad (5.102)$$

where the spectrum of these new quasiparticles $\varepsilon(p)$ (5.101) is radically different from the spectrum of free Bosons due to interaction effects. The ground state energy is given by:

$$E_0 = \frac{N^2}{2V} v_0 + \frac{1}{2} \sum_{p \neq 0} \left[\varepsilon(p) - \frac{p^2}{2m} - \frac{N}{V} v_0 \right] \quad (5.103)$$

At small momenta the quasiparticle energy (5.101) can be written as:

$$\varepsilon(p) = \sqrt{\frac{v_0}{mV_0}} p \equiv up \quad (5.104)$$

where $V_0 = V/N$ is volume per particle, while u , which is completely determined by interactions, represents the speed of Bogolyubov's sound. At large momenta (5.101) reduces to $\varepsilon(p) \approx \frac{p^2}{2m} + \frac{v_0}{V_0}$, i.e. to the spectrum of free particles.

Thus, at small momenta interactions between Bosons leads to complete transformation of the spectrum of elementary excitations, which becomes similar to that postulated by Landau, and satisfies the criterion for superfluidity, so that:

$$v_c = \left(\frac{\varepsilon(p)}{p} \right)_{p \rightarrow 0} = \sqrt{\frac{v_0}{mV_0}} > 0 \quad (5.105)$$

defines the appropriate critical velocity, coinciding in this model with the speed of (Bogolyubov) sound.

From this analysis it becomes clear that the phenomenon of Bose condensation is crucial for the appearance of superfluidity.

5.8 Fermi liquids.

Liquid of interacting particles with half-integer spin (Fermi liquid) is characterized by the spectrum of elementary excitations and other properties, which are radically different from those of Bose liquid. An example of real Fermi liquid is He^3 . Probably most common case is the liquid of conduction electrons in metals. More exotic examples are nucleons in atomic nuclei, neutron stars matter etc. We shall see below that the energy spectrum of elementary excitations in Fermi liquid is somehow similar to that of an ideal Fermi gas, while the role of interactions reduces to relatively minor "renormalization" of experimental observables.

Phenomenological theory of Fermi liquids was proposed by Landau. The starting point of this theory is the statement that classification of energy levels in Fermi system remains the same after adiabatic “switching” of interaction between particles, as we go from Fermi gas to *normal* Fermi liquid. Elementary excitations (quasiparticles) in Fermi liquid are in one to one correspondence with free particle excitations of an ideal Fermi gas. Thus, free particles of the gas are replaced by some effective quasiparticles of the liquid, moving in self-consistent field created by interactions. Criteria for these quasiparticles to have well defined momentum will be discussed shortly below. Let n_p be momentum distribution function of quasiparticles in Fermi liquid. The ground state contains no quasiparticle excitations and corresponds to distribution function of quasiparticles with all states below Fermi momentum (i.e. for $p < p_F$) occupied. This is equivalent to an assumption of existence of well defined Fermi surface (sphere) in momentum space. The value of p_F is related to particle density of the liquid (the number of particles in unit volume) by the same expression (4.43), as in Fermi gas¹²:

$$p_F = (3\pi^2)^{1/3} \left(\frac{N}{V} \right)^{1/3} \hbar. \quad (5.106)$$

It must be stressed that the total energy of a liquid E does not reduce to the sum of quasiparticle energies: E is represented by a functional¹³ of distribution function of some general form, which does not reduce to $\int d\tau n_p \varepsilon_p$, as in an ideal gas. At $T = 0$ this functional defines the ground state energy of Fermi liquid E .

We can normalize distribution function as:

$$\int d\tau n_p = \frac{N}{V} \quad (5.109)$$

where N is the number of particles in liquid, $d\tau = d^3p/(2\pi\hbar)^3$. The change of E under a small variation of distribution function can be written as:

$$\frac{\delta E}{V} = \int d\tau \varepsilon_p \delta n_p, \quad (5.110)$$

$$\varepsilon_p = \frac{\delta E}{\delta n_p} \quad (5.111)$$

The value of ε_p is given by functional (variational) derivative of E by distribution function and corresponds the change of ground state energy of the system due

¹²This is directly related to our assumption about classification of levels in Fermi liquid and Pauli principle. In fact this result can be proved within modern quantum-field theoretic (microscopic) approach to Fermi liquid, where it is known as Luttinger theorem.

¹³The usual function defines some mapping of one set of numbers into another set of numbers. The functional defines mapping of a set *functions* into a set of *numbers*. Typical example of a functional is definite integral: $F[f(x)] = \int_a^b dx f(x)$. Note that function of function is again some function, not a functional. Functional (variational) differentiation used below is formally defined as follows:

$$\frac{\delta F[f(x)]}{\delta f(y)} = \lim_{\varepsilon \rightarrow 0} \frac{F[f(x) + \varepsilon \delta(x-y)] - F[f(x)]}{\varepsilon}. \quad (5.107)$$

For example, for $F[f(x)]$ in the form of definite integral:

$$\frac{\delta F[f(x)]}{\delta f(y)} = \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} \left[\int dx [f(x) + \varepsilon \delta(x-y)] - \int dx f(x) \right] = \int dx \delta(x-y) = 1 \quad (5.108)$$

to and addition of a single quasiparticle with momentum \mathbf{p} . This energy of a quasiparticle is itself the functional of distribution function, i.e. the form of ε_p is determined by distribution of all other quasiparticles in Fermi liquid.

Distribution function of quasiparticles (at equilibrium) has the form of the usual Fermi distribution. This is due to the same classification of energy levels in the liquid as in ideal Fermi gas — the entropy of liquid is determined by the same combinatorial expression of Eq. (4.15), which for the liquid can be written as:

$$S = - \int d\tau [n_p \ln n_p + (1 - n_p) \ln(1 - n_p)] \quad (5.112)$$

Looking for the maximum (extremum) of this expression with additional conditions of fixed total number of particles and total energy (similarly to our analysis for ideal gas) we obtain at finite T :

$$n_p = \frac{1}{e^{\frac{\varepsilon_p - \mu}{T}} + 1} \quad (5.113)$$

However, it should be stressed that ε_p here is some functional of n_p , so that Eq. (5.113) gives in fact some complicated implicit definition of n_p . In fact it can not be found in explicit form¹⁴.

Let us discuss explicitly the spin of quasiparticles $\vec{\sigma}$. In homogeneous and isotropic liquid the scalar ε can depend only on scalar arguments, so that $\vec{\sigma}$ can enter the quasiparticle energy (in the absence of external magnetic field!) only as $\hat{\sigma}^2$ or $(\vec{\sigma}\mathbf{p})^2$ (first order term like $\vec{\sigma}\mathbf{p}$ is not allowed, as it is pseudoscalar due to the axial vector nature of spin). For spin $s = 1/2$ we have:

$$\vec{\sigma}^2 = \frac{3}{4} \quad (\vec{\sigma}\mathbf{p})^2 = \frac{1}{4}\mathbf{p}^2 \quad (5.114)$$

so that σ drops completely and quasiparticle energy does not depend on spin. Accordingly, all energy levels are twice degenerate and we have to write everywhere $d\tau = 2 \frac{d^3p}{(2\pi\hbar)^3}$.

We have attributed each quasiparticle a well defined momentum. Necessary requirement is that any indeterminacy of this momentum is to be small compared to the value of momentum itself and also in comparison to the size of the “smearing” region of distribution function in momentum space (which is defined by small excitation energies or temperatures). Pauli principle restricts possible scatterings of quasiparticles precisely to this region, and after the scattering quasiparticles should arrive also to free (empty) states from this same region. Thus, the probability of quasiparticle scattering is to be proportional to the square of the width Δp of the “smearing” region. This obviously leads to scattering induced indeterminacy of quasiparticle momentum of the order of Δp^2 . Now it is clear that for small enough Δp indeterminacy of momentum will be small not only in comparison to momentum $p \sim p_F$ itself, but also compared to Δp , if we consider it to be small enough. Thus, the quasiparticles in Fermi liquid are well defined only *close enough to the Fermi surface* and quasiparticle

¹⁴Within the microscopic approach to Fermi liquid it was shown by Migdal that distribution function of particles (not quasiparticles!) at $T = 0$ contains a finite discontinuity at $\varepsilon_p = \mu$, proving the existence of Fermi surface in the case of interacting Fermions. The size of this discontinuity in Fermi liquid < 1 , which differs liquid from an ideal gas, where it is equal to 1 (see more detailed discussion below in Chapter 11).

energy ε_p is also well defined only in this narrow region of energies (or temperatures!). Expanding quasiparticle energy in Taylor series in powers of $p - p_F$ we obtain:

$$\xi_p = \varepsilon_p - \mu \approx v_F(|\mathbf{p}| - p_F) \quad \mu = \varepsilon_F \quad (5.115)$$

where $v_F = \left. \frac{\partial \varepsilon_p}{\partial p} \right|_{p=p_F}$ is Fermi velocity.

We have already noted above that during quasiparticle creation or annihilation the angular momentum of any quantum system can only change by integer. If we are dealing with Fermions of spin $s = 1/2$ this means that quasiparticles can be created (annihilated) in pairs. In Fermi liquid the creation of a quasiparticle with energy given by Eq. (5.115) above the ground state takes place via its excitation from the completely filled Fermi sphere to some state above the Fermi surface, with simultaneous creation of a “hole” (of the same energy) below the Fermi surface. Elementary excitation in Fermi liquid is just this process of quasiparticle – quasihole pair creation. This is quite similar to the case of an ideal Fermi gas, but the major difference is that such excitations are well defined only close enough to Fermi surface, where scattering (interaction) processes between quasiparticles are strongly suppressed due to Pauli principle limitations.

In an ideal Fermi gas we have $\varepsilon_p = p^2/2m$ and $v_F = p_F/m$. By analogy, in Fermi liquid we may introduce the value of

$$m^* = \frac{p_F}{v_F} \quad (5.116)$$

which is called an effective mass of a quasiparticle¹⁵. Then the specific heat of Fermi liquid is given by the usual “gas-like” expression (4.70), with simple replacement $m \rightarrow m^*$:

$$C = \frac{\pi^2}{3} \nu_F T \quad \nu_F = \frac{m^* p_F}{\pi^2 \hbar^3} \quad (5.117)$$

To analyze systems with variable number of particles it is convenient to use thermodynamic potential $\Omega = F - \mu N$. At $T = 0$ obviously we have $F = E$, so that $\Omega = E - \mu N$. Consider an “excited” state of the system described by the difference:

$$\Omega - \Omega_0 = E - E_0 - \mu(N - N_0) \quad (5.118)$$

where index 0 denotes the ground state. We can write:

$$N - N_0 = \sum_p \delta n_p = \int d\tau \delta n_p \quad (5.119)$$

According to Eq. (5.111):

$$E[n_p] = E_0 + \sum_p \varepsilon_p \delta n_p + O(\delta n_p^2) \quad (5.120)$$

so that:

$$\Omega - \Omega_0 = \sum_p (\varepsilon_p - \mu) \delta n_p + O(\delta n_p^2) \quad (5.121)$$

¹⁵For example, in liquid He^3 it is known from experiments that $m^* \approx 2.4m_{He^3}$, $p_F/\hbar \approx 0.8 \cdot 10^8 \text{cm}^{-1}$. The region where quasiparticles (i.e. the concept of Fermi liquid itself) are well defined for He^3 is limited to temperatures $T < 0.5K$.

We consider only small variations δn_p close to the Fermi surface, i.e. in a narrow energy layer $\sim \delta$ around it, so that $\varepsilon_p - \mu \sim \delta$. But $\delta n_p \sim \delta$ itself, so that $\Omega - \Omega_0 \sim \delta^2$, and in an expansion of Eq. (5.121) we have to keep all terms of the order of $\sim \delta^2$. Then we can write:

$$\Omega - \Omega_0 = \sum_p (\varepsilon_p - \mu) \delta n_p + \frac{1}{2} \sum_{pp'} f(\mathbf{p}, \mathbf{p}') \delta n_p \delta n_{p'} + O(\delta_p^3) \quad (5.122)$$

where we have introduced:

$$f(\mathbf{p}, \mathbf{p}') = \frac{\delta^2 E}{\delta n_p \delta n_{p'}} \quad (5.123)$$

– the so called Landau function, describing the *interaction* between quasiparticles. In fact, from definitions of Eqs. (5.111) and (5.122) we can see that variation δn_p leads to a change of quasiparticle energy:

$$\delta \varepsilon_{\mathbf{p}} = \int d\tau' f(\mathbf{p}, \mathbf{p}') \delta n_{p'} \quad (5.124)$$

which is completely determined by Landau function. Here is the main difference of Fermi liquid theory from the model of an ideal fermi gas.

Let us assume that $f(\mathbf{p}, \mathbf{p}')$ is a continuous function for \mathbf{p} and \mathbf{p}' close to p_F . In practice it is sufficient to know $f(\mathbf{p}, \mathbf{p}')$ only on the Fermi surface itself, i.e. for $|\mathbf{p}| = |\mathbf{p}'| = p_F$. Then $f(\mathbf{p}, \mathbf{p}')$ depends only on the mutual orientation of vectors \mathbf{p} and \mathbf{p}' (angle in between) and on spins σ, σ' . It is convenient to write $f(\mathbf{p}, \mathbf{p}')$ separating explicitly independent parts, corresponding to parallel or antiparallel orientations of spins of quasiparticles:

$$f_{\uparrow\uparrow}(\mathbf{p}, \mathbf{p}') = f^s(\mathbf{p}, \mathbf{p}') + f^a(\mathbf{p}, \mathbf{p}') \quad (5.125)$$

$$f_{\uparrow\downarrow}(\mathbf{p}, \mathbf{p}') = f^s(\mathbf{p}, \mathbf{p}') - f^a(\mathbf{p}, \mathbf{p}') \quad (5.126)$$

$$(5.127)$$

We can say that antisymmetric part $f^a(\mathbf{p}, \mathbf{p}')$ is due to some exchange interaction $2f^a(\mathbf{p}, \mathbf{p}')$, which appears only when spins are parallel. Another representation of Landau function is also widely used in the literature:

$$f_{\sigma, \sigma'}(\mathbf{p}, \mathbf{p}') = \varphi(\mathbf{p}, \mathbf{p}') + (\hat{\sigma} \hat{\sigma}') \psi(\mathbf{p}, \mathbf{p}') \quad (5.128)$$

where $\hat{\sigma}$ and $\hat{\sigma}'$ are spin matrices of two fermions.

Thus, in isotropic Fermi liquid functions $f^a(\mathbf{p}, \mathbf{p}')$ and $f^s(\mathbf{p}, \mathbf{p}')$ depend only on the angle θ between \mathbf{p} and \mathbf{p}' . Then these functions can be represented as expansions over Lagrange polynomials:

$$f^{s(a)}(\mathbf{p}, \mathbf{p}') = \sum_{l=0}^{\infty} P_l(\cos \theta) f_l^{s(a)} \quad (5.129)$$

so that both functions $f(\mathbf{p}, \mathbf{p}')$ are completely determined by the sets of coefficients f_l^s and f_l^a , which are called Fermi liquid constants. It is convenient to introduce dimensionless constants $F_l^{s,(a)}$ via:

$$\nu_F f_l^{s,(a)} = \frac{m^* p_F}{\pi^2 \hbar^3} f_l^{s,(a)} \equiv F_l^{s,(a)} \quad (5.130)$$

The value of these constants determine renormalization of a number of physical characteristics of Fermi liquid and at least some of them can be determined from experiments. In most cases only few constants are important. In particular, the following relation between the “bare” mass of the particle and effective mass of the quasiparticle can be derived using Galilean invariance [2, 21]:

$$\frac{1}{m} = \frac{1}{m^*} + \frac{p_F}{(2\pi\hbar)^3} 4\pi \int d\cos\theta \cos\theta f(\mathbf{p}, \mathbf{p}') \quad (5.131)$$

Using (5.129), (5.130) and properties of Lagrange polynomials we can get:

$$\frac{m^*}{m} = 1 + \frac{F_1^s}{3} \quad (5.132)$$

From here it is obvious that $F_1^s > -3$. Similarly, taking into account interaction with external magnetic field (see also below), we can derive the spin (paramagnetic) susceptibility of Fermi liquid as [2, 21]:

$$\chi_p = \mu_B^2 \frac{m^* p_F}{\pi^2 \hbar^3} \frac{1}{1 + F_0^a} \quad (5.133)$$

which differs from similar Fermi gas expression (4.79) by the replacement $m \rightarrow m^*$ and Fermi liquid renormalization $1 + F_0^a$.

5.9 Electron liquid in metals*.

In our previous discussion we implicitly assumed that Fermi liquid consists of neutral particles (e.g. like He^3), so that interaction is short range. For Fermi liquid of electrons in metals long range Coulomb interaction becomes important. In case of long range interactions the basic Fermi liquid theory relation (5.124) becomes, strictly speaking, invalid. However, certain generalization of the standard Fermi liquid approach for the case of charged Fermi liquids, proposed by Silin, correctly takes into account Coulomb interaction and reduces the theory to the form quite similar to that of neutral Fermi liquid theory.

Note, first of all, that for the general case of local in time relation we can write the generalization of Eq. (5.124) in the following form:

$$\delta\varepsilon(\mathbf{p}, \mathbf{r}) = Sp_{\sigma'} \int d\mathbf{r}' \int \frac{d^3p'}{(2\pi\hbar)^3} F(\mathbf{p}, \mathbf{p}'; \mathbf{r}, \mathbf{r}') \delta n(\mathbf{p}', \mathbf{r}') \quad (5.134)$$

where we have introduced an explicit dependence on coordinates, necessary for the analysis of spatially inhomogeneous perturbations and taken Sp over spin¹⁶. Function $F(\mathbf{p}, \mathbf{p}'; \mathbf{r}, \mathbf{r}')$ here represents the second variational derivative of the ground state energy of Fermi liquid and also depends not only on momenta \mathbf{p} , \mathbf{p}' and spins, but also on coordinates \mathbf{r} and \mathbf{r}' . In simplest case (self-consistent field in Hartree approximation), neglecting the exchange effects, for particles interacting via potential $U(|\mathbf{r} - \mathbf{r}'|)$, we have:

$$F_H(\mathbf{p}, \mathbf{p}'; \mathbf{r}, \mathbf{r}') = U(|\mathbf{r} - \mathbf{r}'|). \quad (5.135)$$

¹⁶Distribution function of quasiparticles here is understood to be in Wigner representation, to account for coordinate dependence.

This expression neglects the so called correlation effects, while the difference $F - F_H$ by definition is determined by these effects, including the most important effects of exchange correlations. It is important to note that characteristic distances for correlation effects are of the order of electron wavelength at the Fermi level, i.e. of the order of average distance between particles (electrons) $(N/V)^{-1/3} \sim 10^{-8}\text{cm}$ (in metals). Thus, for the most interesting case, when the characteristic scale of a change of distribution of quasiparticles is significantly larger than the correlation range, we may assume:

$$F(\mathbf{p}, \mathbf{p}'; \mathbf{r}, \mathbf{r}') - F_H(\mathbf{p}, \mathbf{p}'; \mathbf{r}, \mathbf{r}') \approx \delta(\mathbf{r} - \mathbf{r}')f(\mathbf{p}, \mathbf{p}') \quad (5.136)$$

Then Eq. (5.134) can be rewritten as:

$$\delta\varepsilon(\mathbf{p}, \mathbf{r}) = Sp_{\sigma'} \int d\mathbf{r}' \int \frac{d^3p'}{(2\pi\hbar)^3} U(|\mathbf{r} - \mathbf{r}'|) \delta n(\mathbf{p}', \mathbf{r}') + Sp_{\sigma'} \int \frac{d^3p'}{(2\pi\hbar)^3} f(\mathbf{p}, \mathbf{p}') \delta n(\mathbf{p}', \mathbf{r}) \quad (5.137)$$

For electrons in metals $U(r) = e^2/r$. In equilibrium, when distribution of particles does not depend on coordinates, spatially nonlocal coupling in the first term of (5.137) is irrelevant and the properties of the system of charged particles are, in some sense, similar to those considered above for neutral Fermi liquid. Note, however, that the first term in (5.137), taken literally, diverges in the case of spatially homogeneous distributions. This divergence is actually fictitious, as we have to take into account the existence in a metal of the homogeneous background of positive ions, guaranteeing the total electrical neutrality of the system. For spatially inhomogeneous distributions this term can be considered as a manifestation of self-consistent scalar potential $\varphi(\mathbf{r})$:

$$e\varphi(\mathbf{r}) = Sp_{\sigma'} \int d\mathbf{r}' \int \frac{d^3p'}{(2\pi\hbar)^3} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \delta n(\mathbf{p}', \mathbf{r}'). \quad (5.138)$$

This potential can be determined by the solution of Poisson equation:

$$\nabla^2\varphi(\mathbf{r}) = -4\pi eSp_{\sigma'} \int \frac{d^3p'}{(2\pi\hbar)^3} \delta n(\mathbf{p}', \mathbf{r}) \quad (5.139)$$

which is an integral part of Landau – Silin theory of charged Fermi liquids.

Let us now take into account the interaction with an external magnetic field \mathbf{B} . Then Eq. (5.137) for the charged Fermi liquid is rewritten as:

$$\delta\varepsilon(\mathbf{p}, \mathbf{r}) = -\mu_B \vec{\sigma} \mathbf{B} + e\varphi(\mathbf{r}) + Sp_{\sigma'} \int \frac{d^3p'}{(2\pi\hbar)^3} f(\mathbf{p}, \mathbf{p}') \delta n(\mathbf{p}, \mathbf{r}) \quad (5.140)$$

It is important that both $\delta\varepsilon$ and φ are determined now by the system of coupled equations (5.139) and (5.140) in a self-consistent way. In particular, it leads to the phenomenon of screening of long range Coulomb forces in quantum system (metallic Fermi liquid), which will be discussed later in Chapter 11.

Neglecting relativistic effects like spin – orbital coupling, we can again write down interaction function $f(\mathbf{p}, \mathbf{p}')$ as in (5.127) or (5.128). Then again we can introduce Fermi liquid constants (5.129) and (5.130), which are to be determined from experiments. Finally, for the charged Fermi liquid we can also obtain expressions for specific heat (5.117), effective mass (5.132) and spin susceptibility (5.133), which are just the same as for the neutral Fermi liquid [21]. Obviously, the values of Fermi liquid constants in different metals are different and

also different from those in liquid He^3 , being the characteristics of quasiparticle interactions in a given system (metal). Beside that, in real metals electronic Fermi liquid may be anisotropic, with non spherical Fermi surface, due to the effects of the given crystal lattice. This requires the appropriate generalizations of isotropic model considered here.

Chapter 6

SUPERCONDUCTIVITY

6.1 Cooper instability.

Up to now we have analyzed the so called *normal* Fermi liquid with repulsive interaction between particles. However, as we shall see shortly, the ground state of Fermi liquid becomes unstable in case of weak (even infinitesimal!) *attraction* between quasiparticles in the vicinity of the Fermi surface. This instability, discovered by Cooper, leads to formation of bound states of Fermions (Cooper pairs), i.e. effective Bosons in Fermion system. It is basic for understanding of such physical phenomena as superconductivity in metals and superfluidity in liquid He^3 .

Below we shall present a simplified analysis of Cooper instability, which gives “almost” correct answer [22]. We have already noted that quasiparticles in Fermi liquid are created in pairs (particle above the Fermi surface and hole below). Close to Fermi surface, according to Eq. (5.115), we can introduce quasiparticle energies as:

$$\begin{aligned}\xi_p &= v_F(|\mathbf{p}| - p_F) \quad (\text{particle}) \\ \xi_p &= v_F(p_F - |\mathbf{p}|) \quad (\text{hole})\end{aligned}\tag{6.1}$$

so that quasiparticle energy in general can be written as $|\xi_p|$.

Consider interaction of two particles (or two holes) close to Fermi surface. Schroedinger equation for two quasiparticles interacting via potential $U(\mathbf{r}_1, \mathbf{r}_2)$ can be written as¹:

$$[H_0(\mathbf{r}_1) + H_0(\mathbf{r}_2) + U(\mathbf{r}_1, \mathbf{r}_2)]\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)\tag{6.2}$$

where $H_0(\mathbf{r})$ is the Hamiltonian of a free quasiparticle:

$$H_0(\mathbf{r})\psi_{\mathbf{p}}(\mathbf{r}) = |\xi_p|\psi_{\mathbf{p}}(\mathbf{r})\tag{6.3}$$

where $\psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{p}\mathbf{r}/\hbar}$ is the wave function of a free quasiparticle. Let us analyze the possibility of formation of the bound state of these two such particles (Cooper pair). In the ground state the momentum of the bound pair should be

¹It is the point where we actually oversimplify the real many-particle problem – here we analyze two separate quasiparticles on the background of “rigid” Fermi surface.

zero and we assume it have zero spin (singlet state)² Thus, the pair is described by the superposition of two quasiparticles with opposite momenta and spins:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mathbf{p}} c_{\mathbf{p}} \psi_{\mathbf{p}\uparrow}(\mathbf{r}_1) \psi_{-\mathbf{p}\downarrow}(\mathbf{r}_2) \quad (6.4)$$

Substituting this expression into Eq. (6.2) we obtain the equation for coefficients $c_{\mathbf{p}}$:

$$2|\xi_{\mathbf{p}}|c_{\mathbf{p}} + \sum_{\mathbf{p}'} U_{\mathbf{p}\mathbf{p}'} c_{\mathbf{p}'} = E c_{\mathbf{p}} \quad (6.5)$$

where $U_{\mathbf{p}\mathbf{p}'}$ is matrix element of interaction. Let us assume that this matrix element has the following form:

$$U_{\mathbf{p}\mathbf{p}'} = \begin{cases} -g & \text{for } p_F - \frac{\hbar\omega_D}{v_F} < |\mathbf{p}|, |\mathbf{p}'| < p_F + \frac{\hbar\omega_D}{v_F} \\ 0 & \text{outside this interval.} \end{cases} \quad (6.6)$$

The sign of the coupling constant g corresponds to attraction, while the limitations on momenta mean that this attraction exists only in rather thin energy layers of the width of $2\hbar\omega_D$ around the Fermi level. The appearance of Debye frequency here is connected to the well established fact that in most metals the microscopic mechanism of this attraction is due to electron – phonon interaction, and phonons can effectively interact with electrons only in energy layer $2\hbar\omega_D \ll \varepsilon_F$ near the Fermi surface.

From (6.5) and (6.6) we find the following expression for the coefficient $c_{\mathbf{p}}$:

$$c_{\mathbf{p}} = \frac{gI}{2|\xi_{\mathbf{p}}| - E} \quad (6.7)$$

where

$$I = \sum_{p'=p_F - \frac{\hbar\omega_D}{v_F}}^{p'=p_F + \frac{\hbar\omega_D}{v_F}} c_{\mathbf{p}'} \quad (6.8)$$

The bound state of two particles corresponds to the negative value of energy $E = -2\Delta$ ($\Delta > 0$). Substituting this to (6.7), and (6.7) into (6.8), we get:

$$\begin{aligned} I &= \frac{1}{2} g I \sum_{p'=p_F - \frac{\hbar\omega_D}{v_F}}^{p'=p_F + \frac{\hbar\omega_D}{v_F}} \frac{1}{|\xi_{p'}| + \Delta} = \\ &= \frac{1}{4} g I \nu_F \int_{-\hbar\omega_D}^{\hbar\omega_D} d\xi \frac{1}{|\xi| + \Delta} \approx \frac{1}{2} g I \nu_F \ln \frac{\hbar\omega_D}{\Delta} \end{aligned} \quad (6.9)$$

where we have transformed summation over p to integration over $\xi = v_F(p - p_F)$, introducing the density of states at the Fermi level $\nu_F = \frac{m p_F}{\pi^2 \hbar^3}$ and taken into account that $\Delta \ll \hbar\omega_D$. The extra coefficient 1/2 is due to summation here being done over the states of one of the particles of the pair, with fixed spin

²We consider here the simplified model with almost point-like attraction of quasiparticles and Pauli principle forbids two Fermions to have the same spin at the same point.

projection, while the expression for the density of states ν_F is written for both spin projections. Accordingly, from (6.9) we obtain the equation for Δ :

$$1 = \frac{1}{2} g \nu_F \ln \frac{\hbar \omega_D}{\Delta} \quad (6.10)$$

which always (even for infinitesimal values of g) possesses the nontrivial solution:

$$\Delta = \hbar \omega_D \exp \left[-\frac{2}{g \nu_F} \right] \quad (6.11)$$

determining the finite binding energy of the pair. Now we see that our system is unstable to formation of bound pairs of electrons even in the case of very weak attraction near the Fermi surface. This is called Cooper instability. Our analysis is slightly inaccurate, as we discussed two separate electrons above the fixed or “rigid” Fermi surface, but it gives the correct order of magnitude estimate of binding energy. Obviously, Cooper pairs are Bosons and can undergo Bose condensation at low enough temperatures. This is the main physical idea in explanation of microscopic nature of superfluidity in Fermi systems (superconductivity in metals).

6.2 Energy spectrum of superconductors.

The physical nature of superconductivity in metals is Cooper pairing of electrons, i.e. the formation of bound states of pairs particles, which are close (in momentum space) to Fermi surface, with equal and opposite momenta and spins. Microscopic mechanism of attractive interaction in traditional superconductors (with critical temperature of superconducting transition $T_c < 30K$) is, in most cases, attributed to electron – phonon interaction. The nature of this attraction in high – temperature superconductors (copper oxides, iron pnictides and chalcogenides) with $T_c > 30K$ is up to now not clear, most probably it is connected with interaction of current carriers (electrons or holes) with antiferromagnetic spin fluctuations. In superfluid He^3 (where in temperature region $T < 2.610^{-3}K$ exists several superfluid phases) this is definitely an exchange by spin fluctuations (paramagnons) among quasiparticles in Helium. A number of other pairing mechanisms were proposed in the literature, e.g. the so called excitonic mechanism. In any case we speak about interaction due to the exchange of some quanta of collective (Boson) excitations between Fermionic quasiparticles. In the following we shall not discuss these microscopic mechanisms of pairing, but shall limit ourselves to traditional and simplified model of superconductivity, proposed by Bardeen, Cooper and Schrieffer (BCS model)³.

Bardeen, Cooper and Schrieffer proposed the following *model* Hamiltonian of a superconductor:

$$H = \sum_{\mathbf{p}\sigma} \xi_{\mathbf{p}} a_{\mathbf{p}\sigma}^+ a_{\mathbf{p}\sigma} - \frac{g}{V} \sum_{\mathbf{p}\mathbf{p}'} a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} \quad (6.12)$$

³We shall consider only spin singlet pairing (opposite spins in pair) of electrons with zero orbital momentum of the pair (*s*-wave pairing), though in some metals and in superfluid He^3 Cooper pairing takes place in spin triplet state (parallel spins in pair) and not necessarily in *s*-wave orbital state. For example in high – temperature copper oxide superconductors *d*-wave singlet Cooper pairs are well confirmed by many experiments.

where $\xi_p = v_F(|\mathbf{p}| - p_F)$ is electron energy in *normal metal* in the vicinity of Fermi level, $a_{\mathbf{p}\sigma}^+$ and $a_{\mathbf{p}\sigma}$ creation and annihilation operators of electron with momentum \mathbf{p} and spin projection σ . The sign of coupling constant g is taken here corresponding to attraction and it is assumed that this constant is different from zero only in some energy layer around the Fermi surface, as in Eq. (6.6). Note that this Hamiltonian is much “reduced” – only electrons with opposite momenta and spins interact with each other, all other interactions are just dropped⁴.

To solve the Hamiltonian (6.12) we shall use the method proposed by Bogolyubov. Let us write down the interaction part of Hamiltonian (6.12):

$$H_{int} = -\frac{g}{V} \sum_{\mathbf{p}\mathbf{p}'} a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} \quad (6.13)$$

and make the following approximate replacement of operator part:

$$\begin{aligned} a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} &\rightarrow \langle a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ \rangle \langle a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} \rangle + \\ &+ \langle a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ \rangle a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} + \langle a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} \rangle a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ \end{aligned} \quad (6.14)$$

where angular brackets denote ground state averaging at $T = 0$ or statistical averaging for $T > 0$, i.e. $\langle \dots \rangle = Z^{-1} Sp(e^{-\frac{H}{T}} \dots)$ (assuming that these averages exist and are nonzero!). This replacement effectively excludes four operator terms in the Hamiltonian, reducing it to the following form, describing interaction with some self-consistent field, determined by these averages:

$$\begin{aligned} H_{int} = -\frac{g}{V} \sum_{\mathbf{p}\mathbf{p}'} \left\{ \langle a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ \rangle a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} + \langle a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} \rangle a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ \right\} - \\ - \frac{g}{V} \sum_{\mathbf{p}\mathbf{p}'} \langle a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ \rangle \langle a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} \rangle \end{aligned} \quad (6.15)$$

Finally the total Hamiltonian of the system can be written as⁵:

$$H = \sum_{\mathbf{p}\sigma} \xi_p a_{\mathbf{p}\sigma}^+ a_{\mathbf{p}\sigma} + \sum_{\mathbf{p}} \left\{ \Delta^* a_{\mathbf{p}\uparrow} a_{-\mathbf{p}\downarrow} + \Delta a_{-\mathbf{p}\downarrow}^+ a_{\mathbf{p}\uparrow}^+ \right\} + \frac{1}{g} V |\Delta|^2 \quad (6.16)$$

where we have introduced by definition:

$$\Delta^* = \frac{g}{V} \sum_{\mathbf{p}'} \langle a_{\mathbf{p}'\uparrow}^+ a_{-\mathbf{p}'\downarrow}^+ \rangle \quad (6.17)$$

$$\Delta = \frac{g}{V} \sum_{\mathbf{p}'} \langle a_{-\mathbf{p}'\downarrow} a_{\mathbf{p}'\uparrow} \rangle \quad (6.18)$$

the so called *anomalous averages*, directly related to *order parameter* of superconducting transition. Combinations of creation and annihilation operators,

⁴As a result of this simplification (separation of most important interactions) the problem may be studied in detail. BCS theory remains one of the best achievements of modern theoretical physics and its ideas are applied in many other systems (besides metals), energy scales and temperatures. Besides the examples given above, we can mention nucleon pairing in atomic nuclei, superfluidity in neutron star matter and also some models of modern theory of elementary particles.

⁵Note the sign change due to permutation of anticommuting Fermi operators.

standing here under the averaging (as well as in Eqs. (6.14) and (6.15)), are in fact creation and annihilation operators Cooper pairs (Bosons!) with zero momentum, similar to (5.89). Then, using Bogolyubov's idea applied before to Bose gas, we can replace these combination of *operators* in Hamiltonian (6.13) by *c*-numbers, defined by the averages in Eqs. (6.14), (6.15), or by directly related (6.17) and (6.18), i.e. assume, that Cooper pairs undergo Bose condensation at low enough temperatures. Without any limitations we can put here $\Delta^* = \Delta$, i.e. choose the phase of a complex number $\Delta = |\Delta|e^{i\phi}$ (order parameter) equal to zero: $\phi = 0$. In the absence of an external magnetic field this can be done, as energy of the system does not depend on phase⁶. Note that the existence of anomalous averages of the type (6.18) explicitly breaks the particle conservation law (compare again with Bose gas case!), in normal metal these averages are obviously zero [18]. The appearance of such averages corresponds to the breaking of this invariance during the phase transition from normal metal to superconductor⁷. Further analysis is aimed to confirm self-consistently, that such averages are really different from zero at low enough temperatures, corresponding to phase transition to superconducting state.

Now Hamiltonian (6.16) is quadratic over Fermion operators and can be diagonalized by Bogoliubov's $u - v$ -transformation. Let us introduce new operators as:

$$b_{\mathbf{p}\downarrow} = u_p a_{\mathbf{p}\downarrow} + v_p a_{-\mathbf{p}\uparrow}^+ \quad b_{\mathbf{p}\uparrow} = u_p a_{\mathbf{p}\uparrow} - v_p a_{-\mathbf{p}\downarrow}^+ \quad (6.19)$$

$$b_{\mathbf{p}\downarrow}^+ = u_p a_{\mathbf{p}\downarrow}^+ + v_p a_{-\mathbf{p}\uparrow} \quad b_{\mathbf{p}\uparrow}^+ = u_p a_{\mathbf{p}\uparrow}^+ - v_p a_{-\mathbf{p}\downarrow} \quad (6.20)$$

Due to the assumed isotropy of electronic liquid coefficients u_p and v_p depend only on $|\mathbf{p}|$. Linear transformation (6.20) "intermixes" operators quasiparticles with opposite momenta and spins. "Old" operators satisfied the usual Fermion commutation relations

$$\{a_{\mathbf{p}\sigma}, a_{\mathbf{p}'\sigma'}^+\} = \delta_{\mathbf{p}\mathbf{p}'}\delta_{\sigma\sigma'} \quad \{a_{\mathbf{p}\sigma}, a_{\mathbf{p}'\sigma'}\} = \{a_{\mathbf{p}\sigma}^+, a_{\mathbf{p}'\sigma'}^+\} = 0 \quad (6.21)$$

where figure brackets denote anticommutators. We have to require that new operators satisfy the same commutation relations:

$$\{b_{\mathbf{p}\sigma}, b_{\mathbf{p}'\sigma'}^+\} = \delta_{\mathbf{p}\mathbf{p}'}\delta_{\sigma\sigma'} \quad \{b_{\mathbf{p}\sigma}, b_{\mathbf{p}'\sigma'}\} = \{b_{\mathbf{p}\sigma}^+, b_{\mathbf{p}'\sigma'}^+\} = 0 \quad (6.22)$$

so that "new" quasiparticles are also Fermions. It is easy to see that this leads to the following relation between coefficients u and v :

$$u_p^2 + v_p^2 = 1 \quad (6.23)$$

Inverse transformations have the form:

$$a_{\mathbf{p}\uparrow} = u_p b_{\mathbf{p}\uparrow} + v_p b_{-\mathbf{p}\downarrow}^+ \quad a_{\mathbf{p}\downarrow} = u_p b_{\mathbf{p}\downarrow} - v_p b_{-\mathbf{p}\uparrow}^+ \quad (6.24)$$

$$a_{\mathbf{p}\uparrow}^+ = u_p b_{\mathbf{p}\uparrow}^+ + v_p b_{-\mathbf{p}\downarrow} \quad a_{\mathbf{p}\downarrow}^+ = u_p b_{\mathbf{p}\downarrow}^+ - v_p b_{-\mathbf{p}\uparrow} \quad (6.25)$$

⁶This was done before also in (5.89) for Bose gas model.

⁷Here again we meet the phenomenon of spontaneous symmetry breaking — new ground state of the system (superconductor) has lower symmetry, than the initial Hamiltonian (6.12). This is typical for any phase transition of second order.

Substituting (6.25) into Hamiltonian (6.16) we obtain:

$$\begin{aligned}
H = & 2 \sum_p \xi_p v_p^2 - 2\Delta \sum_p u_p v_p + \frac{1}{g} V \Delta^2 + \\
& + \sum_p \left\{ [\xi_p (u_p^2 - v_p^2) + 2\Delta u_p v_p] (b_{\mathbf{p}\uparrow}^+ b_{\mathbf{p}\uparrow} + b_{\mathbf{p}\downarrow}^+ b_{\mathbf{p}\downarrow}) \right\} + \\
& + \sum_p \left\{ [2\xi_p u_p v_p - \Delta (u_p^2 - v_p^2)] (b_{\mathbf{p}\uparrow}^+ b_{-\mathbf{p}\downarrow}^+ + b_{-\mathbf{p}\downarrow} b_{\mathbf{p}\uparrow}) \right\}
\end{aligned} \tag{6.26}$$

Now it is seen that if we demand coefficients u and v to satisfy:

$$2\xi_p u_p v_p - \Delta (u_p^2 - v_p^2) = 0 \tag{6.27}$$

nondiagonal terms in (6.26) vanish. Then we finally obtain the Hamiltonian of new “free” (!) quasiparticles:

$$H = E_0 + \sum_p \varepsilon(p) [b_{\mathbf{p}\uparrow}^+ b_{\mathbf{p}\uparrow} + b_{\mathbf{p}\downarrow}^+ b_{\mathbf{p}\downarrow}] \tag{6.28}$$

where

$$E_0 = 2 \sum_p [\xi_p v_p^2 - \Delta u_p v_p] + \frac{1}{g} V \Delta^2 \tag{6.29}$$

defines the ground state energy, while

$$\varepsilon(p) = \xi_p (u_p^2 - v_p^2) + 2\Delta u_p v_p \tag{6.30}$$

gives the energy of new quasiparticles. From Eqs. (6.23) and (6.27) it is easy to obtain the explicit expressions for coefficients u and v :

$$\left. \begin{matrix} u_p^2 \\ v_p^2 \end{matrix} \right\} = \frac{1}{2} \left(1 \pm \frac{\xi_p}{\sqrt{\xi_p^2 + \Delta^2}} \right) \tag{6.31}$$

Then for the spectrum of new quasiparticles from (6.30) we get:

$$\varepsilon(p) = \sqrt{\xi_p^2 + \Delta^2} \tag{6.32}$$

— BCS spectrum with *energy gap* of the width 2Δ around the Fermi surface! Qualitatively, this spectrum is shown in Fig.6-1. Obviously, this spectrum satisfies Landau criterion for superfluidity – $Min \frac{\varepsilon(p)}{p} > 0$, i.e. guarantees superconductivity in the system of charged quasiparticles⁸.

⁸If there is a current, the whole Fermi surface is shifted in momentum space by some vector \mathbf{q} , such that $m\mathbf{v}_s = \hbar\mathbf{q}$, where \mathbf{v}_s is drift velocity of electrons. Then the energy of an elementary excitation close to Fermi surface can be written as $\varepsilon(p) \approx \sqrt{\xi_p^2 + \Delta^2} + \mathbf{p}_F \mathbf{v}_s$, where we have taken into account the smallness of drift velocity (compared to Fermi velocity), so that $\xi_{\mathbf{p}+\mathbf{q}} \approx \xi_p + \mathbf{v}_F \mathbf{q}$. For an electron with momentum parallel or antiparallel to \mathbf{v}_s we have $\varepsilon(p) \approx \sqrt{\xi_p^2 + \Delta^2} \pm p_F v_s$. Thus, an energy difference appears $\hbar\omega = 2p_F v_s$ between opposite points on the Fermi surface, so that excitation spectrum becomes asymmetric. However, until $\hbar\omega = 2p_F v_s < 2\Delta$, the gap in the spectrum persists and for $T = 0$ there are no excited BCS quasiparticles. Accordingly, there is no dissipation of current. For $v_s p_f > \Delta$ the upper and lower quasiparticle bands overlap and excitation of quasiparticles into upper band becomes possible even for $T = 0$ and superconductivity vanishes. This leads to the simplest estimate of the critical current of superconductor: $j_c = ev_s^c = \frac{e\Delta}{p_F}$.

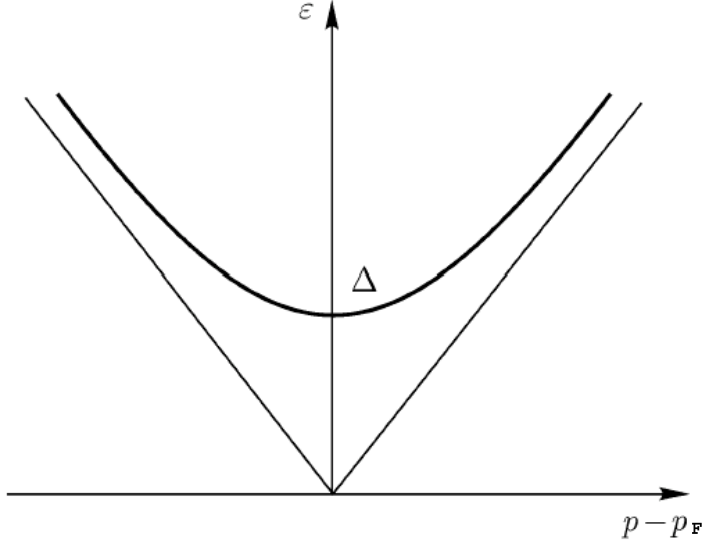


Figure 6.1: Energy spectrum of electrons in BCS theory.

Thus, for finite values of Δ (i.e. qualitatively, when there is Bose condensate of Cooper pairs present) the system becomes a superconductor. However, we still have to show that such situation is possible, i.e. we have to define conditions when anomalous averages (6.17), (6.18) become nonzero. Making $u - v$ transformation in (6.17) we can write:

$$\Delta = \frac{g}{V} \sum_p \langle a_{p\uparrow}^+ a_{-p\downarrow}^+ \rangle = \frac{g}{V} \sum_p u_p v_p (1 - n_{p\uparrow} - n_{p\downarrow}) \quad (6.33)$$

where

$$n_{p\uparrow} = \langle b_{p\uparrow}^+ b_{p\uparrow} \rangle \quad 1 - n_{p\downarrow} = \langle b_{p\downarrow} b_{p\downarrow}^+ \rangle \quad (6.34)$$

In fact:

$$\begin{aligned} \langle a_{p\uparrow}^+ a_{-p\downarrow}^+ \rangle &= \langle (u_p b_{p\uparrow}^+ + v_p b_{-p\downarrow}) (u_p b_{-p\downarrow}^+ - v_p b_{p\uparrow}) \rangle = \\ &= u_p^2 \langle b_{p\uparrow}^+ b_{-p\downarrow}^+ \rangle - u_p v_p \langle b_{p\uparrow}^+ b_{p\uparrow} \rangle + v_p u_p \langle b_{-p\downarrow} b_{-p\downarrow}^+ \rangle - v_p^2 \langle b_{-p\downarrow} b_{p\uparrow} \rangle = \\ &= u_p v_p (1 - n_{p\uparrow} - n_{p\downarrow}) \end{aligned} \quad (6.35)$$

as in the correct ground state we have to satisfy the condition: $\langle b_{p\uparrow}^+ b_{-p\downarrow}^+ \rangle = \langle b_{-p\downarrow} b_{p\uparrow} \rangle = 0$, i.e. new quasiparticles should not be spontaneously created or annihilated⁹. Similarly:

$$\langle a_{p\uparrow} a_{-p\downarrow} \rangle = u_p v_p (1 - n_{p\downarrow} - n_{p\uparrow}) = \langle a_{p\uparrow}^+ a_{-p\downarrow}^+ \rangle \quad (6.36)$$

⁹Mathematically this follows from the presence of only diagonal elements of the density matrix, corresponding to diagonalized Hamiltonian (6.28). Accordingly, the averages of diagonal products of operators (6.34) are different from zero, while the averages of nondiagonal products (6.35) are zero.

Substituting explicit expression (6.31) for u_p and v_p into (6.33), we obtain:

$$1 = \frac{g}{2V} \sum_p \frac{1 - n_{p\uparrow} - n_{p\downarrow}}{\sqrt{\xi_p^2 + \Delta^2}} \quad (6.37)$$

the fundamental *gap equation* of BCS theory.

In the absence of external magnetic field occupation numbers $n_{p\uparrow} = n_{p\downarrow}$ and are defined by the usual Fermi distribution of quasiparticles with spectrum (6.32):

$$n_{p\uparrow} = n_{p\downarrow} = \frac{1}{e^{\frac{\varepsilon(p)}{T}} + 1} \quad (6.38)$$

Consider first the case of $T = 0$. For $\Delta \neq 0$ there are no (excited) quasiparticles at all, i.e. $n_{p\uparrow} = n_{p\downarrow} = 0$. For $T > 0$ they can be thermally excited in pairs (particles and holes) and appear above (below) the gap. Then in Eq. (6.37) we can transform from summation over p to integration and write:

$$1 = \frac{g}{2} \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1 - 2n_p}{\sqrt{\xi_p^2 + \Delta^2}} \quad (6.39)$$

For $T = 0$ we have:

$$1 = \frac{g}{2} \int \frac{dp}{(2\pi\hbar)^3} \frac{4\pi p^2}{\sqrt{\xi_p^2 + \Delta_0^2}} \quad (6.40)$$

It is immediately seen that this equation does not have solutions for Δ_0 in case of $g < 0$, i.e. for repulsive interaction, as both sides of this equation has different signs. Remember now that the coupling constant g is nonzero only in a narrow energy layer of the width $\sim 2\omega_D$ around the Fermi surface (see Eq. (6.6)). Then in (6.40):

$$\int dp p^2 \frac{1}{\sqrt{\Delta_0^2 + v_F^2(p - p_F)^2}} \approx \frac{p_F^2}{v_F} \int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{d\xi_p}{\sqrt{\xi_p^2 + \Delta_0^2}} \approx \frac{2p_F^2}{v_F} \ln \frac{2\hbar\omega_D}{\Delta_0} \quad (6.41)$$

so that Eq. (6.40) takes the form:

$$1 = \frac{gm p_F}{2\pi^2 \hbar^3} \ln \frac{2\hbar\omega_D}{\Delta_0} \quad (6.42)$$

giving the solution:

$$\Delta_0 = 2\hbar\omega_D \exp\left(-\frac{2}{g\nu_F}\right) \equiv 2\hbar\omega_D \exp\left(-\frac{1}{\lambda_p}\right) \quad (6.43)$$

where $\nu_F = \frac{m p_F}{\pi^2 \hbar^3}$ is electron density of states at the Fermi level and $\lambda_p = g\nu_F/2$ is dimensionless coupling constant of pairing interaction. Thus, at $T = 0$ the energy gap Δ_0 is different from zero, formally, even for infinitesimal values of pairing coupling constant λ_p ¹⁰.

¹⁰Note an extra factor of 2 in (6.43), as compared with Eq. (6.11), obtained above from more simple approach. Inaccuracy of Eq. (6.11) is connected with the approximation of separate pair of electrons on the background of a rigid Fermi surface. The correct solution is given by (6.43).

Table 6.1: Temperature of superconducting transition for a number of metals and compounds (K).

<i>Al</i>	<i>Sn</i>	<i>In</i>	<i>Hg</i>	<i>Pb</i>	<i>Nb</i>	<i>Nb₃Sn</i>	<i>Nb₃Ge</i>	<i>YBa₂Cu₃O₇</i>
1.2	3.75	3.4	4.16	7.22	7.78	18.0	23.2	92

At finite temperatures, putting in Eq. (6.39) $\Delta = 0$, we obtain the equation for critical temperature of superconducting transition:

$$1 = \frac{g}{2} \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1 - 2n_p}{|\xi_p|} = \lambda_p \int_{-\hbar\omega_D}^{\hbar\omega_D} d\xi_p \frac{1}{2\xi_p} \text{th} \frac{\xi_p}{2T_c} \quad (6.44)$$

which solution is [22]:

$$T_c = \frac{2\gamma}{\pi} \hbar\omega_D \exp\left(-\frac{1}{\lambda_p}\right) \quad (6.45)$$

where $\gamma \approx 1.78$ is Euler constant. At this temperature the energy gap goes to zero (cf. below), and superconductor becomes the normal metal¹¹.

In Table 6-1 we give temperatures of superconducting transition for a number of metals and compounds. In the last row we show the most popular copper oxide high – temperature superconductor. These compounds are actively studied since 1987. Maximal temperature of superconducting transition $T_c \sim 135K$ (under pressure up to $\sim 150K$) was observed in $Hg_2Ba_2Ca_2Cu_3O_8$. In 2008 a new class of high–temperature superconductors was discovered, based on iron pnictides and chalcogenides. The highest $T_c = \text{sim}55K$ was observed in this class for $Nd(\text{Sm})\text{FeAsO}$ system. High – temperature superconductors are not described by the simplified version of BCS theory described above, though basic qualitative conclusions are still valid. In fact there is no general consensus only on the nature of microscopic mechanism of Cooper pairing in these systems, though most researchers believe it to be non phonon, most probably connected with antiferromagnetic spin fluctuations. There are some other differences with simple BCS approach, e.g. it is well established that in copper oxides the pairing is singlet, but anisotropic (d -wave pairing). In iron based superconductors theoretical picture is complicated by their multiple band electronic structure.

In traditional superconductors BCS theory gives more or less complete description of this phenomenon and there is no doubts in electron – phonon nature of Cooper pairing. In Table 6-2 [24] we give the values of λ_p and $\hbar\omega_D$ for a number of superconductors, where the weak coupling BCS model gives pretty good description¹² As was noted above, in superfluid He^3 Cooper pairing between neutral atoms of Helium takes place at temperatures below $2.6mK$, leading to superfluidity. Microscopic mechanism of pairing in He^3 is related to the exchange by spin fluctuations (paramagnons). There are several superfluid phases

¹¹If microscopic mechanism is not of electron – phonon nature, the frequency in preexponential factor in this approximation is replaced by the characteristic frequency of Bosons, responsible for attraction between current carriers. In particular, for so called excitonic mechanism this is replaced by some energy $\sim E_F \gg \hbar\omega_D$, leading to the possible high–temperature superconductivity (Little – Ginzburg). In real high – temperature superconductors, discovered thus far, we deal here with a characteristic frequency of antiferromagnetic spin fluctuations, while the basic point of BCS theory are conserved.

¹²For the case of strong electron – phonon coupling BCS theory was generalized by Eliashberg and McMillan, producing more complicated equations but conserving all the main ideas of BCS approach.

Table 6.2: Experimental values of $\hbar\omega_D$, T_c and coupling constant λ_p .

	$\hbar\omega_D(K)$	$T_c(K)$	λ_p
<i>Zn</i>	235	0.9	0.18
<i>Cd</i>	164	0.56	0.18
<i>Hg</i>	70	4.16	0.35
<i>Al</i>	375	1.2	0.18
<i>Tl</i>	100	2.4	0.27
<i>Sn</i>	195	3.75	0.25
<i>Pb</i>	96	7.22	0.39

on rather complicated phase diagram, differing by the type of pairing (orbital and spin momentum of pairs). This leads to unusual richness of physical phenomena observed in this system [25].

The concept of bound pairs in BCS theory should not be taken too literally. It is more correct to speak about certain *correlation* between pairs of particles in p -space, leading to a finite probability for particles to have In fact the distribution of momenta δp in the region of these correlations corresponding to the binding energy of a pair (gap) $\sim \Delta$, i.e. $\delta p \sim \Delta/v_F$. Appropriate correlation length given by $\xi \sim \hbar/\delta p \sim \hbar v_F/\Delta$ defines a characteristic scale of distances between correlated particles (the size of a pair). For $T = 0$ this length, called also coherence length, is equal to:

$$\xi_0 \sim \frac{\hbar v_F}{\Delta_0} \sim \frac{v_F}{\omega_D} \exp\left(\frac{1}{\lambda_p}\right) \quad (6.46)$$

Typically in metals $\frac{v_F}{\omega_D} \sim \frac{\hbar}{p_F} \frac{\varepsilon_F}{\hbar\omega_D} \gg a$, where a is a characteristic distance between electrons. Besides that, the exponential factor in (6.46) much exceeds unity, as usually we have $\lambda_p < 1$. From these estimates it is clear that we always have $\xi_0 \gg a$, so that “inside” each pair there is lot of electrons, or in other words, pairs are much overlapped and loose their individual nature. In high – temperature superconductors, due to much higher values of T_c (large binding energy of a pair) and relatively small concentration of current carriers, the size of pairs is not overwhelmingly large in comparison with interparticle distance. These systems belong to a crossover region between very large BCS pairs and “compact” Bosons (BCS-Bose crossover).

In BCS theory electrons of a normal metal are transformed into Fermion quasiparticles with spectrum given by Eq. (6.32). Simultaneously, a reconstruction of the ground state takes place. Here we present (without derivation) main expressions describing the ground state of a superconductor [24]. This state is described by the following state vector:

$$|BCS\rangle = \prod_p (u_p + v_p a_{p\uparrow}^+ a_{-p\downarrow}) |0\rangle \quad (6.47)$$

where $|0\rangle$ is the state without electrons (vacuum), satisfying the obvious condition: $a_{p\sigma}|0\rangle = 0$. Equation $u_p^2 + v_p^2 = 1$ guarantees normalization $\langle BCS|BCS\rangle = 1$. The average number of particles in BCS ground state is

given by:

$$\langle N \rangle = \sum_{p\sigma} \langle BCS | a_{p\sigma}^+ a_{p\sigma} | BCS \rangle = 2 \sum_p v_p^2 = \frac{V}{(2\pi\hbar)^3} \int d^3p 2v_p^2 \quad (6.48)$$

However, the fluctuation of particle number in BCS state is different from zero, as this ground state (as was noted above) breaks the particle conservation:

$$\langle N^2 \rangle - \langle N \rangle^2 = \sum_p 4u_p^2 v_p^2 \quad (6.49)$$

From here it is easily seen that $\langle N^2 \rangle - \langle N \rangle^2 \sim V \sim \langle N \rangle$, but the relative fluctuation:

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} \sim \frac{1}{\langle N \rangle} \quad (6.50)$$

and relative mean square fluctuation behaves as $1/\sqrt{\langle N \rangle}$ for $\langle N \rangle \rightarrow \infty$.

Direct calculations show that BCS ground state satisfies the condition: $b_{p\uparrow} | BCS \rangle = b_{p\downarrow} | BCS \rangle = 0$, i.e. is the correct vacuum state for BCS quasiparticles, originating from quasiparticles of a normal metal via $u - v$ - transformation.

6.3 Thermodynamics of superconductors.

Consider now finite temperatures $T > 0$. Gap equation (6.39) can be rewritten as:

$$-1 + \frac{g}{2} \int \frac{d^3p}{(2\pi\hbar)^3} \frac{1}{\varepsilon(p)} = g \int \frac{d^3p}{(2\pi\hbar)^3} \frac{n_p}{\varepsilon(p)} \quad (6.51)$$

where $\varepsilon(p)$ is given by (6.32). Note that the integral in the left hand side here differs from those in Eq. (6.40) only by the replacement of Δ by Δ_0 . Then, replacing the unity in the left hand side by the logarithm form Eq. (6.42), we can rewrite the left hand side of Eq. (6.51) as $g \frac{m p_F}{2\pi^2 \hbar^3} \ln \frac{\Delta_0}{\Delta}$. In the right hand side we write explicitly the Fermi function $n_p = [e^{\frac{\varepsilon(p)}{T}} + 1]^{-1}$ and transform to integration over $d\xi = v_F dp$. Then (6.51) takes the following form:

$$\ln \frac{\Delta_0}{\Delta} = \int_{-\infty}^{\infty} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2} \left(e^{\frac{\sqrt{\xi^2 + \Delta^2}}{T}} + 1 \right)} = 2I \left(\frac{\Delta}{T} \right) \quad (6.52)$$

where

$$I(u) = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{x^2 + u^2} (\exp \sqrt{x^2 + u^2} + 1)} \quad (6.53)$$

This integral can be calculated in limiting cases [1], and we obtain:

$$I(u) = \begin{cases} \left(\frac{\pi}{2u} \right)^{1/2} e^{-u} & \text{for } u \gg 1 \\ \ln \left(\frac{\pi}{\gamma u} \right) + \frac{7\zeta(3)}{8\pi^2} u^2 & \text{for } u \ll 1 \end{cases} \quad (6.54)$$

where $\gamma \approx 1.78$ is Euler constant, $\zeta(3) \approx 1.202$ is Riemann's ζ -function of argument 3. Substituting these limiting expressions to (6.52), we obtain for low temperatures $T \ll \Delta$:

$$\Delta = \Delta_0 \left[1 - \sqrt{\frac{2\pi T}{\Delta_0}} e^{-\frac{\Delta_0}{T}} \right], \quad (6.55)$$

while in the vicinity of transition to the normal state, where $\Delta \rightarrow 0$, we get:

$$\ln \frac{\Delta_0}{\Delta} = \ln \frac{\pi T}{\gamma \Delta} + \frac{7\zeta(3)}{8\pi^2} \frac{\Delta^2}{T^2} \quad (6.56)$$

From this equation we can see that the gap Δ becomes zero at critical temperature:

$$T_c = \frac{\gamma}{\pi} \Delta_0 \approx 0.57 \Delta_0 \quad (6.57)$$

which, taking into account (6.43), coincides with (6.45). Note the characteristic BCS ratio, following from these expressions: $\frac{2\Delta_0}{T_c} \approx 3.52$, its experimental verification in traditional superconductors was one of the first confirmation of BCS theory¹³.

Close to T_c it follows from (6.56) that:

$$\Delta(T) = T_c \left[\frac{8\pi^2}{7\zeta(3)} \left(1 - \frac{T}{T_c} \right) \right]^{1/2} \approx 3.06 T_c \sqrt{1 - \frac{T}{T_c}} \quad (6.58)$$

demonstrating characteristic square root behavior of the gap, typical for the order parameter of second order phase transition.

The general form of temperature dependence of the gap Δ in BCS theory, following from Eq. (6.52), is shown in Fig. 6-2. This dependence is also well confirmed by the experiments on traditional superconductors with relatively low transition temperature T_c .

Let us consider some other properties of a superconductor at finite temperatures (dropping details of derivation). The difference of free energies of superconducting and normal state close to T_c ($T < T_c$), following from BCS theory [1, 2], is given by:

$$F_s - F_n = -V \frac{2mp_F T_c^2}{7\zeta(3)\hbar^3} \left(1 - \frac{T}{T_c} \right)^2, \quad (6.59)$$

so that superconducting state at $T < T_c$ has lower free energy, than the normal state. The difference of entropies following from (6.59) is:

$$S_s - S_n = -\frac{\partial(F_s - F_n)}{\partial T} = -V \frac{4mp_F T_c}{7\zeta(3)\hbar^3} \left(1 - \frac{T}{T_c} \right) \quad (6.60)$$

Accordingly, we obtain the value of specific heat *discontinuity* at the transition point:

$$C_s - C_n = T \frac{\partial(S_s - S_n)}{\partial T} = V \frac{4mp_F T_c}{7\zeta(3)\hbar^3} \quad (6.61)$$

Taking into account that $C_n = Vmp_F T/3\hbar^3$ (cf. (4.70)), we obtain:

$$\frac{C_s(T_c)}{C_n(T_c)} = \frac{12}{7\zeta(3)} + 1 \approx 2.43. \quad (6.62)$$

¹³In many real superconductors significant deviations from this BCS theory prediction are widely observed. In fact, the “ideal” BCS value of 3.52 the ratio of full width of the energy gap and T_c is characteristic for weakly coupled superconductors (with small values of pairing coupling constant), in accordance with BCS theory. The observed deviations (mostly growth) of this ratio are typical for strongly coupled superconductors and are well described by Eliashberg – McMillan approach.

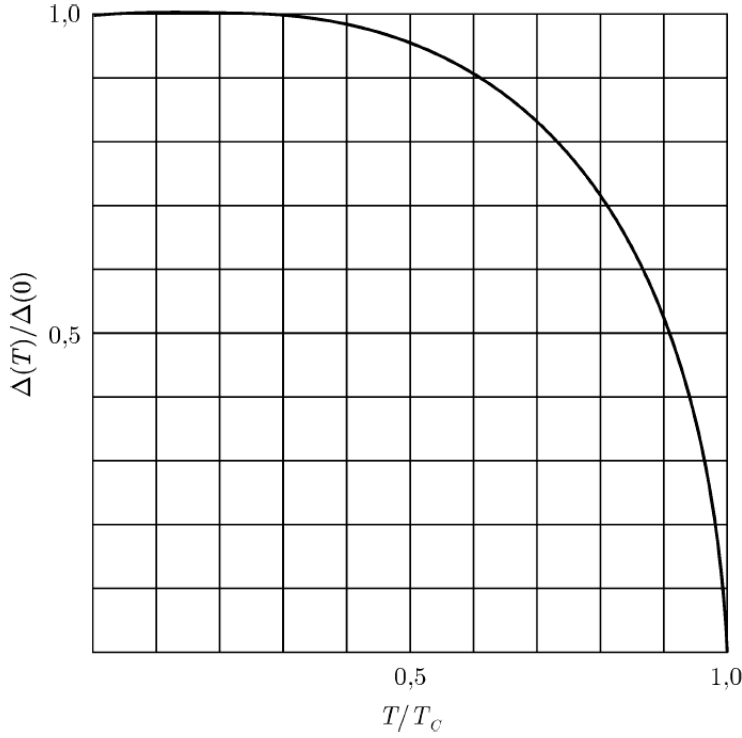


Figure 6.2: Temperature dependence of the gap in BCS theory.

This universal value is also rather well confirmed in specific heat measurements on traditional (weakly coupled) superconductors, while strong coupling leads to significant deviations from this prediction of simple BCS theory.

To calculate specific heat at low temperatures we can use the relation:

$$\delta E = \sum_p \varepsilon(p)(\delta n_{p\uparrow} + \delta n_{p\downarrow}) = 2 \sum_p \varepsilon(p) \delta n_p \quad (6.63)$$

for the total quasiparticle energy change due to variation of occupation numbers. Dividing this expression by δT and going from summation to integration, we obtain specific heat as:

$$C = V \frac{mp_F}{\pi^2 \hbar^3} \int_{-\infty}^{\infty} d\xi_p \varepsilon(p) \frac{\partial n_p}{\partial T} \quad (6.64)$$

For $T \ll \Delta_0$ we can write $n_p \approx e^{-\frac{\varepsilon(p)}{T}}$ and $\varepsilon(p) \approx \Delta_0 + \frac{\xi_p^2}{2\Delta_0}$. Then the simple integration gives:

$$C = V \frac{\sqrt{2} mp_F \Delta_0^{5/2}}{\pi^{3/2} \hbar^3 T^{3/2}} e^{-\frac{\Delta_0}{T}} \quad (6.65)$$

so that at $T \rightarrow 0$ the specific heat of electron gas in a superconductors is exponentially small, due to the existence of a finite gap in quasiparticle spectrum.

At $T = 0$ it can be shown [1, 2] that the difference of ground state energies of superconducting and normal states is given by:

$$E_s - E_n = -V \frac{mp_F}{4\pi^2 \hbar^3} \Delta_0^2 = -\frac{1}{4} V \nu_F \Delta_0^2. \quad (6.66)$$

The negative sign here corresponds to instability of the “normal” ground state in case of attraction between quasiparticles and makes superconducting state the real (stable) ground state of the system. The physical meaning of Eq. (6.66) is pretty clear: in an energy layer of the width of $\sim \Delta_0$ around the Fermi level we have $\sim \nu_F \Delta_0$ quasiparticles, each gaining energy of the order of $\sim \Delta_0$ due to gap formation. The estimate of the total energy gain per one electron is $\sim \Delta^2/\varepsilon_F$.

6.4 Coulomb repulsion*.

Up to now we assumed, that there is attractive interaction between electrons, acting in a narrow energy layer of the width $2\omega_D$ around the Fermi surface¹⁴. Such attraction can exist in metals due to electron – phonon interaction. However, a strong Coulomb repulsion is obviously acting between all electrons in metals, which definitely opposes the formation of Cooper pairs (and thus superconductivity). Let us show how this repulsion can be taken into account in equations of BCS theory.

In general case the energy gap of superconductor with the account of different interaction mechanisms is defined by rather complicated integral equation. Close to T_c this equation can be linearized over Δ as gap goes to zero for $T \rightarrow T_c$. In weak coupling approximation we can write the following gap equation close to T_c , which is the direct generalization of Eq. (6.44) and determines the critical temperature of superconducting transition [24]:

$$\Delta(\xi) = \int_{-\infty}^{\infty} d\tau V(\xi, \xi') N(\xi') \frac{1}{2\xi'} \text{th}\left(\frac{\xi'}{2T_c}\right) \Delta(\xi'), \quad (6.67)$$

where $N(\xi)$ is the density of electron states in normal metal (per one spin projection), and $V(\xi, \xi')$ is the “potential” of an effective interaction between electrons. We assume that $\Delta(\xi)$ here is some unknown function of energy of a quasiparticle ξ , which is to be determined depending on the accepted model of interactions. In our previous discussion Δ was assumed to be a constant and just cancelled out, dropping out from Eq. (6.44).

Effective electron – electron attraction in superconductors is determined in reality by some balance between attraction due to electron – phonon interaction and Coulomb repulsion. We may assume for the “potential” $V(\xi, \xi')$ the following very crude model¹⁵:

$$V(\xi, \xi') = -V_c \theta(\xi, \xi') + V_{ph}(\xi, \xi'), \quad (6.68)$$

where

$$V_c(\xi, \xi') = V_c \theta(\varepsilon_F - |\xi|) \theta(\varepsilon_F - |\xi'|) \quad (6.69)$$

$$V_{ph}(\xi, \xi') = V_{ph} \theta(\omega_D - |\xi|) \theta(\omega_D - |\xi'|) \quad (6.70)$$

are “potentials” of electron – electron and electron – phonon interactions respectively, ω_D is Debye frequency. Constants $V_c > 0$ and $V_{ph} > 0$ describe repulsion

¹⁴In this section we put $\hbar = 1$ and measure frequency ω_D in units of energy.

¹⁵We assume interelectron repulsion to be short-ranged due to the strong screening of Coulomb interaction in metals.

and attraction, acting (due to $\varepsilon_F \gg \omega_D$) in significantly different intervals of energy: electron – phonon attraction acts only on electrons in an energy layer of the width $2\omega_D$ close to the Fermi level, while (screened) Coulomb repulsion acts between all conduction electrons on an energy scale of the order of Fermi energy ε_F .

After substitution of this expression into Eq. (6.67) and simple transformations using (presumably) even gap function $\Delta(\xi)$, we get:

$$\begin{aligned} \Delta(\xi) &= [V_{ph}\theta(\omega_D - \xi) - V_c\theta(\varepsilon_F - \xi)] \int_0^{\omega_D} d\xi' N(\xi') \frac{1}{\xi'} th\left(\frac{\xi'}{2T_c}\right) \Delta(\xi') - \\ &- V_c\theta(\varepsilon_F - \xi) \int_{\omega_D}^{\varepsilon_F} d\xi' N(\xi') \frac{1}{\xi'} th\left(\frac{\xi'}{2T_c}\right) \Delta(\xi'). \end{aligned} \quad (6.71)$$

In rough approximation we can seek a solution of this equation in the form of two “step” functions [24]:

$$\Delta(\xi) = \begin{cases} \Delta_{ph}, & |\xi| < \omega_D, \\ \Delta_c, & \omega_D < |\xi| < \varepsilon_F, \end{cases} \quad (6.72)$$

where Δ_{ph} and Δ_c are some constants, which can be determined (after the substitution of (6.72) into (6.71) from the following system of homogeneous linear equations (obtained after the substitution of (6.72) into (6.71)):

$$\begin{aligned} \left\{ 1 - (V_{ph} - V_c)N(0)K\left(\frac{\omega_D}{2T_c}\right) \right\} \Delta_{ph} + V_cN(0) \left[K\left(\frac{\varepsilon_F}{2T_c}\right) - K\left(\frac{\omega_D}{2T_c}\right) \right] \Delta_c &= 0, \\ V_cN(0)K\left(\frac{\omega_D}{2T_c}\right) \Delta_{ph} + \left\{ 1 + V_cN_0(0) \left[K\left(\frac{\varepsilon_F}{2T_c}\right) - K\left(\frac{\omega_D}{2T_c}\right) \right] \right\} \Delta_c &= 0, \end{aligned} \quad (6.73)$$

where we have replaced the density of states by its constant value $N(0) = \frac{1}{2}\nu_F$ at the fermi level and introduced the notation:

$$K(x) = \int_0^x dx' \frac{1}{x'} th(x'). \quad (6.74)$$

Nontrivial solution of this system exists if the determinant of this system of equations is zero, which gives the equation for T_c :

$$\begin{aligned} (\lambda - \mu^*)K\left(\frac{\omega_D}{2T_c}\right) &= 1, \\ \mu^* &= \mu \left\{ 1 + \mu \left[K\left(\frac{\varepsilon_F}{2T_c}\right) - K\left(\frac{\omega_D}{2T_c}\right) \right] \right\}^{-1}, \end{aligned} \quad (6.75)$$

where we have introduced μ^* – the so called Coulomb pseudopotential, $\mu = V_cN_0(0)$ is dimensionless Coulomb (repulsion) coupling constant, while $\lambda = V_{ph}N_0(0)$ is dimensionless pairing coupling constant due to electron – phonon interaction.

Due to inequality $\varepsilon_F \gg \omega_D \gg T_c$ integral in (6.74) can be calculated for $x \gg 1$, so that $K(x) = \ln\left(\frac{4\gamma}{\pi}x\right)$, where γ is again the Euler constant. Then for the critical temperature of superconducting transition we immediately obtain¹⁶:

$$T_c = \frac{2\gamma}{\pi}\omega_D \exp\left(-\frac{1}{\lambda - \mu^*}\right). \quad (6.76)$$

which coincides with BCS expression (6.45), if we write the pairing constant as $\lambda_p = \lambda - \mu^*$. Coulomb potential μ^* is given here by the following expression:

$$\mu^* \approx \frac{\mu}{1 + \mu \ln \frac{\varepsilon_F}{\omega_D}}. \quad (6.77)$$

From this result we can see that Coulomb repulsion naturally opposes pairing and reduces T_c , diminishing λ_p by μ^* . However, in most metals this effect is largely suppressed due to relatively large (for $\varepsilon_F \gg \omega_D$) value of $\ln(\varepsilon_F/\omega_D)$ (so called Tolmachev's logarithm). In particular, even for $\lambda < \mu$, i.e. when for all energies the total constant of electron – electron interaction is formally repulsive, superconductivity may still persist if $\lambda > \mu^*$.

Using Eq. (6.76) we may propose the following ways to rise the critical temperature of superconducting transition:

1. We may rise the value of ω_D or try to use another (non phonon) mechanism of pairing via the exchange by some collective excitations with characteristic frequencies larger than ω_D . Typical example is the so called excitonic mechanism, for which ω_D is replaced by an energy of the order of ε_F .
2. Another way is to rise the pairing coupling constant λ_p , either by rising attractive coupling λ , or by reducing the Coulomb pseudopotential μ^* .

Nearly all attempts to search for high – temperature superconductivity were undertaken along these ways. Many theoretical explanations of high transition temperatures observed in real high – temperature superconductors are explicitly or implicitly based on these or similar ideas. In fact, practical realization of these tasks is pretty complicated. Even on this elementary level it can be seen that necessary requirements are rather contradictory. For example, rising the preexponential ω_D in (6.76) up to the values of the order of ε_F inevitably leads to the appropriate growth of Coulomb pseudopotential due to diminishing value of Tolmachev's logarithm. On the other hand, the rising of effective pairing constant demands the replacement of weak coupling approximation used in simple BCS theory¹⁷.

In conclusion of our review of microscopic theory of superconductivity we note that above we always supposed that Cooper pairing takes place in singlet

¹⁶This important result was obtained by Tolmachev soon after the BCS work.

¹⁷As an example of the appropriate development of microscopic theory we give here interpolation formula for T_c , proposed by Allen and Dynes, which is valid for the wide interval of dimensionless coupling constant of electron – phonon pairing interaction, including the values $\lambda \sim 1$:

$$T_c = \frac{f_1 f_2}{1.20} \omega_{log} \exp\left\{-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right\} \quad (6.78)$$

where

$$f_1 = [1 + (\lambda/\lambda_1)^{3/2}]^{1/3}; \quad f_2 = 1 + \frac{[\langle \omega^2 \rangle^{1/2} / \omega_{log} - 1]\lambda^2}{\lambda^2 + \lambda_2^2}$$

state (antiparallel spins), and with zero orbital momentum of the pair (s -wave pairing). In real superconductors situation may be more complicated. It was shown by experiments, that in some systems Cooper pairing takes place in triplet state (parallel spins), and also in a state with nonzero orbital moment (He^3 , the so called “heavy Fermion” systems etc.). In copper oxides Cooper pairing is singlet in spin, but d -wave. In iron pnictides situation is complicated by multiple band electronic structure, leading to different superconducting gaps in different bands etc. Obviously, microscopic description of such systems require more complicated theories, but the main ideas and qualitative conclusions of BCS theory remain valid.

6.5 Ginzburg-Landau theory.

Complete microscopic theory, describing behavior of superconductors in external electromagnetic field is too complicated to be discussed here. However, analysis can be very much simplified if we restrict ourselves to the temperature region of $T \rightarrow T_c$, where phenomenological Ginzburg – Landau (GL) theory can be applied. In fact, GL theory is one of most outstanding physical theories, its main ideas play a major role not only in superconductivity, but in many other branches of theoretical physics (such as e.g. the Standard Model of elementary particles). At the same time, from phenomenological point of view GL theory is an impressive example of the use of general Landau theory of phase transitions of second order [1]¹⁸.

In general Landau theory of phase transitions of the second order the difference between “nonsymmetric” and “symmetric” phases is described by the *order parameter*. For a superconductor the natural choice of the order parameter is the complex energy gap, or more precisely, the the anomalous average (6.18), which is proportional to *condensate wave function* of Cooper pairs. In general case this order parameter can be inhomogeneous in space. Assuming for simplicity a cubic symmetry of a crystal lattice, we note that superconducting state is characterized by a scalar n_s – density of superconducting electrons (pairs). Thus it is convenient to normalize condensate wave function by the condition $|\Psi|^2 = n_s/2$, and introducing its phase ϕ write it in the form [2]:

$$\Psi = \sqrt{\frac{n_s}{2}} e^{i\phi} \sim \Delta \quad (6.80)$$

Thus, the order parameter is the complex (two – component) function.

According to general rules of quantum mechanics we can write down the density of supercurrent as:

$$\mathbf{j}_s = -\frac{ie\hbar}{2m} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) = \frac{e\hbar}{2m} n_s \nabla \phi \quad (6.81)$$

$$\lambda_1 = 2.46(1 + 3.8\mu^*); \quad \lambda_2 = 1.82(1 + 6.3\mu^*) \frac{\langle \omega^2 \rangle^{1/2}}{\omega_{log}} \quad (6.79)$$

where ω_{log} is average logarithmic frequency of phonons, while $\langle \omega^2 \rangle$ is the average square of phonon frequency (averaging in both cases is over the phonon spectrum). These parameters replace ω_D of BCS theory, the other parameters were defined above.

¹⁸Note that GL theory can actually be *derived* from microscopic BCS theory, though in fact GL approach was formulated nearly a decade earlier.

where the last equality is valid for the case of spatially homogeneous density n_s , while the doubled mass is introduced here just formally, to stress that supercurrent carriers are Cooper pairs.

The starting point of GL theory is the expression for free energy of a superconductor as a functional of $\Psi(\mathbf{r})$. Consider first a superconductor in the absence of external magnetic field. It is obvious that physical properties should be invariant with respect to gauge (phase) transformation $\Psi \rightarrow \Psi e^{i\alpha}$. This requirement excludes odd power terms in Landau expansion of free energy¹⁹.

Thus, the free energy expansion in powers of the order parameter Ψ for a superconductor can be written as²⁰:

$$F = F_n + \int dV \left\{ \frac{\hbar^2}{4m} |\nabla\Psi|^2 + a|\Psi|^2 + \frac{b}{2} |\Psi|^4 \right\} \quad (6.82)$$

Here F_n is the free energy of normal state, coefficient $b > 0$, and coefficient a is written in usual Landau form:

$$a = \alpha(T - T_c) \quad \alpha > 0 \quad (6.83)$$

so that for $T < T_c$ we have $a < 0$. Coefficient before $|\nabla\Psi|^2$ is taken in the form which leads to the expression (6.81) for current (see below). Identification of m with electron mass is of no importance, as well as the definition of n_s .

For the case of homogeneous order parameter we have:

$$F = F_n + \alpha V(T - T_c) |\Psi|^2 + \frac{bV}{2} |\Psi|^4 \quad (6.84)$$

The value of $|\Psi|^2$ at equilibrium is determined by the minimum of this expression and is given by:

$$|\Psi|^2 = -\frac{a}{b} = \frac{\alpha}{b}(T_c - T) \quad (6.85)$$

for $T < T_c$, and is zero for $T > T_c$. The value of the order parameter $|\Psi|$ goes to zero for $T \rightarrow T_c$ according to the square root law, in complete accord with Eq. (6.58). The value of $n_s \sim |\Psi|^2 \rightarrow 0$ linearly in $T_c - T$.

Substituting (6.85) into (6.84) we obtain:

$$F_s - F_n = -V \frac{\alpha^2}{2b} (T - T_c)^2 \quad (6.86)$$

which is equivalent to Eq. (6.59)²¹. Differentiating Eq. (6.86) by T , similarly to (6.60), we can find the difference of entropies and specific heat discontinuity at the transition point:

$$C_s - C_n = V \frac{\alpha^2 T_c}{b} \quad (6.87)$$

¹⁹Note that phase invariance in quantum mechanics is responsible for particle conservation. Order parameter itself is not invariant with respect to this transformation. In this sense, as was noted above, in superconducting state this symmetry is broken. Symmetry breaking takes place at any second order phase transition, so that the condensed phase is always "nonsymmetric".

²⁰The basic postulate of Landau theory is precisely the possibility to perform such an expansion due to the smallness of the order parameter close to transition temperature [1].

²¹GL theory was derived from microscopic BCS theory of superconductivity by Gorkov, giving explicit microscopic expression for GL coefficients α and b . These expressions can be easily obtained by direct comparison of Eqs. (6.85), (6.58) with Eqs. (6.58), (6.86). Thus, for "pure" superconductors (without impurities) we have: $\alpha = \frac{6\pi^2 T_c}{7\zeta(3)\varepsilon_F}$ and $b = \frac{\alpha T_c}{n}$, where $n = \frac{p_F^3}{3\pi^2 \hbar^3}$ is electron density, with T_c is given by BCS expression (6.45).

which agrees with Eq. (6.87).

Close to T_c (6.86) gives a small correction to free energy, according to thermodynamics it also represents (being expressed via T, P instead of T, V) the difference of Gibbs thermodynamic potentials $\Phi_s - \Phi_n$. This difference coincides with the value of $-V \frac{B_{ct}^2}{8\pi}$, where B_{ct} is thermodynamic critical field destroying superconducting state. Then we easily obtain:

$$B_{ct} = \left(\frac{4\pi a^2}{b} \right)^{1/2} = \left(\frac{4\pi \alpha^2}{b} \right) (T_c - T). \quad (6.88)$$

In the presence of an external magnetic field Eq. (6.82) for free energy can be written as:

$$F = F_n + \int dV \left\{ \frac{\mathbf{B}^2}{8\pi} + \frac{\hbar^2}{4m} \left| \left(\nabla - \frac{2ie}{\hbar c} \mathbf{A} \right) \Psi \right|^2 + a |\Psi|^2 + \frac{b}{2} |\Psi|^4 \right\} \quad (6.89)$$

where $\mathbf{B} = \text{rot} \mathbf{A}$. The structure of gradient term here is determined by gauge invariance of electrodynamics, in particular the coefficient $\frac{2ie}{\hbar c}$ here is expressed via fundamental constants, in contrast to $\hbar^2/4m$. The presence of $2e$ reflects the charge of a Cooper pair — in GL theory we are dealing with charged order parameter!

Looking for an extremum of F as functional of three independent variables Ψ, Ψ^*, \mathbf{A} ²², we can find differential equation determining distribution of Ψ and magnetic field in superconductor. Varying (6.89) with respect to Ψ^* and transforming the integral of $(\nabla - 2ie\mathbf{A}/\hbar c) \nabla \delta \Psi^*$ by partial integration, we get:

$$\delta F = \int dV \left\{ -\frac{\hbar^2}{4m} (\nabla - \frac{2ie}{\hbar c} \mathbf{A})^2 \Psi + a \Psi + b |\Psi|^2 \Psi \right\} \delta \Psi^* + \frac{\hbar^2}{4m} \oint ds (\nabla \Psi - \frac{2ie}{\hbar c} \mathbf{A} \Psi) \delta \Psi^* \quad (6.90)$$

where the second integral is taken over the surface of superconductor. Demanding $\delta F = 0$, we get the condition of volume integral being zero for arbitrary $\delta \Psi^*$, in the form of the following Ginzburg – Landau equation:

$$\frac{1}{4m} \left(-i\hbar \nabla - \frac{2e}{c} \mathbf{A} \right)^2 \Psi + a \Psi + b |\Psi|^2 \Psi = 0 \quad (6.91)$$

Variation over Ψ gives the complex conjugate equation for Ψ^* . Variation of (6.89) over \mathbf{A} leads to Maxwell's equation:

$$\text{rot} \mathbf{B} = \frac{4\pi}{c} \mathbf{j} \quad (6.92)$$

where

$$\mathbf{j} = -\frac{ie\hbar}{2m} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) - \frac{2e^2}{mc} |\Psi|^2 \mathbf{A} \quad (6.93)$$

Here we have written \mathbf{j} as superconducting current because in equilibrium state the normal current is absent.

Boundary condition for these equations is obtained from the condition of surface integral in (6.90) being zero:

$$\mathbf{n} \left(-i\hbar \nabla \Psi - \frac{2e}{\hbar c} \mathbf{A} \right) \Psi = 0 \quad (6.94)$$

²²Complex Ψ consists of independent real and imaginary parts, so it is convenient to consider Ψ and Ψ^* , as independent variables.

where \mathbf{n} unit vector normal to the surface of superconductor. It leads to the equivalent relation: $\mathbf{n}\mathbf{j} = 0$. Eq. (6.94) is valid on the boundary of superconductor with vacuum (insulator), in case of boundary with normal metal it takes another form. Boundary condition for \mathbf{B} reduces to continuity of \mathbf{B} at the border.

In weak magnetic field we may neglect its influence on $|\Psi|^2$ and put it equal to (6.85). For spatially homogeneous $n_s = 2|\Psi|^2$ from (6.93) we get (cf. (6.81)):

$$\mathbf{j} = \frac{\hbar e}{2m} n_s (\nabla\phi - \frac{2e}{\hbar c} \mathbf{A}) \quad (6.95)$$

Applying *rot* to both parts of this equation and using *rot* $\mathbf{A} = \mathbf{B}$ we obtain London's equation:

$$\text{rot}\mathbf{j} = -\frac{n_s e^2}{mc} \mathbf{B} \quad (6.96)$$

From Maxwell's equations (6.92) and *div* $\mathbf{B} = 0$, substituting \mathbf{j} from the first equation into (6.96) and using *rot**rot* $\mathbf{B} = \text{grad } \text{div}\mathbf{B} - \nabla^2 \mathbf{B} = -\nabla^2 \mathbf{B}$, we can write London's equation as:

$$\nabla^2 \mathbf{B} = \frac{1}{\delta^2} \mathbf{B} \quad (6.97)$$

where

$$\delta^2 = \frac{mc^2}{4\pi e^2 n_s} \quad \delta = \left(\frac{mc^2 b}{8\pi e^2 |a|} \right)^{1/2} = \left[\frac{mc^2 b}{8\pi e^2 \alpha (T_c - T)} \right]^{1/2}. \quad (6.98)$$

Near the flat surface of superconductor, taking it as yz - plane and directing x - axis into the body of superconductor, we can reduce Eq. (6.97) to:

$$\frac{d^2 \mathbf{B}}{dx^2} = \frac{1}{\delta^2} \mathbf{B} \quad (6.99)$$

and immediately get the solution:

$$\mathbf{B}(x) = \mathbf{B}_0 e^{-x/\delta}, \quad (6.100)$$

where vector \mathbf{B}_0 is parallel to the surface. This gives the description of Meissner effect – “exclusion” of external magnetic field from superconductor. Characteristic length δ is called penetration depth and it is directly measurable. Its typical values for real superconductors at low temperatures $\delta \sim 10^{-5} - 10^{-6}$ cm. For $T \rightarrow T_c$ it diverges according to (6.98), which corresponds to complete penetration of external magnetic field into normal metal.

In addition to δ another characteristic length appears in GL theory — the so called coherence length or correlation length of order parameter fluctuations $\xi(T)$. Using the standard expressions of Landau theory of second order phase transitions (see below) this length is expressed via GL coefficient as follows:

$$\xi(T) = \frac{\hbar}{2(m|a|)^{1/2}} = \frac{\hbar}{2(m\alpha)^{1/2}(T - T_c)^{1/2}} \sim \xi_0 \sqrt{\frac{T_c}{T_c - T}}; \quad \xi_0 \sim \frac{\hbar v_F}{T_c} \quad (6.101)$$

where in last estimates we used microscopic expressions for GL coefficients and the estimate of BCS coherence length (6.46), determining the size of Cooper

pairs. We can see that coherence length $\xi(T)$ (pair size) also diverges for $T \rightarrow T_c$ (pairs grow and become destroyed at $T = T_c$).

Dimensionless ratio of these characteristic lengths:

$$\kappa = \frac{\delta(T)}{\xi(T)} = \frac{mcb^{1/2}}{(2\pi)^{1/2}|e|\hbar} \quad (6.102)$$

defines the so called Ginzburg – Landau parameter. Depending on its value, all superconductors are divided into two classes with significantly different properties in external magnetic field: superconductors with $\kappa < \frac{1}{\sqrt{2}}$ are called type I superconductors, while those with $\kappa > \frac{1}{\sqrt{2}}$ are called type II superconductors. Most of superconductors used for practical applications, as well as all high – temperature superconductors are in fact type II superconductors.

Let us derive one remarkable result following from Eq. (6.95) and Meissner effect. Consider a superconductor forming a torus and place it in external magnetic field. We assume that both diameters of torus are much larger than penetration depth and coherence length (macroscopic torus). Now we can show that the value of magnetic flux through the torus is quantized — it may only be some integer in units of elementary “flux quantum” expressed via fundamental constants (flux quantization). Deep inside the superconducting torus (outside the border region defined by penetration depth) current density is obviously zero $\mathbf{j} = 0$ (where is no field to induce the current), while vector potential is non zero (only its rotor is zero, so that $\mathbf{B} = 0$). Consider some closed contour C , going around the torus inside its body, far from its surface. Circulation of \mathbf{A} along contour C coincides with magnetic flux through of the contour, i.e. with the flux Φ through the torus:

$$\oint \mathbf{A}d\mathbf{l} = \int \text{rot}\mathbf{A}d\mathbf{f} = \int \mathbf{B}d\mathbf{f} \equiv \Phi \quad (6.103)$$

On the other hand, taking (6.95) equal to zero and integrating it around the contour we get:

$$\oint \mathbf{A}d\mathbf{l} = \frac{\hbar c}{2e} \oint \nabla\phi d\mathbf{l} = \frac{\hbar c}{2e} \delta\phi \quad (6.104)$$

where $\delta\phi$ is the change of the phase of the wave function while we go around the contour. Demanding the single valuedness of the wave function, after we perform a total circulation (one or several times), we conclude that this change of phase can only be 2π multiplied by an integer. Thus we obtain:

$$\Phi = n\phi_0 \quad \text{where} \quad \phi_0 = \frac{\pi\hbar c}{|e|} = 2 \cdot 10^{-7} \text{Gauss cm}^2 \quad (6.105)$$

where n is an integer. The value of ϕ_0 represents an elementary quantum of magnetic flux. This remarkable result is directly confirmed by the experiments, which is, by the way, a direct proof that (super)current carriers in superconductors are quasiparticles with electric charge equal to $2e$ (Cooper pairs).

If we consider a massive cylinder in an external (longitudinal) magnetic field B made of type I superconductor, it will undergo first order phase transition to normal state if we reach thermodynamic critical field B_{ct} discussed above. For type II superconductor, even before we reach the thermodynamic critical field B_{ct} it becomes favorable thermodynamically to form some small regions of

normal phase inside the cylinder and the unusual penetration of magnetic field to the body of superconductor, in the form of the so called Abrikosov's vortices of normal phase, oriented along the field, and allowing magnetic field to penetrate inside. It first becomes possible, when the external field reaches the value of the so called first (or lower) critical field B_{c1} . For $B < B_{c1}$ superconductor is in the usual Meissner state (no field inside). If we start from metal in normal state in high external field, the lowering of this field up to some second (or upper) critical magnetic field $B_{c2} > B_c$ makes it favorable for finite regions of superconducting phase forming inside the normal metal. Thus, in the field region $B_{c1} < B < B_{c2}$ type II superconductors is in the mixed (Shubnikov) phase. Phase diagram of such superconductor in magnetic field is shown schematically in Fig.6-3.

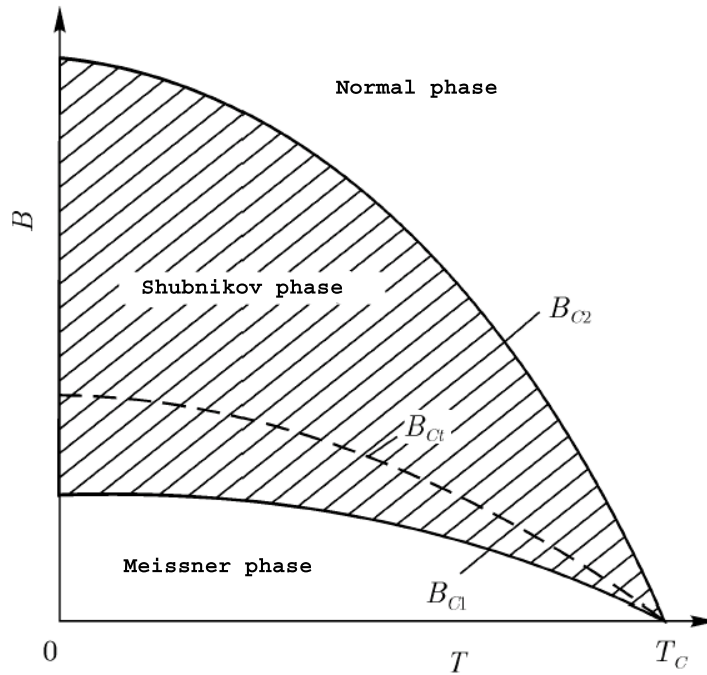


Figure 6.3: Phase diagram of type II superconductor in magnetic field. Dashed line shows thermodynamic critical field B_{ct} .

The value of B_{c2} can be determined from GL theory. It is clear that for $B < B_{c2}$, but close to it, nuclei of superconducting phase possess small values of the order parameter Ψ ($\Psi \rightarrow 0$ for $B \rightarrow B_{c2}$). Then we can write down the linearized GL equation:

$$\frac{1}{4m}(-i\hbar\nabla - \frac{2e}{c}\mathbf{A})^2\Psi = |a|\Psi, \quad (6.106)$$

which has the form of Schroedinger equation for a particle with mass $2m$ and charge $2e$ in magnetic field. The value of $|a|$ in the right hand side of this equation plays the role of an energy level. Boundary condition at infinity is $\Psi = 0$. Now remember the quantum mechanical (Landau) problem of a charged particle in constant homogeneous magnetic field [5]. Minimal value of energy for

such a particle is $E_0 = \hbar\omega_B/2$, where cyclotron frequency $\omega_B = 2|e|B/2mc = |e|B/mc$. Starting from this value we have the continuous energy spectrum. Thus our superconducting nuclei can exist only for:

$$|a| > \frac{|e|\hbar}{2mc}B \quad (6.107)$$

so that

$$B_{c2} = \frac{2mc|a|}{|e|\hbar} = \sqrt{2}\kappa B_c = \phi_0 \frac{1}{2\pi\xi^2(T)} \quad (6.108)$$

where we have introduced $\phi_0 = \frac{\pi c\hbar}{|e|}$ – elementary flux quantum of superconductivity theory introduced above, and also determining the magnetic flux through a single Abrikosov's vortex. During the derivation of the last equalities we have used Eqs. (6.88), (6.101) and (6.102).

Description of the vortex structure of the mixed state of type II superconductors by Abrikosov remains one of the most remarkable achievements of Ginzburg – Landau theory. Unfortunately, we have to limit ourselves only to this qualitative discussion.

Finally, let us discuss shortly the limits of applicability of GL theory. First of all it is necessary to satisfy the condition of $T_c - T \ll T_c$, which is equivalent to $\xi(T) \gg \xi_0$. Then we can use Landau expansion. However, for $T \rightarrow T_c$ the validity of GL theory is limited also by the general condition of applicability of Landau theory of phase transitions, connected with the growth of order parameter fluctuations in immediate vicinity of T_c (in the so called critical region to be discussed later). In case of superconductivity this is a very weak limitation. Later, during the discussion of order parameter fluctuations in Landau theory we shall see that its region of validity (where we can neglect fluctuations) is expressed via GL coefficients by the following inequality:

$$T_c - T \gg \frac{b^2 T_c^2}{\alpha(\hbar^2/m)^3} \quad (6.109)$$

Estimating the right hand side here using microscopic values of these coefficients derived in BCS theory, we get:

$$\frac{T_c - T}{T_c} \gg \left(\frac{T_c}{\varepsilon_F} \right)^4 \quad (6.110)$$

Due to the smallness of the ratio $T_c/\varepsilon_F \sim 10^{-3} - 10^{-4}$ in usual superconductors (usual metals), we can conclude that this limitation is practically irrelevant. Situation change in high – temperature superconductors, where the critical region becomes observable.

Chapter 7

FLUCTUATIONS

7.1 Gaussian distribution.

Physical observables, characterizing the macroscopic body, with high accuracy are equal to their average values. However, small deviations from the average value always take place – there are fluctuations! Let us discuss the ways to find probability distributions for fluctuations¹.

Consider an arbitrary closed system, and let x is some physical parameter, characterizing our system or its part. In the following it is convenient to assume that the average value $\langle x \rangle$ is already subtracted from x , so that below we always have $\langle x \rangle = 0$. In most case $\langle x \rangle = x^*$, where x^* is the most probable value of x . During our general discussion of entropy we have seen (cf. (1.180)), knowledge of the entropy as a function of some macroscopic parameters $x = (x_1, x_2, \dots, x_n)$, we can find the probability of their specific values as:

$$w(x) = C \exp\{S(E, N, V, x)\} \quad (7.1)$$

which is called Boltzmann's principle. Thus, the probability to find a value of some physical characteristic x in the interval $x, x + dx$ is proportional to $\exp S(x)$, where $S(x)$ is entropy as function of an exact value of x . This is a way to define probability distribution of x in most general way, allowing to find the appropriate average values and fluctuations. Eq. (7.1) is the starting point of theory of fluctuations developed by Einstein.

If $\langle x \rangle$ is not subtracted from x , we should note that in equilibrium the entropy is equal to $S_0 = S(\langle x \rangle)$. Then the probability for system to be in a state, characterized by the value of x , belonging to the interval $\langle x \rangle, \langle x \rangle + dx$, takes the form:

$$dw = w(x)dx = \tilde{C} \exp[S(x) - S(\langle x \rangle)]dx = \tilde{C} e^{\Delta S} dx \quad (7.2)$$

where ΔS is the entropy change due to fluctuation dx . In Eq. (7.1) the value of $e^{-S(\langle x \rangle)}$ is simply absorbed into normalization constant C .

Consider the limits of applicability of Eqs. (7.1) and (7.2). All previous arguments implicitly assumed the classical nature of x . Thus, it is necessary to find the condition for quantum effects to be neglected. From quantum mechanics

¹Below we mainly follow [1].

it is known [5] that quantum indeterminacy of energy and some other physical variable x are related by the following relation:

$$\Delta E \Delta x \sim \hbar \dot{x} \quad (7.3)$$

where \dot{x} is the classical time derivative of x ².

Let τ be a characteristic time of change of x , so that $\dot{x} \sim x/\tau$ and

$$\Delta E \Delta x \sim \frac{\hbar x}{\tau} \quad (7.8)$$

It is clear that we can speak about well defined value of x only if $\Delta x \ll x$, so that it is necessary to have

$$\Delta E \gg \frac{\hbar}{\tau} \quad (7.9)$$

i.e. the quantum indeterminacy of energy must be large in comparison to \hbar/τ . Then the entropy of the system has indeterminacy

$$\Delta S \gg \frac{\hbar}{T\tau} \quad (7.10)$$

For Eqs. (7.1) and (7.2) to be valid, it is necessary for indeterminacy of entropy to be small in comparison to unity:

$$T \gg \frac{\hbar}{\tau} \quad \tau \gg \frac{\hbar}{T} \quad (7.11)$$

This is the condition we seek. At low enough temperatures and in case of very fast changes of x in time (small τ !), fluctuations can not be considered as classical (thermodynamic), they become quantum! Below we shall limit ourselves only to the case of classical fluctuations.

Let us return to Eq. (7.1). Entropy S has a maximum at $x = \langle x \rangle = 0$. Then:

$$\left. \frac{\partial S}{\partial x} \right|_{x=0} = 0, \quad \left. \frac{\partial^2 S}{\partial x^2} \right|_{x=0} < 0. \quad (7.12)$$

The value of x due to fluctuation is small. Expanding $S(x)$ in powers of x up to the second order, we have:

$$S(x) = S(0) - \frac{\beta}{2} x^2; \quad \beta > 0 \quad (7.13)$$

²Consider two physical variables f and g , described by operators satisfying commutation relations:

$$\hat{f}\hat{g} - \hat{g}\hat{f} = -i\hbar\hat{c} \quad (7.4)$$

where \hat{c} is also some operator. In quasiclassical limit $\hbar \rightarrow 0$, in first approximation \hat{c} can be replaced by c -number. Then:

$$\hat{f}\hat{g} - \hat{g}\hat{f} = -i\hbar c \quad (7.5)$$

This commutation relation is similar to $p_x x - x p_x = -i\hbar$, but with $\hbar \rightarrow \hbar c$. Then, in analogy with Heisenberg relation $\Delta x \Delta p_x \sim \hbar$, we can conclude that in quasiclassical approximation f and g satisfy the following indeterminacy relation:

$$\Delta f \Delta g \sim \hbar c \quad (7.6)$$

In particular, when one of the variables is energy $f \equiv H$ and the second operator (\hat{g}) does not depend on time, using $\hat{g} = \frac{i}{\hbar}(\hat{H}\hat{g} - \hat{g}\hat{H})$, we obtain $c = \dot{g}$ and quasiclassical indeterminacy relation takes the form:

$$\Delta E \Delta g \sim \hbar \dot{g} \quad (7.7)$$

For $g = x$ it reduces to (7.3).

Substituting this to (7.1), we obtain:

$$w(x)dx = Ae^{-\frac{\beta}{2}x^2} dx \quad (7.14)$$

Normalization constant A is defined by $\int_{-\infty}^{\infty} dxw(x) = 1$, giving $A = \sqrt{\beta/2\pi}$.

We see that probability distribution of fluctuations of x is given by *Gaussian law*:

$$w(x) = \sqrt{\frac{\beta}{2\pi}} e^{-\frac{\beta}{2}x^2} \quad (7.15)$$

The average square of fluctuation is equal to:

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} dx x^2 w(x) = \frac{1}{\beta} \quad (7.16)$$

Thus, the Gaussian distribution can also be written as:

$$w(x) = \frac{1}{\sqrt{2\pi \langle x^2 \rangle}} \exp\left(-\frac{x^2}{2 \langle x^2 \rangle}\right) \quad (7.17)$$

Function $w(x)$ has a sharper maximum for smaller values of $\langle x^2 \rangle$.

The knowledge of $\langle x^2 \rangle$ allows to find a similar characteristic for any function $\varphi(x)$. Due to smallness of x we have:

$$\langle (\Delta\varphi)^2 \rangle = \left(\frac{d\varphi}{dx}\right)_{x=0}^2 \langle x^2 \rangle. \quad (7.18)$$

Similarly we can determine the probability of simultaneous fluctuations of several thermodynamic variables. Let us denote these deviations from equilibrium (average) values as x_1, x_2, \dots, x_n . Introducing entropy $S(x_1, x_2, \dots, x_n)$ we write this probability distribution as $w dx_1 \dots dx_n \sim \exp[S(x_1, \dots, x_n)] dx_1 \dots dx_n$. Expanding S in powers of x_i up to terms of second order, we get:

$$\Delta S = -\frac{1}{2} \sum_{i,k=1}^n \beta_{ik} x_i x_k = -\frac{1}{2} \beta_{ik} x_i x_k \quad (7.19)$$

which is a negative quadratic form. Obviously $\beta_{ik} = \beta_{ki}$. In last equality we assume the usual rule of summation over repeating indices. Then:

$$w = A \exp\left(-\frac{1}{2} \beta_{ik} x_i x_k\right) \quad (7.20)$$

where A is defined by normalization $\int dx_1 \dots dx_n w = 1$. Further calculations proceed as follows. Let us make a linear transformation of x_i :

$$x_i = a_{ik} x'_k \quad (7.21)$$

diagonalizing the quadratic form $\beta_{ik} x_i x_k$. To get:

$$\beta_{ik} x_i x_k = x_i'^2 \equiv x'_i x'_k \delta_{ik} \quad (7.22)$$

we require that coefficients of our transformation (7.22) satisfy the condition:

$$\beta_{ik} a_{il} a_{km} = \delta_{lm} \quad (7.23)$$

Determinant of the matrix in the left hand side is equal to the product of determinants:

$$\beta a^2 = 1 \quad \beta = \text{Det}\beta_{ik} \quad a = \text{Det}a_{ik} \quad (7.24)$$

The Jacobian of linear transformation $x_i \rightarrow x'_i$ is equal to a . Then, after the linear transformation (7.21) the integral is factorized into the product of n identical integrals, and taking into account (7.24) we get:

$$Aa \left[\int_{-\infty}^{\infty} dx' \exp\left(-\frac{1}{2}x'^2\right) \right]^n = \frac{A}{\sqrt{\beta}} (2\pi)^{n/2} = 1 \quad (7.25)$$

Finally, the Gaussian distribution for several variables is written as:

$$w = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \exp\left(-\frac{1}{2}\beta_{ik}x_ix_k\right) \quad \beta = \text{Det}|\beta_{ik}| \quad (7.26)$$

using it we can find:

$$\langle x_ix_k \rangle = \beta_{ik}^{-1} \quad (7.27)$$

where β_{ik}^{-1} is the matrix element of the matrix inverse to β_{ik} . For statistically independent fluctuations of x_1 and x_2 the average of their product factorizes: $\langle x_1x_2 \rangle = \langle x_1 \rangle \langle x_2 \rangle = 0$, so that $\beta_{12}^{-1} = 0$. In case of Gaussian distribution, the inverse theorem is also valid. If $\langle x_1x_2 \rangle = 0$ (i.e. $\beta_{12}^{-1} = 0$), then fluctuations of x_1 and x_2 are statistically independent.

7.2 Fluctuations of basic physical properties.

Let us calculate mean square fluctuations of basic thermodynamic variables of some separate small part of macroscopic body. This small part is assumed still to contain large enough number of particles.

For such variables as energy or volume, which also have direct mechanical interpretation, the notion of fluctuation is obvious. However, it needs clarification for such variables as entropy and temperature, as definition of these variables is necessarily connected with system evolution during finite time intervals.

Probability w can be written as:

$$w \sim \exp \Delta S \quad (7.28)$$

where ΔS is entropy change due to fluctuation. From thermodynamics we know [1] that

$$\Delta S = -\frac{R_{min}}{T_0} \quad (7.29)$$

where R_{min} is minimal work, necessary for reversible change of thermodynamic variables in the given small part of the body (due to fluctuation), while the rest of the system plays a role of a bath with temperature T_0 . Thus:

$$w \sim \exp\left(-\frac{R_{min}}{T_0}\right) \quad (7.30)$$

Now we can substitute here (for fixed temperature and pressure of the bath):

$$R_{min} = \Delta E - T_0\Delta S + P_0\Delta V \quad (7.31)$$

where $\Delta E, \Delta S, \Delta V$ are changes of energy, entropy and volume of the small part of the system due to fluctuation, while T_0 and P_0 are temperature and pressure of the bath, i.e. temperature and pressure of our system in equilibrium. Below we drop index zero and understand that coefficients are taken at equilibrium. Then we obtain:

$$w \sim \exp\left(-\frac{\Delta E - T\Delta S + P\Delta V}{T}\right) \sim \exp\left(-\frac{\Delta\Phi}{T}\right) \quad (7.32)$$

where $\Delta\Phi$ is the change of thermodynamic potential due to fluctuation. For $\Delta V = 0$, i.e. in the absence of volume fluctuations, we have:

$$w \sim \exp\left(-\frac{\Delta F}{T}\right) \quad (7.33)$$

here ΔF is the free energy change due to fluctuation.

Note that Eqs. (7.32) and (7.33) are actually applicable to arbitrary fluctuations, both small and large. In case of small fluctuations we may proceed as follows. Expanding ΔE in power series we get:

$$\Delta E - T\Delta S + P\Delta V = \frac{1}{2} \left[\frac{\partial^2 E}{\partial S^2} (\Delta S)^2 + 2 \frac{\partial^2 E}{\partial S \partial V} \Delta S \Delta V + \frac{\partial^2 E}{\partial V^2} (\Delta V)^2 \right] \quad (7.34)$$

where first order terms in the expansion of ΔE cancelled out as $\frac{\partial E}{\partial S} = T$ and $\frac{\partial E}{\partial V} = -P$. It is easily seen that (7.34) can be rewritten as:

$$\frac{1}{2} \left[\Delta S \Delta \left(\frac{\partial E}{\partial S} \right)_V + \Delta V \Delta \left(\frac{\partial E}{\partial V} \right)_S \right] = \frac{1}{2} (\Delta S \Delta T - \Delta P \Delta V). \quad (7.35)$$

Then we obtain the probability of fluctuation as:

$$w \sim \exp\left(\frac{\Delta P \Delta V - \Delta T \Delta S}{2T}\right). \quad (7.36)$$

From this general expression we can find fluctuations of different thermodynamic variables.

First, let us choose V and T as independent variables. Then:

$$\Delta S = \left(\frac{\partial S}{\partial T} \right)_V \Delta T + \left(\frac{\partial S}{\partial V} \right)_T \Delta V = \frac{C_v}{T} \Delta T + \left(\frac{\partial P}{\partial T} \right)_V \Delta V \quad (7.37)$$

$$\Delta P = \left(\frac{\partial P}{\partial T} \right)_V \Delta T + \left(\frac{\partial P}{\partial V} \right)_T \Delta V. \quad (7.38)$$

Substituting these expressions into (7.36) we can see, that terms with $\Delta V \Delta T$ cancel, and what remains is:

$$w \sim \exp\left\{-\frac{C_v}{2T^2} (\Delta T)^2 + \frac{1}{2T} \left(\frac{\partial P}{\partial V} \right)_T (\Delta V)^2\right\}. \quad (7.39)$$

This expression factorizes into two factors, depending only on ΔT or ΔV . Thus, the fluctuations of temperature and volume are statistically independent:

$$\langle \Delta T \Delta V \rangle = 0 \quad (7.40)$$

Comparing each of two factors in Eq. (7.39) with general expression for Gaussian distribution (7.17), we find the following expressions for mean square fluctuations of temperature and volume:

$$\langle (\Delta T)^2 \rangle = \frac{T^2}{C_v} \quad (7.41)$$

$$\langle (\Delta V)^2 \rangle = -T \left(\frac{\partial V}{\partial P} \right)_T. \quad (7.42)$$

Positivity of these expressions is guaranteed by thermodynamic inequalities $C_v > 0$ and $(\partial P/\partial V)_T < 0$ [1].

Choose now P and S as independent variables in Eq. (7.36). Then:

$$\Delta V = \left(\frac{\partial V}{\partial P} \right)_S \Delta P + \left(\frac{\partial V}{\partial S} \right)_P \Delta S \quad (7.43)$$

$$\Delta T = \left(\frac{\partial T}{\partial S} \right)_P \Delta S + \left(\frac{\partial T}{\partial P} \right)_S \Delta P = \frac{T}{C_p} \Delta S + \left(\frac{\partial T}{\partial P} \right)_S \Delta P \quad (7.44)$$

But according to $dW = TdS + VdP$ we have $(\frac{\partial V}{\partial S})_P = \frac{\partial^2 W}{\partial P \partial S} = (\frac{\partial T}{\partial P})_S$, then:

$$\Delta V = \left(\frac{\partial V}{\partial P} \right)_S \Delta P + \left(\frac{\partial T}{\partial P} \right)_S \Delta S \quad (7.45)$$

Substituting ΔV and ΔT into (7.36), we obtain:

$$w \sim \exp \left\{ \frac{1}{2T} \left(\frac{\partial V}{\partial P} \right)_S (\Delta P)^2 - \frac{1}{2C_p} (\Delta S)^2 \right\} \quad (7.46)$$

As before, this expression factorizes in two factors, depending on ΔP and ΔS . Thus:

$$\langle (\Delta S)^2 \rangle = C_p \quad (7.47)$$

$$\langle (\Delta P)^2 \rangle = -T \left(\frac{\partial P}{\partial V} \right)_S \quad (7.48)$$

From relations obtained above it is seen that mean square fluctuations of additive thermodynamic variables, such as volume and entropy, are proportional to the size (volume) of those part of the system, to which they are related. Accordingly, these fluctuations are $\sim \sqrt{V}$, while relative fluctuations are $\sim 1/\sqrt{V}$. At the same time, for temperature and pressure already mean square fluctuations are inversely proportional to the square root of volume.

Expressions for fluctuations of thermodynamic variables can also be obtained directly from Gibbs distribution. As an example, let us consider fluctuations of particle number. Using the grand canonical distribution we have:

$$\langle N \rangle = e^{\frac{\Omega}{T}} \sum_N N e^{\frac{\mu N}{T}} \sum_n e^{-\frac{E_n N}{T}} \quad (7.49)$$

Differentiating this expression by μ (at constant V and T), we get:

$$\begin{aligned} \frac{\partial \langle N \rangle}{\partial \mu} &= \frac{1}{T} e^{\frac{\Omega}{T}} \sum_N \left(N^2 + N \frac{\partial \Omega}{\partial \mu} \right) e^{\frac{\mu N}{T}} \sum_n e^{-\frac{E_n N}{T}} = \\ &= \frac{1}{T} \left(\langle N^2 \rangle + \langle N \rangle \frac{\partial \Omega}{\partial \mu} \right) \end{aligned} \quad (7.50)$$

But $\partial\Omega/\partial\mu = -\langle N \rangle$, so that:

$$\frac{\partial \langle N \rangle}{\partial \mu} = \frac{1}{T}(\langle N^2 \rangle - \langle N \rangle^2) = \frac{1}{T} \langle (\Delta N)^2 \rangle, \quad (7.51)$$

and accordingly:

$$\langle (\Delta N)^2 \rangle = T (\partial \langle N \rangle / \partial \mu)_{T,V}. \quad (7.52)$$

From these expressions it is clear that mean square fluctuations of such variables as energy, volume and pressure tend to zero as $T \rightarrow 0$. This is a general property of all thermodynamic variables, which also have direct mechanical meaning, but it is not so in general for such purely thermodynamic variables as entropy and temperature. According to Eq. (7.41), for fixed energy, we can not attribute to our system the well defined temperature, it fluctuates and Eq. (7.41) characterizes the limits for precise determination of the temperature of an isolated system.

7.3 Fluctuations in ideal gases.

Consider now calculations of $\langle (\Delta N)^2 \rangle$ from another point of view. According to Eq. (7.42) fluctuations of volume are given by $\langle (\Delta V)^2 \rangle = -T \left(\frac{\partial V}{\partial P} \right)_T$. Dividing both parts of this equality by N^2 , we find fluctuation of the volume per one particle:

$$\langle \left(\Delta \frac{V}{N} \right)^2 \rangle = -\frac{T}{N^2} \left(\frac{\partial V}{\partial P} \right)_T \quad (7.53)$$

This allows us to find fluctuation of particle number in any separate volume inside the body. The volume V is fixed, so that $\Delta \frac{V}{N} = V \Delta \frac{1}{N} = -\frac{V}{N^2} \Delta N$, and substitution into Eq. (7.53) gives:

$$\langle (\delta N)^2 \rangle = -T \frac{N^2}{V^2} \left(\frac{\partial V}{\partial P} \right)_T \quad (7.54)$$

Using now the equation of state of an ideal gas giving $V = NT/P$, we obtain:

$$\langle (\Delta N)^2 \rangle = N \quad (7.55)$$

Then the relative fluctuation is:

$$\frac{\langle (\Delta N)^2 \rangle^{1/2}}{N} = \frac{1}{\sqrt{N}}. \quad (7.56)$$

Consider now fluctuations of particle distribution over different quantum states. Let n_k be the number of particles in k -th quantum state. Due to total independence of this (sub)system of particles from the rest of the system (gas), we may apply to it Eq. (7.52):

$$\langle (\Delta n_k)^2 \rangle = T \frac{\partial \langle n_k \rangle}{\partial \mu} \quad (7.57)$$

For Fermi - gas, after the substitution of $\langle n_k \rangle = [e^{(\epsilon_k - \mu)/T} + 1]^{-1}$ we obtain:

$$\langle (\Delta n_k)^2 \rangle = \langle n_k \rangle (1 - \langle n_k \rangle). \quad (7.58)$$

Similarly, for Bose – gas:

$$\langle (\Delta n_k)^2 \rangle = \langle n_k \rangle (1 + \langle n_k \rangle). \quad (7.59)$$

For Boltzmann gas, after substitution of $\langle n_k \rangle = e^{(\mu - \varepsilon_k)/T}$, we obtain:

$$\langle (\Delta n_k)^2 \rangle = \langle n_k \rangle \quad (7.60)$$

Previous expressions of Eqs. (7.58) and (7.59) reduce to (7.60) for $n_k \ll 1$. Let us sum (7.58) and (7.59) over the group of G_j close levels, containing $N_j = \sum n_k$ particles. Due to statistical independence of fluctuations of different n_k we have:

$$\langle (\Delta N_j)^2 \rangle = G_j \langle n_j \rangle (1 + \langle n_j \rangle) = N_j \left(1 + \frac{\langle N_j \rangle}{G_j} \right) \quad (7.61)$$

where $\langle n_j \rangle$ is the average value of $\langle n_k \rangle$ close to each other, and $\langle N_j \rangle = \langle n_j \rangle G_j$.

These expressions can be applied e.g. to photon gas, putting in (7.59) $\mu = 0$. Consider the set of quantum states of photons (in volume V) with close frequencies, belonging to a small interval $\Delta\omega_j$. The number of the relevant states is $G_j = V\omega_j^2\Delta\omega_j/\pi^2c^3$. The total energy of the quanta in this frequency interval is given by $E_{\Delta\omega_j} = N_j\hbar\omega_j$. Multiplying (7.61) by $(\hbar\omega_j)^2$ and dropping index j , we obtain the following Einstein expression for the fluctuation of photon gas energy $E_{\Delta\omega}$ in the given frequency interval $\Delta\omega$:

$$\langle (\Delta E_{\Delta\omega})^2 \rangle = \hbar\omega E_{\Delta\omega} + \frac{\pi^2c^3(E_{\Delta\omega})^2}{V\omega^2\Delta\omega}. \quad (7.62)$$

Let us consider also fluctuations of particle number within the given volume of an ideal gas V . In principle we can analyze big enough fluctuations with $N - \langle N \rangle$ of the order of $\langle N \rangle$. This is relevant only for Boltzmann gas, as in Fermi and Bose gases probability of such fluctuations becomes noticeable only in such small volumes, that quantum fluctuations become important. According to grand canonical ensemble, distribution of N particles of the gas over different quantum states is proportional to

$$\exp \left\{ \frac{\Omega + \mu N - \sum \varepsilon_k}{T} \right\}, \quad (7.63)$$

where $\sum \varepsilon_k$ is the sum of energies of particles. To obtain probability distribution w_N we have to sum this expression over all states of the particles in the given volume V . Performing summation independently over the states of each particle, we have to divide the result by $N!$, so that:

$$w_N = \frac{e^{\Omega/T}}{N!} \left(\sum_k e^{\frac{\mu - \varepsilon_k}{T}} \right)^N \quad (7.64)$$

The sum standing here is simply the average number of particles in the given volume:

$$\sum_k e^{\frac{\mu - \varepsilon_k}{T}} = \langle N \rangle. \quad (7.65)$$

Then:

$$w_N = \text{const} \frac{\langle N \rangle^N}{N!}, \quad (7.66)$$

and finding $const = e^{-\langle N \rangle}$ from normalization³ we obtain:

$$w_N = \frac{\langle N \rangle^N e^{-\langle N \rangle}}{N!} \quad (7.67)$$

which is the so called Poisson distribution. Using it we can directly show [1], that the mean square fluctuation of particle number is again:

$$\langle (\Delta N)^2 \rangle = \langle N \rangle \quad (7.68)$$

and this expression is valid not only for large, but for arbitrary values of $\langle N \rangle$.

³This reduces to $\Omega = -PV = -\langle N \rangle T$, in accordance with equation of state of an ideal gas.

Chapter 8

PHASE TRANSITIONS AND CRITICAL PHENOMENA

8.1 Mean-field theory of magnetism.

This Chapter is devoted to an elementary introduction into theory of second order phase transitions and critical phenomena. The simplest microscopic model of such phase transition is mean (or molecular) field theory of Curie and Weiss, which gives a qualitative description of a phase transition in ferromagnets. This model allows us to study the main aspects of the general problem, which are also characteristic for all other types of second order phase transitions.

Consider first statistical mechanics of free spins in an external magnetic field (e.g. paramagnet with localized magnetic moments). The Hamiltonian of the system of N non interacting spins \mathbf{S}_i in an external magnetic field \mathbf{H} is written as:

$$H = -g\mu_B \sum_{i=1}^N \mathbf{S}_i \mathbf{H} \quad (8.1)$$

where g is gyromagnetic ratio and $\mu_B = \frac{e\hbar}{2mc}$ is Bohr magneton. To shorten notations in the following we introduce $\tilde{\mu} = g\mu_B$. Quantum states of spin are defined by its projections on external magnetic field, which are given $2S + 1$ possible values ($m_i = -S, -S + 1, \dots, S - 1, S$).

Partition functions of this system of spins takes the form:

$$Z = \sum_S \exp \left(-\frac{\tilde{\mu}}{T} \sum_{i=1}^N \mathbf{S}_i \mathbf{H} \right) = \sum_{m_1=-S}^{m_1=S} \dots \sum_{m_N=-S}^{m_N=S} \exp \left(x \sum_{i=1}^N m_i \right) \quad (8.2)$$

where

$$x \equiv \frac{\tilde{\mu}H}{T} \quad (8.3)$$

Summation in Eq. (8.2) is especially simple in case of $S = 1/2$:

$$\begin{aligned} Z &= \prod_{i=1}^N \left\{ \sum_{m_i=-1/2}^{m_i=1/2} \exp(xm_i) \right\} = \\ &= \prod_{i=1}^N 2ch\left(\frac{1}{2}x\right) = 2^N ch^N\left(\frac{1}{2}x\right) \end{aligned} \quad (8.4)$$

For arbitrary S we have:

$$Z = \left\{ \frac{\exp(-xS)[1 - \exp\{(2S+1)x\}]}{1 - \exp(x)} \right\}^N = \left[\frac{sh\{(S+1/2)x\}}{sh(x/2)} \right]^N \quad (8.5)$$

The free energy is now given by:

$$F(T, H) = -T \ln Z = -NT \ln \left[\frac{sh\{(S+1/2)x\}}{sh(x/2)} \right] \quad (8.6)$$

Then the magnetization is obtained as:

$$M(T, H) = - \left(\frac{\partial F}{\partial H} \right)_T = T \frac{\partial}{\partial H} \ln Z = M_0 B_S(Sx) \quad (8.7)$$

where $M_0 \equiv M(T=0, H=0) = NS\tilde{\mu} = NSg\mu_B$ is the maximal possible value of magnetization, while

$$B_S(x) \equiv \frac{2S+1}{2S} cth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S} cth\left(\frac{1}{2S}x\right) \quad (8.8)$$

is the so called Brillouin function. This function relates the magnetization of paramagnet and the value of an external magnetic field, graphically it is shown in Fig. 8-1. For the case of $S = 1/2$ Brillouin function is given by:

$$B_{1/2}\left(\frac{1}{2}x\right) = 2cth(x) - cth(x/2) = th(x/2). \quad (8.9)$$

From Fig. 8-1 we see that $M = 0$ for $H = 0$, in fact it is obvious for paramagnet state. In ferromagnets situation is different, spins interact with each other and at low temperatures the system acquires spontaneous magnetization, which exists also in the absence of external magnetic field, i.e. for $H = 0$. Basic assumption of mean field theory approach to magnetic ordering is that spin – spin interaction produces within the system some mean (or “molecular”) magnetic field H_m , which is to be added to external field H . It is also assumed that this field is just proportional to internal magnetization of the system:

$$H_m = \lambda M(T, H) \quad (8.10)$$

so that an effective field acting upon each spin is given by:

$$H_{eff} = H + \lambda M(T, H) \quad (8.11)$$

Parameter $\lambda > 0$ is called molecular field parameter. All relations derived above remain valid, we only have to substitute $H \rightarrow H_{eff}$. In particular, after such substitution Eq. (8.7) reduces to:

$$M = M_0 B_S \left[\frac{\tilde{\mu}S}{T} (H + \lambda M) \right] \quad (8.12)$$

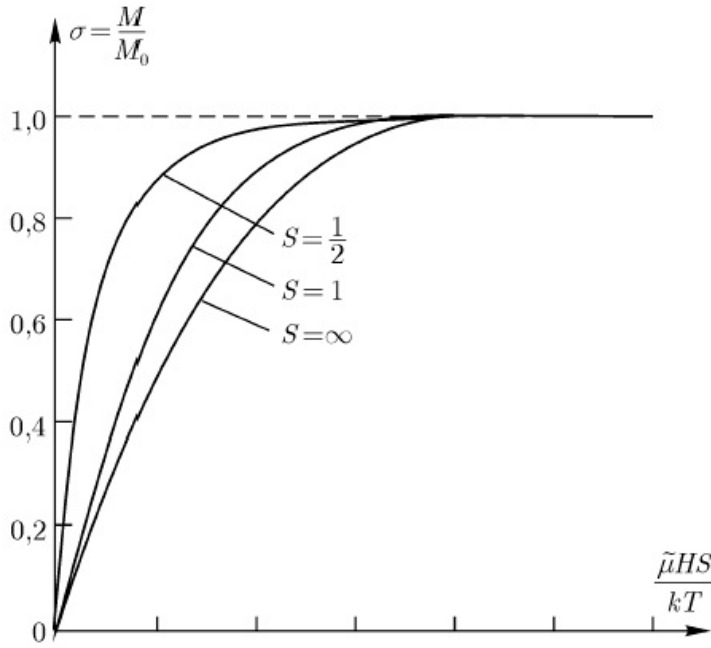


Figure 8.1: Dependence of relative magnetization of paramagnet $\sigma = M/M_0$ on parameter $\tilde{\mu}HS/T$, described by Brillouin function for different values of spin S .

Putting now $H = 0$ we get the equation determining magnetization M :

$$M = M_0 B_S \left(\frac{\tilde{\mu} \lambda M}{T} S \right) \quad (8.13)$$

Graphic solution of this equation is shown in Fig. 8-2. Eq. (8.13) possesses the trivial solution $M = 0$ for arbitrary values of temperature T . However, there is also the possibility of the second (non trivial) solution for $M \neq 0$, when the initial slope of the curve, representing the right hand side of Eq. (8.13), is more steep than left hand side. To analyze this situation analytically, we perform Taylor expansion of Brillouin function:

$$B_S(x) = \frac{S+1}{3S} x - \frac{S+1}{3S} \frac{2S^2+2S+1}{30S^2} x^3 + \dots \quad (8.14)$$

Then the initial slope of the curve for the right hand side of (8.13) is defined by:

$$M_0 \left(\frac{S+1}{3S} \right) \frac{\tilde{\mu} S \lambda}{T} = C \frac{\lambda}{T} \quad (8.15)$$

where we have introduced the so called Curie constant:

$$C \equiv \frac{N \tilde{\mu}^2 S(S+1)}{3} \quad (8.16)$$

expressing M_0 via microscopic parameters, in accordance with an expression after Eq. (8.7). Now from Eq. (8.15) we can see that the non trivial solution

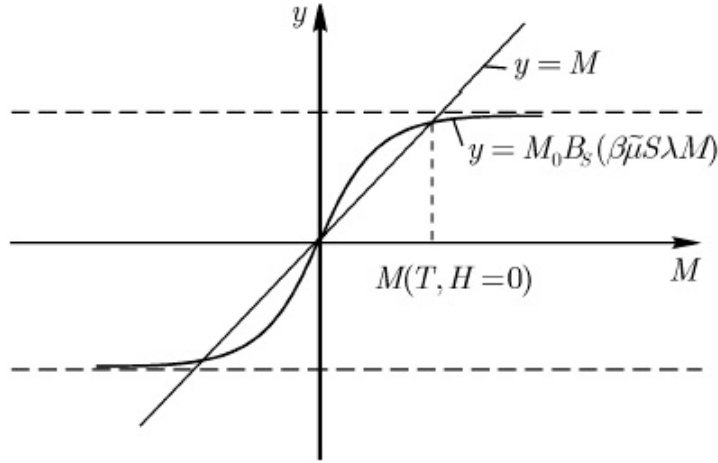


Figure 8.2: Graphic solution of equation for magnetization in molecular (mean) field theory ($\beta = 1/T$).

exists for $T < \lambda C$, giving the value of the critical temperature of ferromagnetic phase transition in mean field theory:

$$T_c = \lambda C \quad (8.17)$$

For lower temperatures $M \neq 0$ even in the absence of an external magnetic field. Transition temperature T_c obviously tends to zero as $\lambda \rightarrow 0$, when we return to the case of a paramagnet.

Let us consider the origin of molecular field from microscopic point of view. The majority of models of magnetic ordering is based upon the concept of exchange interaction between spins, which in the simplest case can be described by Heisenberg model, with interaction Hamiltonian written as:

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{S}_i \mathbf{S}_j - \tilde{\mu} \sum_i \mathbf{S}_i \mathbf{H} \quad (8.18)$$

where J_{ij} is the so called exchange integral, which is taken to be positive (the case of ferromagnetic ordering).

Very popular is also the simplified version of this model called Ising model, described by the hamiltonian (8.18) with only S_z spin components left. Usually, Ising Hamiltonian is written as:

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} s_i s_j - \tilde{\mu} \sum_i s_i H \quad (8.19)$$

where Ising “spins” $s_i = \pm 1$, i.e. take only two values. Actually, the Ising model can be solved exactly on two – dimensional lattice [1]. This solution, first obtained by Onsager, is very important for the theory of phase transitions, but we shall not describe it here.

Mean (molecular) field approximation reduces to the approximate replacement of microscopic Hamiltonian (8.18) by an *effective* Hamiltonian of the fol-

lowing form:

$$H = - \sum_{i \neq j} J_{ij} \langle S_z \rangle S_{iz} - \tilde{\mu} \sum_i S_{iz} H \quad (8.20)$$

where external magnetic field is assumed to be oriented along z - axis, while $\langle S_z \rangle$ denotes the average value of z -component of spin on an arbitrary lattice site. It is clear that (8.20) describes the system of free (non interacting) spins in an effective (mean or molecular) field, oriented along z -axis and given by:

$$H_{eff} = H + \frac{J_0}{\tilde{\mu}} \langle S_z \rangle = H + \frac{J_0}{N\tilde{\mu}^2} M \quad (8.21)$$

where

$$J_0 = \sum_j J_{ij} \quad J_{ii} = 0 \quad (8.22)$$

It can be said that molecular field on the given lattice site is actually the mean magnetic field, which is self-consistently created on this site by all other spins of the system. Comparing Eqs. (8.21) and (8.11), we can see that molecular field constant λ is determined in this model by the following expression:

$$\lambda = \frac{J_0}{N\tilde{\mu}^2} \quad (8.23)$$

From Eq. (8.17) it follows now, that the critical temperature of ferromagnetic phase transition (Curie temperature) is given by:

$$T_c = \frac{1}{3} J_0 S(S+1) \quad (8.24)$$

In case of spins interacting with nearest neighbors only, i.e. for $J_{ij} = J$ when the site j is one of the z nearest neighbors of site i , while for other cases $J_{ij} = 0$, we have:

$$T_c = \frac{1}{3} zJS(S+1) \quad (8.25)$$

Let us return to the simplest case of $S = 1/2$. According to Eqs. (8.9) and (8.12) we can write:

$$M = M_0 th \left[\frac{1}{2T} \tilde{\mu} (H + \lambda M) \right] \quad (8.26)$$

Introducing dimensionless (relative) variables $\sigma = M/M_0$ and $t = T/T_c$, we can rewrite Eq. (8.26) as:

$$\sigma = th \left(\frac{1}{2} \frac{\tilde{\mu} H}{T} + \frac{\sigma}{t} \right) \quad (8.27)$$

Using $th(x+y) = \frac{thx+thy}{1+(thx)(thy)}$ we rewrite (8.27) as:

$$h \equiv th \left(\frac{\tilde{\mu} H}{2T} \right) = \frac{\sigma - th(\sigma/t)}{1 - \sigma th(\sigma/t)} \quad (8.28)$$

Near the critical point ($H = 0$, $M = 0$, $T = T_c$) all arguments of hyperbolic functions in (8.28) are small and we can perform Taylor expansions: $thx = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 + \dots$. Then:

$$h = \sigma \left(1 - \frac{1}{t} \right) + \sigma^3 \left[\frac{1}{3t^3} + \frac{1-1/t}{t} \right] \quad (8.29)$$

This is the so called magnetic equation of state, which determines the behavior of all the relevant physical characteristics of magnet close to the critical point.

For example we can consider magnetization and magnetic susceptibility. From Eq. (8.28) it is seen, that in zero external field $h = 0$ and for $T < T_c$ Eq. (8.29) takes the form:

$$\sigma^2 = \frac{T_c/T - 1}{\frac{T_c^3}{3T^3} + \frac{T_c}{T} \left(1 - \frac{T_c}{T}\right)} + \dots \approx 3 \left(\frac{T}{T_c}\right)^2 \frac{T_c - T}{T_c} \quad (8.30)$$

Thus, we obtain the following behavior of magnetization in zero field close to T_c (for $T < T_c$):

$$\sigma \sim |\tau|^\beta \quad \tau = \frac{T - T_c}{T_c} \quad (8.31)$$

where the *critical exponent* of magnetization (order parameter) $\beta = 1/2$.

Isothermal susceptibility in zero field $\chi_T = \left(\frac{\partial M}{\partial H}\right)_T$ satisfy the following relation:

$$\chi_T = \left(\frac{\partial M}{\partial \sigma}\right)_T \left(\frac{\partial \sigma}{\partial h}\right)_T \left(\frac{\partial h}{\partial H}\right)_T = \left(\frac{1}{2} N \tilde{\mu}\right) \left(\frac{\tilde{\mu}}{2T}\right) \left(\frac{\partial \sigma}{\partial h}\right)_T = \frac{C}{T} \left(\frac{\partial \sigma}{\partial h}\right)_T \quad (8.32)$$

where Curie constant was taken from (8.16) for the case of $S = 1/2$. Differentiating both sides of (8.29) over h for $T \approx T_c$, we get:

$$1 = \frac{\partial \sigma}{\partial h} \left[\left(1 - \frac{1}{t}\right) + 3\sigma^2 \left(\frac{1}{3t^3}\right) \right] \quad (8.33)$$

or, using (8.32),

$$\chi_T = \frac{C}{T} \left[\frac{\tau}{t} + \frac{\sigma^3}{t^3} \right]^{-1} \quad (8.34)$$

Then, for $T > T_c$ we have $\sigma = 0$ for $H = 0$ and (8.34) reduces to:

$$\chi_T = \frac{C}{T} \left(\frac{T_c T - T_c}{T T_c}\right)^{-1} = \frac{C}{T - T_c} \sim \tau^{-\gamma} \quad (8.35)$$

where the critical exponent of susceptibility $\gamma = 1$. For $T < T_c$, according to (8.30) we have $\sigma^2 \approx -3\tau$, so that from (8.34) we get:

$$\chi_T \approx \frac{1}{2} \frac{C}{T} \frac{1}{(-\tau)} \sim |\tau|^{-1} \quad (8.36)$$

and the critical exponent of susceptibility for $T < T_c$ is also $\gamma' = 1$.

Direct calculations within mean (molecular) field model show that the specific heat of the system at $T = T_c$ has a discontinuity $\Delta C_H = 3/2N$. Within this model we can also study the critical behavior of a number of other physical characteristics of the system, described by appropriate critical exponents.

In general, molecular field model (approximation) gives rather satisfactory qualitative description of ferromagnetic phase transition. It is easily generalized to the case of antiferromagnetic transition. In fact, this model is the origin of a number of similar mean field models for microscopic description of different phase transitions in many physical systems. For example, the BCS model of

superconductivity, described above, is the typical mean field model, where the relevant “mean field” is described by anomalous averages (6.17), (6.18), while the Hamiltonians (6.15) or (6.16) are direct analogs of (8.20)¹. In superconductivity theory, this approach actually gives very accurate description of system behavior close to T_c . For majority of other phase transitions, e.g. in real magnetics, this description is only qualitative, the experimental values of critical exponents are significantly different from mean field theory predictions. The physical reason for these discrepancies is due to the increasing role of fluctuations in the critical region close to T_c . We shall return to this problem below.

8.2 Quasiaverages*.

Microscopic theory of phase transitions addresses very important question of degeneracy of the system ground state and closely related problem of proper definition of statistical averages. Consider as an example Heisenberg ferromagnet, described by the Hamiltonian (8.18). In the absence of an external magnetic field (for $\mathbf{H} = 0$) this Hamiltonian is obviously invariant with respect to rotations in three-dimensional space. It is clear as in this case (8.18) depends only on scalar products of spins on different lattice sites. However, ferromagnetic ground state is not invariant with respect to three-dimensional rotations — spontaneous magnetization has a definite direction in space and system is invariant only with respect to rotations around this direction. At the same time, it is obvious that the other ground state of the same system, characterized by other direction of magnetization vector, corresponds to the same energy. Accordingly, there is an infinite set of ground states, differing only by the directions of magnetization. Introduction of an external magnetic field (even infinitesimal) breaks this degeneracy and allows well defined calculations of all statistical averages. This leads to the concept of *quasiaverages* [23] — one of the central concepts in the theory of phase transitions.

Let us return to Heisenberg model in the absence of an external magnetic field:

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{S}_i \mathbf{S}_j \quad (8.37)$$

The total spin of this system:

$$\mathbf{S} = \sum_j \mathbf{S}_j \quad (8.38)$$

is an integral of motion (this is valid for each of its components, in quantum mechanics each one commutes with the Hamiltonian of the system). Consider now commutation relations:

$$\begin{aligned} S_x S_y - S_y S_x &= i S_z \\ S_y S_z - S_z S_y &= i S_x \\ S_z S_x - S_x S_z &= i S_y \end{aligned} \quad (8.39)$$

Using these relations we can write:

$$iSp(S_z e^{-\frac{H}{T}}) = Sp[(S_x S_y - S_y S_x) e^{-\frac{H}{T}}] \quad (8.40)$$

¹BCS Hamiltonian can even be rewritten via some “pseudospin” operators (introduced by Anderson), when it is reduced practically to the same form as (8.20).

As S_x commutes with H we get:

$$Sp(S_y S_x e^{-\frac{H}{T}}) = Sp(S_y e^{-\frac{H}{T}} S_x) = Sp(S_x S_y e^{-\frac{H}{T}}), \quad (8.41)$$

so that

$$Sp(S_z e^{-\frac{H}{T}}) = 0. \quad (8.42)$$

Similarly we find that:

$$Sp(S_x e^{-\frac{H}{T}}) = 0 \quad Sp(S_y e^{-\frac{H}{T}}) = 0 \quad (8.43)$$

Let us introduce the magnetization of the unit volume as:

$$\mathbf{M} = \frac{\tilde{\mu}}{V} \sum_j \mathbf{S}_j = \frac{\tilde{\mu}}{V} \mathbf{S}. \quad (8.44)$$

Then:

$$Sp(\mathbf{M} e^{-\frac{H}{T}}) = 0 \quad (8.45)$$

so that the average magnetization:

$$\langle \mathbf{M} \rangle = \lim_{V \rightarrow \infty} \frac{Sp(\mathbf{M} e^{-\frac{H}{T}})}{Sp(e^{-\frac{H}{T}})} = 0. \quad (8.46)$$

Thus, the standard definition of statistical (Gibbs) average leads to the zero average magnetization, which correspond to the invariance of the system with respect to three-dimensional rotations.

Let us stress that this result is valid for arbitrary temperatures, e.g. for temperatures below the Curie temperature. It may seem paradoxical, as for $T < T_c$ the system acquires spontaneous magnetization. However, the direction of magnetization vector in the absence of an external field is arbitrary, so that the (statistical) equilibrium state is actually infinitely degenerate.

Let us introduce the external magnetic field $\nu \mathbf{e}$ ($\nu > 0$, $\mathbf{e}^2 = 1$), replacing the Hamiltonian (8.37) by

$$H_{\nu \mathbf{e}} = H + \nu V \mathbf{e} \mathbf{M}. \quad (8.47)$$

Then, for temperatures below the Curie temperature we have

$$\langle \mathbf{M} \rangle = \mathbf{e} M_\nu \quad (8.48)$$

where M_ν will have a finite (nonzero) limit as the intensity ν of the external field tends to zero. Formally we can say that here we observe a kind of “instability” of usual definition of averages due to the addition to Hamiltonian a term with infinitesimal external field² and the average value of $\langle \mathbf{M} \rangle$ acquires finite value:

$$\mathbf{e} m \quad \text{where} \quad m = \lim_{\nu \rightarrow 0} M_\nu. \quad (8.49)$$

Now it is convenient to introduce the concept of the *quasiaverage*. Consider some dynamic variable A , built on spin operators. Then its quasiaverage is defined as:

$$\langle A \rangle = \lim_{\nu \rightarrow 0} \langle A \rangle_{\nu \mathbf{e}} \quad (8.50)$$

²It is assumed that we first perform thermodynamic limit of statistical mechanics $V \rightarrow \infty$, and only after that we tend ν to zero.

where $\langle A \rangle_{\nu \mathbf{e}}$ is the usual statistical average of A with Hamiltonian $H_{\nu \mathbf{e}}$.

Thus, the degeneracy is actually reflected in quasiaverages via their dependence on the arbitrary direction of the unit vector \mathbf{e} . The usual average is given by:

$$\langle A \rangle = \int \langle A \rangle_{\mathbf{e}} d\mathbf{e} \quad (8.51)$$

i.e. is obtained by integration over all directions of \mathbf{e} . Obviously quasiaverages are more convenient and “physical”, in comparison with usual averages, if we are dealing with degenerate equilibrium states. In fact, in practical calculations in phase transition theory we are always using quasiaverages (explicitly or implicitly).

As another example we can mention BCS theory of superconductivity. As we noted above, BCS state breaks gauge symmetry related to particle number conservation, which is reflected in the appearance of anomalous averages like (6.17), (6.18). Here we do not have the real physical field, breaking this symmetry, as in the case of external magnetic field breaking rotational symmetry of Heisenberg ferromagnet. However, instead we can introduce the fictitious infinitesimal “source” of Cooper pairs in BCS Hamiltonian (6.12), writing it as:

$$H_\nu = H - \nu \sum_{\mathbf{p}} [a_{-\mathbf{p}\downarrow} a_{\mathbf{p}\uparrow} + a_{\mathbf{p}\uparrow}^+ a_{-\mathbf{p}\downarrow}^+] \quad (8.52)$$

which explicitly breaks particle number conservation (gauge symmetry). Accordingly, all the averages in superconducting state are to be understood as quasiaverages obtained with Hamiltonian (8.52), with $\nu \rightarrow 0$ at the end of calculations. Naturally, all these averages depend on the arbitrary phase angle ϕ . While discussing the superconducting state above we just assumed $\phi = 0$, which is quite similar to fixing the direction of magnetization of Heisenberg ferromagnet in mean field theory approach, which we oriented along the arbitrary direction of z -axis, defined by the direction of an external magnetic field. Quite similarly we can analyze the Bose condensation [23].

In fact, discussing any kind of phase transition we always assume the introduction of an infinitesimal Bogolyubov’s field or “source”, lifting (breaking) the appropriate symmetry. Then, during all calculations we have to take into account for appropriate anomalous averages, breaking the symmetry of the initial Hamiltonian. “Condensed” state after the phase transition (appearing for $T < T_c$) is characterized by finite values of anomalous averages, which remain nonzero even after the external field (or “source”) is put to zero, i.e. for $\nu \rightarrow 0$. In “normal” phase (for $T > T_c$) anomalous averages tend to zero as $\nu \rightarrow 0$, and the appropriate symmetry remains unbroken. In this sense, all phase transitions of the second order are associated with “spontaneous” breaking of some (usually continuous) symmetry.

8.3 Fluctuations of the order parameter.

Let us discuss now fluctuations of the order parameter. We have already noted above that these fluctuations become important near the critical temperature of transition, significantly modifying the results of mean field theories. Our analysis will be essentially based on Landau theory, as a typical mean field theory of second order phase transitions.

In most cases, the order parameter in Landau theory can be represented by n – component vector, either in the usual coordinate space, or in some associated space, according to the nature of symmetry breaking during the phase transition. In Heisenberg model this is the usual three – component vector (magnetization), in Ginzburg – Landau superconductivity theory this is the complex (i.e. two – component) wave function of Cooper pairs condensate etc. Below we shall analyze the simplest possible variant of the phase transition, described by single – component order parameter η , which corresponds e.g. to the Ising model³.

In thermodynamics, the minimal work necessary to create some fluctuation out of equilibrium state of the system (at fixed pressure and temperature) is equal to the appropriate change of thermodynamic potential $\Delta\Phi$. Thus, according to Eq. (7.32) the probability of fluctuation at fixed P and T is estimated as:

$$w \sim \exp\left(-\frac{\Delta\Phi}{T}\right) \quad (8.53)$$

Let us denote the equilibrium value of η as $\bar{\eta}$. For small deviation from equilibrium write:

$$\Delta\Phi = \frac{1}{2}(\eta - \bar{\eta})^2 \left(\frac{\partial^2\Phi}{\partial\eta^2}\right)_{P,T} \quad (8.54)$$

The equilibrium value of the order parameter is determined by Landau expansion:

$$\Phi(T, P, \eta) = \Phi_0(P, T) + at\eta^2 + B\eta^4 - \eta hV \quad (8.55)$$

where $t = T - T_c(P)$, and h is an external field interacting with order parameter (e.g. magnetic field in Ising model). Using Eq. (8.55) we define the equilibrium value of the order parameter $\bar{\eta}$ from:

$$\left(\frac{\partial\Phi}{\partial\eta}\right)_{T,h} = 0 \quad (8.56)$$

which reduces to:

$$2at\bar{\eta} + 4B\bar{\eta}^3 = hV \quad (8.57)$$

which is equivalent to the result (8.29) derived from mean (molecular) field theory. The solution of Eq. (8.57) for $h \rightarrow 0$ has the form:

$$\begin{aligned} \bar{\eta}^2 &= 0 & \text{for } t > 0 \\ \bar{\eta}^2 &= -\frac{at}{2B} & \text{for } t < 0 \end{aligned} \quad (8.58)$$

so that the critical exponent of the order parameter is equal to $1/2$, the same value as in Eq. (8.31).

Susceptibility is defined as:

$$\chi = \left(\frac{\partial\bar{\eta}}{\partial h}\right)_{T;h \rightarrow 0} \quad (8.59)$$

Differentiating (8.57), we obtain for $h \rightarrow 0$:

$$\frac{\partial\bar{\eta}}{\partial h} = \frac{V}{2at + 12B\bar{\eta}^2} \quad (8.60)$$

³We drop the discussion of very important symmetry aspects of Landau theory, related to specific type of the crystal lattice [1] and assume our system homogeneous and isotropic.

Substituting now (8.58) we get:

$$\chi = \frac{V}{2at} \quad \text{for } t > 0$$

$$\chi = \frac{V}{-4at} \quad \text{for } t < 0 \quad (8.61)$$

which is similar to Eqs. (8.35), (8.36) and demonstrate the divergence of $\chi \sim |T - T_c|^{-1}$, so that the critical exponent of susceptibility $\gamma = \gamma' = 1$, as we obtained in molecular field approximation. In fact, Landau theory is a typical mean field theory and all critical exponents are obtained the same as in similar microscopic models.

Using (8.60) we can write:

$$\chi = V \left[\left(\frac{\partial^2 \Phi}{\partial \eta^2} \right)_{h=0} \right]^{-1} \quad (8.62)$$

Thus, the probability of fluctuation is determined from (8.53) and (8.54) by the following expression:

$$\Delta \Phi = \frac{1}{2} (\eta - \bar{\eta})^2 \frac{V}{\chi} \quad (8.63)$$

$$w \sim \exp \left[- \frac{(\eta - \bar{\eta})^2 V}{2\chi T_c} \right] \quad (8.64)$$

Now, in accordance with general form of Gaussian distribution (7.17), we obtain the mean square of order parameter fluctuation as:

$$\langle (\Delta \eta)^2 \rangle = \frac{T_c \chi}{V} \sim \frac{1}{|t|} \quad \text{for } T \rightarrow T_c \quad (8.65)$$

We see that fluctuations grow close to T_c and diverge as $\sim |T - T_c|^{-1}$.

For more deep understanding of physical nature of this phenomenon, it is useful to find the spatial correlation function of order parameter fluctuations. For inhomogeneous system (fluctuations actually create inhomogeneities!) thermodynamic potential is conveniently written as $\Phi = \int dV \Phi(\mathbf{r})$, where $\Phi(\mathbf{r})$ is its density (which is a function of coordinate). We shall actually use thermodynamic potential $\Omega(T, \mu)$ and consider some volume V within the body, containing variable number of particles N . Potential $\Omega(T, \mu, \eta)$, for the unit volume, can be expanded in the usual Landau form, similar to (8.55):

$$\Omega(T, \mu, \eta) = \Omega_0(T, \mu) + \alpha t \eta^2 + b \eta^4 - \eta h \quad (8.66)$$

where $\alpha = a/V$, $b = B/V$, $t = T - T_c(\mu)$. This form of expansion is valid for homogeneous case. In inhomogeneous system it must contain spatial derivatives of the order parameter η . For long wavelength fluctuations we can limit ourselves to lowest order derivatives and their lowest powers. Terms linear in derivatives like $f(\eta) \frac{\partial \eta}{\partial x_i}$ reduce to surface integrals after volume integration, thus corresponding to irrelevant surface effects. We shall limit ourselves to the simplest case (valid for crystals of cubic symmetry), when the density of thermodynamic potential can be written as:

$$\Omega = \Omega_0 + \alpha t \eta^2 + b \eta^4 + g(\nabla \eta)^2 - \eta h \quad (8.67)$$

For homogeneous state to be stable, we have to require that $g > 0$, in opposite case Ω does not have minimum for $\eta = const.$

Considering fluctuations at fixed μ and T , we write fluctuation probability as:

$$w \sim \exp\left(-\frac{\Delta\Omega}{T}\right) \quad (8.68)$$

because the minimal work required to bring the system out of equilibrium under these conditions is given by $R_{min} = \Delta\Omega$.

Let us consider fluctuations in symmetric (e.g. paramagnetic) phase (at $h = 0$), when $\bar{\eta} = 0$, so that $\Delta\eta = \eta$. Limiting ourselves to second order terms over fluctuations, we can write the change of Ω as⁴:

$$\Delta\Omega = \int dV \{\alpha t(\eta)^2 + g(\nabla\eta)^2\} \quad (8.70)$$

Let us introduce Fourier expansion of $\eta(\mathbf{r})$:

$$\eta(\mathbf{r}) = \sum_{\mathbf{k}} \eta_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \quad \eta_{-\mathbf{k}} = \eta_{\mathbf{k}}^* \quad (8.71)$$

Then its gradient can be written as:

$$\nabla\eta(\mathbf{r}) = \sum_{\mathbf{k}} i\mathbf{k}\eta_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} \quad (8.72)$$

Substitution of these expressions into Eq. (8.70) and volume integration leaves non zero only terms containing the products like $\eta_{\mathbf{k}}\eta_{-\mathbf{k}} = |\eta_{\mathbf{k}}|^2$. Then we obtain:

$$\Delta\Omega = V \sum_{\mathbf{k}} (gk^2 + \alpha t) |\eta_{\mathbf{k}}|^2 \quad (8.73)$$

so that:

$$\langle |\eta_{\mathbf{k}}|^2 \rangle = \frac{T}{2V(gk^2 + \alpha t)} \quad (8.74)$$

This expression is usually called Ornstein - Zernike correlator. From this expression it is clear that only the long wavelength fluctuations with $k \sim \sqrt{\alpha t/g}$ grow as $t \rightarrow 0$. Actually, the expression (8.74) is valid only for long enough wavelengths k^{-1} , which are large in comparison to average interatomic distance a .

Let us define correlation function in coordinate space as:

$$G(\mathbf{r}_1 - \mathbf{r}_2) = \langle \eta(\mathbf{r}_1)\eta(\mathbf{r}_2) \rangle \quad (8.75)$$

This can be calculated as:

$$G(\mathbf{r}) = \sum_{\mathbf{k}} \langle |\eta_{\mathbf{k}}|^2 \rangle e^{i\mathbf{k}\mathbf{r}} = V \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\mathbf{r}} \langle |\eta_{\mathbf{k}}|^2 \rangle \quad (8.76)$$

⁴Note that quite similar results can be obtained at the other side of transition, in broken symmetry phase. Here we have non zero $\bar{\eta} = (-\alpha t/2b)^{1/2}$ and the change of Ω , up to terms of the order of $\sim (\Delta\eta)^2$, we get:

$$\Delta\Omega = \int dV \{-2\alpha t(\Delta\eta)^2 + g(\nabla\eta)^2\} \quad (8.69)$$

Thus, for any characteristics of the system we obtain expressions, which differ from those for symmetric phase by substitution of αt by $2\alpha|t|$.

Then from (8.74) we obtain⁵:

$$G(r) = \frac{T_c}{8\pi gr} \exp\left(-\frac{r}{\xi}\right) \quad (8.78)$$

where

$$\xi = \sqrt{\frac{g}{\alpha t}} \sim (T - T_c)^{-1/2} \quad (8.79)$$

Parameter ξ is called correlation length of fluctuations and defines the characteristic distance for decay of their correlations. We have already met with this length in Ginzburg – Landau theory, where it was called coherence length. Divergence of ξ for $T \rightarrow T_c (T > T_c)$ corresponds to the appearance (at $T = T_c$) of *long range order*. Correlation length critical exponent $\nu = 1/2$, which is again the standard result of the mean field theory.

For $r = 0$ the integral in (8.76) determines the average square of order parameter fluctuation $\eta(\mathbf{r})$ at the given point of space. Its divergence is directly related to inapplicability of Eq. (8.74) for large $k \sim a^{-1}$. This is easily avoided by the introduction of the cutoff:

$$G(0) = \frac{T}{4\pi^2} \int_0^{k_0} dk k^2 \frac{1}{gk^2 + \alpha t} \quad (8.80)$$

where $k_0 \sim 1/a$. Here we observe the significant dependence on the spatial dimensions. For d -dimensional space instead of (8.80) we have to write:

$$G(0) \sim \int_0^{k_0} dk k^{d-1} \frac{1}{k^2 + \xi^{-2}} \quad (8.81)$$

This integral is easily estimated as:

$$G(0) \sim \int_{\xi^{-1}}^{k_0} dk k^{d-3} \sim \begin{cases} k_0 - \xi^{-1} & d = 3 \\ \ln(k_0 \xi) & d = 2 \\ \xi - \frac{1}{k_0} & d = 1 \end{cases} \quad (8.82)$$

From this estimate we see that for $T \rightarrow T_c$, when $\xi \rightarrow \infty$, the average square of the order parameter fluctuation at the given point is finite for $d = 3$ and diverges for $d = 1, 2$. This reflects the impossibility of the existence of long range order in one – dimensional and two – dimensional systems [1]. Let us stress that here the relevant divergence of the integral in (8.82) is at low integration limit (“infrared” divergence), not at the upper limit, where it is regularized by cutoff. In the theory of critical phenomena spatial dimensionality $d = 2$ is called the *lower critical dimensionality*. The reasoning presented here is rather

⁵Here we use the following expressions for Fourier transformation:

$$\begin{aligned} \int dV \frac{e^{-\kappa r}}{r} e^{i\mathbf{k}\mathbf{r}} &= \frac{4\pi}{k^2 + \kappa^2} \\ \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{e^{i\mathbf{k}\mathbf{r}}}{k^2 + \kappa^2} &= \frac{e^{-\kappa r}}{4\pi r} \end{aligned} \quad (8.77)$$

These are most easily obtained if we note that $\varphi(r) = \frac{e^{-\kappa r}}{4\pi r}$ satisfies differential equation: $\nabla^2 \varphi - \kappa^2 \varphi = -4\pi \delta(r)$. Multiplying both sides of this equation by $e^{-i\mathbf{k}\mathbf{r}}$ and integrating over whole space (performing partial integration of $e^{-i\mathbf{k}\mathbf{r}} \nabla^2 \varphi$ twice) we obtain the required result.

crude, but it qualitatively valid. More accurate proof of the impossibility of the long range order in low – dimensional systems requires also an analysis of situation for $T < T_c$ [26]. In fact, the lower critical dimensionality $d = 2$ only for phase transitions breaking the continuous symmetry, while for Ising like single – component order parameter the lower critical dimension $d = 1$. This is clear, for example, from an exact Onsager solution for two – dimensional Ising model, which demonstrates the existence of the phase transition for $d = 2$ [1].

To avoid confusion we note that Eq. (8.65) determines fluctuations of order parameter η , averaged over the volume V with linear dimensions $L \gg \xi$. Let us denote it by $\langle \eta^2 \rangle_V$. The average of $\eta(\mathbf{r})$ over the volume V is given by $\eta_{\mathbf{k}=0}$. Thus, it is natural that for $k = 0$ (8.74) coincides with (8.65), so that:

$$\chi = \frac{V}{T_c} \int d\mathbf{r} G(\mathbf{r}) \quad (8.83)$$

The value of $\langle \eta^2 \rangle_V$ can be directly obtained also from correlation function:

$$\langle \eta^2 \rangle_V = \frac{1}{V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 \langle \eta(\mathbf{r}_1) \eta(\mathbf{r}_2) \rangle = \frac{1}{V} \int dV G(r) \quad (8.84)$$

Now we can formulate the criterion of applicability of Landau theory of phase transitions (or mean field theory), based on expansion (8.67). For the validity of this theory we have to demand that the mean square fluctuations of the order parameter η , averaged over the correlation volume $\sim \xi^3$, be small compared with the equilibrium value of the order parameter $\eta^2 \sim \alpha|t|/b$. Using (8.65) with $V \sim \xi^3$ we come to the condition:

$$\frac{T_c \chi}{\xi^3} \ll \frac{\alpha|t|}{b} \quad (8.85)$$

or, taking χ and ξ from (8.61) and (8.79):

$$\alpha|t| \gg \frac{T_c^2 b^2}{g^3} \quad (8.86)$$

This condition is usually called Ginzburg criterion for the applicability of Landau theory of phase transitions⁶. This inequality define the size of the so called *critical region* around T_c , where fluctuations are large and significantly change the mean field picture of the phase transition, e.g. the critical exponents⁷. The description of the system within the critical region is the field of the theory of critical phenomena [26]. Some aspects of this theory will be discussed in the next section.

8.4 Scaling.

The theory of critical phenomena introduces the following standard set of characteristics of the system and appropriate critical exponents, determining the

⁶Expansion in powers of $t = T - T_c$ in Landau coefficients requires also the validity of condition $t \ll T_c$. For this to be in agreement with (8.86) it is necessary also to satisfy: $\frac{T_c b^2}{\alpha g^3} \ll 1$.

⁷Above we already mentioned Ginzburg criterion while discussing the limits of Ginzburg – Landau theory of superconductivity. We have seen that in superconductors the size of the critical region is negligible.

singular behavior of these characteristics at the critical point, as function of the parameter $\tau = \frac{T-T_c}{T_c} \rightarrow 0$.

Order parameter:

$$\bar{\eta} \sim |\tau|^\beta \quad T \rightarrow T_c - 0 \quad (8.87)$$

$$\bar{\eta} \sim h^{\frac{1}{\delta}} \quad T = T_c \quad (8.88)$$

Susceptibility:

$$\chi \sim \begin{cases} \tau^{-\gamma} & T \rightarrow T_c + 0 \\ |\tau|^{-\gamma'} & T \rightarrow T_c - 0 \end{cases} \quad (8.89)$$

Correlation function of order parameter (d is spatial dimensionality):

$$G(r) \sim \frac{\exp(-r/\xi)}{r^{d-(2-\eta)}} \quad (8.90)$$

where correlation length:

$$\xi \sim \begin{cases} \tau^{-\nu} & T \rightarrow T_c + 0 \\ |\tau|^{-\nu'} & T \rightarrow T_c - 0 \end{cases} \quad (8.91)$$

At the critical point itself:

$$G(r) \sim \frac{1}{r^{d-(2-\eta)}} \quad (8.92)$$

$$G(k) \sim \frac{1}{k^{2-\eta}} \quad (8.93)$$

Critical exponent α of specific heat is introduced in a similar way:

$$C(\tau, h = 0) = \frac{A^+}{\alpha} [\tau^{-\alpha} - 1] + B^+ \quad T \rightarrow T_c + 0 \quad (8.94)$$

$$C(\tau, h = 0) = \frac{A^-}{\alpha'} [|\tau|^{-\alpha'} - 1] + B^- \quad T \rightarrow T_c - 0 \quad (8.95)$$

with $\alpha = 0$ corresponding to logarithmic singularity.

Theoretical problem of description of critical phenomena reduces to derivation of these expressions and calculation of critical exponents $\alpha, \alpha', \beta, \gamma, \gamma', \delta, \eta, \nu, \nu'$.

Significant progress in the studies of critical phenomena was achieved after the introduction of the concept of *scaling* or scale invariance. This is essentially based on the idea that the growth of correlation length close to T_c leads to significant interaction of fluctuations, which defines the singular behavior of physical characteristics at critical point. At the same time, as correlation length becomes much larger than interatomic spacing $\xi \gg a$, the microscopic details of interactions are probably not so important. Hypothesis of scale invariance (scaling) assumes that the singular dependence of physical characteristics on $T - T_c$ is controlled by divergence of correlation length ξ , and it becomes the only relevant parameter of length in the problem.

Let us discuss scaling using the simple qualitative arguments due to Kadanoff. For simplicity we consider the system of N Ising spins (cf. (8.19)) in d -dimensional lattice, with interaction parameter J , different from zero only between nearest neighbors. External magnetic field is H . Then the Hamiltonian (8.19) can be rewritten in units of T as:

$$\frac{H}{T} = -K \sum_{\langle ij \rangle} s_i s_j - h \sum_{i=1}^N s_i \quad (8.96)$$

where we have introduced dimensionless parameters $K = J/2T$ and $h = \tilde{\mu}H/T$.

Let us break the lattice into cells with linear dimensions La , where a is lattice parameter and L is an arbitrary integer ($L \gg 1$). (cf. Fig. 8-3). Then we obtain in total $\mathcal{N} = N/L^d$ cells, each containing L^d spins. Below we consider

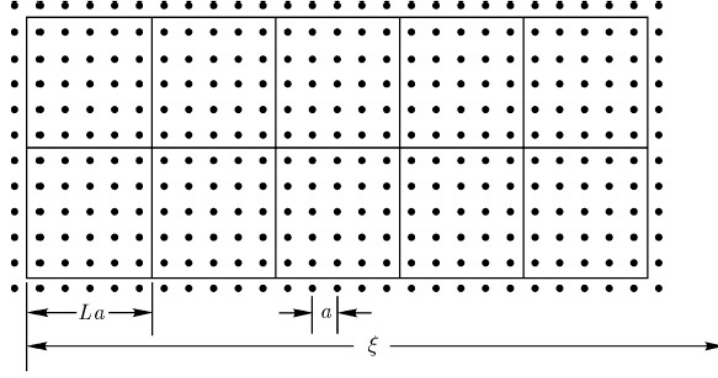


Figure 8.3: Kadanoff construction for Ising lattice.

only temperatures close enough to T_c , so that correlation length ξ is much larger than the size of a cell, i.e. $\xi \gg La$. It guarantees that each cell, containing L^d spins, with $1 \ll L \ll \xi/a$, contains only spins oriented “up” or “down”. Then the total magnetic moment of each cell s_α ($\alpha = 1, 2, \dots, \mathcal{N}$) can be, in some sense, be considered similarly to the single site moment s_i . This assumption is qualitatively valid if the given cell is inside the group of correlated spins. The resulting moment of this cell is given by L^d , with \pm sign. It is convenient to introduce $\tilde{s}_\alpha = s_\alpha/L^d$, i.e. normalize spin of the cell by unity. Then, if try to rewrite the Hamiltonian as a function of cell moments s_α (not site moments s_i), we can expect it to be of the same form as (8.96) for the standard Ising model, but with different values of parameters, i.e. with K and h replaced by some K_L and h_L :

$$\frac{H}{T} = -K_L \sum_{\langle \alpha, \alpha' \rangle} \tilde{s}_\alpha \tilde{s}_{\alpha'} - h_L \sum_{\alpha} \tilde{s}_\alpha \quad (8.97)$$

where the summation is performed over Kadanoff cells numbered by α .

The an external magnetic field $h \rightarrow 0$, the effective field h_L in cell formulation obviously also tends to zero. Similarly, as $T \rightarrow T_c$ and $K \rightarrow K_c$, with $K_c = \frac{J}{2T_c}$ given by the initial Ising model, we should get $K_L \rightarrow K_c$. Thus, we can assume the following scaling relations:

$$\tau_L = \tau L^y \quad \dots \quad K_L = K_c - \tau L^y \quad (8.98)$$

$$h_L = h L^x \quad (8.99)$$

where $\tau = K_c - K$, $\tau_L = K_c - K_L$. Critical values of interaction parameters are the same in both formulations, as we assumed their equivalence⁸. Critical exponents x and y remain undetermined, but we shall see that all other (physical)

⁸Parameter τ , defined here, has the same meaning as above in case of $J = \text{const.}$ In principle, we can also consider the phase transition with the change of J at fixed temperature.

critical exponents can be expressed via these, so that only two critical exponents are independent.

Consider the change of free energy of the system under a small change of h . Let us assume that magnetic field is different at different sites of the lattice, but these changes are smooth enough, so that it is effectively constant within each Kadanoff cell. Then the change of the free energy is given by:

$$\delta \left(\frac{F}{T} \right) = - \sum_i \langle s_i \rangle \delta h_i = - \sum_\alpha \langle s_\alpha \rangle \delta h_{L\alpha} \quad (8.100)$$

where $\langle s_i \rangle$ is an average spin at the lattice site, and $\langle s_\alpha \rangle$ is an average spin of a cell. Both expressions should be equivalent. Due to assumption of smooth change of magnetic field in space, we can write within each cell:

$$L^d \langle s_i \rangle \delta h_i = \langle s_\alpha \rangle \delta h_{L\alpha} \quad (8.101)$$

Using (8.99), we obtain:

$$\langle s_i \rangle = L^{x-d} \langle s_\alpha \rangle \quad (8.102)$$

Consider now the homogeneous field, independent of site number i . Then the magnetization at the site (which is equivalent to the order parameter $\bar{\eta}$) is the function of τ and h only:

$$\langle s_i \rangle = F(\tau, h) \quad (8.103)$$

According to our basic assumption, in terms of s_α we are describing the same system, but with new values of τ_L and h_L , so that the value of $\langle s_\alpha \rangle$ is represented by the *same* function, depending on *new* variables:

$$\langle s_\alpha \rangle = F(\tau_L, h_L) \quad (8.104)$$

Then from Eqs. (8.100), (8.102), (8.103), (8.104) we can see that the order parameter can be written as:

$$\bar{\eta} = \langle s \rangle = F(\tau, h) = L^{x-d} F(L^y \tau, L^x h) \quad (8.105)$$

Now, the length L introduced above is purely mathematical invention and should cancel from all physical characteristics of the system! This is possible only if the function $F(\tau, h)$ has the following form:

$$\bar{\eta} = \left(\frac{h}{|h|} \right) |\tau|^{\frac{d-x}{y}} f \left(\frac{\tau}{|h|^{\frac{y}{x}}} \right) \quad (8.106)$$

The factor of $h/|h|$ here is added just to guarantee the change of magnetization sign with the sign of an external magnetic field.

The explicit form of function $f(z)$, entering (8.106), is unknown. However, these arguments allowed us to transform an unknown function of two variables τ and h into a function of a single variable $z = \tau/|h|^{\frac{y}{x}}$. Remarkably, this is sufficient to express all physical critical exponents of our system via exponents x and y , or, in other words, express all physical critical exponents via any two of them (which can be determined from experiments).

For example, remembering (8.87), i.e. $\bar{\eta} \sim |\tau|^\beta$, which is valid for small negative values of τ and $h \rightarrow 0$, we note that $f(-\infty) = \text{const}$ and

$$\beta = \frac{d-x}{y} \quad (8.107)$$

Differentiating (8.106) over h for $h \rightarrow 0$, we get the susceptibility: $\chi \sim |\tau|^{\frac{d-x}{y}} \frac{\partial}{\partial h} f(\tau/|h|^{\frac{y}{x}}) \sim |\tau|^{\frac{d-x}{y}+1} |h|^{-\frac{y}{x}-1} f'(z)$. However, the dependence on h in χ should cancel for $h \rightarrow 0$. Then it is clear that $f'(z) \sim z^{-\frac{x}{y}-1}$ and $\chi \sim |\tau|^{-\gamma} \sim |\tau|^{\frac{d-2x}{y}}$. Thus we obtain:

$$\gamma = \gamma' = \frac{2x-d}{y} \quad (8.108)$$

Similarly, for $\tau = 0$ according to (8.88) we should have $\bar{\eta} \sim h^{\frac{1}{\delta}}$. Eq. (8.106) for $\tau = 0$, should become independent of τ , which is only possible if $f(z \rightarrow 0) \sim z^{\frac{x-d}{y}}$. Then from (8.106) we immediately obtain $\bar{\eta} \sim |h|^{\frac{d-x}{x}}$, so that

$$\delta = \frac{x}{d-x} \quad (8.109)$$

From these relations we get:

$$d/y = \gamma + 2\beta = \beta(\delta + 1) \quad (8.110)$$

which gives the scaling relation between experimentally measurable exponents β, γ, δ .

Integrating $\bar{\eta} \sim \frac{\partial F}{\partial h} \sim |\tau|^{\frac{d-x}{y}} f(\tau/|h|^{\frac{y}{x}})$ it is easy to get $F \sim |\tau|^{\frac{d-x}{y}} \int dh f(\tau/|h|^{\frac{y}{x}}) \sim |\tau|^{\frac{d}{y}} \int dz \tilde{f}(z)$. Then the specific heat is:

$$C \sim -T \frac{\partial^2 F}{\partial T^2} \sim |\tau|^{\frac{d}{y}-2} \quad (8.111)$$

Comparing with (8.95), we obtain:

$$\alpha = \alpha' = 2 - \frac{d}{y} \quad \text{or} \quad \frac{d}{y} = 2 - \alpha \quad (8.112)$$

so that comparison with (8.110) gives:

$$\gamma + 2\beta = \beta(\delta + 1) = 2 - \alpha \quad (8.113)$$

Consider now correlation function, which is in general defined as:

$$G(\mathbf{r}_i - \mathbf{r}_j) = G(R, \tau, h) = \langle [s_i - \langle s \rangle][s_j - \langle s \rangle] \rangle \quad (8.114)$$

where R is the distance between two lattice sites: $R = |\mathbf{r}_i - \mathbf{r}_j|/a$. In a similar way we can write down correlation function in terms of cell variables s_α , defined in (8.102). This expression is to be identical to $G(R, \tau, h)$, but with different scales of length, τ and h :

$$\begin{aligned} R &\rightarrow R/L \\ \tau &\rightarrow \tau_L = \tau L^y \\ h &\rightarrow h_L = h L^x \end{aligned} \quad (8.115)$$

From here we get:

$$G(R, \tau, h) = L^{2(x-d)} \langle [s_{\alpha-} \langle s_{\alpha} \rangle] [s'_{\alpha-} \langle s_{\alpha} \rangle] \rangle = L^{2(x-d)} G(R/L, \tau L^y, h L^x) \quad (8.116)$$

and $G(R, \tau, h)$ is independent of an arbitrary parameter L if we take:

$$G(R, \tau, h) = |\tau|^{2(d-x)/y} \tilde{G}(R|\tau|^{1/y}, \tau/|h|^{y/x}) \quad (8.117)$$

for $R \gg 1$, $|\tau| \ll 1$ and $h \ll 1$.

Eq. (8.117) determines critical exponents ν, ν', η . We immediately observe (cf. (8.90), (8.91)) that for $h = 0$ correlation length $\xi \sim |\tau|^{-1/y}$. Accordingly, its critical exponent is given by:

$$\frac{1}{y} = \nu = \nu' = \frac{2 - \alpha}{d} \quad (8.118)$$

Finally, the last of critical exponents η is determined from (cf. (8.93)):

$$G(R, \tau = 0, h = 0) \sim \frac{1}{R^{d-2+\eta}} \quad (8.119)$$

Then, demanding cancellation of τ -dependence in (8.117) for $\tau \rightarrow 0$, we obtain $G(R) \sim R^{2(x-d)} \sim R^{2-d-\eta}$, so that:

$$-(d - 2 + \eta) = 2(x - d). \quad (8.120)$$

From Eq. (8.109) we have $x = \frac{d\delta}{\delta+1}$, then from (8.120), using (8.113), we get:

$$d - 2 + \eta = \frac{2d}{\delta + 1} = \frac{2d\beta}{2 - \alpha} = \frac{2\beta}{\nu} \quad (8.121)$$

or

$$\beta = \frac{1}{2}(d - 2 + \eta)\nu \quad (8.122)$$

From (8.110) and (8.118) we have $\gamma = \frac{d}{y} - 2\beta = d\nu - 2\beta$, and using (8.122) we obtain one more scaling relation:

$$(2 - \eta)\nu = \gamma. \quad (8.123)$$

It is rather easy to derive also the following relations:

$$\begin{aligned} \frac{d\gamma}{2 - \eta} &= 2 - \alpha, \\ \delta &= \frac{d + 2 - \eta}{d - 2 + \eta}. \end{aligned} \quad (8.124)$$

In conclusion of our discussion we give the summary of most widely used scaling relations between physical critical exponents:

$$\nu = \nu' = \frac{\gamma}{2 - \eta} \quad (8.125)$$

$$\alpha = \alpha' = 2 - \nu d \quad (8.126)$$

$$\beta = \frac{1}{2}\nu(d - 2 + \eta) \quad (8.127)$$

Remarkably, all experiments in the critical region of widely different physical systems, undergoing phase transitions of the second order, confirm scaling relations for critical exponents, derived here.

Theoretical problem of *calculation* of the values of critical exponents for rather long time remained one of the most difficult problems of statistical physics. The physical reason for these difficulties was the strong interaction between fluctuations in the critical region and the absence of a natural small parameter for the development of some kind of perturbation theory. This problem was successfully solved by Wilson using *renormalization group* approach, originating from quantum field theory. Renormalization group transformations are actually the modern and rigorous realization of scaling transformations, extending elementary discussion given above. We shall not discuss this formalism here referring the reader to special literature on modern theory of critical phenomena [26] and limiting ourselves only to some qualitative results of this theory.

First of all, note that the values of critical exponents obtained in Landau theory (mean field approximation):

$$\begin{aligned} \nu &= \frac{1}{2} & \gamma &= 1 & \eta &= 0 \\ \alpha &= 0 & \beta &= \frac{1}{2} & \delta &= 3 \end{aligned} \quad (8.128)$$

do not satisfy scaling relations (8.127) and most experiments in real three – dimensional systems. At the same time, it is easy to see that Landau theory exponents (8.128) *satisfy* scaling relations if we formally take space dimensionality $d = 4$. In this sense we can say that Landau theory gives the correct description of critical phenomena for spatial dimensionality $d = 4$ and, as is actually shown in modern theory [26], for all $d > 4$. Spatial dimensionality $d = 4$ is usually called the *upper critical dimension*. Remarkable result of the modern theory of critical phenomena is the *universality* of critical behavior — the values of critical exponents in different physical systems actually are determined only by the spatial dimensionality of the system and the number of components n of the order parameter (i.e. by the type of the symmetry broken at the phase transition).

Wilson proposed an original method of calculation of critical exponents, based on perturbation theory over an artificial small parameter $\varepsilon = 4 - d$ – small deviation from the upper critical dimension $d = 4$, for which critical exponents coincide with predictions of Landau (mean field) theory (ε – expansion). Below we present the values of critical exponents up to terms of the order of $\sim \varepsilon^2$ in theory with n – component order parameter [26]:

$$\gamma = 1 + \frac{n+2}{n+8} \frac{\varepsilon}{2} + \frac{n+2}{n+8} \frac{n^2 + 22n + 52}{(n+8)^2} \frac{\varepsilon^2}{4} + \dots \quad (8.129)$$

$$2\nu = 1 + \frac{n+2}{n+8} \frac{\varepsilon}{2} + \frac{n+2}{n+8} \frac{n^2 + 23n + 60}{(n+8)^2} \frac{\varepsilon^2}{4} + \dots \quad (8.130)$$

$$\eta = \frac{n+2}{2(n+8)^2} \varepsilon^2 + \frac{n+2}{2(n+8)^2} \left[\frac{6(3n+14)}{(n+8)^2} - \frac{1}{4} \right] \varepsilon^3 + \dots \quad (8.131)$$

$$\delta = 3 + \varepsilon + \left[\frac{1}{2} - \frac{n+2}{(n+8)^2} \right] \varepsilon^2 + \dots \quad (8.132)$$

Table 8.1: Critical exponents for the model with $n = 1$ (Ising).

Exponent	Wilson	Numerical	Landau
ν	0.626	0.642	0.5
η	0.037	0.055	0
γ	1.244	1.250	1
α	0.077	0.125	0
β	0.340	0.312	0.5
δ	4.460	5.15	3

$$\beta = \frac{1}{2} - \frac{3}{n+8} \frac{\varepsilon}{2} + \frac{(n+2)(2n+1)}{2(n+8)} \varepsilon^2 + \dots \quad (8.133)$$

$$\alpha = \frac{4-n}{n+8} \frac{\varepsilon}{2} + \dots \quad (8.134)$$

In Table 8.1 we compare the values of critical exponents, obtained from these expressions for the case of $d = 3$ ($\varepsilon = 1$) and $n = 1$ (Ising case), with the results of numerical calculations (high temperature expansions) for three – dimensional Ising model. Also we give in the Table the values of critical exponents from Landau theory. We can see that ε – expansion gives rather satisfactory agreement with the results of numerical analysis⁹.

Modern methods of calculation significantly improve the results of the simplest form of ε – expansion, taking into account the higher orders and asymptotic behavior of appropriate perturbation series, produce the values of critical exponents in full agreement with the results of numerical calculations and experiments.

⁹Another effective method of calculation of critical exponents is based on perturbation expansion in powers of the inverse number of order parameter components $1/n$ [26], as for $n \rightarrow \infty$ it can be shown that critical exponents are also given by mean field approximation (Landau theory).

Chapter 9

LINEAR RESPONSE

9.1 Linear response to mechanical perturbation.

Up to now we mainly discussed the problems of equilibrium statistical mechanics. Actually, there is a wide class of problems related to non – equilibrium processes, which can be rigorously formulated and solved within the general formalism of equilibrium theory. We are speaking about rather common situation, when the system is initially in equilibrium state, but later it is perturbed by some weak external perturbation. This class of problems is analyzed within the linear response theory, which gives the well developed and general approach to the solution such non – equilibrium problems¹.

There are two major types of external perturbations, which can be applied to an arbitrary physical system at equilibrium. First of all, we may consider mechanical perturbations, corresponding to the action of some external physical fields, which can be introduced by additional terms in Hamiltonian, describing the physical interactions with these fields. Perturbations, which can not be described in this way, are called in non–equilibrium statistical mechanics thermal perturbations. Typical examples are temperature or concentration gradients. For simplicity, below we are dealing only with mechanical perturbations, though the general formalism of linear response theory is also well developed for thermal perturbations.

Consider the response of a quantum Gibbs ensemble, corresponding to time independent Hamiltonian H , towards an external perturbation H_t^1 , explicitly dependent on time. Total Hamiltonian of the system is given by:

$$\mathcal{H} = H + H_t^1 \quad (9.1)$$

Let us assume that at $t = -\infty$ external perturbation was absent, so that:

$$H_t^1|_{t=-\infty} = 0 \quad (9.2)$$

In majority of practical cases perturbation H_t^1 can be written as:

$$H_t^1 = - \sum_j B_j F_j(t) \quad (9.3)$$

¹Below we follow mainly Ref. [3].

where $F_j(t)$ are some functions of time (c -numbers, external fields), while B_j are operators with no explicit time dependence, which are “conjugated” to fields $F_j(t)$. Explicit examples will be given below.

For definiteness we shall consider adiabatic “switching on” of periodic (in time) external perturbation written as:

$$H_t^1 = - \sum_{\omega} e^{\varepsilon t - i\omega t} B_{\omega} \quad (\varepsilon \rightarrow +0) \quad (9.4)$$

where $B_{\omega}^+ = B_{-\omega}$ due to Hermiticity of the Hamiltonian.

In general case, statistical operator (density matrix) of the system ρ satisfies quantum Liouville equation:

$$i\hbar \frac{\partial \rho}{\partial t} = [H + H_t^1, \rho] \quad (9.5)$$

and initial condition in our case is to written as:

$$\rho|_{t=-\infty} = \rho_0 = \frac{1}{Z} e^{-\frac{H}{T}} \quad (9.6)$$

which simply means that at initial moment $t = -\infty$ our system is at the state of thermodynamic (statistical) equilibrium and described by canonical Gibbs ensemble. Of course, grand canonical ensemble can also be used to describe the initial state of the system.

Let us perform now the canonical transformation of the following form:

$$\rho_1 = e^{\frac{iHt}{\hbar}} \rho e^{-\frac{iHt}{\hbar}} \quad (9.7)$$

Then the Liouville equation is reduced to the following form:

$$i\hbar \frac{\partial \rho_1}{\partial t} = [H_t^1(t), \rho_1] \quad (9.8)$$

with initial condition:

$$\rho_1|_{t=-\infty} = \rho_0 \quad (9.9)$$

Here we introduced

$$H_t^1(t) = e^{\frac{iHt}{\hbar}} H_t^1 e^{-\frac{iHt}{\hbar}} \quad (9.10)$$

perturbation operator in Heisenberg representation with Hamiltonian H , so that with respect to the total Hamiltonian (9.1) this defines the so called interaction representation.

Eq. (9.8) with initial condition given by (9.9) can be integrated and written as a single integral equation:

$$\rho_1(t) = \rho_0 + \int_{-\infty}^t dt' \frac{1}{i\hbar} [H_{t'}^1(t'), \rho_1(t')] \quad (9.11)$$

or, making transformation to the initial form of density matrix $\rho(t)$ using (9.7):

$$\rho(t) = \rho_0 + \int_{-\infty}^t dt' e^{-\frac{iH(t-t')}{\hbar}} \frac{1}{i\hbar} [H_{t'}^1, \rho] e^{\frac{iH(t-t')}{\hbar}} \quad (9.12)$$

where we have also used (9.10).

If perturbation H_t^1 is small, solution of Eq. (9.12) can be obtained by iterations, taking ρ_0 as initial value. In the first order (linear) approximation we get:

$$\rho = \rho_0 + \int_{-\infty}^t dt' \frac{1}{i\hbar} [H_{t'}^1(t' - t), \rho_0]. \quad (9.13)$$

The second term in the right hand side represents *non - equilibrium* correction to density matrix, calculated in linear approximation over external perturbation. Up to now we have not used the explicit form of ρ_0 . Now we can do it, taking into account the explicit form of canonical distribution (9.6).

Let us use the so called Kubo identity, which is valid for any quantum operator A :

$$[A, e^{-\beta H}] = -e^{-\beta H} \int_0^\beta d\lambda e^{\lambda H} [A, H] e^{-\lambda H} \quad (9.14)$$

The proof of this identity will be given shortly, but now we can use it to rewrite (9.13) as:

$$\rho = \rho_0 \left\{ 1 - \int_0^\beta d\lambda \int_{-\infty}^t dt' e^{\lambda H} \dot{H}_{t'}^1(t' - t) e^{-\lambda H} \right\} \quad (9.15)$$

where

$$\dot{H}_{t'}^1(t' - t) = \frac{1}{i\hbar} [H_{t'}^1(t' - t), H] \quad (9.16)$$

If take ρ_0 in the form of grand canonical distribution, Eq. (9.15) remains valid, we only have to make the replacement $H \rightarrow H - \mu N$.

Let us derive now Kubo identity. We write:

$$[A, e^{-\beta H}] = e^{-\beta H} S(\beta) \quad (9.17)$$

where $S(\beta)$ is an operator to be determined. Differentiating (9.17) over β , we obtain differential equation for $S(\beta)$:

$$\frac{\partial S}{\partial \beta} = -e^{\beta H} [A, H] e^{-\beta H} \quad (9.18)$$

with initial condition $S|_{\beta=0} = 0$. Integrating it with this initial condition we get (9.14).

Eqs. (9.13) and (9.15) allow to calculate (in linear approximation over H_t^1) the average value of an arbitrary physical variable, represented by some operator A :

$$\begin{aligned} \langle A \rangle &= Sp \rho A \\ \langle A \rangle &= \langle A \rangle_0 + \int_{-\infty}^t dt' \frac{1}{i\hbar} \langle [A(t), H_{t'}^1(t')] \rangle_0 \end{aligned} \quad (9.19)$$

where we used (9.13) and taken into account the invariance of Sp with respect to cyclic permutation of operators² and

$$A(t) = e^{\frac{iHt}{\hbar}} A e^{-\frac{iHt}{\hbar}} \quad (9.20)$$

²We have $Sp[H_{t'}^1(t' - t), \rho_0]A = Sp\rho_0[A, H_{t'}^1(t' - t)]$ etc. Expression for $A(t)$ appears here with the account of (9.10) and further permutations of operators under Sp .

is A operator in Heisenberg representation, and $\langle \dots \rangle_0 = Sp \rho_0 \dots$ is the averaging with *equilibrium* density matrix. This means that non-equilibrium problem of linear response is reduced to equilibrium problem, as all the averages to be calculated now are, in fact, calculated for the equilibrium state. This remarkable result (Kubo) allows the applications of the powerful apparatus of equilibrium statistical mechanics to solution of this kind of (weakly) non-equilibrium problems.

Eq. (9.19) describes the response of the average value of an operator A to external perturbation H_t^1 . Note that here we are dealing with the retarded response – it appears at the moments of time, which are later than perturbation is switched on. This reflects the causality principle, which is basic for all physical processes. Extending formally integration over time in (9.20) to $+\infty$, which may be done by the introduction of step – like $\theta(t - t')$ – function, it is convenient to rewrite (9.19) as:

$$\langle A \rangle = \langle A \rangle_0 + \int_{-\infty}^{\infty} dt' \langle \langle A(t) H_{t'}^1(t') \rangle \rangle \quad (9.21)$$

where we have introduced the *retarded* double-time (commutator) Green's function (Bogolyubov, Tyablikov), defined for the pair of arbitrary operators A and B as [27]:

$$\langle \langle A(t), B(t') \rangle \rangle = \theta(t - t') \frac{1}{i\hbar} \langle [A(t), B(t')] \rangle_0 \quad (9.22)$$

where

$$\theta(t - t') = \begin{cases} 1 & \text{for } t \geq t' \\ 0 & \text{for } t < t' \end{cases} \quad (9.23)$$

As a result the problem is reduced to calculation of appropriate double-time Green's functions, using the well-developed mathematical formalism [27].

The response to external perturbations can be expressed also in another form, using the time correlation functions. Let us use Kubo identity (9.14). Then:

$$\begin{aligned} \langle A \rangle &= \langle A \rangle_0 - \int_0^\beta d\lambda \int_{-\infty}^t dt' \langle e^{\lambda H} \dot{H}_{t'}^1(t') e^{-\lambda H} A(t) \rangle_0 = \\ &= \langle A_0 \rangle + \int_0^\beta d\lambda \int_{-\infty}^t dt' \langle e^{\lambda H} H_{t'}^1(t') e^{-\lambda H} \dot{A}(t) \rangle_0 \end{aligned} \quad (9.24)$$

where we have used the so called stationarity condition:

$$\langle A \dot{H}_{t'}^1(t' - t) \rangle_0 = - \langle \dot{A}(t - t') H_{t'}^1 \rangle_0 . \quad (9.25)$$

The last equality follows from the fact that equilibrium average of the product of dynamic variables depends only on the time difference:

$$\langle A H_{t'}^1(t' - t) \rangle_0 = \langle A(t - t') H_{t'}^1 \rangle_0 \quad (9.26)$$

which is obtained by cyclic permutations of operators like $e^{\frac{iHt}{\hbar}}$ under the averaging. Differentiating (9.26) by t we obtain (9.25).

Eq. (9.24) can also be rewritten as:

$$\begin{aligned} \langle A \rangle &= \langle A \rangle_0 - \int_0^\beta d\lambda \int_{-\infty}^t dt' \langle \dot{H}_{t'}^1(t' - i\hbar\lambda) A(t) \rangle_0 = \\ &= \langle A \rangle_0 + \int_0^\beta d\lambda \int_{-\infty}^t dt' \langle H_{t'}^1(t' - i\hbar\lambda) \dot{A}(t) \rangle . \end{aligned} \quad (9.27)$$

Eqs. (9.21) and (9.27) give the general expressions for linear response of the system to mechanical perturbation. For an external perturbation (9.3) these can be written as:

$$\langle A \rangle = \langle A \rangle_0 - \sum_j \int_{-\infty}^{\infty} dt' \langle\langle A(t)B_j(t') \rangle\rangle F_j(t') \quad (9.28)$$

$$\langle A \rangle = \langle A \rangle_0 + \sum_j \int_{-\infty}^t dt' \int_0^{\beta} d\lambda \langle e^{\lambda H} B_j(t') e^{-\lambda H} A(t) \rangle_0 F_j(t') \quad (9.29)$$

These are the so called Kubo formulas for the linear response of quantum mechanical system, which reduce the non – equilibrium problem to calculations of equilibrium correlators. This last task is, in general, quite nontrivial and requires the development of special formalism, such as e.g. the theory of double – time commutator Green’s functions.

The physical meaning of the retarded double – time Green function can be easily understood considering the reaction of the system towards instantaneous δ -like perturbation:

$$H_t^1 = B\delta(t - t_1) \quad (9.30)$$

substituting which into (9.21) gives:

$$\langle A \rangle = \langle A \rangle_0 + \langle\langle A(t)B(t_1) \rangle\rangle \quad (9.31)$$

There is a number of well developed methods of calculations of such Green’s functions. Here we briefly describe the approach based on the method of equations of motion (chain equations) [27]. Equation of motion for Green’s function (9.22):

$$G_{AB}(t, t') \equiv \langle\langle A(t), B(t') \rangle\rangle = \theta(t - t') \frac{1}{i\hbar} \langle [A(t), B(t')] \rangle_0 \quad (9.32)$$

can be easily obtained from the general equation of motion for an arbitrary quantum operator in Heisenberg representation:

$$i\hbar \frac{dA}{dt} = [A, H] = AH - HA \quad (9.33)$$

The right hand side of this equation can be calculated for each concrete problem, using the explicit form of Hamiltonian and commutation relations for operators. Differentiating (9.32) by t we obtain the equation:

$$i\hbar \frac{dG_{AB}}{dt} = \frac{d\theta(t - t')}{dt} \langle [A(t), B(t')] \rangle_0 + \langle\langle i\hbar \frac{dA(t)}{dt}, B(t') \rangle\rangle \quad (9.34)$$

Taking into account the obvious relation of $\theta(t)$ step – like function with δ -function of t :

$$\theta(t) = \int_{-\infty}^t dt' \delta(t') \quad (9.35)$$

as well as equations of motion for operator A (9.33), we can write the equation of motion for the Green’s function in the following form:

$$i\hbar \frac{dG_{AB}}{dt} = \delta(t - t') \langle [A(t), B(t')] \rangle_0 + \langle\langle \{A(t)H(t) - H(t)A(t)\}, B(t') \rangle\rangle. \quad (9.36)$$

The right hand side of Eq. (9.36), in general, contains double – time Green’s functions of higher order, than the initial one, which is connected with the nontrivial interaction in any many – particle system. For these Green’s functions we can again write equations of motion similar to (9.36) and obtain the *chain* of interconnected equations of motion for the set of Green’s functions of higher and higher orders. This chain of equations is, in general case, infinite, so that we are dealing with the infinite system of integro – differential equations, which can not be solved. However, in most practical cases this chain of equations can be approximately “decoupled”, expressing in some way the higher order Green’s functions via the low order ones. Then we obtain the finite system of equations (or sometime even the single equation), which is much easier to solve. Unfortunately, there is no general theoretical recipe for decoupling of this chain of equations, everything depends on the skills and abilities of a theorist, trying to solve the problem. Examples of successful decouplings and solutions of a number of physical models by this method can be found in the literature [27].

9.2 Electrical conductivity and magnetic susceptibility.

Consider reaction of the system to external electric field. Perturbation (9.3) in this case can be written as:

$$H_t^1 = - \sum_j e_j (\mathbf{E} \mathbf{x}_j) \cos \omega t e^{\varepsilon t} = -(\mathbf{E} \mathbf{P}) \cos \omega t e^{\varepsilon t} \quad (9.37)$$

where e_j is the charge of j -th particle, \mathbf{x}_j is its coordinate, \mathbf{E} is the electric field in a , playing the role of an external (c -number) “force”,

$$\mathbf{P} = \sum_j e_j \mathbf{x}_j \quad (9.38)$$

is polarization vector, considered here as quantum mechanical operator. This perturbation induces the electric current, which according to (9.21) it can be written as:

$$\langle J_\alpha \rangle = \int_{-\infty}^{\infty} dt' \langle\langle J_\alpha(t), H_{t'}^1(t') \rangle\rangle \quad (9.39)$$

Here we do not have the constant term, as in equilibrium the electric current is just zero, $\langle J_\alpha \rangle = 0$. Also in Eq. (9.39) we have:

$$H_t^1(t) = -(\mathbf{E} \mathbf{P}(t)) \cos \omega t e^{\varepsilon t} \quad J_\alpha(t) = \sum_j e_j \dot{x}_{j\alpha}(t) = \dot{P}_\alpha(t) \quad (9.40)$$

where J_α is an electric current operator, $\dot{x}_{j\alpha}$ is the appropriate velocity component of j -th particle.

Taking into account (9.40) expression (9.39) can be written as:

$$\langle J_\alpha \rangle = - \sum_\beta \int_{-\infty}^{\infty} dt' \langle\langle J_\alpha(t) P_\beta(t') \rangle\rangle E_\beta \cos \omega t' e^{\varepsilon t'} \quad (9.41)$$

Accordingly:

$$\langle J_\alpha \rangle = \sum_\beta \text{Re} \{ \sigma_{\alpha\beta}(\omega) e^{-i\omega t + \varepsilon t} \} E_\beta \quad (9.42)$$

where

$$\sigma_{\alpha\beta}(\omega) = - \int_{-\infty}^{\infty} dt e^{-i\omega t + \varepsilon t} \langle\langle J_{\alpha} P_{\beta}(t) \rangle\rangle \quad (9.43)$$

is conductivity tensor in periodic external field. The limit of $\varepsilon \rightarrow 0$ is to be performed here after the thermodynamic limit $V \rightarrow \infty, N \rightarrow \infty (V/N \rightarrow const)$.

Thus, adiabatic switching on of electric field leads to the appearance of electric current in the system with finite conductivity (irreversible process). Static conductivity can be obtained from (9.43) taking the limit of $\omega \rightarrow 0$:

$$\sigma_{\alpha\beta} = \lim_{\varepsilon \rightarrow 0} \int_{-\infty}^{\infty} dt e^{\varepsilon t} \langle\langle J_{\alpha} P_{\beta}(t) \rangle\rangle \quad (9.44)$$

Let us rewrite (9.43) as (making permutations of operators under Sp):

$$\sigma_{\alpha\beta}(\omega) = - \frac{1}{i\hbar} \int_{-\infty}^0 dt e^{-i\omega t + \varepsilon t} Sp\{[P_{\beta}(t), \rho_0] J_{\alpha}\} \quad (9.45)$$

and apply Kubo identity:

$$[P_{\beta}(t), \rho_0] = -i\hbar\rho_0 \int_0^{\beta} d\lambda e^{\lambda H} \dot{P}_{\beta}(t) e^{-\lambda H} \quad (9.46)$$

Then we obtain:

$$\begin{aligned} \sigma_{\alpha\beta} &= \int_0^{\beta} d\lambda \int_0^{\infty} dt e^{i\omega t - \varepsilon t} \langle e^{\lambda H} J_{\beta} e^{-\lambda H} J_{\alpha}(t) \rangle_0 = \\ &= \int_0^{\beta} d\lambda \int_0^{\infty} dt e^{i\omega t - \varepsilon t} \langle J_{\beta} J_{\alpha}(t + i\hbar\lambda) \rangle_0 \end{aligned} \quad (9.47)$$

which is the notorious Kubo formula for conductivity.

In static limit we have:

$$\sigma_{\alpha\beta} = \lim_{\varepsilon \rightarrow 0} \int_0^{\beta} \int_0^{\infty} dt e^{-\varepsilon t} \langle J_{\beta} J_{\alpha}(t + i\hbar\lambda) \rangle_0 \quad (9.48)$$

Thus, the problem of calculation of conductivity is reduced to calculation of time correlation functions of currents in thermodynamic equilibrium. In concrete systems this is obviously a rather complicate task, which can be analyzed and solved by different methods, which we shall not discuss here.

Consider now the response of the system to the switching of homogeneous (in space) time – dependent (periodic) magnetic field (periodic) $\mathbf{H}(t)$ with frequency ω :

$$\mathbf{H}(t) = \mathbf{H} \cos \omega t e^{\varepsilon t} = \text{Re} e^{-i\omega t + \varepsilon t} \mathbf{H} \quad (9.49)$$

This perturbation is described by operator (9.3) of the following form:

$$H_t^1 = -\mathbf{M}\mathbf{H}(t) = -\mathbf{M}\mathbf{H} \cos \omega t e^{\varepsilon t} \quad (9.50)$$

where \mathbf{M} is the operator of (total) magnetic moment the system. Under the influence of this perturbation the magnetic moment of the system changes, according to (9.21), as:

$$\langle M_{\alpha} \rangle = \langle M_{\alpha} \rangle_0 + \int_{-\infty}^{\infty} dt' \langle\langle M_{\alpha}(t) H_t^1(t') \rangle\rangle \quad (9.51)$$

where $\langle M_\alpha \rangle_0$ is the average projection of magnetic moment on α -axis at equilibrium. If there is magnetic field present at equilibrium we have $\langle M_\alpha \rangle_0 \neq 0$. Expression (9.51) can be written as:

$$\langle M_\alpha \rangle = \langle M_\alpha \rangle_0 + \sum_\beta \text{Re} \{ \chi_{\alpha\beta}(\omega) e^{-i\omega t + \varepsilon t} \} H_\beta \quad (9.52)$$

where

$$\chi_{\alpha\beta}(\omega) = - \int_{-\infty}^{\infty} dt e^{-i\omega t + \varepsilon t} \langle \langle M_\alpha M_\beta(t) \rangle \rangle \quad (9.53)$$

is the tensor of magnetic susceptibility in periodic magnetic field. With the help of Kubo identity Eq. (9.53) can be rewritten also as:

$$\chi_{\alpha\beta} = \int_0^\beta d\lambda \int_0^\infty dt e^{i\omega t - \varepsilon t} \langle \dot{M}_\beta M_\alpha(t + i\hbar\lambda) \rangle \quad (9.54)$$

These expressions are widely used e.g. in the theory of magnetic resonance.

As an elementary example of the use of Kubo formulas we consider electric conductivity, making simplest assumptions for time behavior of correlation functions. Using Eqs. (9.22), (9.44) we get:

$$\sigma_{\alpha\beta} = - \lim_{\varepsilon \rightarrow 0} \frac{1}{i\hbar} \int_{-\infty}^0 dt e^{\varepsilon t} \langle [J_\alpha, P_\beta(t)] \rangle_0 \quad (9.55)$$

Let us assume that

$$\langle [J_\alpha, P_\beta(t)] \rangle_0 \approx \langle [J_\alpha, P_\beta] \rangle_0 e^{-\frac{|t|}{\tau}} \quad (9.56)$$

where τ is some relaxation time. Correlation function at coinciding times can be found in elementary way as:

$$\begin{aligned} \langle [J_\alpha, P_\beta] \rangle_0 &= \langle \left[\sum_i \frac{e}{m} p_i^\alpha, \sum_j e x_j^\beta \right] \rangle_0 = \\ &= \frac{e^2}{m} \sum_i [p_i^\alpha, x_i^\beta] = -i\hbar \delta_{\alpha\beta} \frac{e^2}{m} N \end{aligned} \quad (9.57)$$

where N is the total number of particles, and we used the standard commutation relation $[x_i^\beta, p_i^\alpha] = i\hbar \delta_{\alpha\beta}$. Then we find:

$$\sigma_{\alpha\beta} = \frac{Ne^2}{m} \delta_{\alpha\beta} \lim_{\varepsilon \rightarrow 0} \int_{-\infty}^0 dt e^{(\varepsilon + 1/\tau)t} = \frac{Ne^2}{m} \tau \delta_{\alpha\beta} \quad (9.58)$$

or, per unit volume:

$$\sigma_{\alpha\beta} = \frac{ne^2}{m} \tau \delta_{\alpha\beta} \quad (9.59)$$

which is the usual Drude expression for conductivity. Let us stress that the real problem for theory is, of course, the derivation of behavior like that given by Eq. (9.56) from some microscopic model, which allows also the calculation of dependencies of τ on temperature (or concentration of impurities) for different mechanisms of scattering. These problems can be solved by modern theoretical methods, such as Green's functions formalism.

9.3 Dispersion relations.

Now we shall discuss some general properties of response functions. Consider again time – depending mechanical perturbation, which is switched on adiabatically and described by the following term in Hamiltonian:

$$H_t^1 = - \sum_{j=1}^n F_j(t) B_j \quad (9.60)$$

where $F_j(t) \sim e^{\varepsilon t}$ for $t \rightarrow -\infty$, $\varepsilon \rightarrow +0$, B_j are some dynamical variables (operators), while $F_j(t)$ are c – number “forces”, representing external fields acting upon variables B_j . For simplicity we assume below, that in equilibrium state (for $F_j = 0$) we have $\langle A_j \rangle_0 = 0$, so that the response of the system to external perturbation (9.60) is written, according to (9.21), in the following form:

$$\langle A_i \rangle = \int_{-\infty}^t dt' \kappa_{ij}(t-t') F_j(t') \quad (9.61)$$

where

$$\kappa_{ij}(t-t') = - \langle\langle A_i(t) B_j(t') \rangle\rangle \quad (9.62)$$

is the generalized response matrix. Retarded Green’s function is different from zero only for the positive values of time difference, so that:

$$\kappa_{ij}(t-t') = 0 \quad \text{for } t < t' \quad (9.63)$$

which reflects the *causality*: response of the system can not be before in time than perturbation, due to which it appears.

Let us make Fourier expansion of $F_j(t)$ and $\langle A_i \rangle$:

$$\langle A_i \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} A_i(\omega) \quad (9.64)$$

$$F_j(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} F_j(\omega) \quad (9.65)$$

where Fourier components:

$$A_i(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} \langle A_i(t) \rangle \quad (9.66)$$

$$F_j(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} F_j(t) \quad (9.67)$$

Making Fourier transformation in (9.61) we reduce the integral relation to the algebraic one:

$$A_i(\omega) = \kappa_{ij}(\omega) F_j(\omega) \quad (9.68)$$

where

$$\begin{aligned} \kappa_{ij}(\omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} \kappa_{ij}(t) = - \langle\langle A_i | B_j \rangle\rangle_{\omega} = \\ &= \int_0^{\infty} dt e^{-i\omega t - \varepsilon t} \int_0^{\beta} d\lambda \langle \dot{B}_j A_i(t + i\hbar\lambda) \rangle \end{aligned} \quad (9.69)$$

is Fourier transformed generalized susceptibility matrix. The last expression is sometimes called Kubo's fluctuation – dissipation theorem³.

As both A_i and F_j are real, we have:

$$A_i(\omega) = A_i^*(-\omega) \quad F_j(\omega) = F_j^*(-\omega) \quad (9.70)$$

so that

$$\kappa_{ij} = \kappa_{ij}^*(-\omega) \quad (9.71)$$

and we obtain

$$\begin{aligned} \text{Re}\kappa_{ij}(\omega) &= \text{Re}\kappa_{ij}(-\omega) \\ \text{Im}\kappa_{ij}(\omega) &= -\text{Im}\kappa_{ij}(-\omega) \end{aligned} \quad (9.72)$$

We see that the real part of generalized susceptibility $\kappa_{ij}(\omega)$ is even, while imaginary part is odd over frequency ω ⁴.

Due to causality (cf. (9.63)) the first integral in (9.69) is in fact reduced to (in the following for brevity we drop indices i, j):

$$\kappa(\omega) = \int_0^\infty dt \kappa(t) e^{i\omega t} \quad (9.73)$$

From this fact alone we can obtain some quite general relations for $\kappa(\omega)$, considering it as a function of complex frequency $\omega = \omega' + i\omega''$. Consider the properties of $\kappa(\omega)$ in the upper half-plane of ω . From (9.73) and the fact that $\kappa(t)$ is finite for all positive values of t it follows, that $\kappa(\omega)$ is finite single-valued function in all upper half-plane of ω , it never becomes infinite there, i.e. does not have any singularities there. The proof is simple: for $\omega'' > 0$ there is an exponential dumping factor of $\exp(-t\omega'')$ in the integrand of (9.73), the function $\kappa(t)$ is finite in all integration range, so that the integral in (9.73) converges. Let us stress that the conclusion on the absence of singularities of $\kappa(\omega)$ in the upper half-plane, from physical point of view is the direct consequence of causality. Causality alone transforms integration in (9.73) to the limits from 0 to ∞ (instead of $-\infty$ to ∞). The function $\kappa(\omega)$ is non-singular also at the real axis of frequency ($\omega'' = 0$), except probably the origin ($\omega = 0$).

Let us derive now the general formulas connecting the real and imaginary parts of $\kappa(\omega)$. Let us choose some real and positive value of $\omega = \omega_0$ and integrate $\frac{\kappa(\omega)}{\omega - \omega_0}$ over the contour C , shown in Fig. 9-1. At the infinity $\kappa \rightarrow 0$ so that $\frac{\kappa(\omega)}{\omega - \omega_0}$ tends to zero faster than $1/\omega$. Thus the integral $\int_C d\omega \frac{\kappa(\omega)}{\omega - \omega_0}$ converges. Function $\kappa(\omega)$ does not have singularities in the upper half-plane and point $\omega = \omega_0$ is excluded from integration, so that $\frac{\kappa(\omega)}{\omega - \omega_0}$ is analytic inside contour C , so that our integral is just zero (Cauchy theorem).

Integral over semicircle at the infinity becomes zero due to fast dumping of the integrand. The point ω_0 is surpassed by small semicircle (with radius $\rho \rightarrow 0$). This encirclement is performed clockwise and leads to the contribution

³Fluctuation – dissipation theorem can be written in different forms and gives the relation between susceptibilities (or transport coefficients) and appropriate equilibrium correlators (fluctuations).

⁴It can be shown that $\text{Im}\kappa_{ij}$ determines dissipation of energy of an external field, so that $\text{Im}\kappa_{ij}(\omega > 0) > 0$.

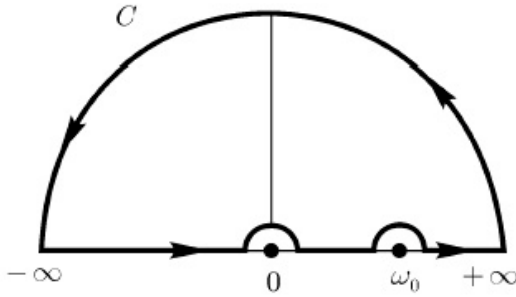


Figure 9.1: Contour of integration used in derivation of Kramers – Kronig relations.

$-i\pi\kappa(\omega_0)$ (integral over the complete circle gives $-2i\pi\kappa(\omega_0)$). If $\kappa(0)$ is finite, surpassing the origin is excessive and integration along the real axis leads to:

$$\lim_{\rho \rightarrow 0} \left\{ \int_{-\infty}^{\omega_0 - \rho} d\omega \frac{\kappa(\omega)}{\omega - \omega_0} + \int_{\omega_0 + \rho}^{\infty} d\omega \frac{\kappa(\omega)}{\omega - \omega_0} \right\} - i\pi\kappa(\omega_0) = 0 \quad (9.74)$$

The first term here is the integral from $-\infty$ to ∞ , understood as a principal value, thus we obtain:

$$i\pi\kappa(\omega_0) = P \int_{-\infty}^{\infty} d\omega \frac{\kappa(\omega)}{\omega - \omega_0} \quad (9.75)$$

This relation is obtained immediately if we consider the integral of $\frac{\kappa(\omega)}{\omega - \omega_0 + i\delta}$ along the real axis and use the famous relation for generalized functions:

$$\frac{1}{x + i\delta} = P \frac{1}{x} - i\pi\delta(x) \quad \delta \rightarrow +0 \quad (9.76)$$

Previous discussion in fact just gives the derivation of this useful relation.

Integration variable ω in (9.75) takes only real values. Let us denote it ξ , and from now on use ω to denote the fixed real value of frequency ω_0 . Then, separating the real and imaginary parts in (9.75), we obtain:

$$Re\kappa(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} d\xi \frac{Im\kappa(\xi)}{\xi - \omega} \quad (9.77)$$

$$Im\kappa(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} d\xi \frac{Re\kappa(\xi)}{\xi - \omega} \quad (9.78)$$

These are the notorious Kramers – Kronig relations. The only property of $\kappa(\omega)$ use in our derivation was the absence of singularities of this function in the upper half-plane⁵. Thus we may say, that Kramers – Kronig relations directly follow from causality principle.

⁵As to the property of $\kappa \rightarrow 0$ for $\omega \rightarrow \infty$, it is not so important: if the limit of κ_∞ is finite, we can simply consider the difference $\kappa - \kappa_\infty$ instead of κ , with appropriate changes in all expressions.

Using the oddness of $Im\kappa(\xi)$ we can rewrite the first of these relations as:

$$Re\kappa(\omega) = \frac{1}{\pi}P \int_0^\infty d\xi \frac{Im\kappa(\xi)}{\xi - \omega} + P \int_0^\infty d\xi \frac{Im\kappa(\xi)}{\xi + \omega} \quad (9.79)$$

or

$$Re\kappa(\omega) = \frac{2}{\pi} \int_0^\infty d\xi \frac{\xi Im\kappa(\omega)}{\xi^2 - \omega^2} \quad (9.80)$$

If $\kappa(\omega)$ has a pole at $\omega = 0$, so that close to it $\kappa = iA/\omega$, surpassing of this pole over the semicircle produces an additional $-A/\omega$ contribution to the integral, which is to be added to the left hand side of (9.75). Accordingly, a similar term will appear in (9.78):

$$Im\kappa(\omega) = -\frac{1}{\pi}P \int_{-\infty}^\infty d\xi \frac{Re\kappa(\xi)}{\xi - \omega} + \frac{A}{\omega} \quad (9.81)$$

Kramers – Kronig relations are the most important exact expressions, allowing to control theoretical models and calculations, with important experimental applications: measurements of $Re\kappa(\omega)$ in a wide frequency interval allow to restore the values of $Im\kappa(\omega)$ (and vice versa), performing numerical integration of experimental data.

Chapter 10

KINETIC EQUATIONS

10.1 Boltzmann equation.

Theory of linear response is appropriate to describe system reaction to weak external perturbations, moving it slightly outside thermodynamic equilibrium. In principle, it can be applied to systems of quite general nature. Another problem is description of arbitrary nonequilibrium states. Up to now there is no general theory of this kind applicable for arbitrary systems of particles. However, much progress was made in the studies of general nonequilibrium behavior of gases of weakly interacting (or rarefied) particles (or quasiparticles). Historically, this was the first branch of nonequilibrium statistical mechanics, started in works of Boltzmann. This is often called *physical kinetics* or the theory of kinetic equations.

Here we shall rather briefly discuss the derivation of basic equation of kinetic theory of gases, determining the distribution function $f(\mathbf{p}, \mathbf{r}, t)$ of separate particles in general nonequilibrium case¹. This equation is basic for the solution of plenty of problems of the physical kinetics of gases [4, 15]. Similar quantum kinetic equations describe nonequilibrium processes in gases of quasiparticles in quantum liquids and solids at low temperatures.

If we neglect atomic collisions each atom represents a closed subsystem and its distribution function satisfies Liouville equation:

$$\frac{df}{dt} = 0 \quad (10.1)$$

Total derivative here denotes differentiation along the phase trajectory of an atom, determined by equations of motion. In the absence of an external field the value of a freely moving atom remains constant, only its coordinates \mathbf{r} change. Then:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \nabla f \quad (10.2)$$

where \mathbf{v} is the velocity. If our gas is in an external field, defined by the potential $U(\mathbf{r})$, we have:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \nabla f + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} \quad (10.3)$$

¹Previously, during our discussion of Boltzmann's statistics (cf. e.g Eqs. (3.8), (3.28) etc.), we denoted this function as $n(p, q)$. For simplicity we limit ourselves to one atom gases.

where $\mathbf{F} = -\nabla U$ is the force, acting upon atom due to this field. In the following, for brevity, we assume that an external field is absent, so that $\mathbf{F} = 0$.

Atomic collisions break the equality in Eq. (10.1) and distribution function is not conserving along the phase trajectories, so that instead of (10.1) we have to write:

$$\frac{df}{dt} = St f \quad (10.4)$$

where $St f$ denotes the rate of the change of distribution function due to these collisions. Using Eq. (10.2) we can write:

$$\frac{\partial f}{\partial t} = -\mathbf{v}\nabla f + St f, \quad (10.5)$$

which defines the total change of distribution function at a given point in the phase space, where the first term in the right hand side determines the number of atoms leaving the given phase space element due to the free motion. The most important term $St f$ is called *collision integral*, while Eq. (10.4) itself is called *kinetic equation*².

Obviously, kinetic equation become well defined only after we establish the explicit form of collision integral. For qualitative estimates of kinetics in gases, very common (and crude) form of collision term can be introduced using the concept of *mean free time* τ , i.e. the average time between two successive atomic collisions (the so called τ - approximation):

$$St f \approx -\frac{f - f_0}{\tau} \quad (10.6)$$

where f_0 denotes the equilibrium distribution function. The numerator of this expression guarantees the vanishing of collision integral in equilibrium, while the minus sign reflects the fact that collisions, in general, lead to the equilibrium state of the system, i.e. diminish the deviation of distribution function from its equilibrium value. In this sense the value of τ plays the role of relaxation time for the establishment of equilibrium in each elementary volume of the gas.

The consistent derivation of collision integral for classical gas can be performed using Bogolyubov's method, which gives the regular procedure of derivation of not only simplest Boltzmann's equation (which can also obtained by from purely heuristic approach [15]), but also corrections to it. However, below we limit ourselves to derivation of Boltzmann's collision integral, which is sufficient for us to illustrate the general method.

The starting point of Bogolyubov's approach is the use of chain of equations for partial distribution functions (1.93):

$$\frac{\partial F_s}{\partial t} = \{H^{(s)}, F_s\} + \frac{N}{V} \sum_{i=1}^s \int \frac{\partial U(|\mathbf{r}_i - \mathbf{r}_{s+1}|)}{\partial \mathbf{r}_i} \frac{\partial F_{s+1}}{\partial \mathbf{p}_i} d\mathbf{r}_{s+1} d\mathbf{p}_{s+1} \quad (10.7)$$

Our aim is to construct the *closed* equation for one particle distribution function $f(\mathbf{p}, \mathbf{r}, t) = \frac{N}{V} F_1(\mathbf{r}, \mathbf{p}, t)$ ³.

²Sometimes it is also called transport equation.

³Distribution function $f(\mathbf{p}, \mathbf{r})$ is normalized to the total number of particles (3.28), while $F_1(\mathbf{r}, \mathbf{p}, t)$ is normalized to unity, according to (1.80).

Using the definition of Poisson brackets and Eq. (10.7) we immediately obtain the first equation of the chain for $F_1(\mathbf{r}, \mathbf{p}, t)$ as:

$$\frac{\partial F_1(t, \tau_1)}{\partial t} + \mathbf{v}_1 \frac{\partial F_1(t, \tau_1)}{\partial \mathbf{r}_1} = \frac{N}{V} \int \frac{\partial U_{12}}{\partial \mathbf{r}_1} \frac{\partial F_2(t, \tau_1, \tau_2)}{\partial \mathbf{p}_1} d\tau_2 \quad (10.8)$$

where for brevity we introduced the variables $\tau = \mathbf{r}, \mathbf{p}$.

Similarly, the second equation of the chain takes the form:

$$\begin{aligned} \frac{\partial F_2}{\partial t} + \mathbf{v}_1 \frac{\partial F_2}{\partial \mathbf{r}_1} + \mathbf{v}_2 \frac{\partial F_2}{\partial \mathbf{r}_2} - \frac{\partial U_{12}}{\partial \mathbf{r}_1} \frac{\partial F_2}{\partial \mathbf{p}_1} - \frac{\partial U_{12}}{\partial \mathbf{r}_2} \frac{\partial F_2}{\partial \mathbf{p}_2} = \\ = \frac{N}{V} \int d\tau_3 \left[\frac{\partial F_3}{\partial \mathbf{p}_1} \frac{\partial U_{13}}{\partial \mathbf{r}_1} + \frac{\partial F_3}{\partial \mathbf{p}_2} \frac{\partial U_{23}}{\partial \mathbf{r}_2} \right] \end{aligned} \quad (10.9)$$

It is not difficult to see that the integral in the r.h.s. of the last equation is small. In fact, the interaction potential $U(r)$ is effectively nonzero only within the limits defined by the radius of forces it creates, which we denote by d , i.e. for $r < d$. Thus, integration over coordinates in $d\tau_3$ is performed over the region defined by $|\mathbf{r}_1 - \mathbf{r}_3| < d$ or $|\mathbf{r}_2 - \mathbf{r}_3| < d$, i.e. the volume of the order of $\sim d^3$. Using (1.81) we have $\frac{1}{V} \int F_3 d\tau_3 = F_2$, where integration is over the whole phase space. Then we get the following estimate:

$$\frac{N}{V} \int \left[\frac{\partial F_3}{\partial \mathbf{p}_1} \frac{\partial U_{13}}{\partial \mathbf{r}_1} \right] d\tau_3 \sim \frac{\partial U(r)}{\partial r} \frac{\partial F_2}{\partial p_1} \frac{d^3}{a^3} \quad (10.10)$$

where a is the average distance between particles in our gas. Then it is clear that the r.h.s. of Eq. (10.9) is small over the parameter $(d/a)^3$ (we assume gas to be rarefied!), as compared with terms containing $\partial U/\partial r$ in the l.h.s. Thus the r.h.s. can be neglected. The sum of all terms in the l.h.s. of the equation in fact represents the total derivative dF_2/dt , where $\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2$ are considered as the functions of time, satisfying the equations of motion for the two particle problem, defined by the Hamiltonian:

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + U(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (10.11)$$

Thus, we have:

$$\frac{d}{dt} F_2(t, \tau_1, \tau_2) = 0 \quad (10.12)$$

Up to now our analysis was purely mechanical. To derive kinetic equation we have to make some assumptions of *statistical* nature. Let us assume that all colliding particles of the gas are statistically independent. This assumption will be used as a kind of initial condition for differential equation (10.12). This assumption introduces time asymmetry, which leads to *irreversible* kinetic equation, despite our use of time reversible equations of motion of classical mechanics. The essence of the problem here is that any correlation between coordinates and momenta of particles in the gas appears only during pretty short collision time of the order of $\sim d/v$ (v is the average velocity of gas particles), and affects particles up to the distances of the order of d only.

Let t_0 be some moment of time before the collision, when two particles are rather far from each other, so that $(|\mathbf{r}_{10} - \mathbf{r}_{20}| \gg d$, where the subscript zero denotes the values at this given moment). Statistical independence of colliding

particles means, that in this moment t_0 the two particle distribution function F_2 is factorized into the product of one particle functions F_1 . Then, integration of Eq. (10.12) from t_0 to t gives:

$$F_2(t, \tau_1, \tau_2) = F_1(t_0, \tau_{10})F_1(t_0, \tau_{20}) \quad (10.13)$$

Here $\tau_{10} = (\mathbf{r}_{10}, \mathbf{p}_{10})$ and $\tau_{20} = (\mathbf{r}_{20}, \mathbf{p}_{20})$ are to be understood as the values of coordinates and momenta, which particles should have had at the moment t_0 to achieve the given values of $\tau_1 = (\mathbf{r}_1, \mathbf{p}_1)$ and $\tau_2 = (\mathbf{r}_2, \mathbf{p}_2)$ by the moment t . In this sense τ_{10} τ_{20} are the functions of τ_1, τ_2 and $t - t_0$. Furthermore, only \mathbf{r}_{10} and \mathbf{r}_{20} depend on $t - t_0$, while the values of \mathbf{p}_{10} and \mathbf{p}_{20} , related to the free moving particles before the collision do not depend on $t - t_0$.

Let us return to Eq. (10.8) — the future kinetic equation. The left hand side here is of required form, but we are interested in the right hand side, which should become the collision integral. Let us substitute there F_2 from (10.13) and introduce $f(\mathbf{p}, \mathbf{r}, t) = \frac{N}{V} F_1(\mathbf{r}, \mathbf{p}, t)$ instead of F_1 . Then we obtain:

$$\frac{\partial f(t, \tau_1)}{\partial t} + \mathbf{v}_1 \frac{\partial f(t, \tau_1)}{\partial \mathbf{r}_1} = St f \quad (10.14)$$

where

$$St f = \int d\tau_2 \frac{\partial U_{12}}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{p}_1} [f(t_0, \tau_{10})f(t_0, \tau_{20})] \quad (10.15)$$

In (10.15) the relevant region for integration is determined by $|\mathbf{r}_2 - \mathbf{r}_1| \sim d$, i.e. by the region where real collision takes place. In this region, in first approximation we can simply neglect the coordinate dependence of f , as it significantly changes only on the scale of the order of the mean free path l , which is much greater than d . The final form of collision integral does not change at all, if we consider from the very beginning only the spatially homogeneous case, assuming that f does not depend on coordinates. In accordance with previous remarks this means that in functions $f(t_0, \mathbf{p}_{10})$ and $f(t_0, \mathbf{p}_{20})$ we can just neglect an explicit time dependence via $\mathbf{r}_{10}(t)$ and $\mathbf{r}_{20}(t)$.

Let us transform the integrand in (10.15) using (10.12) and taking into account the absence of an explicit dependence on time:

$$\begin{aligned} & \frac{d}{dt} f(t_0, \mathbf{p}_{10})f(t_0, \mathbf{p}_{20}) = \\ & = \left(\mathbf{v}_1 \frac{\partial}{\partial \mathbf{r}_1} + \mathbf{v}_2 \frac{\partial}{\partial \mathbf{r}_2} - \frac{\partial U_{12}}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial U_{12}}{\partial \mathbf{r}_2} \frac{\partial}{\partial \mathbf{p}_2} \right) f(t_0, \mathbf{p}_{10})f(t_0, \mathbf{p}_{20}) = 0 \end{aligned} \quad (10.16)$$

Now we can express the derivative over \mathbf{p}_1 via derivatives over $\mathbf{r}_1, \mathbf{r}_2$ \mathbf{p}_2 and substitute the expression obtained in this way into (10.15). The term with derivative $\partial/\partial \mathbf{p}_2$ disappears after transformation into surface integral in momentum space (using Gauss theorem). After that we get:

$$St f(t, \mathbf{p}_1) = \int \mathbf{v}_{12} \frac{\partial}{\partial \mathbf{r}} [f(t_0, \mathbf{p}_{10})f(t_0, \mathbf{p}_{20})] d^3 r d^3 p_2 \quad (10.17)$$

where we have introduced the relative velocity of particles $\mathbf{v}_{12} = \mathbf{v}_1 - \mathbf{v}_2$, and taken into account that both \mathbf{p}_{10} and \mathbf{p}_{20} and, correspondingly, the whole expression in square brackets depend not on \mathbf{r}_1 and \mathbf{r}_2 separately, but only on

the difference $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. Let us introduce instead of $\mathbf{r} = (x, y, z)$ cylindrical coordinates z, ρ, φ , with z -axis along \mathbf{v}_{12} . Noting that $\mathbf{v}_{12}\partial/\partial\mathbf{r} = v_{12}\partial/\partial z$, and performing integration over dz , we rewrite (10.17) as:

$$St f(t, \mathbf{p}_1) = \int [f(t_0, \mathbf{p}_{10})f(t_0, \mathbf{p}_{20})] \Big|_{-\infty}^{\infty} v_{12}\rho d\rho d\varphi d^3p_2 \quad (10.18)$$

where limits $z = \pm\infty$ should be understood as distances large in comparison with d , but small in comparison with mean free path l . This is due to our use of Eq. (10.16) during transformation from (10.15) to (10.18), which is valid until the particles under consideration do not collide once more.

Remember now that \mathbf{p}_{10} and \mathbf{p}_{20} are the initial momenta (at the moment t_0) of particles, which at the final moment t possess \mathbf{p}_1 and \mathbf{p}_2 . If in the final moment $z = z_1 - z_2 = -\infty$, the particles 1 and 2 are at a distance, which is obviously greater than d and do not interact with each other, and there were no collision between them, so that initial and final momenta just coincide: $\mathbf{p}_{10} = \mathbf{p}_1$, $\mathbf{p}_{20} = \mathbf{p}_2$ for $z = -\infty$. If at the final moment $z = +\infty$, there was a collision and particles acquired momenta \mathbf{p}_1 and \mathbf{p}_2 as a result of it. In this case we denote $\mathbf{p}_{10} = \mathbf{p}'_1(\rho)$ and $\mathbf{p}_{20} = \mathbf{p}'_2(\rho)$ for $z = \infty$. These values of momenta are functions of coordinate ρ , which is actually the impact parameter, while the product

$$\rho d\rho d\varphi = d\sigma \quad (10.19)$$

represents the classical differential scattering crosssection [11].

Note finally, that the explicit dependence of functions $f(t_0, \mathbf{p}_{10})$ and $f(t_0, \mathbf{p}_{20})$ on t_0 can be replaced, on the same level of approximation, by the similar dependence on t . In fact, the validity of (10.13) requires only that $t - t_0 \gg d/v$: at the moment t_0 the distance between particles must be great in comparison with the effective radius of the forces d . At the same time, the time difference $t - t_0$ can be chosen to satisfy $t - t_0 \ll l/v$, where l is the mean free path. The ratio of l/v gives the mean free time, which is just a characteristic time for significant change of distribution function. Then, the change of distribution function during the time interval $t - t_0$ will be relatively small and can be neglected.

Taking into account these remarks we can reduce (10.18) to the final form:

$$St f(t, \mathbf{p}_1) = \int [f(t, \mathbf{p}'_1)f(t, \mathbf{p}'_2) - f(t, \mathbf{p}_1)f(t, \mathbf{p}_2)] v_{12} d\sigma d^3p_2 \quad (10.20)$$

which is called Boltzmann's collision integral. Kinetic equation (10.5) with such collision integral is called Boltzmann's kinetic equation.

Boltzmann obtained his collision integral from simple heuristic considerations, based on the so called *Stosszahlansatz*. It is clear that the collision integral can be written as $St f = \bar{R} - R$, where \bar{R} represents the growth rate of distribution function $f(\mathbf{r}, \mathbf{p}_1, t)$ due to atomic collisions in gas, while R is its drop rate due to similar collisions. Let us determine first R . Consider some atom within the volume element d^3r surrounding point \mathbf{r} , with its momentum belonging to some element d^3p_1 of momentum space, around \mathbf{p}_1 . Within the same spatial volume we have atoms with arbitrary momenta \mathbf{p}_2 , which can be considered as a beam of particles, scattered by an atom with momentum \mathbf{p}_1 . The flow of these scattered atoms is given by:

$$I = f(\mathbf{r}, \mathbf{p}_2, t) d^3p_2 |\mathbf{v}_1 - \mathbf{v}_2|. \quad (10.21)$$

According to *Stosszahlansatz*, distribution function f in (10.21) coincide with our distribution function, to be determined from kinetic equation. This seems almost obvious assumption, but actually it is the central point of derivation, with no rigorous justification. The number of collisions like $\mathbf{p}_2, \mathbf{p}_2 \rightarrow \mathbf{p}'_1, \mathbf{p}'_2$, taking place in volume element d^3r during the unit of time, is given by:

$$Id\sigma = f(\mathbf{r}, \mathbf{p}_2, t)|\mathbf{v}_1 - \mathbf{v}_2|d\sigma \quad (10.22)$$

The drop rate R of distribution function is obtained by summation of (10.22) over all values of \mathbf{p}_2 and multiplication of the result by the density of atoms in volume element d^3p_1 in velocity space:

$$R = f(\mathbf{r}, \mathbf{p}_1, t) \int d^3p_2 d\sigma |\mathbf{v}_1 - \mathbf{v}_2| f(\mathbf{r}, \mathbf{p}_2, t) \quad (10.23)$$

In a similar way we can determine also the value of \bar{R} . Consider collisions $\mathbf{p}'_1, \mathbf{p}'_2 \rightarrow \mathbf{p}_1, \mathbf{p}_2$, where momentum \mathbf{p}_1 is considered as fixed. Consider the beam of atoms with momenta \mathbf{p}'_2 , colliding with atom possessing the momentum \mathbf{p}'_1 . Flow density of this beam is given by:

$$f(\mathbf{r}, \mathbf{p}'_2, t) d^3p'_2 |\mathbf{v}'_2 - \mathbf{v}'_1|. \quad (10.24)$$

The number of collision of this type per unit of time is:

$$f(\mathbf{r}, \mathbf{p}'_2, t) d^3p'_2 |\mathbf{v}'_2 - \mathbf{v}'_1| d\sigma'. \quad (10.25)$$

The growth rate of distribution function \bar{R} is determined by the integral:

$$\bar{R} d^3p_1 = \int d^3p'_2 d\sigma' |\mathbf{v}'_2 - \mathbf{v}'_1| [f(\mathbf{r}, \mathbf{p}'_1, t) d^3p'_1] f(\mathbf{r}, \mathbf{p}'_2, t). \quad (10.26)$$

Due to time invariance of equations of motion, the differential crosssections of direct and inverse scatterings are the same: $d\sigma = d\sigma'$. Besides that, conservation laws (we consider only elastic scatterings!) give:

$$\begin{aligned} |\mathbf{v}_1 - \mathbf{v}_2| &= |\mathbf{v}'_1 - \mathbf{v}'_2| \\ d^3p_1 d^3p_2 &= d^3p'_1 d^3p'_2. \end{aligned} \quad (10.27)$$

Then:

$$\bar{R} = \int d^3p_2 d\sigma |\mathbf{v}_1 - \mathbf{v}_2| f(\mathbf{r}, \mathbf{p}'_1, t) f(\mathbf{r}, \mathbf{p}'_2, t). \quad (10.28)$$

It is necessary to note that momentum \mathbf{p}_1 here is fixed, while \mathbf{p}'_1 and \mathbf{p}'_2 are functions of $\mathbf{p}_1, \mathbf{p}_2$.

Using the derived expressions for R and \bar{R} , and introducing the obvious shortened notations, we obtain:

$$St f = \bar{R} - R = \int d^3p_2 d\sigma |\mathbf{v}_1 - \mathbf{v}_2| (f'_1 f'_2 - f_1 f_2) \quad (10.29)$$

which coincides with Eq. (10.20).

10.2 H-theorem.

Nonequilibrium gas freely evolving with no external perturbations tends to equilibrium. Similar behavior is characteristic for any closed macroscopic system. This should be accompanied by corresponding entropy growth. This is experimentally observed behavior, and the evolution of nonequilibrium distribution function, following from kinetic equation should satisfy this observation. In fact, we can derive this (irreversible!) behavior directly from Boltzmann's equation.

We have shown above (cf. Eqs. (3.25), (3.30)), that entropy of an ideal gas in nonequilibrium (macroscopic) state, described by distribution function f , is equal to:

$$S = \int f \ln \frac{e}{f} dV d^3p. \quad (10.30)$$

Differentiating this expression over time, we can write:

$$\frac{dS}{dt} = \int \frac{\partial}{\partial t} \left(f \ln \frac{e}{f} \right) dV d^3p = - \int \ln f \frac{\partial f}{\partial t} dV d^3p. \quad (10.31)$$

Equilibrium state in gas is achieved via atomic (molecular) collisions, and corresponding entropy growth should be related precisely with the change of distribution functions due to these collisions. The change of distribution function due free motion of atoms can not change entropy of the gas. This change is determined (for the gas in an external field) by the first two terms in the right hand side of:

$$\frac{\partial f}{\partial t} = -\mathbf{v} \nabla f - \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} + St f. \quad (10.32)$$

Corresponding contribution to dS/dt is given by:

$$- \int \ln f \left[-\mathbf{v} \frac{\partial f}{\partial \mathbf{r}} - \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} \right] dV d^3p = \int \left[\mathbf{v} \frac{\partial}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial}{\partial \mathbf{p}} \right] \left(f \ln \frac{f}{e} \right) dV d^3p. \quad (10.33)$$

Integral over dV of the term with derivative $\partial/\partial \mathbf{r}$ is transformed via Gauss theorem to the surface integral at infinity, it is actually zero, as outside the volume occupied by gas, we have $f = 0$. Similarly, the term with derivative $\partial/\partial \mathbf{p}$ integrated over d^3p is transformed to the surface integral at infinity in momentum space and it is also just equal to zero.

Thus, we obtain the rate of change of entropy as:

$$\frac{dS}{dt} = - \int \ln f St f d^3p dV. \quad (10.34)$$

Substituting here Boltzmann's collision integral (10.29), we get:

$$\frac{dS}{dt} = - \int d^3p_1 \int dp_2^3 d\sigma |\mathbf{v}_1 - \mathbf{v}_2| (f_2' f_1' - f_2 f_1) \ln f_1. \quad (10.35)$$

The integral here does not change after permutation of variables \mathbf{p}_1 and \mathbf{p}_2 , as scattering crosssection is invariant to this permutation. Performing this change of integration variables and taking the half of the sum of the new and previous expression (10.35), we obtain:

$$\frac{dS}{dt} = - \frac{1}{2} \int d^3p_1 \int d^3p_2 d\sigma |\mathbf{v}_2 - \mathbf{v}_1| (f_2' f_1' - f_2 f_1) \ln(f_1 f_2). \quad (10.36)$$

This integral is also invariant with respect to mutual permutation of $\mathbf{p}_1, \mathbf{p}_2$ and $\mathbf{p}'_1, \mathbf{p}'_2$, as to each direct collision process correspond the inverse collision with the same crosssection. Accordingly we can write::

$$\frac{dS}{dt} = -\frac{1}{2} \int d^3 p'_1 \int d^3 p'_2 d\sigma' |\mathbf{v}'_2 - \mathbf{v}'_1| (f_2 f_1 - f'_2 f'_1) \ln(f'_1 f'_2). \quad (10.37)$$

Noting that $d^3 p'_1 d^3 p'_2 = d^3 p_1 d^3 p_2$ and $|\mathbf{v}'_2 - \mathbf{v}'_1| = |\mathbf{v}_2 - \mathbf{v}_1|$ and $d\sigma' = d\sigma$, we take half sum of Eqs. (10.36), (10.37), and obtain:

$$\frac{dS}{dt} = -\frac{1}{4} \int d^3 p_1 \int d^3 p_2 d\sigma |\mathbf{v}_2 - \mathbf{v}_1| (f'_2 f'_1 - f_2 f_1) [\ln(f_1 f_2) - \ln(f'_1 f'_2)]. \quad (10.38)$$

The integrand in (10.38) is never positive, which is clear from previously used inequality $x \ln x > x - 1$ (valid for $x > 0$). Thus, we have proved the notorious Boltzmann's H -theorem: $\frac{dS}{dt} \geq 0$, which is equivalent to the law of entropy growth⁴.

It is easy to see, that $\frac{dS}{dt} = 0$ only in case of the integrand in (10.38) being identically zero. This is only so when all distribution functions, entering the collision integral, are equal to corresponding equilibrium (Boltzmann distribution) values. It is now also clear, that the arbitrary initial (nonequilibrium) distribution function $f(\mathbf{p}, t)$ tends to the equilibrium value as $t \rightarrow \infty$.

10.3 Quantum kinetic equations*.

Let us consider now the derivation of quantum kinetic equations. Our task now is to derive the closed equation for one particle density matrix from Bogolyubov's chain of equations for partial density matrices (1.163). The version of Bogolyubov's approach discussed below was proposed by Zyrianov [28].

Let us start from quantum Liouville equation (1.128) for general (N - particle) density matrix:

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho] \equiv H\rho - \rho H \quad (10.39)$$

We shall work in secondary quantization representation, built upon eigenfunctions of the Hamiltonian of "free" particles (quasiparticles):

$$H_0 |\nu \rangle = E_\nu |\nu \rangle \quad (10.40)$$

$$H_0 = \sum_{\nu} E_\nu a_\nu^+ a_\nu \quad (10.41)$$

where a_ν^+, a_ν are creation and annihilation operators of Fermions or Bosons in the quantum state $|\nu \rangle$. Here ν denotes the quantum numbers, characterizing elementary excitations in our system. In most cases these correspond to free particles with definite momenta (or quasimomenta) and spin: $|\nu \rangle = |\mathbf{p}, \sigma \rangle = \chi_\sigma e^{i\mathbf{p}\mathbf{r}/\hbar}$, where χ_σ is spinor part of the wave function. In the absence of external fields $E_\nu \equiv E_p = p^2/2m$. However, within this formalism, we can also discuss less trivial cases. For example, ν may correspond to the set of Landau quantum numbers of an electron in external (homogeneous) magnetic field: $\nu = \{n, p_z, \sigma\}$,

⁴The name H -theorem is historical, as Boltzmann used the notation $H = -S$.

or these may be some quantum numbers of energy levels for some other exactly soluble model, when the Hamiltonian can be written in diagonal form (10.41).

Operators of second quantization satisfy the usual commutation relations:

$$[a_\nu, a_{\nu'}^\pm]_\pm = \delta_{\nu\nu'} \quad (10.42)$$

$$[a_\nu, a_{\nu'}]_\pm = 0 \quad [a_\nu^\pm, a_{\nu'}^\pm]_\pm = 0 \quad (10.43)$$

where \pm refers to Fermions and Bosons respectively. It is supposed here that these operators are written in Schroedinger representation and are time independent.

Our aim is to derive equation for one particle density matrix, defined in Eq. (1.163) as:

$$F_{1\nu\nu'} = \langle \nu | F_1 | \nu' \rangle = Sp \rho a_\nu^\dagger a_{\nu'} \equiv \langle a_\nu^\dagger a_{\nu'} \rangle \quad (10.44)$$

Naturally, we are going to discuss the case of interacting particles, when the total Hamiltonian is written as:

$$H = H_0 + V \quad (10.45)$$

where V represents some interaction Hamiltonian, which is also written in secondary quantization representation.

Using the Liouville equation (10.39), we can write:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} Sp \rho a_\nu^\dagger a_{\nu'} &= i\hbar \frac{\partial}{\partial t} \langle a_\nu^\dagger a_{\nu'} \rangle = Sp [H, \rho] a_\nu^\dagger a_{\nu'} = \\ &= Sp \rho [a_\nu^\dagger a_{\nu'}, H] = \langle [a_\nu^\dagger a_{\nu'}, H] \rangle \end{aligned} \quad (10.46)$$

where we have performed an obvious cyclic permutation of operators under Sp . Thus, our problem is reduced to calculation of the average value of the commutator, standing in the r.h.s. of this equation. Now we have to introduce some specific model of interaction.

10.3.1 Electron-phonon interaction.

Consider (not the simplest possible case!) the system of electrons (Fermions), occupying the states $|\nu\rangle$, interacting with phonons (Bosons), with states characterized by quasimomentum $|\mathbf{k}\rangle$. Then we write:

$$H_0 = H_{el}^0 + H_{ph}^0 \quad (10.47)$$

$$H_{el}^0 = \sum_{\nu} E_{\nu} a_{\nu}^{\dagger} a_{\nu} \quad H_{ph}^0 = \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} \quad (10.48)$$

$$V = H_{el-ph} = \sum_{\nu, \nu', \mathbf{k}} A(\nu', \nu, \mathbf{k}) a_{\nu}^{\dagger} a_{\nu'} (b_{\mathbf{k}} + b_{-\mathbf{k}}^{\dagger}) \quad (10.49)$$

where $A(\nu', \nu, \mathbf{k}) = g_{\mathbf{k}} \langle \nu | e^{i\mathbf{k}\mathbf{r}} | \nu' \rangle$ is the matrix element of electron - phonon interaction and $g_{\mathbf{k}}$ is corresponding coupling constant.

In this problem we have actually to construct the system of interconnected kinetic equations for one particle density matrices of electrons (10.44) and phonons:

$$N_{1\mathbf{k}\mathbf{k}'} = \langle \mathbf{k} | N_1 | \mathbf{k}' \rangle = Sp \rho b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}'} = \langle b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}'} \rangle \quad (10.50)$$

Consider first the exact equations of motion similar to Eq. (10.46):

$$i\hbar \frac{\partial}{\partial t} \langle a_{\kappa}^+ a_{\kappa'} \rangle = \langle [a_{\kappa}^+ a_{\kappa'}, H_{el}^0 + H_{ph}^0 + H_{el-ph}] \rangle \quad (10.51)$$

$$i\hbar \frac{\partial}{\partial t} \langle b_{\mathbf{k}}^+ b_{\mathbf{k}'} \rangle = \langle [b_{\mathbf{k}}^+ b_{\mathbf{k}'}, H_{el}^0 + H_{ph}^0 + H_{el-ph}] \rangle \quad (10.52)$$

Now it is necessary to perform explicit calculations of different commutators here, using the basic commutation relations (10.42), (10.43). In particular, it is pretty easy to get the following relations:

$$[a_{\nu}^+ a_{\nu'}, a_{\kappa}^+ a_{\kappa'}] = a_{\nu}^+ a_{\kappa'} \delta_{\nu'\kappa} - a_{\kappa}^+ a_{\nu'} \delta_{\nu\kappa'} \quad (10.53)$$

$$[b_{\mathbf{q}}^+ b_{\mathbf{q}'}, b_{\mathbf{k}}^+ b_{\mathbf{k}'}] = b_{\mathbf{q}}^+ b_{\mathbf{q}'} \delta_{\mathbf{q}'\mathbf{k}} - b_{\mathbf{k}}^+ b_{\mathbf{q}'} \delta_{\mathbf{q}\mathbf{k}'} \quad (10.54)$$

Then, using (10.53) in (10.51), we obtain:

$$\begin{aligned} \left(i\hbar \frac{\partial}{\partial t} + E_{\kappa} - E_{\kappa'} \right) F_{1\kappa\kappa'} &= \sum_{\nu\nu'} \{ A(\nu', \nu, \mathbf{q}) [\delta_{\nu\kappa'} H_{\kappa\nu'}^* - \delta_{\kappa\nu'} H_{\nu\kappa'}^*] + \\ &\quad + A^*(\nu', \nu, \mathbf{q}) [\delta_{\nu\kappa'} H_{\kappa\nu'} - \delta_{\kappa\nu'} H_{\nu\kappa}] \} \end{aligned} \quad (10.55)$$

where we have introduced:

$$H_{\kappa\kappa'\mathbf{q}}^* = \langle a_{\kappa}^+ a_{\kappa'} b_{\mathbf{q}} \rangle \quad H_{\kappa\kappa'\mathbf{q}} = \langle a_{\kappa}^+ a_{\kappa'} b_{\mathbf{q}}^+ \rangle \quad (10.56)$$

Similarly, using (10.54) in (10.52) we obtain:

$$\left(i\hbar \frac{\partial}{\partial t} + \hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'} \right) N_{1\mathbf{k}\mathbf{k}'} = \sum_{\nu\nu'} \{ A^*(\nu', \nu, \mathbf{k}) H_{\nu\nu'\mathbf{k}} - A(\nu', \nu, \mathbf{k}) H_{\nu\nu'\mathbf{k}'}^* \} \quad (10.57)$$

These are the first equations of Bogolyubov's chain. On the next step we have to write down equations of motion for $H_{\kappa\kappa'\mathbf{q}}$ and $H_{\kappa,\kappa'\mathbf{q}}^*$:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \langle a_{\kappa}^+ a_{\kappa'} b_{\mathbf{q}} \rangle &= \langle [a_{\kappa}^+ a_{\kappa'} b_{\mathbf{q}}, H_{el}^0 + H_{ph}^0 + H_{el-ph}] \rangle \\ i\hbar \frac{\partial}{\partial t} \langle a_{\kappa}^+ a_{\kappa'} b_{\mathbf{q}}^+ \rangle &= \langle [a_{\kappa}^+ a_{\kappa'} b_{\mathbf{q}}^+, H_{el}^0 + H_{ph}^0 + H_{el-ph}] \rangle \end{aligned} \quad (10.58)$$

Using again (10.53) and (10.54) and also

$$[b_{\mathbf{q}}, b_{\mathbf{k}}^+ b_{\mathbf{k}}] = b_{\mathbf{k}} \delta_{\mathbf{k}\mathbf{q}} \quad [b_{\mathbf{q}}^+, b_{\mathbf{k}}^+ b_{\mathbf{k}}] = -b_{\mathbf{k}}^+ \delta_{\mathbf{k}\mathbf{q}} \quad (10.59)$$

we get:

$$\begin{aligned} \left(i\hbar \frac{\partial}{\partial t} + E_{\kappa} - E_{\kappa'} + \hbar\omega_{\mathbf{q}} \right) H_{\kappa',\kappa,\mathbf{q}} &= \sum_{\gamma\gamma'\mathbf{q}'} A(\gamma', \gamma, \mathbf{q}') \{ \langle a_{\kappa}^+ a_{\gamma'} b_{\mathbf{q}'} b_{\mathbf{q}}^+ \rangle \delta_{\gamma\kappa'} + \\ &\quad + \langle a_{\kappa}^+ a_{\gamma'} b_{-\mathbf{q}'} b_{\mathbf{q}}^+ \rangle \delta_{\gamma\kappa'} - \langle a_{\gamma}^+ a_{\kappa'} b_{\mathbf{q}'} b_{\mathbf{q}}^+ \rangle \delta_{\gamma'\kappa} - \\ &\quad - \langle a_{\gamma}^+ a_{\kappa'} b_{-\mathbf{q}'} b_{\mathbf{q}}^+ \rangle \delta_{\gamma'\kappa} - \langle a_{\kappa}^+ a_{\kappa'} a_{\gamma'}^+ a_{\gamma'} \rangle \delta_{\mathbf{q}\mathbf{q}'} \} \end{aligned} \quad (10.60)$$

$$\begin{aligned}
\left(i\hbar\frac{\partial}{\partial t} + E_{\kappa} - E_{\kappa'} - \hbar\omega_{\mathbf{q}}\right) H_{\kappa',\kappa,\mathbf{q}}^* &= \sum_{\gamma\gamma'\mathbf{q}'} A^*(\gamma', \gamma, \mathbf{q}') \left\{ \langle a_{\kappa}^+ a_{\gamma'} b_{\mathbf{q}'} b_{\mathbf{q}} \rangle \delta_{\gamma'\kappa'} + \right. \\
&+ \langle a_{\kappa}^+ a_{\gamma'} b_{-\mathbf{q}'} b_{\mathbf{q}} \rangle \delta_{\gamma'\kappa'} - \langle a_{\gamma}^+ a_{\kappa'} b_{\mathbf{q}'} b_{\mathbf{q}} \rangle \delta_{\gamma'\kappa} - \\
&\left. - \langle a_{\gamma}^+ a_{\kappa'} b_{-\mathbf{q}'} b_{\mathbf{q}} \rangle \delta_{\gamma'\kappa} - \langle a_{\kappa}^+ a_{\kappa'} a_{\gamma}^+ a_{\gamma'} \rangle \delta_{\mathbf{q}\mathbf{q}'} \right\}
\end{aligned} \tag{10.61}$$

In principle this procedure can be continued and we shall obtain the next equations of the chain, but for most practical problems it is sufficient to limit ourselves to equations derived above (at least for weak enough interactions). The only way to “cut” Bogolyubov’s chain is to use some approximate “decoupling” of higher order correlators (density matrices) via lower order correlators (e.g. factorize higher order density matrices into products of lower order density matrices). Unfortunately, in general case, this procedure is not completely unambiguous and there may be several ways to perform such “decoupling”. For the problem under consideration, the two particle correlators may be expressed via one particle correlators in the following way⁵:

$$\begin{aligned}
\langle a_{\kappa}^+ a_{\kappa'} b_{\mathbf{k}}^+ b_{\mathbf{k}'} \rangle &\approx F_{1\kappa\kappa'} N_{1\mathbf{k}\mathbf{k}'} \\
\langle a_{\kappa}^+ a_{\kappa'} b_{\mathbf{k}} b_{\mathbf{k}'}^+ \rangle &\approx \langle a_{\kappa}^+ a_{\kappa'} \rangle \langle \delta_{\mathbf{k}\mathbf{k}'} + b_{\mathbf{k}}^+ b_{\mathbf{k}} \rangle = F_{1\kappa\kappa'} (\delta_{\mathbf{k}\mathbf{k}'} + N_{1\mathbf{k}\mathbf{k}'}) \\
\langle a_{\kappa}^+ a_{\kappa'} a_{\nu'}^+ a_{\nu'} \rangle &\approx F_{1\kappa\kappa'} F_{1\nu\nu'} + F_{1\kappa\nu'} (\delta_{\kappa'\nu'} - F_{1\nu\kappa'}) \\
\langle a_{\kappa}^+ a_{\kappa'} b_{\mathbf{k}'} b_{\mathbf{k}} \rangle &= \langle a_{\kappa} a_{\kappa'} b_{\mathbf{k}}^+ b_{\mathbf{k}}^+ \rangle = 0
\end{aligned} \tag{10.62}$$

Using (10.62) in (10.60) and performing formal integration we get:

$$H_{\kappa\kappa'\mathbf{q}}(t) = e^{\frac{i}{\hbar}(E_{\kappa} - E_{\kappa'} + \hbar\omega_{\mathbf{q}})(t-t_0)} \left\{ H_{\kappa\kappa'\mathbf{q}}(t_0) + \frac{1}{i\hbar} \int_{t_0}^t dt' e^{\frac{i}{\hbar}(E_{\kappa} - E_{\kappa'} + \hbar\omega_{\mathbf{q}})(t-t')} I_{\kappa\kappa'\mathbf{q}}^{FN}(t') \right\} \tag{10.63}$$

where t_0 is the initial moment of time, and we used the notation:

$$\begin{aligned}
I_{\kappa\kappa'\mathbf{q}}^{FN}(t') &= \sum_{\gamma\gamma'\mathbf{q}'} A(\gamma', \gamma, \mathbf{q}') [(F_{1\kappa\gamma'} \delta_{\gamma'\kappa'} - \\
&- F_{1\gamma'\kappa} \delta_{\gamma'\kappa}) (\delta_{\mathbf{q}\mathbf{q}'} + N_{1\mathbf{q}\mathbf{q}'}) - (F_{1\kappa\kappa'} F_{1\kappa\gamma'} (\delta_{\gamma'\kappa'} - F_{1\gamma'\kappa'}) \delta_{\mathbf{q}\mathbf{q}'}]_{t'}
\end{aligned} \tag{10.64}$$

where the last index denotes that all the density matrices (correlators) in square brackets are taken at the time moment t' .

Let us introduce now Bogolyubov’s condition of “weak correlations ” far away in the past:

$$\lim_{t_0 \rightarrow -\infty} H_{\kappa\kappa'\mathbf{q}}(t_0) = 0 \tag{10.65}$$

The choice of this condition in the past is obviously connected with causality and Eq. (10.65) explicitly introduces the “arrow of time”.

Then Eq. (10.63) can be rewritten as:

$$H_{\kappa\kappa'\mathbf{q}}(t) = \frac{1}{i\hbar} \int_{-\infty}^t dt' e^{-\frac{i}{\hbar}(E_{\kappa} - E_{\kappa'} + \hbar\omega_{\mathbf{q}})(t-t')} I_{\kappa\kappa'\mathbf{q}}^{FN}(t') \tag{10.66}$$

⁵It is easy to see that here we have taken all possible combinations of the pair products of creation and annihilation operators (called “pairings”), the average values of those giving one particle density matrices. Such decoupling is equivalent to the use of the so called Wick theorem, which is strictly valid if we make averaging over the equilibrium density matrix [29].

so that after the change of the variable $t' - t = \tau$ we obtain:

$$H_{\kappa\kappa'\mathbf{q}}(t) = \frac{1}{i\hbar} \int_{-\infty}^0 d\tau e^{-i(E_\kappa - E_{\kappa'} + \hbar\omega_{\mathbf{q}})\frac{\tau}{\hbar}} I_{\kappa\kappa'\mathbf{q}}^{FN}(t + \tau) \quad (10.67)$$

Thus, in principle, the values of correlator $H_{\kappa\kappa'\mathbf{q}}$ at the time moment t are determined by the values of the density matrices F_1 and N_1 in all previous moments of time (solution with “memory”). Following Bogolyubov we shall assume that characteristic time scale of this “memory” is of the order of typical (microscopic) time scale of electron – phonon interaction τ_0 , so that afterwards the time evolution of all (kinetic) variables is determined only by the time dependence of one particle density matrices. Then, being interested the evolution of the system on the time scale $t \gg \tau_0$, we can totally neglect “memory” effects in Eq. (10.67). Accordingly, using

$$\begin{aligned} \frac{1}{i} \int_{-\infty}^0 dt e^{\mp ixt} &= \lim_{\varepsilon \rightarrow 0^+} \frac{1}{i} \int_{-\infty}^0 dt e^{\mp i(x \pm i\varepsilon)t} = \\ &= \lim_{\varepsilon \rightarrow 0^+} \frac{1}{x \pm i\varepsilon} = P \frac{1}{x} \mp i\delta(x) \end{aligned} \quad (10.68)$$

we immediately obtain:

$$\begin{aligned} H_{\kappa\kappa'\mathbf{q}} &= \lim_{\varepsilon \rightarrow 0^+} \frac{1}{E_\kappa - E_{\kappa'} + \hbar\omega_{\mathbf{q}} + i\varepsilon} \sum_{\gamma\gamma'\mathbf{q}'} A(\gamma', \gamma, \mathbf{q}') \{ (F_{1\kappa\gamma'} \delta_{\gamma\kappa'} - \\ &- F_{1\gamma\kappa'} \delta_{\gamma'\kappa'}) (\delta_{\mathbf{q}\mathbf{q}'} + N_{1\mathbf{q}\mathbf{q}'}) - (F_{1\kappa\kappa'} F_{1\gamma\gamma'} + F_{1\kappa\gamma'} (\delta_{\gamma\kappa'} - F_{1\gamma\kappa'})) \delta_{\mathbf{q}\mathbf{q}'} \} \end{aligned} \quad (10.69)$$

Similarly, from Eq. (10.61) we get:

$$\begin{aligned} H_{\kappa\kappa'\mathbf{q}}^* &= \lim_{\varepsilon \rightarrow 0^+} \frac{1}{E_\kappa - E_{\kappa'} - \hbar\omega_{\mathbf{q}} + i\varepsilon} \sum_{\gamma\gamma'\mathbf{q}'} A^*(\gamma', \gamma, \mathbf{q}') \{ (F_{1\kappa\gamma'} \delta_{\gamma\kappa'} (N_{1\mathbf{q}'\mathbf{q}} + \delta_{\mathbf{q}\mathbf{q}'}) - \\ &- F_{1\gamma\kappa'} \delta_{\gamma'\kappa'} N_{1\mathbf{q}\mathbf{q}'}) - (F_{1\gamma\kappa'} F_{1\kappa\gamma'} - F_{1\kappa\kappa'} F_{1\gamma\gamma'}) \delta_{\mathbf{q}\mathbf{q}'} \} \end{aligned} \quad (10.70)$$

Note that solutions (10.67) and (10.67) immediately follow from (10.60) and (10.61) (after the decoupling (10.62)), if we assume the absence of an *explicit* time dependence of H and H^* , which allows us to perform in Eqs. (10.60) and (10.61) the formal substitution $i\hbar \frac{\partial}{\partial t} \rightarrow i\varepsilon^6$.

We see that the substitution of (10.69) and (10.70) into (10.55) and (10.57) already produces the closed system of kinetic equations for F_1 and N_1 . However, their general form becomes much simpler, if we assume the diagonal nature of one particle density matrices:

$$F_{1\kappa\kappa'} = F_{1\kappa} \delta_{\kappa\kappa'} \quad N_{1\mathbf{k}\mathbf{k}'} = N_{1\mathbf{k}} \delta_{\mathbf{k}\mathbf{k}'} \quad (10.71)$$

The validity of this assumption actually depends on the properties of the system under consideration and on the quantum number of electrons ν , as well as on the possibility to neglect spatial inhomogeneities in phonon gas. If these conditions

⁶This corresponds to Bogolyubov’s assumption, that on time scales typical for kinetic phenomena, higher order density matrices (or distribution functions) depend on time only through the appropriate time dependence of one particle density matrices (distribution functions).

are satisfied, the quantum kinetic equations for electrons and phonons acquire the final form:

$$\begin{aligned} \frac{\partial F_{1\kappa}}{\partial t} = & \\ \frac{2\pi}{\hbar} \sum_{\nu\mathbf{q}} \{ & |A(\kappa, \nu, \mathbf{q})|^2 \delta(E_\kappa - E_\nu + \hbar\omega_{\mathbf{q}}) [F_{1\nu}(1 - F_{1\kappa})(N_{1\mathbf{q}} + 1) - F_{1\kappa}(1 - F_{1\nu})N_{1\mathbf{q}}] \\ & + |A(\nu, \kappa, \mathbf{q})|^2 \delta(E_\kappa - E_\nu - \hbar\omega_{\mathbf{q}}) [F_{1\nu}(1 - F_{1\kappa})N_{1\mathbf{q}} - F_{1\kappa}(1 - F_{1\nu})(N_{1\mathbf{q}} + 1)] \} \end{aligned} \quad (10.72)$$

$$\frac{\partial}{\partial t} N_{1\mathbf{k}} = \frac{2\pi}{\hbar} \sum_{\nu\nu'} |A(\nu, \nu', \mathbf{k})|^2 \delta(E_{\nu'} - E_\nu - \hbar\omega_{\mathbf{k}}) \{ [F_{1\nu'} - F_{1\nu}] N_{1\mathbf{k}} + F_{1\nu'}(1 - F_{1\nu}) \} \quad (10.73)$$

These kinetic equations (collision integrals) for electron – phonon system form the basis for the solution of numerous problems of physical kinetics in solids [28].

10.3.2 Electron-electron interaction.

Let us discuss briefly the derivation of quantum kinetic equation for the case of interacting electrons (Fermions), described by the Hamiltonian:

$$H = \sum_{\nu} E_{\nu} a_{\nu}^{\dagger} a_{\nu} + \sum_{\mu\mu'\nu\nu'} \langle \mu\nu | U | \mu'\nu' \rangle a_{\nu}^{\dagger} a_{\mu}^{\dagger} a_{\nu'} a_{\mu'} \quad (10.74)$$

where we assume that interaction is of short range (screened) nature (the case of Coulomb interaction requires special treatment). The matrix element of this interaction can be written as:

$$\langle \mu\nu | U(\mathbf{r}) | \mu'\nu' \rangle = \int \frac{d^3\mathbf{k}}{(2\pi)^3} U(\mathbf{k}) \langle \mu | e^{i\mathbf{k}\mathbf{r}} | \mu' \rangle \langle \nu | e^{i\mathbf{k}\mathbf{r}} | \nu' \rangle \quad (10.75)$$

Let us introduce again the partial density matrices:

$$F_{1\kappa\kappa'} = Spp a_{\kappa}^{\dagger} a_{\kappa'} = \langle a_{\kappa}^{\dagger} a_{\kappa'} \rangle \quad (10.76)$$

$$\langle \kappa\kappa' | F_2 | \nu\nu' \rangle = Spp a_{\kappa}^{\dagger} a_{\kappa'}^{\dagger} a_{\nu} a_{\nu'} = \langle a_{\kappa}^{\dagger} a_{\kappa'}^{\dagger} a_{\nu} a_{\nu'} \rangle \quad (10.77)$$

Then the appropriate Bogolyubov's chain looks like:

$$\begin{aligned} \left(i\hbar \frac{\partial}{\partial t} + E_{\kappa} - E_{\kappa'} \right) F_{1\kappa\kappa'} = & \sum_{\nu\nu'\mu\mu'} \langle \mu\nu | U | \mu'\nu' \rangle [\langle \nu\mu | F_2 | \mu'\nu' \rangle \delta_{\kappa\mu'} - \\ & - \langle \nu\mu | F_2 | \mu'\kappa' \rangle \delta_{\nu'\kappa} + \langle \kappa\mu | F_2 | \mu'\nu' \rangle \delta_{\kappa'\nu} - \langle \kappa\nu | F_2 | \mu'\nu' \rangle \delta_{\mu\kappa'}] \end{aligned} \quad (10.78)$$

$$\begin{aligned} & \left(i\hbar \frac{\partial}{\partial t} + E_{\kappa'} + E_{\kappa} - E_{\gamma} - E_{\gamma'} \right) \langle \kappa\kappa' | F_2 | \gamma\gamma' \rangle = \\ & = \sum_{\mu\mu'\nu\nu'} \langle \mu\nu | U | \mu'\nu' \rangle \langle [a_{\nu}^{\dagger} a_{\mu}^{\dagger} a_{\nu'} a_{\mu'}, a_{\kappa}^{\dagger} a_{\kappa'}^{\dagger} a_{\gamma} a_{\gamma'}] \rangle \end{aligned} \quad (10.79)$$

After calculations of commutators in (10.79) we obtain the averages of the product of three creation and three annihilation operators, which can be decoupled in the following way:

$$\begin{aligned} \langle a_\nu^+ a_\mu^+ a_{\nu'} a_{\kappa'}^+ a_\gamma a_{\gamma'} \rangle &\approx F_{1\nu\gamma'} F_{1\mu\nu'} F_{1\kappa'\gamma} + F_{1\nu\nu'} F_{1\mu\gamma} F_{1\kappa'\gamma'} + \\ &\quad + F_{1\nu\gamma} F_{1\mu\gamma'} (\delta_{\nu'\kappa'} - F_{1\kappa'\nu'}) \\ \langle a_\kappa^+ a_\nu^+ a_\mu^+ a_{\mu'} a_\gamma a_{\gamma'} \rangle &\approx F_{1\mu\mu'} F_{1\nu\gamma} F_{1\kappa\gamma'} + F_{1\kappa\mu'} F_{1\nu\gamma'} F_{1\kappa'\gamma'} + F_{1\kappa\gamma} F_{1\nu\mu'} F_{1\mu\gamma'} \end{aligned} \quad (10.80)$$

As before, analyzing only slow enough kinetic processes, in Eq. (10.79) we can replace $i\hbar \frac{\partial}{\partial t} \rightarrow i\varepsilon$, which allows (taking into account (10.80)) an immediate solution. After substitution of this solution into Eq. (10.78), we obtain the kinetic equation for $F_{1\kappa\kappa'}$. Assuming diagonal nature of $F_{1\kappa\kappa'} = F_{1\kappa} \delta_{\kappa\kappa'}$, we can reduce our kinetic equation to the following form:

$$\begin{aligned} \frac{\partial F_{1\kappa}}{\partial t} &= \frac{2\pi}{\hbar} \sum_{\nu\nu'\kappa'} |\langle \nu\nu' | U | \kappa\kappa' \rangle|^2 \delta(E_\nu + E_{\nu'} - E_\kappa - E_{\kappa'}) \\ &\quad [F_{1\nu}(1 - F_{1\kappa}) F_{1\nu'}(1 - F_{1\kappa'}) - F_{1\kappa}(1 - F_{1\nu}) F_{1\kappa'}(1 - F_{1\nu'})] \end{aligned} \quad (10.81)$$

In momentum representation:

$$|\kappa \rangle = \frac{1}{\sqrt{V}} e^{\frac{i}{\hbar} \mathbf{p} \mathbf{r}} \quad (10.82)$$

$$F_{1\kappa} \rightarrow n_{\mathbf{p}} \quad (10.83)$$

$$E_\kappa \rightarrow \varepsilon(\mathbf{p}) = p^2/2m \quad (10.84)$$

$$\langle \mu | e^{i\mathbf{k}\mathbf{r}} | \nu \rangle = \frac{1}{V} \int d\mathbf{r} e^{\frac{i}{\hbar} (\mathbf{p}' - \mathbf{p} + \mathbf{k}) \mathbf{r}} \quad \text{etc.} \quad (10.85)$$

so that kinetic equation for electrons is written as:

$$\begin{aligned} \frac{\partial n_{\mathbf{p}}}{\partial t} &= \frac{2\pi}{(2\pi\hbar)^6 \hbar} \int d\mathbf{p}'_1 d\mathbf{p}'_2 d\mathbf{p}_2 |U(\mathbf{p}_1 - \mathbf{p}'_1)|^2 \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}'_1 - \mathbf{p}'_2) \\ &\quad \delta(\varepsilon(\mathbf{p}_1) + \varepsilon(\mathbf{p}_2) - \varepsilon(\mathbf{p}'_1) - \varepsilon(\mathbf{p}'_2)) [n_{\mathbf{p}'_1} n_{\mathbf{p}'_2} (1 - n_{\mathbf{p}_1}) (1 - n_{\mathbf{p}_2}) - \\ &\quad - n_{\mathbf{p}_1} n_{\mathbf{p}_2} (1 - n_{\mathbf{p}'_1}) (1 - n_{\mathbf{p}'_2})] \end{aligned} \quad (10.86)$$

where $U(\mathbf{p})$ is the Fourier transform of interaction potential.

Writing the entropy of electron gas as in Eq. (4.15):

$$S = 2 \int \frac{d^3 p}{(2\pi)^3} [(1 - n_{\mathbf{p}}) \ln(1 - n_{\mathbf{p}}) - n_{\mathbf{p}} \ln n_{\mathbf{p}}] \quad (10.87)$$

and using (10.86) we can (after some tedious calculations) prove the quantum version of H - theorem: $\frac{dS}{dt} \geq 0$.

Equilibrium Fermi distribution:

$$n_{\mathbf{p}}^0 = \frac{1}{e^{\frac{\varepsilon(\mathbf{p}) - \mu}{T}} + 1} \quad (10.88)$$

leads to zero value of collision integral in Eq. (10.86), which can be checked by direct calculations, taking into account energy conservation law for scattering

particles, expressed by δ – function in collision integral. It can be easily seen in this case, that combination of (equilibrium) distribution functions in square brackets in (10.86) becomes an identical zero.

The derived expression for collision integral for the system of interacting electrons plays a major role in studies of low temperature kinetics in metals and other Fermi – liquids.

Chapter 11

BASICS OF THE MODERN THEORY OF MANY-PARTICLE SYSTEMS

11.1 Quasiparticles and Green's functions.

We have seen above the major role played by the concept of quasiparticles in the modern theory of condensed matter. Rigorous justification of this concept is achieved within the formalism of Green's functions, which is at present the standard apparatus of the theory of many particle systems. Green's functions approach allows clear formulation of the criteria of existence of quasiparticles in concrete systems (models) and gives the universal method of calculations, practically of any physical characteristics of many particle systems, with the account of different interactions. This method first appeared in quantum field theory, where it was widely accepted after the formulation of quite effective and convenient approach, based on the use of *Feynman diagrams*. Later it was applied to general many particle systems, which in fact lead to the creation of modern condensed matter theory [2]. Obviously, here we are unable to give the complete and coherent presentation of Green's functions formalism, our aim is only to introduce some of its major definitions and give the qualitative illustrations of some simple applications¹.

Below we mainly consider the case of temperature $T = 0$. Generalization of Green's functions approach to finite temperatures is rather straightforward and we shall briefly discuss it at the end of this Chapter. Let us start from the case

¹The most clear presentation of Green's functions method, as well as Feynman diagram technique, with applications to the problems of statistical physics, was given in the classic book by Abrikosov, Gorkov and Dzyaloshinskii [29]. Rather detailed material can be found in Ref. [2]. More elementary presentation on Green's functions is given in Refs. [30, 31, 32].

of a single quantum particle, described by Schroedinger equation²:

$$i\frac{\partial\psi(\mathbf{r},t)}{\partial t} - H\psi(\mathbf{r},t) = 0 \quad (11.1)$$

Instead of this equation, we may introduce the equation of motion for Green's function $G(\mathbf{r},t;\mathbf{r}',t')$:

$$i\frac{\partial G}{\partial t} - HG = i\delta(\mathbf{r} - \mathbf{r}')\delta(t - t') \quad (11.2)$$

with initial condition $G(\mathbf{r},t+0;\mathbf{r}',t) = \delta(\mathbf{r} - \mathbf{r}')$. Green's function represents the *probability amplitude* of particle transition from point \mathbf{r}' at the time moment t to point \mathbf{r} at the time moment t . The squared modulus of this amplitude gives the probability of this transition. We can see this expressing the ψ -function at the time moment $t + \tau$ via ψ -function at the time moment t :

$$\psi(\mathbf{r},t + \tau) = \int d\mathbf{r}' G(\mathbf{r},t + \tau;\mathbf{r}',t)\psi(\mathbf{r}',t) \quad (11.3)$$

It is easily seen, that $\psi(\mathbf{r},t + \tau)$ written in this way, satisfies Schroedinger equation (11.1), while for $\tau \rightarrow 0$ it transforms into $\psi(\mathbf{r},t)$ due to initial condition $G(\mathbf{r},t+0;\mathbf{r}',t) = \delta(\mathbf{r} - \mathbf{r}')$. Besides that, we assume (by definition) that $G = 0$ for $\tau < 0$ (causality!).

Consider eigenfunctions and eigenvalues of our Schroedinger equation:

$$H\varphi_\lambda(\mathbf{r}) = \varepsilon_\lambda\varphi_\lambda(\mathbf{r}) \quad (11.4)$$

The physical meaning of quantum numbers λ may be different, depending on the nature of the problem under discussion. In translation invariant system $\lambda \rightarrow \mathbf{p}$ – the momentum, for an electron in external magnetic field λ represents Landau quantum numbers etc. Let us consider a particle in potential field:

$$H = \frac{p^2}{2m} + V(\mathbf{r}) \quad (11.5)$$

In particular, this may correspond to a nontrivial problem of nucleons in potential well – an atomic nuclei [31], so that λ represents the quantum numbers of the shell model. Any solution of Schroedinger equation can be expanded over this (complete) system of eigenfunctions:

$$\psi(\mathbf{r},t) = \sum_\lambda c_\lambda(t)\varphi_\lambda(\mathbf{r}) \quad (11.6)$$

so that (11.3) can be written as:

$$c_\lambda(t + \tau) = \sum_{\lambda'} G_{\lambda\lambda'}(\tau)c_{\lambda'}(t) \quad (11.7)$$

$$G_{\lambda\lambda'}(\tau) = \int d^3r d^3r' G(\mathbf{r},\mathbf{r}'\tau)\varphi_\lambda^*(\mathbf{r})\varphi_{\lambda'}(\mathbf{r}') \quad (11.8)$$

²Below we use the system of units with $\hbar = 1$, which is standard in most modern texts. If necessary, the value of \hbar can be easily restored in final expressions.

which gives Green's function in λ -representation. As φ_λ is an eigenfunction of Hamiltonian H , which is time independent, there are no transitions to other states, so that $c_\lambda(t + \tau) = e^{-i\varepsilon_\lambda\tau}c_\lambda(t)$, i.e.

$$G_{\lambda\lambda'}(\tau) = G_\lambda(\tau)\delta_{\lambda\lambda'} = e^{-i\varepsilon_\lambda\tau}\theta(\tau) \quad (11.9)$$

where $\theta(\tau) = 1$ for $\tau \geq 0$ and $\theta(\tau) = 0$ for $\tau < 0$. Let us make Fourier transformation:

$$G_\lambda(\varepsilon) = \frac{1}{i} \int_{-\infty}^{\infty} d\tau e^{i\varepsilon\tau} G_\lambda(\tau) \quad (11.10)$$

$$G_\lambda(\tau) = i \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} e^{-i\varepsilon\tau} G_\lambda(\varepsilon) \quad (11.11)$$

Then, after an elementary integration we obtain:

$$G_\lambda(\varepsilon) = \frac{1}{\varepsilon - \varepsilon_\lambda + i\delta} \quad \delta \rightarrow +0 \quad (11.12)$$

The sign of $\delta \rightarrow 0$ is chosen to guarantee $G_\lambda(\tau) = 0$ for $\tau < 0$. In fact, we have:

$$\begin{aligned} G_\lambda(\tau) &= i \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} \frac{e^{-i\varepsilon\tau}}{\varepsilon - \varepsilon_\lambda + i\delta} \\ &= \begin{cases} e^{-i\varepsilon_\lambda\tau} & \text{for } \tau > 0 \\ 0 & \text{for } \tau < 0 \end{cases} \end{aligned} \quad (11.13)$$

The integrand here possesses a pole at $\varepsilon = \varepsilon_\lambda - i\delta$. Then, for $\tau > 0$ we can perform integration over ε closing the integration contour in lower half - plane of complex variable ε (as the factor of $e^{-i\varepsilon\tau}$ guarantees exponential damping of the integrand on semicircle at infinity), so that the pole is inside integration contour and the integral is easily calculated using Cauchy theorem, giving the result shown above. For $\tau < 0$, in a similar way, to make zero the contribution of semicircle at infinity, it is necessary to close integration contour in the upper half - plane of ε . Then, there is no pole inside integration contour and the integral is zero.

In the mixed $(\mathbf{r}, \varepsilon)$ representation we get:

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}', \varepsilon) &= \sum_{\lambda, \lambda'} G_{\lambda\lambda'}(\varepsilon) \varphi_\lambda(\mathbf{r}) \varphi_{\lambda'}^*(\mathbf{r}') = \\ &= \sum_{\lambda} \frac{\varphi_\lambda(\mathbf{r}) \varphi_\lambda^*(\mathbf{r}')}{\varepsilon - \varepsilon_\lambda + i\delta} \end{aligned} \quad (11.14)$$

Here the sum over λ is performed over all bound states of a particle in a field, as well as over the continuous spectrum. We see that $G(\mathbf{r}, \mathbf{r}', \varepsilon)$ possesses the poles at the values of ε equal to ε_λ - the energies of the bound states, and a cut (continuum of the poles) at the part of the real ε - axis, corresponding to continuous spectrum.

Let us consider now the many particle system. Below we are only dealing with systems consisting of Fermions. For the systems of Bose particles we may construct a similar approach, but we shall not discuss it here due to the lack of space, proper presentation can be found in Refs. [2, 29]. We shall start with the case of noninteracting Fermions (ideal Fermi gas). We have seen above, that

elementary excitations in this system are formed by pairs of particles (above the Fermi surface) and holes (below the Fermi surface).

Let us find the explicit form of Green's function $G_{\lambda\lambda'}(\tau)$, i.e. the transition amplitude of a single particle from state λ to state λ' , in a system of noninteracting Fermions. We have to take into account Pauli principle and exclude all transitions into occupied states. This is achieved by the introduction into the definition of Green's function of an extra factor $(1 - n_\lambda)$, where

$$n_\lambda = \begin{cases} 1 & \text{for } \varepsilon_\lambda \leq \varepsilon_F \\ 0 & \text{for } \varepsilon_\lambda > \varepsilon_F \end{cases} \quad (11.15)$$

is the number of particles in a state λ (Fermi distribution at $T = 0$). Thus, we obtain:

$$G_{\lambda\lambda'}^+(\tau) = (1 - n_\lambda)\delta_{\lambda\lambda'} \begin{cases} e^{-i\varepsilon_\lambda\tau} & \tau > 0 \\ 0 & \tau < 0 \end{cases} \quad (11.16)$$

Let us find similar expression for a hole. The number of "free" places for holes in a state λ is proportional to n_λ , so that

$$G_{\lambda\lambda'}^-(\tau) = n_\lambda\delta_{\lambda\lambda'} \begin{cases} e^{i\varepsilon_\lambda\tau} & \tau > 0 \\ 0 & \tau < 0 \end{cases} \quad (11.17)$$

where we have taken into account that energy of the hole, calculated with respect to Fermi level, has the sign opposite to that of a particle.

It is convenient to introduce Green's function $G_\lambda(\tau)$, defined both for $\tau > 0$ and $\tau < 0$:

$$G_\lambda(\tau) = \begin{cases} G_\lambda^+(\tau) & \text{for } \tau > 0 \\ -G_\lambda^-(\tau) & \text{for } \tau < 0 \end{cases} \quad (11.18)$$

Fourier transform of this function is easily calculated as:

$$\begin{aligned} G_\lambda(\varepsilon) &= -i(1 - n_\lambda) \int_0^\infty d\tau e^{-i\varepsilon_\lambda\tau + i\varepsilon\tau} + in_\lambda \int_{-\infty}^0 d\tau e^{i\varepsilon_\lambda\tau + i\varepsilon\tau} = \\ &= \frac{1 - n_\lambda}{\varepsilon - \varepsilon_\lambda + i\delta} + \frac{n_\lambda}{\varepsilon - \varepsilon_\lambda - i\delta} \end{aligned} \quad (11.19)$$

where $\delta \rightarrow +0$ is necessary to guarantee the convergence of integrals. This expressions is conveniently rewritten as:

$$\begin{aligned} G_\lambda(\varepsilon) &= \frac{1}{\varepsilon - \varepsilon_\lambda + i\delta \text{sign}\varepsilon_\lambda} = \\ &= \begin{cases} \frac{1}{\varepsilon - \varepsilon_\lambda + i\delta} & \varepsilon_\lambda > \varepsilon_F \\ \frac{1}{\varepsilon - \varepsilon_\lambda - i\delta} & \varepsilon_\lambda < \varepsilon_F \end{cases} \end{aligned} \quad (11.20)$$

where we have introduced the sign function: $\text{sign}(x) = 1$ for $x > 0$ and $\text{sign}(x) = -1$ for $x < 0$. Note that the Fourier transform of Green's function possesses a pole at ε equal to the energy of particle (hole).

Consider now the system of interacting Fermions (Fermi liquid). Single particle Green's function in the system of interacting particles is defined by the following expression:

$$G^+(\mathbf{r}t; \mathbf{r}'t')_{t > t'} = \langle 0 | \hat{\psi}(\mathbf{r}t) \hat{\psi}^+(\mathbf{r}'t') | 0 \rangle \quad (11.21)$$

where $|0\rangle$ is an exact eigenfunction of the ground state (“vacuum”), corresponding to the filled Fermi sphere, $\hat{\psi}(\mathbf{r}t)$ is Fermion creation operator in Heisenberg representation:

$$\hat{\psi}(\mathbf{r}t) = e^{iHt}\hat{\psi}(\mathbf{r})e^{-iHt} \quad (11.22)$$

where H is the total Hamiltonian of many particle system, which includes interactions. Operator $\hat{\psi}(\mathbf{r})$ can be expressed via annihilation operators a_λ of particles in eigenstates λ ($\hat{\psi}^+$ is similarly expressed via creation operators a_λ^+):

$$\hat{\psi}(\mathbf{r}) = \sum_{\lambda} a_{\lambda} \varphi_{\lambda}(\mathbf{r}) \quad (11.23)$$

Expression (11.21) obviously represents the amplitude of a particle propagation³ from point $(\mathbf{r}'t')$ to point $(\mathbf{r}t)$.

For a hole propagation we can write similarly:

$$G^-(\mathbf{r}t; \mathbf{r}'t')_{t > t'} = \langle 0 | \hat{\psi}^+(\mathbf{r}t) \hat{\psi}(\mathbf{r}'t') | 0 \rangle \quad (11.24)$$

where we have taken into account that (in Fermion system) annihilation of particle in a given point is equivalent to creation of a hole.

Expressions (11.21) and (11.24) are defined for $t > t'$. It is convenient to define a single Green's function, which for $t > t'$ describes a particle, while for $t < t'$ – hole (similarly to (11.18)):

$$G(\mathbf{r}t; \mathbf{r}'t') = \begin{cases} G^+(\mathbf{r}t; \mathbf{r}'t') & \text{for } t > t' \\ -G^-(\mathbf{r}'t'; \mathbf{r}t) & \text{for } t < t' \end{cases} \quad (11.25)$$

Another way to write this definition is:

$$G(x, x') = \langle 0 | T \hat{\psi}(x) \hat{\psi}^+(x') | 0 \rangle \quad (11.26)$$

where we have denoted $x = (\mathbf{r}t)$ and introduced an operator of T -ordering, which places all operators to the right of T in order of diminishing times in their arguments, taking also into account the change of signs due to (possible) permutations of Fermion operators. Formal definition of T -ordering (originating in quantum field theory) is written as:

$$T \{F_1(t_1)F_2(t_2)\} = \begin{cases} F_1(t_1)F_2(t_2) & \text{for } t_1 > t_2 \\ -F_2(t_2)F_1(t_1) & \text{for } t_1 < t_2 \end{cases} \quad (11.27)$$

for Fermion operators, and

$$T \{B_1(t_1)B_2(t_2)\} = \begin{cases} B_1(t_1)B_2(t_2) & \text{for } t_1 > t_2 \\ B_2(t_2)B_1(t_1) & \text{for } t_1 < t_2 \end{cases} \quad (11.28)$$

for Boson operators.

Green's function defined according to (11.26) is called Feynman or casual (T -ordered)⁴.

³Green's functions are often called *propagators*.

⁴Let us stress, that this definition is different from the definition of double time Green's function given in (9.22), and naturally appearing in the linear response theory, even if go to the limit of zero temperature. The advantage of the use of Feynman Green's functions is the possibility to construct diagram technique, much simplifying all calculations. There is no diagram technique to calculate double time Green's functions (9.22). There are certain exact relations and methods, allowing to express Green's functions of linear response theory via Feynman functions at $T = 0$ [29], as well as appropriate generalizations for the case of finite temperatures, to be considered below [2, 29]

Let us limit our consideration to an infinite (translation invariant) system, when $G(\mathbf{r}t; \mathbf{r}'t') = G(\mathbf{r} - \mathbf{r}', t - t')$. Accordingly, it is convenient to introduce the Fourier representation over $t - t'$ and $\mathbf{r} - \mathbf{r}'$:

$$G(\mathbf{p}\tau) = \int d^3r G(\mathbf{r}\tau) e^{-i\mathbf{p}\mathbf{r}} \quad (11.29)$$

where

$$G(\mathbf{p}\tau) = \begin{cases} \langle 0 | a_{\mathbf{p}} e^{-iH\tau} a_{\mathbf{p}}^{\dagger} | 0 \rangle e^{iE_0\tau} & \tau > 0 \\ - \langle 0 | a_{\mathbf{p}}^{\dagger} e^{iH\tau} a_{\mathbf{p}} | 0 \rangle e^{-iE_0\tau} & \tau < 0 \end{cases} \quad (11.30)$$

and E_0 is the ground state energy.

Quasiparticles in our system can be introduced, if the one particle Green's function can be written in the following form ($\tau > 0$):

$$G(\mathbf{p}\tau) \approx Z e^{-i(\varepsilon(\mathbf{p}) - \gamma(\mathbf{p}))\tau} + \dots \quad \text{and} \quad \gamma(\mathbf{p}) \ll \varepsilon(\mathbf{p}) \quad (11.31)$$

i.e. it contains a contribution, reminding the Green's function of an ideal Fermi gas, which we derived above. Eq. (11.31) means, that the state $|0\rangle$ contains a wave packet with amplitude Z , representing a quasiparticle with energy $\varepsilon(\mathbf{p})$ and *damping* $\gamma(\mathbf{p})$. The necessary requirement is the weakness of this damping $\gamma(\mathbf{p}) \ll \varepsilon(\mathbf{p})$, i.e. the requirement for a quasiparticle to be "well-defined"⁵. Similarly, for $\tau < 0$ we can define Green's function of a quasihole. Thus, in a system with well-defined quasiparticles, the Fourier transform of the Green's function (11.26) can be written as:

$$\begin{aligned} G(\mathbf{p}\varepsilon) &= Z \left\{ \frac{1 - n_{\mathbf{p}}}{\varepsilon - \varepsilon(\mathbf{p}) + i\gamma(\mathbf{p})} + \frac{n_{\mathbf{p}}}{\varepsilon - \varepsilon(\mathbf{p}) - i\gamma(\mathbf{p})} \right\} + G_{reg}(\mathbf{p}\varepsilon) = \\ &= \frac{Z}{\varepsilon - \varepsilon(\mathbf{p}) + i\gamma(\mathbf{p}) \text{sign}(p - p_F)} + G_{reg}(\mathbf{p}\varepsilon) \end{aligned} \quad (11.32)$$

We see that the pole of this expression defines the spectrum of quasiparticles and their damping. This is the most important property of Green's functions, allowing to determine the spectrum of elementary excitations in many particle system. The value of nonsingular term G_{reg} in (11.32) is determined by multiparticle excitations and, in most cases, is not of great interest. At the same time, we have to note that in systems with strong interactions (correlations) there are cases, when we can not separate a singular pole – like contribution to the Green's function, related to single particle elementary excitations (quasiparticles). Then, all physics is in fact determined by G_{reg} and situation becomes more complicated.

What for else do we need Green's functions? Actually, with their help we can calculate the averages (over the ground state) of different physical characteristics of our system. Using the *one particle* Green's function, introduced above, we can calculate the ground state averages of operators, which are represented by sums over all particles (one particle operators):

$$\hat{A} = \sum_i \hat{A}_i(\xi_i, \mathbf{p}_i) \quad (11.33)$$

⁵This condition is valid in Landau Fermi liquids, where close to Fermi surface we have $\varepsilon(\mathbf{p}) \approx v_F(|\mathbf{p}| - p_F)$, and $\gamma(\mathbf{p}) \sim (|\mathbf{p}| - p_F)^2$.

where ξ_i is the set of spatial and spin variables, while \mathbf{p}_i are momenta of all the particles of the system. Typical examples are:

$$n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (11.34)$$

– particle density at point \mathbf{r} ,

$$\mathbf{j}(\mathbf{r}) = \frac{e}{m} \sum_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (11.35)$$

– current density at point \mathbf{r} etc.

Operator \hat{A} in secondary quantization representation can be written as:

$$\hat{A} = \int d\xi \psi^+(\xi) A(\xi, \mathbf{p}) \psi(\xi) \quad (11.36)$$

Consider Green's function (11.25), (11.26) at $t = t' - 0$:

$$G(\xi, \xi', \tau)|_{\tau \rightarrow -0} = - \langle 0 | \psi^+(\xi') \psi(\xi) | 0 \rangle \quad (11.37)$$

Then, the ground state average value of operator \hat{A} is given by:

$$\langle A \rangle = \int d\xi A(\xi, \mathbf{p}) G(\xi, \xi', \tau = -0)|_{\xi = \xi'} = -SpAG|_{\tau = -0} \quad (11.38)$$

We conclude, that $G|_{\tau = -0}$ just coincides (up to a sign) with one particle density matrix (cf. (1.163)) at $T = 0$:

$$\rho(\xi', \xi) = \langle 0 | \psi^+(\xi') \psi(\xi) | 0 \rangle = -G|_{\tau = -0} \quad (11.39)$$

To find the averages of two particle operators like:

$$\hat{B} = \sum_{ik} B_{ik}(\xi_i \mathbf{p}_i; \xi_k \mathbf{p}_k) \quad (11.40)$$

we need to calculate two particle Green's function:

$$G_2(1, 2; 3, 4) = \langle 0 | T \psi(1) \psi(2) \psi^+(3) \psi^+(4) | 0 \rangle \quad (11.41)$$

etc.

From (11.37) we immediately obtain particle momentum distribution function as:

$$n(\mathbf{p}) = -i \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} G(\mathbf{p}\varepsilon) e^{-i\varepsilon\tau} |_{\tau \rightarrow -0} \quad (11.42)$$

Here we can not simply go to the limit of $\tau = 0$, as $G \sim \frac{1}{\varepsilon}$ and for $\varepsilon \rightarrow \infty$ the integral $\int d\varepsilon G(\mathbf{p}\varepsilon)$ diverges. For finite and negative τ we can transform the integral over real axis of ε to integral over the closed contour C , shown in Fig. 10-1. After that we can put $\tau = 0$, so that:

$$n(\mathbf{p}) = -i \int_C \frac{d\varepsilon}{2\pi} G(\mathbf{p}\varepsilon) \quad (11.43)$$

Consider Green's function like that of Eq. (11.32) (quasiparticles!):

$$G(\mathbf{p}\varepsilon) = \frac{Z}{\varepsilon - \varepsilon(\mathbf{p}) + i\gamma(\mathbf{p}) \text{sign}(p - p_F)} + G_{reg}(\mathbf{p}\varepsilon) \quad (11.44)$$

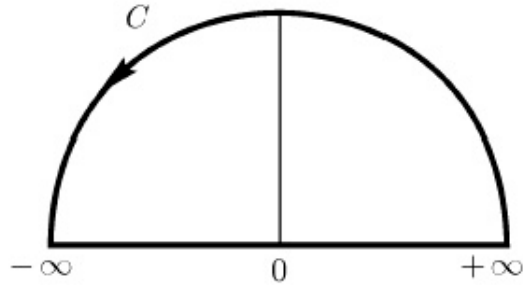


Figure 11.1: Integration contour used in calculations of distribution function.

We see that damping (imaginary part in the denominator of the first term) changes sign at $p = p_F$: it is positive for $p > p_F$ and negative for $p < p_F$. Thus, for $p < p_F$ we have a pole inside contour C , so that the integral is equal to Z , while for $p > p_F$ the pole is in the lower half-plane and the integral over C is equal to zero. Neglecting the regular many particle contribution G_{reg} we have:

$$n(p_F - 0) - n(p_F + 0) = Z \quad (11.45)$$

As $0 \leq n(p) \leq 1$, it follows that $0 < Z < 1$. Now it is clear, that the qualitative form of distribution function of Fermions at $T = 0$ (interacting Fermions, Fermi liquid!) has the form, shown in Fig. 10-2. Thus, despite the presence of

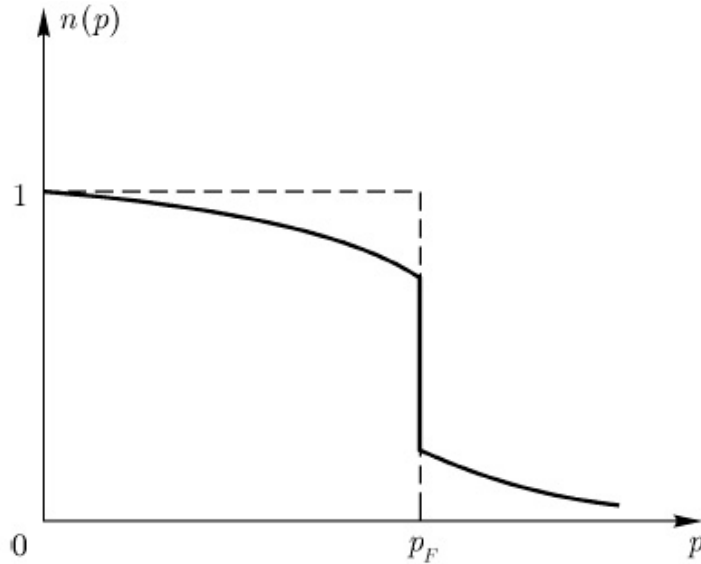


Figure 11.2: Qualitative form of distribution function of particles in Fermi liquid at $T = 0$.

interactions (not necessarily weak!), which “smears” momentum distribution of particles, there is still a “trace” of Fermi distribution for an ideal gas — even

in Fermi liquid there is a finite discontinuity in distribution function at $p = p_F$. This important result was first derived by Migdal, it gives a major microscopic justification of one of the most important assumptions of phenomenological Fermi liquid theory, introduced by Landau. Surely, our analysis is valid only for momenta p close enough to p_F , where concept of quasiparticles “works” due to $\gamma \sim (p - p_F)^2$, making damping small in comparison to the real part of the spectrum $\varepsilon(\mathbf{p}) \approx v_F(|\mathbf{p}| - p_F)$.

11.2 Feynman diagrams for many-particle systems.

Feynman diagram technique is an elegant and compact formulation of perturbation theory rules to calculate Green’s functions. Unfortunately, we are unable to present here the detailed derivation of these rules and the reader should address to Refs. [29, 2] for the complete presentation of Feynman’s approach. An elementary, though detailed enough, presentation can be found in Ref. [30]. Many examples of practical use of Feynman diagrams are given in Ref. [32]. Here we shall limit ourselves to formulation of elementary rules of diagram technique (without derivation), which is sufficient to get some impression of the method and not to be “frightened” by the appearance of Feynman diagrams, which are rather ubiquitous in modern literature.

To be concrete, let us consider the system of interacting Fermions, with the Hamiltonian, written in secondary quantization formalism as:

$$H = \sum_{\mathbf{p}} \varepsilon(\mathbf{p}) a_{\mathbf{p}}^+ a_{\mathbf{p}} + \frac{1}{2} \sum_{\mathbf{p}\mathbf{q}\mathbf{k}} V_{\mathbf{k}} a_{\mathbf{p}+\mathbf{k}}^+ a_{\mathbf{q}-\mathbf{k}}^+ a_{\mathbf{q}} a_{\mathbf{p}} \quad (11.46)$$

By definition, Green’s function $G(\mathbf{p}\tau)$ is dealing with the motion of a single particle. In the absence of interactions (free Green’s function) we can represent this motion by a straight line, e.g. directed from right to left. As unperturbed ground state of the system is the filled Fermi sphere, there is a possibility of a hole motion, which we shall represent by a straight line, directed from left to right. Thus, directed line represents the free Green’s function $G(\mathbf{p}\tau)$, corresponding to a free particle with momentum \mathbf{p} .

Interaction corresponds to scattering of one particle by another. In the first order of perturbation theory over $V_{\mathbf{k}}$, we have two types of scattering processes, represented by Feynman diagrams, shown in Fig. 10-3. Process corresponding

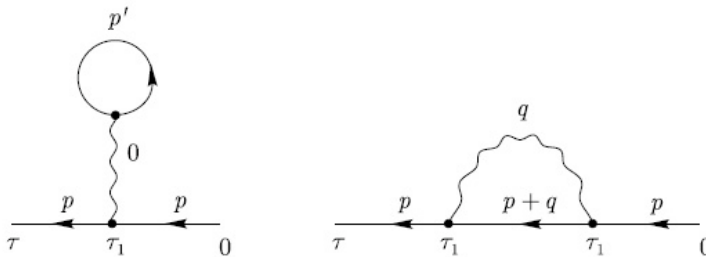


Figure 11.3: Diagrams of the first order for the Green’s function.

to the first diagram corresponds to a particle moving in a free way until it is directly scattered by particles inside the Fermi sphere (surface) at the time moment τ_1 , while afterwards it continues the free motion from time moment τ_1 to time moment τ . The act of interaction (scattering) is represented by the wavy line and a closed circle describes the process, when a particle is scattered from the state with some momentum below the Fermi surface and returned again to the same state. Process corresponding to second diagram represents the so called exchange scattering on particles below the Fermi surface, its meaning is obvious from the diagram itself – the free motion after scattering is continued by a particle excited from below of the Fermi surface, while initial particle has gone to a state below.

In the second order of perturbation theory, the number of possible scattering processes increases, examples of appropriate Feynman diagrams are shown in Fig. 10-4. All diagrams here, except the last one, show different combinations

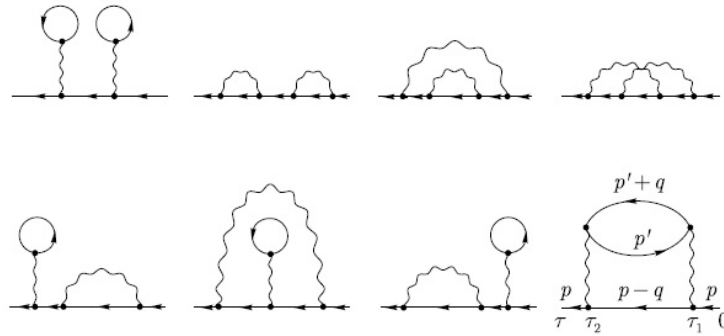


Figure 11.4: Examples of diagrams of the second order for the Green's function.

of scattering of the first order, considered above. The last diagram describes something new — at the moment τ_1 the particle is scattered, creating a particle – hole pair, exciting it from the states below the Fermi surface. At the moment τ_2 the particle is scattered again, as particle – hole pair annihilates, returning to the initial state. Physically, this process corresponds to polarization of particles below the Fermi surface.

Most conveniently, the rules of diagram technique are formulated for calculations of the Fourier transform of Green's function $G(\mathbf{p}\varepsilon)$. In this case arrows on lines, representing Green's functions, does not denote the direction of time, but correspond simple to incoming and outgoing “energies” ε and momenta \mathbf{p} , which are conserved in each vertex (interaction point). The rules to construct an analytic expression, corresponding to a given Feynman diagram, are formulated as follows:

1. To each straight line we attribute the value of momentum \mathbf{p} and “energy” ε , and write corresponding analytic expression:

$$iG_0(\mathbf{p}\varepsilon) = \frac{i}{\varepsilon - \varepsilon(\mathbf{p}) + i\delta \text{sign}\varepsilon(\mathbf{p})}. \quad (11.47)$$

2. To each interaction (wavy) line corresponds the factor $-iV_{\mathbf{q}}$ (in case of instantaneous interaction) or $-iV(\mathbf{q}\omega)$ for retarded interaction.

3. In each vertex (point, where wavy line is attached to Green's function lines) energy and momentum are conserved, with energies and momenta attributed to lines directed towards the vertex, taken with plus - sign, while energies and momenta attributed to outgoing lines are taken with minus - sign.

4. It is necessary to perform integration over each \mathbf{p} and ε not fixed by conservation laws:

$$\frac{1}{(2\pi)^4} \int d^3\mathbf{p} \int d\varepsilon \dots \quad (11.48)$$

5. Each closed Fermion loop is attributed an extra factor of (-1) .

6. Summation over spins (e.g. in a loop) introduces a factor of 2 (for Fermions with spin 1/2).

Consider the simplest expressions, corresponding to specific diagrams. For example, the first diagram of Fig. 11-3 corresponds to an analytic expression:

$$i^2 G_0(\mathbf{p}\varepsilon)(-iV_0) \left\{ \frac{2}{(2\pi)^3} \int d^3p' (-n(\mathbf{p}')) \right\} iG_0(\mathbf{p}\varepsilon) = G_0(\mathbf{p}\varepsilon)(-iV_0)NG_0(\mathbf{p}\varepsilon) \quad (11.49)$$

where in the first expression we already taken into account (11.43) and N is the total number of particles. This gives the so called Hartree correction. The second diagram of Fig. 11-3 gives:

$$i^2 G_0(\mathbf{p}\varepsilon) \frac{1}{(2\pi)^3} \int d^3q (-iV_{\mathbf{q}}) (-n(\mathbf{p} + \mathbf{q})) G_0(\mathbf{p}\varepsilon) \quad (11.50)$$

which is Fock correction. The last diagram of Fig. 11-4 corresponds to:

$$G_0(\mathbf{p}\varepsilon) \frac{1}{(2\pi)^4} \int d^3q \int d\omega iG_0(\mathbf{p} - \mathbf{q}\varepsilon - \omega) (-iV_{\mathbf{q}})^2 [-i\Pi_0(\mathbf{q}\omega)] G_0(\mathbf{p}\varepsilon) \quad (11.51)$$

where we have introduced the so called polarization operator, corresponding to the loop in this graph:

$$\begin{aligned} -i\Pi_0(\mathbf{q}\omega) &= 2(-i)(-1) \int \frac{d^3p'}{(2\pi)^3} \int \frac{d\varepsilon'}{2\pi} (i)^2 G_0(\mathbf{p}' + \mathbf{q}\varepsilon + \omega) G_0(\mathbf{p}'\varepsilon') = \\ &= i \int \frac{d^3p}{(2\pi)^3} \frac{n(\mathbf{p}) - n(\mathbf{p} - \mathbf{q})}{\varepsilon(\mathbf{p} - \mathbf{q}) - \varepsilon(\mathbf{p}) + \omega + i\delta \text{sign}\omega} \end{aligned} \quad (11.52)$$

Note that this expression gives only the simplest contribution to polarization operator, in general case we have to deal with higher order corrections, e.g. of the type shown in Fig. 10-5.

11.3 Dyson equation.

Remarkable property of Feynman diagram technique is the possibility to perform intuitively clear *graphical summation* of infinite series of diagrams. Let us denote an *exact* Green's function (taking into all interaction corrections) by a "fat"

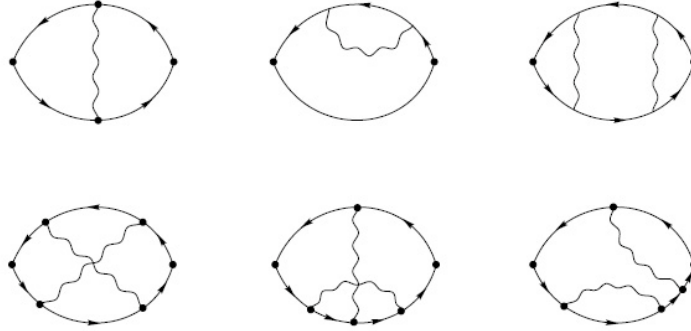


Figure 11.5: Higher corrections for polarization operator.

(or “dressed”) line, while the free particle Green’s function is denoted by a “thin” line as above. The total transition amplitude from point 2 to point 1 is, obviously, equal to the sum of all possible transition amplitudes, appearing in all orders of perturbation theory, i.e. to the sum of *all* diagrams of the type shown in Fig. 10-6. Now we can classify these diagrams in the following way. First of

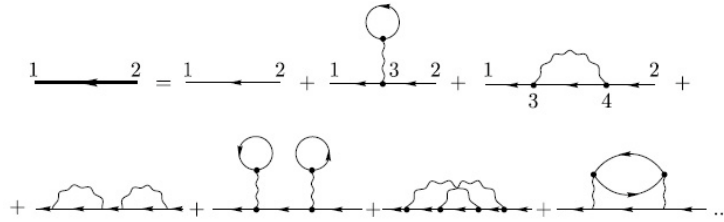


Figure 11.6: Diagrammatic series for the total (exact) Green’s function.

all we separate the single graph, corresponding to a free particle motion. All the remaining diagrams has the following form: up to some point the particle moves freely, then it is scattered, which leads to creation and annihilation of several particles and holes (or it is scattered by particles below the Fermi surface), then again it performs free motion, then it is scattered again etc. Let us denote as Σ the sum of all diagrams *which can not be cut over the single particle line*. Examples of such diagrams are shown in Fig. 10-7. Σ is called the *irreducible self-energy part*, or simply self-energy. It is easily seen, that the full (“dressed”) Green’s function is determined by the so called Dyson equation, derived graphically in Fig. 10-8. Analytically, it corresponds to the following integral equation:

$$G(1, 2) = G_0(1, 2) + \int d\tau_3 d\tau_4 G_0(1, 3) \Sigma(3, 4) G(4, 2) \quad (11.53)$$

Iterating this equation, we obviously obtain the complete perturbation series for the Green’s function. After Fourier transformation Dyson equations becomes a simple algebraic equation:

$$G(\mathbf{p}\varepsilon) = G_0(\mathbf{p}\varepsilon) + G_0(\mathbf{p}\varepsilon) \Sigma(\mathbf{p}\varepsilon) G(\mathbf{p}\varepsilon), \quad (11.54)$$

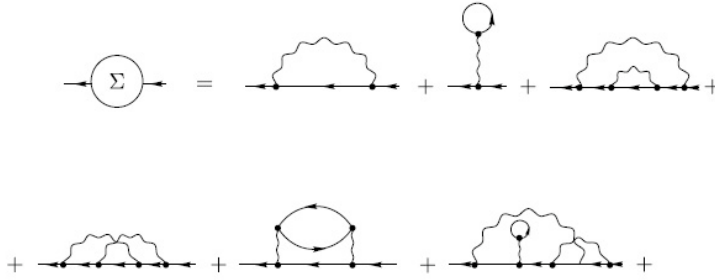


Figure 11.7: Simplest diagrams for irreducible self-energy part.

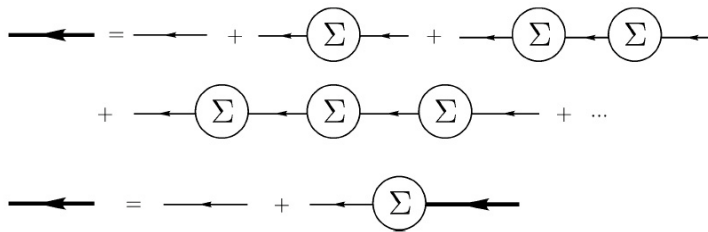


Figure 11.8: Diagrammatic derivation of Dyson equation.

which is easily solved as:

$$G(\mathbf{p}\varepsilon) = \frac{1}{\varepsilon - \varepsilon(\mathbf{p}) - \Sigma(\mathbf{p}\varepsilon)} \quad (11.55)$$

where we have taken into account the explicit form of $G_0(\mathbf{p}\varepsilon)$. It is clear that self-energy part $\Sigma(\mathbf{p}\varepsilon)$ describes in a compact way all the changes of a particle motion due to its interactions with all other particles in the system. In general case, self-energy is a complex function consisting of real and imaginary parts (this why in Eq. (11.55) we have dropped infinitesimally small imaginary contribution from free particle Green's function $i\delta\text{sign}(\varepsilon - \varepsilon_F)$). The energy of quasiparticle can be determined now as a solution of the equation, determining the pole of the total Green's function:

$$\varepsilon = \varepsilon(\mathbf{p}) + \Sigma(\mathbf{p}\varepsilon) \quad (11.56)$$

In real case the solution of this equation for ε may be quite complicated.

For the examples given above in Eqs. (11.49), (11.50) and (11.51), the appropriate contributions to self-energy part are:

$$\Sigma_H = NV_0 \quad (11.57)$$

$$\Sigma_F = - \int \frac{d^3q}{(2\pi)^3} V_{\mathbf{q}} n(\mathbf{p} + \mathbf{q}) \quad (11.58)$$

$$\Sigma_{pol} = \int \frac{d^3q}{(2\pi)^3} \int \frac{d\omega}{2\pi} V_{\mathbf{q}}^2 \Pi_0(\mathbf{q}\omega) G_0(\mathbf{p} - \mathbf{q}\varepsilon - \omega) \quad (11.59)$$

Let us return once again to the question of possibility to introduce well-defined quasiparticles, i.e. to reduce the *exact* Green's function to the form given by

Eq. (11.32). In Fermi system, it is convenient to count all energies from the chemical potential μ . For free particles we have $\varepsilon(\mathbf{p}) = \frac{p^2}{2m} - \mu$. In isotropic system (Fermi liquid) $\Sigma(\mathbf{p}\varepsilon)$ depends only on the absolute value of \mathbf{p} . Let us define the value of Fermi momentum p_F (radius of Fermi sphere) for the system of *interacting* Fermions by the following equation:

$$\frac{p_F^2}{2m} + \Sigma(p_F, 0) = \mu \quad (11.60)$$

This definition assumes, of course, that $Im\Sigma(p, 0) \rightarrow 0$ for $p \rightarrow p_F, \varepsilon \rightarrow 0$ (Fermi liquid behavior!). For the system of interacting Fermions we can prove in rather general form, that $Im\Sigma(p\varepsilon) \sim Max\{\varepsilon^2, (p-p_F)^2\}sign\varepsilon$. Then, expanding $\Sigma(p\varepsilon)$ in power series over $p - p_F$ and ε , we obtain the following expression for $G(p\varepsilon)$ close to the Fermi surface:

$$\begin{aligned} G^{-1} &= \varepsilon - \frac{p^2}{2m} + \mu - \Sigma(p\varepsilon) \approx \\ &\approx \varepsilon - \frac{p^2}{2m} + \mu - \Sigma(p_F, 0) - \left(\frac{\partial\Sigma}{\partial p}\right)_F (p - p_F) - \left(\frac{\partial\Sigma}{\partial\varepsilon}\right)_F \varepsilon + i\alpha|\varepsilon|\varepsilon = \\ &= \left[1 - \left(\frac{\partial\Sigma}{\partial\varepsilon}\right)_F\right] \varepsilon - \left[\frac{p_F}{m} + \left(\frac{\partial\Sigma}{\partial p}\right)_F\right] (p - p_F) + i\alpha'|\varepsilon|\varepsilon \end{aligned} \quad (11.61)$$

where $\alpha' = const.$ From Eq. (11.61) we can see, that Green's function can be written in the required form:

$$G(p\varepsilon) = \frac{Z}{\varepsilon - v_F(p - p_F) + i\alpha|\varepsilon|\varepsilon} + G_{reg} \quad (11.62)$$

where G_{reg} contains all contributions dropped in (11.61), and we defined:

$$Z^{-1} = 1 - \left(\frac{\partial\Sigma}{\partial\varepsilon}\right)_F = \left(\frac{\partial G^{-1}}{\partial\varepsilon}\right)_F \quad (11.63)$$

$$v_F = \frac{p_F}{m^*} = \frac{\frac{p_F}{m} + \left(\frac{\partial\Sigma}{\partial p}\right)_F}{\left(\frac{\partial G^{-1}}{\partial\varepsilon}\right)_F} = -\frac{\left(\frac{\partial G^{-1}}{\partial p}\right)_F}{\left(\frac{\partial G^{-1}}{\partial\varepsilon}\right)_F} \quad (11.64)$$

$$(11.65)$$

where $\alpha = Z\alpha'$. Thus, we obtain the Green's function of Fermion quasiparticles with an effective mass m^* , which, as everything else, is determined by the behavior of $\Sigma(p\varepsilon)$ close to the Fermi level (surface). Note that in a simplified case, when $\Sigma(p\varepsilon)$ does not depend on p , so that $\left(\frac{\partial\Sigma}{\partial p}\right)_F = 0$, we have:

$$\frac{p_F}{m^*} = \frac{p_F}{m} Z \quad \text{i.e.} \quad \frac{m^*}{m} = Z^{-1} \quad (11.66)$$

so that Z simply renormalizes mass of the quasiparticle. Due to the general property of $Z < 1$, effective mass in Fermi liquid is larger, than the mass of free particles.

All these properties of $\Sigma(p\varepsilon)$ are rather easily confirmed, if we limit ourselves to the contributions of simplest Feynman diagrams, both for the case of point-like or Coulomb interactions. Rigorous choice and summation of "dominating"

(sub)series of diagrams can be done for the cases of high or (inversely) low density of Fermions, when there exist appropriate small parameters, allowing the use of perturbation theory [29, 2, 30]. All basic assumptions of Fermi liquid theory are thus explicitly confirmed by microscopic calculations. In general case, when there is no small parameter and no “dominating” subseries of diagrams (typical example are electrons in metals!), formally all diagrams are to be taken into account and we can only limit ourselves to rather general analysis, of the kind briefly illustrated above, which constitutes the basis of microscopic version of Landau Fermi liquid approach.

In recent years, the number of models of the so called strongly correlated systems demonstrated non Fermi liquid behavior, breaking the main assumptions of Landau theory, such as the possibility to introduce the well-defined quasiparticles. This is rather typical situation in low dimensional systems, especially in one dimensional case. Two dimensional systems form apparently a kind of borderline between non Fermi liquid and Fermi liquid behavior, situation here is under active discussion at present, e.g. with respect to the properties of high-temperature superconductors in the normal state.

Similar diagram technique can be constructed for all other basic types of interactions in many particle systems, such as electron – phonon interaction, scattering by impurities etc. Depending on the type of interaction, we can have different topologies of Feynman diagrams and diagram rules. For example, in the case of electron – phonon interaction wavy lines denote phonon (Bose) Green’s functions, while in the case of random impurity scattering diagrams do not have closed Fermion loops etc. Details of all these cases can be found e.g. in Refs. [29, 32].

11.4 Effective interaction and dielectric screening.

As another example of the use of diagrammatic approach, below we shall discuss diagram summation, leading to the concept of an effective (screened) interaction in Fermion system. Let us define the effective (renormalized or full) interaction by diagrams, shown in Fig. 10-9. In Fig. 10-10 we show diagrams for the

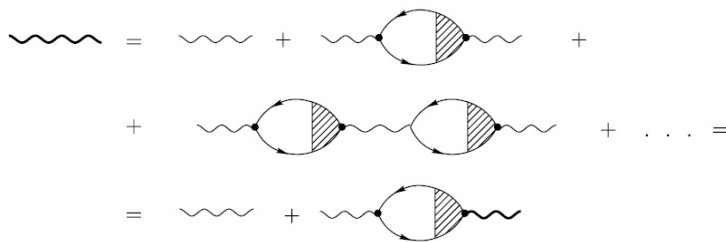


Figure 11.9: Feynman diagrams for effective interaction between particles.

full polarization operator (containing higher order corrections) and for the so called *vertex parts*, representing complicated “blocks” of diagrams, describing the processes of multiple scatterings of Fermions. Unfortunately, for vertex parts we can not find in general the closed integral equations, similar to Dyson

equation discussed above. It is only possible in some specific approximations and models. The screened effective interaction (“fat” wavy line in Fig. 11-

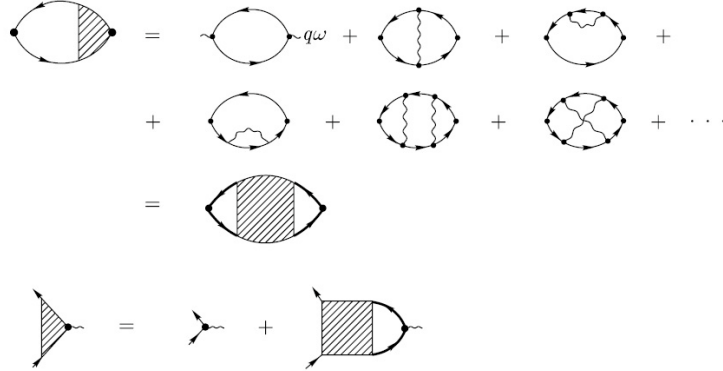


Figure 11.10: Full polarization operator and vertex parts.

9) can be related to frequency and wave vector dependent dielectric function of the system $\epsilon(\mathbf{q}\omega)$. Using diagrams shown in Fig 11-9, we get the screened interaction as:

$$\begin{aligned}
 -i\mathcal{V}(\mathbf{q}\omega) &\equiv -\frac{iV_{\mathbf{q}}}{\epsilon(\mathbf{q}\omega)} = \\
 &= -iV_{\mathbf{q}} + (-iV_{\mathbf{q}})[-i\Pi(\mathbf{q}\omega)](-iV_{\mathbf{q}}) + (-iV_{\mathbf{q}})[-i\Pi(\mathbf{q}\omega)](-iV_{\mathbf{q}})[-i\Pi(\mathbf{q}\omega)](-iV_{\mathbf{q}}) + \dots \\
 &= -iV_{\mathbf{q}} + (-iV_{\mathbf{q}})[-i\Pi(\mathbf{q}\omega)](-i\mathcal{V}(\mathbf{q}\omega)) = \\
 &= -iV_{\mathbf{q}} + (-iV_{\mathbf{q}})[-i\Pi(\mathbf{q}\omega)](-iV_{\mathbf{q}})\frac{1}{\epsilon(\mathbf{q}\omega)} = \\
 &= -iV_{\mathbf{q}} \left\{ 1 - V_{\mathbf{q}}\Pi(\mathbf{q}\omega)\frac{1}{\epsilon(\mathbf{q}\omega)} \right\}
 \end{aligned}$$

so that:

$$\frac{1}{\epsilon(\mathbf{q}\omega)} = 1 - V_{\mathbf{q}}\Pi(\mathbf{q}\omega)\frac{1}{\epsilon(\mathbf{q}\omega)} \quad (11.67)$$

From here we obtain the general expression for dielectric function (permeability) of many particle system via polarization operator:

$$\epsilon(\mathbf{q}\omega) = 1 + V_{\mathbf{q}}\Pi(\mathbf{q}\omega) \quad (11.68)$$

In case of Coulomb interaction in the system of electrons we have $V_q = \frac{4\pi e^2}{q^2}$, so that:

$$\epsilon(\mathbf{q}\omega) = 1 + \frac{4\pi e^2}{q^2}\Pi(\mathbf{q}\omega) \quad (11.69)$$

Consider the simplest approximation for polarization operator (11.52)⁶. After calculation of all integrals, this polarization operator can be written as [29, 30, 32]:

$$\Pi_0(q\omega) = \nu_F\Phi(q\omega) \quad (11.70)$$

⁶This approximation is justified in the limit of high enough density of electrons, when Coulomb interaction can be considered weak. Appropriate estimates were given above during the discussion of basic properties of Fermi gases.

where ν_F is electron density of states at the Fermi level and

$$\begin{aligned}\Phi(q\omega) &= \frac{1}{2} \int_{-1}^1 dx \frac{v_F q x}{\omega - v_F q x} = \\ &= 1 - \frac{\omega}{2v_F q} \ln \left| \frac{\omega + v_F q}{\omega - v_F q} \right| + i\pi \frac{\omega}{2v_F q} \theta(v_F q - \omega).\end{aligned}\quad (11.71)$$

In particular, $\Phi(q0) = 1$, which gives:

$$\Pi(q0) = \nu_F \quad (11.72)$$

Then we obtain:

$$\epsilon(q0) = 1 + \frac{4\pi e^2}{q^2} \nu_F = 1 + \frac{\kappa^2}{q^2} \quad (11.73)$$

where

$$\kappa^2 = 4\pi e^2 \nu_F \quad (11.74)$$

Accordingly:

$$\mathcal{V}(q0) = \frac{4\pi e^2}{q^2 \epsilon(q0)} = \frac{4\pi e^2}{q^2 + \kappa^2} \quad (11.75)$$

which describes the so called debye screening of Coulomb potential in quantum plasma of electrons at temperature $T = 0$. Obviously, in coordinate space we have $\mathcal{V}(r) = \frac{e^2}{r} e^{-\kappa r}$, so that Eq. (11.74), in fact, determines the screening radius κ^{-1} .

In the inverse limit of high frequencies of $\omega \gg v_F q$, we can show that $\Phi(q\omega) = -\frac{v_F^2 q^2}{3\omega^2}$, so that:

$$\epsilon(\omega) = 1 - \frac{4\pi e^2 v_F^2}{3\omega^2} \nu_F = 1 - \frac{4\pi n e^2}{m\omega^2} = 1 - \frac{\omega_p^2}{\omega^2} \quad (11.76)$$

Here we used $\nu_F = \frac{3}{2} \frac{n}{\epsilon_F}$, where n is density (concentration) of electrons. We also introduced the square of plasma frequency:

$$\omega_p^2 = \frac{4\pi n e^2}{m} \quad (11.77)$$

Equation $\epsilon(q\omega) = 0$ determines the frequency of plasma oscillations (plasmons) for the whole range of q . In particular, for small values of q , when plasmon damping is absent, we can find the dispersion (spectrum) of plasmons as:

$$\omega^2 = \omega_p^2 + \frac{3}{5} v_F q^2 \quad (11.78)$$

In fact, the frequency of plasmons is very weakly dependent on their wavelength and this dispersion is just a small correction.

11.5 Green's functions at finite temperatures.

Feynman diagram technique discussed above was generalized by Matsubara to the case of finite temperatures [29]. Below we shall briefly discuss this generalization, limiting discussion to Fermi systems only. Thermodynamic Green's function of a Fermi particle is defined according to Matsubara as:

$$\mathcal{G}(\mathbf{p}, \tau_2 - \tau_1) = -i \langle T a_{\mathbf{p}}(\tau_2) a_{\mathbf{p}}^+(\tau_1) \rangle \quad (11.79)$$

where, by definition:

$$a_{\mathbf{p}}(\tau) = e^{(H-\mu N)\tau} a_{\mathbf{p}} e^{-(H-\mu N)\tau} \quad (11.80)$$

and $0 < \tau_1, \tau_2 < \beta = \frac{1}{T}$ are real variables, while the angular brackets denote averaging over the grand canonical Gibbs distribution, which is convenient to write here as:

$$\langle A \rangle = \frac{Sp\rho A}{Sp\rho} \quad \text{where} \quad \rho = e^{-\beta(H-\mu N)} \quad (11.81)$$

Taking into account that $Z = Sp\rho$, this is equivalent to the definition used above. The reason why the Green's function \mathcal{G} can be represented by the same diagrammatic series as Green's function G , previously defined for the case of $T = 0$, can be seen as follows. We have seen that diagrammatic expansion for G is the fundamental consequence of time dependent Schroedinger equation (11.1). Statistical operator ρ , written in the form of (11.81), satisfies the so called Bloch equation:

$$\frac{\partial \rho}{\partial \beta} = -(H - \mu N)\rho \quad (11.82)$$

which is easily verified by direct differentiation. Now we see the direct correspondence between time dependent Schroedinger equation (11.1):

$$\psi \leftrightarrow \rho \quad H \leftrightarrow H - \mu N \quad it \leftrightarrow \beta \quad (11.83)$$

Thus, making the substitution:

$$H \rightarrow H - \mu N \quad it \rightarrow \tau \quad (11.84)$$

in all expressions of previous paragraphs we can obtain the diagrammatic technique for \mathcal{G} , which is practically of the same form as in the case of $T = 0$. Substitution $H \rightarrow H - \mu N$ only shifts of energy scale of single particle energy by μ :

$$H_0 - \mu N = \sum_{\mathbf{p}} (\varepsilon(\mathbf{p}) - \mu) a_{\mathbf{p}}^+ a_{\mathbf{p}} \quad (11.85)$$

Though Matsubara's Green' functions \mathcal{G} depend on "imaginary time" τ ⁷, we can always perform transformation to real time in final expression putting $\tau \rightarrow it$, or more precisely, making an analytic continuation to the real axis of time.

We noted above that the values of τ_1 and τ_2 in (11.79) vary in the interval from 0 to β . Thus, to make transformation to (\mathbf{p}, ω) representation, we have to introduce the periodically continues function \mathcal{G} , obtained by periodic repetition of \mathcal{G} on the interval from $-\infty$ to ∞ . For this function we can write down an expansion into Fourier *series*:

$$\mathcal{G}(\mathbf{p}\tau) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} e^{-i\omega_n \tau} \mathcal{G}(\mathbf{p}\omega_n) \quad (11.86)$$

where summation is performed over discrete (Matsubara) frequencies $\omega_n = \pi n T$. Accordingly

$$\mathcal{G}(\mathbf{p}\omega_n) = \frac{1}{2} \int_{-\beta}^{\beta} d\tau e^{i\omega_n \tau} \mathcal{G}(\mathbf{p}\tau) \quad (11.87)$$

⁷The variable τ is real, but Green's function \mathcal{G} is obtained from G by the replacement $it \rightarrow \tau$, so that actually we are making transformation to "imaginary time" $t = -i\tau$.

“Time” difference $\tau = \tau_2 - \tau_1$ varies in the interval $(-\beta, \beta)$, as the values of τ_1 and τ_2 vary in the interval $(0, \beta)$. The function $\mathcal{G}(\mathbf{p}\tau)$ periodically repeat itself in the intervals $(-\beta, \beta), (\beta, 3\beta), (3\beta, 5\beta), \dots, (-3\beta, -\beta), \dots$. For the system consisting of Fermions, the even values of n drop out of the series for $\mathcal{G}(\mathbf{p}\tau)$ due to “quasiperiodic” boundary condition:

$$\mathcal{G}(\mathbf{p}, \tau) = -\mathcal{G}(\mathbf{p}, \tau + \beta) \quad \text{for } \tau < 0 \quad (11.88)$$

To see the validity of this relation, we can use the property $SpAB = SpBA$. Assuming $\tau' - \tau > 0$, we have:

$$\begin{aligned} \mathcal{G}(\mathbf{p}, \tau - \tau') &= \frac{i}{Z} Sp e^{-\beta(H-\mu N)} a_{\mathbf{p}}^+(\tau') a_{\mathbf{p}}(\tau) = \\ &= \frac{i}{Z} Sp a_{\mathbf{p}}(\tau) e^{-\beta(H-\mu N)} a_{\mathbf{p}}^+(\tau') e = \\ &= \frac{i}{Z} Sp e^{-\beta(H-\mu N)} e^{\beta(H-\mu N)} a_{\mathbf{p}}(\tau) e^{-\beta(H-\mu N)} a_{\mathbf{p}}^+(\tau') = \\ &= \frac{i}{Z} Sp e^{-\beta(H-\mu N)} a_{\mathbf{p}}(\tau + \beta) a_{\mathbf{p}}^+(\tau') \end{aligned} \quad (11.89)$$

or

$$\mathcal{G}(\mathbf{p}, \tau - \tau') = -\mathcal{G}(\mathbf{p}, \tau - \tau' + \beta) \quad (11.90)$$

which for $\tau' = 0$ just coincides with (11.88). The minus sign appeared here due to anticommutation of Fermi operators. Substituting (11.88) into (11.86) we can see, that all terms with even n become zero. Thus, for Fermions we are always dealing with odd Matsubara frequencies:

$$\omega_n = \frac{(2n+1)\pi}{\beta} = (2n+1)\pi T \quad (11.91)$$

In a similar way, for Bosons only even Matsubara frequencies remain:

$$\omega_n = \frac{2n\pi}{\beta} = 2n\pi T \quad (11.92)$$

Remembering Eqs. (11.16), (11.17) and (11.18) for free particle Green's functions at $T = 0$, we can easily write down Matsubara's Green's for free Fermions as:

$$\mathcal{G}_0(\mathbf{p}, \tau_2 - \tau_1) = -i\{\theta(\tau_2 - \tau_1)(1 - n(\mathbf{p})) - \theta(\tau_1 - \tau_2)n(\mathbf{p})\}e^{-(\varepsilon(\mathbf{p})-\mu)(\tau_2-\tau_1)} \quad (11.93)$$

where $n(\mathbf{p}) = [e^{\beta(\varepsilon(\mathbf{p})-\mu)} + 1]^{-1}$ is Fermi distribution for finite T . Thus, the step-like functions, entering the definition of G_0 at $T = 0$ are “smeared” by finite T , so that the state with a given \mathbf{p} can be filled either by particle or a hole.

Substituting (11.93) into (11.87) we find:

$$\mathcal{G}_0(\mathbf{p}\omega_n) = \frac{i}{i\omega_n - \varepsilon(\mathbf{p}) + \mu} \quad \omega_n = (2n+1)\pi T \quad (11.94)$$

With the only change, related to the transition to discrete frequencies, which also “conserve” in the vertices, Matsubara's diagram technique for $T > 0$ is

practically identical to Feynman technique for $T = 0$. In particular, the full (exact) Green's function is determined by Dyson equation:

$$\mathcal{G}(\mathbf{p}\omega_n) = \frac{i}{i\omega_n - \varepsilon(\mathbf{p}) + \mu - \Sigma(\mathbf{p}\omega_n)}, \quad \omega_n = (2n + 1)\pi T \quad (11.95)$$

However, we must stress that Matsubara's Green's functions are not quantum propagators (transition amplitudes) at all!

Calculation of Matsubara's Green's functions allows, in principle, to find arbitrary thermodynamic characteristics of the many particle system at finite temperatures. In particular, it is possible to construct diagrammatic expansion for interaction correction to thermodynamic potential Ω [29]. Appropriate diagrams of the lowest orders are shown in Fig. 10-11. For concreteness we show

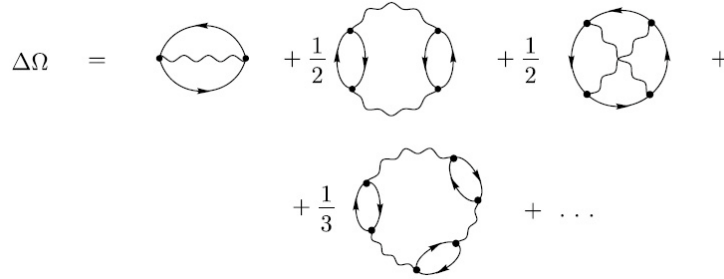


Figure 11.11: Diagrammatic expansion for thermodynamic potential.

here diagrams for the case of interacting Fermions. Perturbation series for $\Delta\Omega$ consists of loop diagrams, restricted to the case of connected diagrams only. Certain difficulty here is related to the appearance in this series of an extra combinatorial factor of $\frac{1}{n}$ for every contribution of the n -th order. This makes a series for $\Delta\Omega$ rather inconvenient for summation. In particular, for $\Delta\Omega$ we can not derive any analogue of Dyson equation. As $\Omega = -VP(\mu, T)$, in fact here we are calculating the corrections to pressure $\Delta P = P - P_0(\mu, T)$, where P_0 is the pressure in a system of free particles (ideal gas), so that we are actually dealing with quantum corrections to the equation of state.

Finally, we shall mention the diagram technique, proposed by Keldysh, which is applicable to finite temperatures and, more importantly, to the analysis of nonequilibrium processes in many particle systems in real time, including the derivation of kinetic equations. Detailed enough presentation of this technique can be found in Ref. [15].

Appendix A

Motion in phase space, ergodicity and mixing.

A.1 Ergodicity.

From classical mechanics it is known, that differential equations of motion of any conservative mechanical system can be written in Hamilton form:

$$\dot{q}_k = \frac{\partial H}{\partial p_k} \quad \dot{p}_k = -\frac{\partial H}{\partial q_k} \quad (\text{A.1})$$

where q_k, p_k are generalized coordinates and momenta ($k = 1, 2, \dots, n = 3N$, i.e. in total we have $2n = 6N$ equations, where N is the number of particles in the system and n is the number of degrees of freedom),

$$H(p, q) = H(p_1, p_2, \dots, p_n; q_1, q_2, \dots, q_n) \quad (\text{A.2})$$

is the Hamiltonian of the system, which is equal to the total energy, expressed as a function of generalized coordinates and momenta. Hamiltonian is related to Lagrangian L by the well known relation:

$$H = \sum_{k=1}^n p_k \dot{q}_k - L \quad (\text{A.3})$$

Equations of motion (A.3) can be integrated and their solutions can be written in the following form¹:

$$p_k = \varphi_k(q_i^0, p_i^0, t) \quad q_k = \psi_k(q_i^0, p_i^0, t) \quad (\text{A.4})$$

where q_i^0, p_i^0 are initial values of coordinates and momenta. Functions φ_k, ψ_k represent (according to Cauchy theorem) single valued and continuous functions of arguments q_i^0, p_i^0 .

To obtain (conserving) integrals of motion we can use the following procedure. Divide by equation $\dot{p}_1 = -\frac{\partial H}{\partial q_1}$ all the other $2n - 1$ equations (A.1). Then we get:

$$\frac{dq_1}{dp_1} = -\frac{\frac{\partial H}{\partial p_1}}{\frac{\partial H}{\partial q_1}}, \quad \dots, \quad \frac{dp_n}{dp_1} = -\frac{\frac{\partial H}{\partial q_n}}{\frac{\partial H}{\partial q_1}} \quad (\text{A.5})$$

¹Below we mainly follow Ref. [10]

This system of equations does not contain time t (for H independent of t) and defines conserving quantities. In total it gives $2n - 1$ integrals of motion, including obviously energy, which we denote as:

$$\Phi_1(q, p) \equiv H(p, q) = \alpha_1 = E \quad (\text{A.6})$$

Then, the rest of $2n - 2$ integrals of motion can be written as:

$$\begin{aligned} \Phi_2(q, p) = \alpha_2, \dots, \Phi_n(q, p) = \alpha_n \\ \Psi_2(q, p) = \beta_2, \dots, \Psi_n(q, p) = \beta_n \end{aligned} \quad (\text{A.7})$$

where $\alpha_1, \dots, \alpha_n; \beta_2, \dots, \beta_n$ are integration constants. One more integral of motion is obtained solving the equation $\dot{p}_1 = -\partial H/\partial q_1$ and using Eqs. (A.6),(A.7). This can be written as:

$$\Psi_1(q, p) = t + \beta_1 \quad (\text{A.8})$$

Addition to t of an arbitrary constant does not change equations of motion, as time t enters only through differentials.

Consider the simplest example of a system with one degree of freedom — the harmonic oscillator. Then (putting the mass $m = 1$) the Hamiltonian is written as:

$$H = \frac{1}{2}(p^2 + \omega^2 q^2). \quad (\text{A.9})$$

Hamilton equations of motion now are:

$$\dot{q} = \frac{\partial H}{\partial p} = p \quad \dot{p} = -\frac{\partial H}{\partial q} = -\omega^2 q \quad (\text{A.10})$$

which give the following solutions (integrals):

$$q = q^0 \cos \omega t + \frac{p^0}{\omega} \sin \omega t, \quad p = -\omega q^0 \sin \omega t + p^0 \cos \omega t \quad (\text{A.11})$$

which can be rewritten as energy integral:

$$2H = p^2 + \omega^2 q^2 = 2E \quad (\text{A.12})$$

and the relation, determining the dependence of p and q on time:

$$\frac{1}{\omega} \arccos \frac{\omega q}{\sqrt{p^2 + \omega^2 q^2}} = t + \beta \quad (\text{A.13})$$

Oscillator with one degree of freedom possesses these two integrals of motion. Mechanical state of oscillator is represented by a point on (p, q) – plane, which is the phase space for this simple system. The motion of the system is represented by phase point movement over the “ergodic surface” (line on (p, q) – plane), determined by the value of energy E . These lines of constant energies, as is obvious from Eq. (A.12), form the ellipses, like those shown in Fig. A-1). The second integral (A.13) determines the velocity of phase point movement over these ellipses. Integrals of motion for oscillator (A.11) can be rewritten, using Eqs. (A.12),(A.13), as:

$$q = \frac{\sqrt{2E}}{\omega} \sin \omega(t + \beta) \quad p = \sqrt{2E} \cos(t + \beta). \quad (\text{A.14})$$

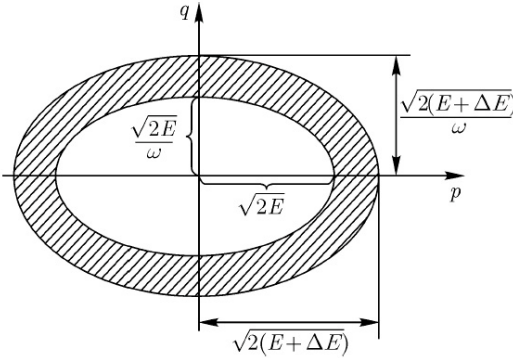


Figure A.1: Phase space of harmonic oscillator. Shown are isoenergetic “surfaces” — ellipses, corresponding to oscillators, with energies differing by ΔE in energy. Microcanonical distribution function is equal to a constant, different from zero in the area Ω between these ellipses.

For this simple system *time average* can be calculated in elementary way. Due to periodicity of motion (A.14), time average of an arbitrary function of dynamic variables $F(q, p)$ on an infinite time interval, can be reduced to the average over the period of motion $T = \frac{2\pi}{\omega}$:

$$\tilde{F} = \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} dt F \left\{ \frac{\sqrt{2E}}{\omega} \sin \omega(t + \beta), \sqrt{2E} \cos \omega(t + \beta) \right\}. \quad (\text{A.15})$$

This average depends on E , with E being fixed here. Without changing the value of (A.15), we can calculate its average over infinitesimally small interval of energies:

$$\begin{aligned} \tilde{F} &= \lim_{\Delta E \rightarrow 0} \frac{1}{\Delta E} \int_E^{E+\Delta E} dE \tilde{F} = \\ &= \lim_{\Delta E \rightarrow 0} \frac{\omega}{2\pi \Delta E} \int_E^{E+\Delta E} dE \int_0^{\frac{2\pi}{\omega}} dt F \left\{ \frac{\sqrt{2E}}{\omega} \sin \omega(t + \beta), \sqrt{2E} \cos \omega(t + \beta) \right\} \end{aligned} \quad (\text{A.16})$$

Let us transform from variables E and t to q and p . Using (A.14), we can calculate the Jacobian of this transformation as:

$$\frac{\partial(q, p)}{\partial(t, E)} = \begin{vmatrix} \sqrt{2E} \cos \omega(t + \beta) & \frac{1}{\omega \sqrt{2E}} \sin \omega(t + \beta) \\ -\omega \sqrt{2E} \sin \omega(t + \beta) & \frac{1}{\sqrt{2E}} \cos \omega(t + \beta) \end{vmatrix} = 1 \quad (\text{A.17})$$

Then we obtain:

$$\tilde{F} = \lim_{\Delta E \rightarrow 0} \frac{\omega}{2\pi \Delta E} \int dq \int dp F(q, p) \quad (\text{A.18})$$

where the integration is performed over the infinitesimally narrow area between the ellipses of constant energies E and $E + \Delta E$ with $\Delta E \rightarrow 0$.

On the other hand we can define *microcanonical* distribution for oscillator, with probability density $\rho(p, q)$ equal to constant (independent of specific values

of p and q) within the area Ω between the ellipse $p^2 + \omega^2 q^2 = 2E$ and ellipse $p^2 + \omega^2 q^2 = 2(E + \Delta E)$, and equal to zero outside this area (cf. Fig. A-1):

$$\rho(p, q) = \begin{cases} \frac{\omega}{2\pi\Delta E} & \text{for } p, q \in \Omega \\ 0 & \text{for } p, q \notin \Omega \end{cases} \quad (\text{A.19})$$

where to guarantee normalization of $\rho(p, q)$ to unity, we have taken into account that the actual area of Ω is:

$$\Delta(\pi ab) = \Delta\left(\frac{2\pi E}{\omega}\right) = \frac{2\pi\Delta E}{\omega}, \quad (\text{A.20})$$

where a and b denote semi-axes of ellipse, corresponding to energy E . Then, microcanonical average (over phase space) of $F(q, p)$ is equal to:

$$\langle F \rangle = \int dpdq \rho(p, q) F(q, p) = \lim_{\Delta E \rightarrow 0} \frac{\omega}{2\pi\Delta E} \int \int_{p^2 + \omega^2 q^2 = 2(E + \Delta E)}^{p^2 + \omega^2 q^2 = 2E} dpdq F(q, p) \quad (\text{A.21})$$

Comparing (A.18) and (A.21) we can see, that in this simplest case of a system with only one degree of freedom, the time average simply coincides with microcanonical average.

In general case the, as we seen above, integrals of Hamilton equations can be written as:

$$\begin{aligned} p_k &= \varphi_k(t + \beta_1, \beta_2, \dots, \beta_n, \alpha_1, \alpha_2, \dots, \alpha_n) \\ q_k &= \psi_k(t + \beta_1, \beta_2, \dots, \beta_n, \alpha_1, \alpha_2, \dots, \alpha_n) \end{aligned} \quad (\text{A.22})$$

or in shortened form:

$$X = \Phi(t + \beta_1, \beta_2, \dots, \beta_n, \alpha_1, \alpha_2, \dots, \alpha_n) \quad (\text{A.23})$$

Time average of an arbitrary dynamic variable $F(X)$ is determined by:

$$\begin{aligned} \tilde{F} &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^{\infty} dt F(X) = \\ &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^{\infty} dt F\{\Phi(t + \beta_1, \beta_2, \dots, \beta_n, \alpha_1, \alpha_2, \dots, \alpha_n)\} \end{aligned} \quad (\text{A.24})$$

This average, in general, depends on *all* $2n - 1$ integration constants (integrals of motion) $\beta_2, \dots, \beta_n, \alpha_1, \alpha_2, \dots, \alpha_n$, except β_1 , on which it does not depend. At the same time, we have shown before that statistical mechanical averages of any dynamic variables in *equilibrium* depend only on one integral of motion — energy². Thus, the many particle systems under consideration should satisfy the special property: time averages of any *single valued* dynamical variable is dependent only on energy $\alpha_1 = E$:

$$\tilde{F}(X) = f_F(E) \quad (\text{A.25})$$

Such systems are called *ergodic*. For ergodic systems the time average of any single valued dynamical variable is equal to its average over microcanonical ensemble.

²For fixed external parameters like volume, pressure, external fields etc.

The proof of this statement is rather simple. Consider microcanonical average:

$$\langle F \rangle = \int dX F(X) w_E(X) \quad (\text{A.26})$$

where

$$w_E(X) = \frac{\delta\{H(X) - E\}}{\Omega(E)}. \quad (\text{A.27})$$

As the value of $\langle F \rangle$ does not depend on time, its time average is equal to itself, so that:

$$\langle F \rangle = \widetilde{\langle F \rangle} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \int dX F(X) w_E(X). \quad (\text{A.28})$$

Variables X determine the state of the system at the moment t , let us make transformation to variables X_0 , determining the state of the system at $t = 0$. These variables are related through the solutions of Hamilton equations, which can be written as:

$$X = \Phi(t, X_0) \quad (\text{A.29})$$

Then

$$F(X) = F\{\Phi(t, X_0)\} \quad (\text{A.30})$$

Obviously $H(X) = H(X_0)$, so that

$$w_E(X) = \frac{\delta\{H(X) - E\}}{\Omega(E)} = \frac{\delta\{H(X_0) - E\}}{\Omega(E)} = w_E(X_0), \quad (\text{A.31})$$

and according to Liouville theorem $dX = dX_0$. Thus, after changing the variables we have:

$$\langle F \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \int dX_0 w_E(X_0) F\{\Phi(t, X_0)\} \quad (\text{A.32})$$

Let us change the order of integration over t and X_0 , then:

$$\langle F \rangle = \int dX_0 w_E(X_0) \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt F\{\Phi(t, X_0)\} = \int dX_0 w_E(X_0) \tilde{F} \quad (\text{A.33})$$

Due to the assumed ergodicity the time average \tilde{F} depends only on energy $H(X_0)$, so that:

$$\tilde{F} = f_F[H(X_0)] \quad (\text{A.34})$$

Thus

$$\langle F \rangle = \int dX_0 w_E(X_0) f_F[H(X_0)] \quad (\text{A.35})$$

But $w_E(X_0)$ is different from zero only for $H = E$, so that $f_F(H)$ can be taken out of integral, putting $H = E$. Then we get:

$$\langle F \rangle = f_F(E) \int dX_0 w_E(X_0) = f_F(E) = \tilde{F} \quad (\text{A.36})$$

where we have taken into account that the integral is equal to unity due to renormalization condition. This ends the proof of equivalence of time and microcanonical averaging for ergodic systems.

It may seem that ergodic mechanical systems just do not exist at all, as the general time average (A.24) definitely depends on other integrals of motion $\alpha_2, \alpha_3, \dots, \beta_n$, besides energy. Consider one of them, e.g. $\Phi_2(X) = \alpha_2$. The time average of $\Phi_2(X)$ is obviously equal to α_2 and depends not on energy integral $E = \alpha_1$, but on α_2 . However, for ergodic systems the left parts of all integrals of motion $\Phi_k = \alpha_k, \Psi_k = \beta_k$ ($k = 2, \dots, n$), besides energy, momentum and angular momentum are *multivalued* functions of coordinates and momenta (and can not be transformed to single valued functions). This is always so for systems with inseparable variables. Systems with separable variables are, in this sense, trivial — they are exactly solvable and are also called *integrable*, their motion is regular (non random) and we do not need statistics at all to describe their properties³. The restriction to single valued functions $F(p, q)$ is quite natural from physical point of view, for systems at rest we can drop momentum and angular momentum integrals of motion. Statistical mechanics is dealing with complicated *non integrable* systems (performing nontrivial motion). In recent decades a number of explicit examples of such systems, sometimes consisting of rather few particles, were demonstrated to show all the properties of ergodic motion [12].

A.2 Poincare recurrence theorem.

Let us continue our discussion of the system motion in phase space using more abstract language. Consider the phase point (p, q) . Let us define the operator of time translation $\hat{T}(t)$ as:

$$(q(t), p(t)) = \hat{T}(t)(q(0), p(0)) \quad (\text{A.37})$$

This operator gives a complete description of phase point motion and is implicitly defined by Hamilton equations. We shall not try to construct such operators explicitly for specific systems, it is clear that, in principle, they always exist. Liouville theorem corresponds to conservation of an arbitrary phase volume Γ under the action of operator \hat{T} :

$$\Gamma(t) = \hat{T}(t)\Gamma(0) = \Gamma(0) \quad (\text{A.38})$$

Using Liouville theorem, it is rather easy to prove the so called Poincare recurrence theorem [12]. Consider conservative (H is time independent) mechanical system, performing motion in a finite region of its phase space. Let us take some region (set of points) of the phase space A and chose an initial point $z_0 = (q_0, p_0)$ in it. We shall show now, that after a certain (finite) time the system will necessarily return to the region A (Poincare theorem), except probably a set of initial points of measure zero. The proof can be done through *reductio ad absurdum*. Let us denote as B the subset of points in A , which never return to A . Suppose that after some large time t_1 the set B moves to B_1 :

$$\hat{T}(t_1)B = B_1 \quad (\text{A.39})$$

³More details on this can be found in Ref. [11], where it is shown that in general case of systems with inseparable variables, the set of single valued integrals of motion is limited to those, which are directly related to general properties of time and translational invariance, as well is to isotropy of space, i.e. to energy, momentum and angular momentum conservation laws.

According to definition of B the intersection of B_1 and A is an empty set:

$$B_1 \cap A = \emptyset \quad (\text{A.40})$$

After time interval $t_2 = 2t_1$ we have:

$$\hat{T}(2t_1)B = \hat{T}(t_1)B_1 \equiv B_2 \quad (\text{A.41})$$

Then also

$$B_2 \cap B_1 = \emptyset \quad (\text{A.42})$$

If this is not so, there exist points, which do not left B_1 . However, due to time reversibility of Hamilton equations that would mean, that these points could not have entered B_1 . This contradicts their past: at $t = 0$, according to our assumption, they belonged to A . Continued application of $\hat{T}(nt_1)$ – operator to B leads to an infinite sequence B_1, B_2, \dots of nonintersecting images of B . According to Liouville theorem:

$$\Gamma(B) = \Gamma(B_1) = \Gamma(B_2) = \dots, \quad (\text{A.43})$$

so that during the motion, the points from B cover the phase volume $\Gamma = \infty$. However, due to a finite nature of the motion of our system, this volume is to be finite. This is possible only in case of $\Gamma(B) = 0$, which proves Poincaré recurrence theorem.

From Poincaré theorem it follows, that the system will infinitely many times return to initial region A . It may seem that this result contradicts the irreversible evolution of many particle systems, observed in the experiments, and possibility of its description along the lines of statistical mechanics. Actually, this is not so. To understand this situation, we have to consider the average recurrence time or the time of *Poincaré cycle*. Let us make a rough estimate of this time for the simplest many particle system — an ideal gas [33]. Consider N molecules of the gas moving in volume V . We may understand the recurrence in the sense of repetition of the state of each molecule with some finite accuracy Δv of its velocity and some Δx for its coordinate. This accuracy corresponds to an element of phase volume $\Delta\Gamma = [m\Delta v\Delta x]^{3N}$, while the total set of possible states of the gas, with fixed energy $E = \sum_i \frac{mv_i^2}{2} = \frac{3}{2}NT$, corresponds the phase volume⁴:

$$\Gamma \approx C_{3N} (m^2 \sum_i v_i^2)^{3N/2} V^N \approx C_{3N} (3NTm)^{3N/2} V^N. \quad (\text{A.44})$$

It is clear, that before returning (with the given accuracy) to initial position, the phase point, representing our system, is to pass through $\sim \frac{\Gamma}{\Delta\Gamma}$ states. Let τ be some characteristic time for gas, e.g. mean free time of the molecule. Then, the recurrence time can be roughly estimated as:

$$\tau_R \sim \tau \frac{\Gamma}{\Delta\Gamma} \sim C_{3N} \left(\frac{V}{\Delta x^3} \right)^N \left(\frac{3NT}{m\Delta v^2} \right)^{3N/2} \tau \sim \left(\frac{V}{\Delta x^3} \right)^N \left(\frac{T}{m\Delta v^2} \right)^{3N/2} \tau. \quad (\text{A.45})$$

⁴Here $C_{3N} \approx \left(\frac{2\pi\epsilon}{3N} \right)^{3N/2}$ is related to a constant in the expression for the volume of n -dimensional sphere $V_n = CR^n$, the exact value of this constant being $C_n = \frac{2\pi^{n/2}}{n\Gamma(n/2)}$. For $n \gg 1$, using the asymptotic expression for Γ -function $\Gamma(n/2) \approx (2\pi)^{1/2} (n/2)^{(n-1)/2} e^{-n/2}$, we get $C_n \approx \left(\frac{2\pi\epsilon}{n} \right)^{n/2}$

Let us take $\Delta x \sim 0.1(V/N)^{1/3}$, i.e. of the order of 10% of interparticle distance in our gas, and $\Delta v \sim 0.1(T/m)^{1/2}$, i.e. of the order of 10% of an average velocity (so that conditions of “return” are rather crude). Then we obtain:

$$\tau_R \sim \tau(10N)^N(10^2)^{3N/2} \sim \tau N^N \quad (\text{A.46})$$

For 1cm^3 of a gas in normal conditions we have $N \sim 10^{18}$, so that

$$\frac{\tau_R}{\tau} \sim (10^{18})^{10^{18}} \sim 10^{2 \cdot 10^{19}} \quad (\text{A.47})$$

and the ratio of recurrence time τ_R to mean free time $\tau \sim 10^{-6}\text{sec}$, or to one second, one year, or even to a characteristic “lifetime” of our Universe ($\sim 10^{10}\text{years} \sim 10^{17}\text{sec}$), with logarithmic accuracy is the same (!) and is of the order of $10^{2 \cdot 10^{19}}$. Thus, the typical time of Poincaré cycle, even for such a simple system, is immensely large, and the probability of such return is immensely small. This leads to an obvious conclusion, that the *most probable* behavior of many particle system is, in fact, the irreversible behavior, observed in reality.

A.3 Instability of trajectories and mixing.

Consider the motion of a drop of “phase liquid” in the phase space. The character of this motion may be very complicated, as time grows, the borders of the drop may become irregular, with drop becoming “amoeba” – like (cf. Fig. A-2), filling different regions of the phase space. The volume of the drop is conserved (Liouville theorem). Such motion is called *mixing*. The phase points, which

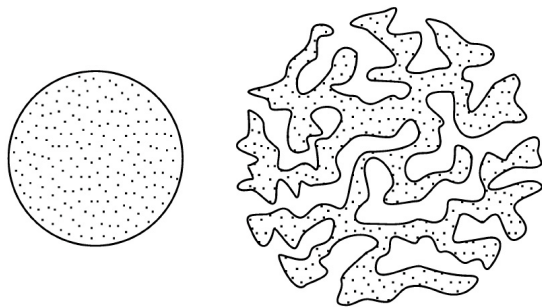


Figure A.2: Qualitative evolution of phase drop during mixing.

were close to each other initially, may become very far from each other during this time evolution, and move in practically independent way. The property of mixing is natural to expect for systems, characterized by *unstable* motion, when phase trajectories, initially close to each other, become exponentially far away from each other with the growth of time, i.e. the small perturbations of initial conditions lead to arbitrary large deviations of phase trajectory from unperturbed motion. If the phase space is finite (and we are interested just in this case — the system moves over the hypersurface of constant energy!), the phase trajectories can not deviate more than to a characteristic size of this space and begin to intermix in very complicated way. Denoting by $D(t)$ the *distance*

between two points in the phase space, belonging to two different trajectories at the moment t , we can formally define the local instability of motion in the following way [12] – there exists a direction in phase space for which:

$$D(t) = D_0 e^{h_0 t} \quad (\text{A.48})$$

where the increment of instability (Lyapunov exponent, $h_0 > 0$) is, in general, the function of a point in phase space and has the statistical meaning [12] of an inverse time of “decoupling” of correlations between trajectories during mixing. It is obvious, that this picture can be directly related to an idea of description of entropy growth, using the coarse grained distribution function, which we used previously. The question arises — whether we can define entropy in such a way, that will allow its use for dynamical systems, using only the properties of phase trajectories (not distribution functions)? This problem was solved by Kolmogorov, who introduced the notion of dynamic of K -entropy. Consider again the evolution of some initial element of the phase volume $\Delta\Gamma_0$. According to Liouville theorem:

$$\Delta\Gamma(t) = \Delta\Gamma_0 \quad (\text{A.49})$$

but the structure of the phase drop changes with time (cf. Fig. A-2). There may appear “bubbles”, empty regions etc. As t grows, the “bubble” structure becomes more and more fine, while the external border of the phase drop becomes wider and wider. Let us take some ε (of dimensionality Γ) and “coarsen” the structure of the phase drop up to an accuracy of the order of ε . Then, qualitatively it is clear that all thin structures of the drop, with thickness smaller than ε , will be effectively “dressed”, so that the coarse grained phase volume $\widetilde{\Delta\Gamma}(t)$ will actually grow with time. Knowing (A.48), it is easy to understand that

$$\widetilde{\Delta\Gamma}(t) = \Delta\Gamma_0 e^{ht} \quad (\text{A.50})$$

where h is some quantity, related to the increment of instability of phase trajectories h_0 . Then we may define entropy as:

$$S = \ln \widetilde{\Delta\Gamma}(t) = \ln(\Delta\Gamma_0 e^{ht}) = ht + \ln \Delta\Gamma_0 \quad (\text{A.51})$$

We are interested in defining physical characteristics, including entropy S , with highest possible accuracy. If coarse graining is defined by ε , then it is obvious, that there is no sense in taking $\Delta\Gamma_0$ less, than ε . Thus, we can put $\Delta\Gamma_0 = \varepsilon$ and go to the limit of $\varepsilon \rightarrow 0$. Consider:

$$\lim_{\varepsilon \rightarrow 0} \lim_{t \rightarrow \infty} \frac{1}{t} \ln \widetilde{\Delta\Gamma}(t) = \lim_{\varepsilon \rightarrow 0} \lim_{t \rightarrow \infty} \frac{1}{t} (ht + \ln \varepsilon) = h \quad (\text{A.52})$$

This expression is the definition of K -entropy h . Let us stress the importance of the order of performing limits here. The basic properties of K -entropy are:

1. K -entropy h determines the velocity of entropy S change due to purely dynamic process of mixing of phase trajectories in phase space.
2. K -entropy h , the increment of local instability h_0 and the inverse time of decoupling of time correlations are of the same order of magnitude.

These properties explain the physical meaning of Kolmogorov's entropy.

How the physical entropy S reaches its maximum? For $\varepsilon \rightarrow 0$, i.e. defining the entropy $S(t) = ht$ ($t \rightarrow \infty$) with arbitrary large accuracy, entropy S does not reach maximum, but situation changes if we fix the finite accuracy of coarse graining ε_0 . Then, from (A.50) it is easy to find the characteristic time t_0 , during which the region $\Delta\Gamma_0 = \varepsilon_0$ is expanded up to the value $\widetilde{\Delta\Gamma} = 1$:

$$t_0 = \frac{1}{h} \ln \frac{1}{\varepsilon_0} \quad (\text{A.53})$$

During this time the phase drop of the size of ε_0 homogeneously fill all the phase volume and the further growth of entropy stops.

Appendix B

Statistical mechanics and information theory.

B.1 Relation between Gibbs distributions and principle of maximal information entropy.

Information entropy.

The notion of entropy in statistical mechanics is closely related to the similar notion in information theory [34]. There exists a wide range literature, where this relation is discussed in detail [35, 36]. Below we shall deal with some of the problems, illustrating the basic principles, connecting these fundamental concepts.

In a narrow sense, information theory represents the statistical theory of communications, i.e. transmission of signals, texts etc. [34]. The main concept in this theory is that of *information* entropy, which acts as a measure of information, contained in a given communication, text, set of signals etc., which are considered as more or less random sequence of symbols or events. More precisely, information entropy gives the measure of indeterminacy of information, corresponding to a given statistical distribution of such events. Let p_k is some discrete probability distribution of events, enumerated by index k . Information entropy is defined as[34]¹:

$$H = - \sum_{k=1}^n p_k \ln p_k; \quad \sum_k p_k = 1 \quad (\text{B.1})$$

In fact, the value of H equals zero if some of $p_k = 1$, while the remaining $p_k = 0$, i.e. when the result can be predicted with certainty and there is no indeterminacy in information at all. The value of H acquires the maximum value, when all p_k are equal to each other, i.e. for $p_k = 1/n$. It is obvious, that this limiting case corresponds to maximal indeterminacy — we do not know anything about specific events, all are equally probable (i.e. letters of the text appear absolutely

¹For us it is irrelevant here, that in information theory this definition normally uses instead of \ln the logarithm with base 2, i.e. \log_2 , which is related to measuring information in *bits*

randomly, in physics this corresponds to absolutely random realization of different states of the system etc.). Maximum of information entropy corresponds to maximum of our *ignorance* about events and our information on these in this case is minimal.

Entropy H is additive for independent events, realized with probabilities u_i and v_i , when $p_{ik} = u_i v_k$, so that

$$H = - \sum_{ik} p_{ik} \ln p_{ik} = - \sum_i u_i \ln u_i - \sum_k v_k \ln v_k; \quad \sum_i u_i = 1; \quad \sum_k v_k = 1 \quad (\text{B.2})$$

For continuous distribution of events x , characterized by probability density $f(x)$, information entropy is given by:

$$H = - \int dx f(x) \ln f(x); \quad \int dx f(x) = 1 \quad (\text{B.3})$$

For independent events, again we have additivity. If $f(x, y) = f_1(x) f_2(y)$, we obtain:

$$H = - \int dx \int dy f(x, y) \ln f(x, y) = - \int dx f_1(x) \ln f_1(x) - \int dy f_2(y) \ln f_2(y) \quad (\text{B.4})$$

Gibbs entropy defined by distribution function $\rho(p, q)$ in phase space essentially is also the information entropy:

$$S = - \int d\Gamma \rho \ln \rho; \quad \int d\Gamma \rho = 1 \quad (\text{B.5})$$

and can be considered as a measure of our ignorance (absence of information) of details of microscopic states of the macroscopic system.

For ensembles with variable number of particles Eq. (B.5) is generalized as:

$$S = - \sum_{N \geq 0} \int d\Gamma_N \rho_N \ln \rho_N; \quad \sum_{N \geq 0} \int d\Gamma_N \rho_N = 1. \quad (\text{B.6})$$

Below we consider extremal properties of Gibbs ensembles, which were established long before the formulation of information theory. The proofs will be given using Gibbs inequality (1.187):

$$\int d\Gamma \rho' \ln \left(\frac{\rho'}{\rho} \right) \geq 0 \quad (\text{B.7})$$

where ρ and ρ' are two normalized distributions, defined in the same phase space. Equality here holds only in case of $\rho = \rho'$.

Extremal properties of microcanonical distribution.

Let us prove that microcanonical distribution corresponds to the maximal information entropy among all distributions with the same number of particles in the same energy layer. Let ρ be distribution function of microcanonical ensemble, while ρ' is an arbitrary distribution function, defined in the same phase space and in the same energy layer, and both satisfy normalization condition:

$$\int d\Gamma \rho' = \int d\Gamma \rho = 1 \quad (\text{B.8})$$

B.1. RELATION BETWEEN GIBBS DISTRIBUTIONS AND PRINCIPLE OF MAXIMAL INFORMATION ENTROPY

Substituting ρ and ρ' into inequality (B.7), we obtain:

$$-\int d\Gamma \rho' \ln \rho' \leq -\int d\Gamma \rho' \ln \rho = -\ln \rho \int d\Gamma \rho' = -\int d\Gamma \rho \ln \rho \quad (\text{B.9})$$

and the proof is complete. In Eq. (B.9) we used the constancy of microcanonical distribution ρ in its energy layer and normalization conditions for ρ and ρ' .

Extremal properties of canonical distribution.

Let us show that Gibbs canonical distribution corresponds to maximal information entropy at fixed average energy of the system:

$$\langle H \rangle = \int d\Gamma H \rho \quad (\text{B.10})$$

with normalization condition:

$$\int d\Gamma \rho = 1. \quad (\text{B.11})$$

Consider canonical distribution:

$$\rho = Z^{-1} \exp(-\beta H); \quad Z = \int d\Gamma \exp(-\beta H) \quad (\text{B.12})$$

where $\beta = 1/T$. Consider ρ' – another normalized distribution, corresponding to the same average energy as canonical distribution ρ :

$$\int d\Gamma \rho', \quad H = \int d\Gamma \rho H \quad (\text{B.13})$$

while in all other respects ρ' is arbitrary. Substituting (B.12) to (B.7), we get:

$$\begin{aligned} -\int d\Gamma \rho' \ln \rho' &\leq -\int d\Gamma \rho' \ln \rho = \ln Z + \beta \int d\Gamma \rho' H = \ln Z + \beta \int d\Gamma \rho H \\ \text{i.e.} \quad -\int d\Gamma \rho' \ln \rho' &\leq -\int d\Gamma \rho \ln \rho \end{aligned} \quad (\text{B.14})$$

which completes the proof.

Extremal properties of grand canonical distribution.

Let us give an example of the proof for the quantum case. The entropy of quantum ensemble is defined as:

$$S = -S p \rho \ln \rho \quad (\text{B.15})$$

where ρ is density matrix. In diagonal representation (cf. (1.175)):

$$S = -\sum_k w_k \ln w_k \quad (\text{B.16})$$

which has the explicit form of (B.1) — the information entropy for discrete sequence of events (in our case quantum states).

Extremal properties of quantum ensembles can be derived using the inequality:

$$Sp\rho' \ln \rho' \geq Sp\rho' \ln \rho \quad (\text{B.17})$$

where ρ and ρ' are arbitrary normalized statistical operators. Equality again holds only for the case of $\rho = \rho'$. This general inequality follows from $\ln x \geq 1 - 1/x$, which is valid for $x > 0$ (equality holds for $x = 1$). Substituting $x = \rho'\rho^{-1}$ and averaging over ρ' , we have:

$$Sp\rho' \ln(\rho'\rho^{-1}) \geq Sp\rho'(1 - \rho\rho'^{-1}) = 0 \quad (\text{B.18})$$

as both density matrices are normalized to unity and we can make permutations of operators under Sp .

Let us demonstrate that grand canonical quantum ensemble corresponds to the maximum of information entropy at fixed average energy:

$$\langle H \rangle = Sp\rho H \quad (\text{B.19})$$

and average number of particles:

$$\langle N \rangle = Sp\rho N \quad (\text{B.20})$$

with normalization:

$$Sp\rho = 1. \quad (\text{B.21})$$

Let us write the grand canonical ensemble as:

$$\rho = \exp\left(\frac{\Omega - H + \mu N}{T}\right); \quad e^{-\frac{\Omega}{T}} = Sp \exp\left(-\frac{H - \mu N}{T}\right). \quad (\text{B.22})$$

Then, from inequality (B.17) we obtain (assuming that ρ' is an arbitrary density matrix with the same averages (B.19), (B.20), (B.21)):

$$-Sp\rho' \ln \rho' \leq -Sp\rho' \ln \rho = -Sp \left[\rho' \left(\frac{\Omega}{T} - \frac{H}{T} + \frac{\mu N}{T} \right) \right] = -Sp\rho \ln \rho \quad (\text{B.23})$$

which proves our statement. Here we used (B.19), (B.20), (B.21), which are valid for ρ and ρ' , i.e.

$$Sp\rho' H = Sp\rho H, \quad Sp\rho' N = Sp\rho N. \quad (\text{B.24})$$

These extremal properties of Gibbs ensembles can be used as their definitions. This gives another approach to justification of *equilibrium* statistical mechanics². From our discussion it becomes clear that the physical entropy describes the lack of information on the real microscopic structure of multi particle system. This lack of information leads to the possibility of different microscopic states, which we can not discern from each other, which corresponds to real randomness in hidden degrees of freedom of the system. It is maximal, when the system is in equilibrium, when we know almost nothing on the details of its microscopic organization, and its state is completely determined by few thermodynamic parameters. Attempts to clarify microscopic details of internal organization of the system will inevitably perturb the equilibrium state and lead to lower values of entropy.

²In fact, we just shown, that different versions of Gibbs distribution correspond to the maximum of thermodynamic entropy with specific additional conditions. This naturally defines corresponding equilibrium states.

B.2 Purging Maxwell's "demon".

Interesting relation between statistical thermodynamics and information theory can be studied analyzing the problem of Maxwell's demon [35]. We just have noted that attempts to get information on the details of microscopic organization of the system via interference with microscopic processes within the system can move it out of equilibrium state. Probably the first example of such interference was proposed by Maxwell, introducing the paradox of a "demon", which "works" against the second law of thermodynamics. The simplest variant of such demon can work as follows. Consider a vessel with gas in equilibrium state, with a wall inside, separating the vessel into parts A and B , and a hole in the wall with a door. We can imagine, that our demon is sitting near this door and can let fast molecules passing through the hole, say from A to B , while from B to A it allows the passage of slow molecules. Then, after some time interval, since the start of these activities, in part B we shall collect more fast molecules, than in part A . Thermodynamic equilibrium will be broken, temperature of



Figure B.1: Maxwell's demon.

the gas in part B will become higher, than in part A . This situation explicitly contradicts the second law, it is not difficult now to make heat pass from more cold part of the vessel to more hot part. Obviously, we may replace demon by some automatic device, which will violate the second law in this way. More so, it seems much more probable, that a kind of "intellectual being" will deal with this process even more effectively. At the same time, we are sure that the second law is of universal nature and all processes in Nature should obey it. In fact, this is a correct conclusion and we shall see shortly, that no demon will be able to overcome this law via decreasing entropy in a closed system, which demon includes himself (itself). The paradox of Maxwell's demon was first resolved by Szillard, who used clear and simple arguments, which will be discussed below [35].

The essence of Szillard's argument is, that demon has to *observe* separate molecules, to separate "fast" molecules from "slow". This observation can be made using some physical methods, e.g. he can shine on molecules using electric light, so that he can see them and start to act. Thus, the closed system to be analyzed may consist of:

- gas at finite temperature $T = T_0$, contained in a vessel with a wall and a door,
- demon, operating the door,

- electric light with a charged cell, giving energy to an electric bulb.

The cell energy heats the wire in the bulb up to some high enough temperature $T_1 > T_0$. This allows to obtain the light with energy of the quanta $\hbar\omega_1 > T_0$, which is necessary for these quanta to be recognized on the background of “black body” radiation, which is always present within the vessel with gas with temperature T_0 . During the experiment, the cell gives the energy E to the bulb, bulb wire radiates this energy and loses entropy. This change of entropy is estimated as:

$$S_f = -\frac{E}{T_1} \quad (\text{B.25})$$

and it is introduced to the gas as a negative entropy. With no interference from demon’s side, energy E is absorbed by gas at temperature T_0 , and we observe the total growth of entropy:

$$S = \frac{E}{T_0} + S_f = \frac{E}{T_0} - \frac{E}{T_1} > 0 \quad (\text{B.26})$$

Consider now demon at work. It (or he) can find a molecule only in case it will scatter at least one quantum of energy $\hbar\omega_1$ from molecule to its (his) “eye” (or to photomultiplier). This inevitably leads to the growth of demon’s entropy:

$$\Delta S_d = \frac{\hbar\omega_1}{T_0} \quad (\text{B.27})$$

The obtained information can be used to decrease the entropy of the system. The initial entropy of the system is given by:

$$S_0 = \ln \Omega_0 \quad (\text{B.28})$$

where Ω_0 is the statistical weight of the (closed) system. After getting the information, the system is defined in more details, Ω_0 is decreased by some value p :

$$\Omega_1 = \Omega_0 - p \quad (\text{B.29})$$

This leads to the decrease of entropy:

$$\Delta S_i = S_1 - S_0 = \ln(\Omega_0 - p) - \ln \Omega_0 \approx -\frac{p}{\Omega_0} \quad (\text{B.30})$$

as in most practical cases we have $p \ll \Omega_0$. The total balance of entropy is expressed by:

$$\Delta S_d + \Delta S_i = \frac{\hbar\omega_1}{T_0} - \frac{p}{\Omega_0} > 0 \quad (\text{B.31})$$

as $\hbar\omega_1/T_0 > 1$, but $p/\Omega_0 \ll 1$. Thus, as a result, the entropy of the closed system increases, in accordance with the second law.

Let us consider this situation in more details. Suppose that after some time, demon has created the temperature difference ΔT between parts A and B of the vessel:

$$\begin{aligned} T_B &> T_A; & T_B - T_A &= \Delta T \\ T_B &= T_0 + \frac{1}{2}\Delta T; & T_A &= T_0 - \frac{1}{2}\Delta T \end{aligned} \quad (\text{B.32})$$

After that, demon chooses a fast molecule in the region A with kinetic energy $\frac{3}{2}T(1 + \varepsilon_1)$ and sends it to the region B . Then he chooses a slow molecule in B with kinetic energy $\frac{3}{2}T(1 - \varepsilon_2)$ and allows it to pass to the region A . To observe both molecules, demon needs at least two light quanta, which leads the decrease of his entropy:

$$\Delta S_d = 2 \frac{\hbar\omega_1}{T_0} > 2 \quad (\text{B.33})$$

The exchange of molecules leads to the transfer of energy from A to B :

$$\Delta Q = \frac{3}{2}T(\varepsilon_1 + \varepsilon_2) \quad (\text{B.34})$$

which, taking into account (B.32), corresponds to the decrease of total entropy:

$$\Delta S_i = \Delta Q \left(\frac{1}{T_B} - \frac{1}{T_A} \right) \approx -\Delta Q \frac{\Delta T}{T^2} = -\frac{3}{2}(\varepsilon_1 + \varepsilon_2) \frac{\Delta T}{T}. \quad (\text{B.35})$$

The values of ε_1 and ε_2 are, most probably, small and $\Delta T \ll T$, then:

$$\begin{aligned} \Delta S_i &= -\frac{3}{2}\eta; \quad \eta \ll 1, \quad \text{so that} \\ \Delta S_d + \Delta S_i &= \left(2 \frac{\hbar\omega_1}{T_0} - \frac{3}{2}\eta \right) > 0 \end{aligned} \quad (\text{B.36})$$

in agreement with the second law.

In principle, we can analyze another situation, that of demon at low temperature, when its temperature $T_2 \ll T_0$. In this case it can absorb quanta $\hbar\omega$, radiated by molecules of the gas at temperature T_0 . Then, instead of conditions $T_1 > T_0$ and $\hbar\omega_1 > T_0$ used above, we have $\hbar\omega > T_2$ and $T_2 < T_0$, and we can repeat our arguments. We always need some difference of temperatures, or demon will not be able to operate. But in any case it will not be able to overcome the second law.

These results lead to an important conclusion: physical measurements of rather general nature can lead to the increase of entropy. There is some low limit, below which most measurements become impossible. Rough estimate for this limit corresponds to the decrease of entropy by ~ 1 ($\sim k_B$). More accurate estimate gives the value of this limit as $k_B \ln 2 \approx 0.7k_B$, per one bit of acquired information [35].

However, this is not the end of the story of Maxwell's demon. Though all the arguments, given above, are undoubtedly valid for typical physical measurements, more recent studies demonstrated the specific ways to determine the positions of molecules, not leading to the appropriate increase of entropy [37]. It was also discovered that some operations with information data, e.g. writing data from one device to the other, can be, under certain conditions, be performed without thermodynamic limitations. However, there is still a deep reason why the appropriate demon will not be able to break the second law. The thing is that it has first to "forget" the results of the previous measurement, i.e. destroy information (and thus "pay" in thermodynamic sense). Any memory state (e.g. of a computer) is represented by appropriate physical states (electric current, voltages, magnetizations etc.). Corresponding cleaning of memory, as was first

noted by Landauer, is *thermodynamically irreversible* operation, leading to the general increase of entropy of the closed system³.

Below we briefly explain the Landauer principle of information erasure analyzing the so called Szillard engine model⁴. The Szillard engine consists of a one-dimensional cylinder, whose volume is V_0 , containing a one-molecule gas and a partition that works as a movable piston. The operator, e.g. a demon, of the engine inserts the partition into the cylinder, measures the position of the molecule, and connects to the partition a string with a weight at its end. These actions by the demon are ideally performed without energy consumption [37]. The demon's memory is also modeled as one-molecule gas in a box with a partition in the middle. Binary information, 0 and 1, is represented by the position of the molecule in the box, the left and the right, respectively.

The following is the protocol to extract work from the engine by information processing of the demon (see Fig. B.2), where we denote "SzE" for the Szillard engine and "DM" for the demon's memory at each step of the protocol. Initially, the molecule in the cylinder moves freely over the volume V_0 .

Step 1 (SzE) The partition is inserted at the center of the cylinder.

Step 2 (SzE, DM) The demon measures the location of the molecule, either the left ("L") or the right ("R") side of the partition. The demon records the measurement outcome in his memory. When it is L (R), his memory is recorded as "0" ("1").

Step 3 (SzE) Depending on the measurement outcome, the demon arranges the device differently. That is, when the molecule was found on the left (right) hand side, i.e., the record is 0 (1), he attaches the string to the partition from the left (right). In either case, by putting the cylinder in contact with the heat bath of temperature T , the molecule pushes the partition, thus exerting work on the weight, until the partition reaches the end of the cylinder. The amount of work extracted by the engine is

$$W = k_B T \ln 2, \quad (\text{B.37})$$

as can be seen by applying the combined gas law in one dimension.

Step 4 (SzE) The demon removes the partition of the engine, letting the molecule return to its initial state.

Step 5 (DM) The demon removes the partition of his memory to erase information.

Step 6 (DM) In order to reset the memory to its initial state, the demon compresses the volume of the gas by half.

In order to complete the cycle for both the Szillard engine and the memory, the demon has to reset the memory, which follows the erasure of one-bit of

³If demon possesses very large memory, it can surely simply remember the results of all measurements, so that there be no irreversible actions. However, this situation does not correspond to thermodynamic cycle. Demon just increases the entropy of its memory to decrease the entropy of surrounding medium.

⁴This example is taken from A. Hosoya, K. Maruyama, Y. Shikano. Phys. Rev. E **84**, 061117 (2011).

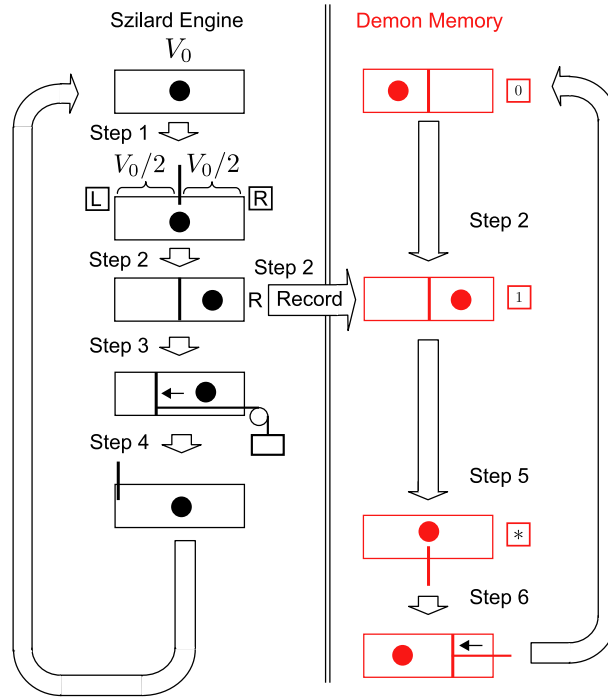


Figure B.2: A protocol of Szillard engine (left side) and demon's memory (right side). This figure shows an example in which the molecule was found in the right hand side of the cylinder. In demon's memory, the state after removing the partition is denoted by "*".

information. More precisely, the physical process of information erasure and memory resetting described in Steps 5 and 6, goes as follows. The box is in contact with the thermal bath at the same temperature T as that of the engine. The record in the memory can be erased simply by removing the partition, since the location of the molecule becomes completely uncertain. To bring the memory back to its initial state, e.g., 0, one has to compress the gas by half by sliding a piston from the right end to the middle. The necessary work for this compression is $k_B T \ln 2$, which exactly cancels out the work gain by the engine (B.37).

Let us look at the same process in terms of thermodynamic entropy. By Steps 1 and 2, the volume of the gas in engine is halved, regardless of the measurement outcome. As the entropy change of an ideal gas under the isothermal process is given by $\Delta S = S(V') - S(V) = k_B \ln(V'/V)$, the entropy of the engine is lowered by $k_B \ln 2$. The isothermal expansion in Step 3 increases the entropy of the gas by $k_B \ln 2$, while that of the heat bath is decreased by the same amount. As far as the Szillard engine and its heat bath are concerned, the net result is an entropy decrease of $k_B \ln 2$. This is exactly canceled out by the entropy increase due to information erasure and reset performed in Steps 5 and 6.

These last two steps are of crucial importance when closing a cycle of the memory. Information erasure in Step 5 is an irreversible process and increases

thermodynamic entropy by $k_B \ln 2$. The isothermal compression to reset the memory in Step 6 requires work and dissipates entropy of $k_B \ln 2$ to its heat bath. This is the essence of Landauer-Bennett mechanism that finally resolves the Maxwell's demon paradox.

Appendix C

Nonequilibrium Statistical Operators.

C.1 Quasi-equilibrium statistical operators.

There were many attempts to construct the general formulation of nonequilibrium statistical mechanics along the lines, similar to the general Gibbs approach to equilibrium statistical mechanics. Below we briefly discuss one of the most popular formulations, developed essentially by Zubarev and coworkers [3, 38].

In classical nonequilibrium statistical mechanics we have to analyze solutions of Liouville equation (1.50) for general statistical distribution function ρ :

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}. \quad (\text{C.1})$$

where $\{H, \rho\}$ denote Poisson brackets (1.49) for H and ρ .

The quantum Liouville equation (1.128) for the general density matrix ρ (statistical operator) in operator form is written as:

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho] \quad (\text{C.2})$$

Below we consider only the quantum case, as classical equations can be formulated in a similar way.

The formal solution of Liouville equation (C.2) can be written as:

$$\rho(t) = U(t, t_0)\rho(t_0)U^+(t, t_0) \quad (\text{C.3})$$

where $\rho(t_0)$ is an arbitrary statistical operator at the initial moment of time t_0 , while $U(t, t_0)$ is the operator of time evolution, determined by equation:

$$\frac{\partial U(t, t_0)}{\partial t} = \frac{1}{i\hbar} HU(t, t_0) \quad (\text{C.4})$$

with initial condition $U(t_0, t_0) = 1$. However, this solution can be useful only in case of appropriate choice of statistical operator $\rho(t_0)$ and initial moment t_0 . Typical example is linear response theory, where we choose $t_0 \rightarrow -\infty$ and

$\rho(-\infty)$ is assumed to be an equilibrium Gibbs ensemble. Thus, the main problem of nonequilibrium statistical mechanics is not reduced to finding the formal solutions of Liouville equation, but to the proper choice of initial conditions.

Note, that depending on specific problem, the number of parameters, necessary to describe the nonequilibrium state of a system, depends on the characteristic time-scale of interest to us. For larger time-scales we need actually smaller number of such parameters. For example, at hydrodynamic stage of nonequilibrium process it is sufficient to deal only with the average values of energy, momentum and particle densities. This idea of reduced description of nonequilibrium processes at large enough intervals of time is basic for almost all theories of nonequilibrium processes (cf. our discussion of derivation of kinetic equations in Chapter 10). It was first clearly formulated by Bogolyubov.

We are interested in solutions of Liouville equation for not very short time intervals, when the description of nonequilibrium state can be achieved with some set of operators P_m , where index m may be both discrete and continuous. We shall look for those solutions of Liouville equation, which depend on these operators and conjugated parameters $F_m(t)$, which will be explained a bit later. Depending on the choice of operators P_m , such an approach is possible both on kinetic or hydrodynamic stage of nonequilibrium process. On hydrodynamic stage we can choose P_m as operators of energy, momentum and particle densities $H(\mathbf{r})$, $\mathbf{p}(\mathbf{r})$ and $n(\mathbf{r})$. On kinetic stage P_m may be chosen as appropriate one-particle density matrices.

To formulate proper initial condition for Liouville equation, we introduce now the notion of *quasiequilibrium* statistical operator. It can be defined in a way similar to that we have used in our discussion of equilibrium statistical operators in Appendix B. Let us assume that our nonequilibrium state is characterized by the set of the averages of operators P_m . Quasiequilibrium statistical operator can be defined as corresponding to the extremum of information entropy:

$$S = -Sp\rho \ln \rho \quad (\text{C.5})$$

under additional conditions of fixing the average values of P_m :

$$Sp\rho P_m = \langle P_m \rangle^t \quad (\text{C.6})$$

and normalization condition:

$$Sp\rho = 1 \quad (\text{C.7})$$

To solve this problem we can look for the extremum of the following functional:

$$L(\rho) = -Sp\rho \ln \rho - \sum_m F_m(t) Sp\rho P_m - (\Phi(t) - 1) Sp\rho \quad (\text{C.8})$$

where $F_m(t)$ and $\Phi(t) - 1$ are appropriate Lagrange multipliers. Demanding:

$$\delta L(\rho) = -Sp\{[\ln \rho + \Phi(t) + \sum_m F_m(t) P_m] \delta \rho\} = 0 \quad (\text{C.9})$$

for arbitrary variations $\delta \rho$, we get quasiequilibrium statistical operator as:

$$\rho_l = \exp\{-\Phi(t) - \sum_m F_m(t) P_m\} \equiv \exp\{-S(P_m, t)\} \quad (\text{C.10})$$

where

$$\Phi(t) = \ln Sp \exp\left\{-\sum_m F_m(t)P_m\right\} \quad (\text{C.11})$$

and

$$S(P_m, t) = \Phi(t) + \sum_m F_m(t)P_m \quad (\text{C.12})$$

is entropy operator for quasiequilibrium ensemble.

Conjugate parameters F_m are determined by demanding that the physical averages with total density matrix coincide with averages, calculated with quasiequilibrium statistical operator:

$$Sp\rho P_m = Sp\rho_l P_m \quad (\text{C.13})$$

or

$$\langle P_m \rangle^t = \langle P_m \rangle_l^t \quad (\text{C.14})$$

Entropy of the quasiequilibrium ensemble is:

$$\begin{aligned} S &= -\langle \ln \rho_l \rangle_l = \langle S(P_m, t) \rangle_l^t = \Phi(t) + \sum_m F_m(t) \langle P_m \rangle_l^t = \\ &= \Phi(t) + \sum_m \langle P_m \rangle^t \end{aligned} \quad (\text{C.15})$$

Thus, by construction, the quasiequilibrium statistical operator (C.10) corresponds to the extremum (in fact maximum!) of information entropy, at fixed values of averages $\langle P_m \rangle$ and normalization, just in the same way as equilibrium Gibbs ensembles correspond to the maximum of information entropy, at fixed average values of appropriate integrals of motion¹ (cf. Appendix B). In particular case of hydrodynamic regime we can take:

$$\begin{aligned} F_0(\mathbf{r}, t) &= \beta(\mathbf{r}, t), & P_0 &= H(\mathbf{r}) \\ F_1(\mathbf{r}, t) &= -\beta(\mathbf{r}, t)\mathbf{v}(\mathbf{r}, t), & P_1 &= \mathbf{p}(\mathbf{r}) \\ F_2(\mathbf{r}, t) &= -\beta(\mathbf{r}, t) \left[\mu(\mathbf{r}, t) - \frac{m}{2} \mathbf{v}^2(\mathbf{r}, t) \right], & P_2 &= n(\mathbf{r}) \end{aligned} \quad (\text{C.18})$$

where $\beta^{-1}(\mathbf{r}, t)$, $\mu(\mathbf{r}, t)$ and $\mathbf{v}(\mathbf{r}, t)$ are (local!) temperature, chemical potential and velocity.

Quasiequilibrium statistical operator (C.10) guarantees the validity of thermodynamic relations between Φ , F_m and S^2 :

$$\frac{\delta \Phi}{\delta F_m(t)} = -\langle P_m \rangle_l^t, \quad \frac{\delta S}{\delta \langle P_m \rangle_l^t} = F_m(t) \quad (\text{C.19})$$

so that $F_m(t)$ and $\langle P_m \rangle_l^t$ are conjugate to each other.

¹In equilibrium state (C.10) naturally reduces either to canonical distribution

$$\rho = \exp\{-\Phi - \beta H\}, \quad \Phi = \ln Z = \ln Sp e^{-\beta H} \quad (\text{C.16})$$

with $\Phi = -F/T$, or to grand canonical distribution

$$\rho = \exp\{-\Phi - \beta(H - \mu N)\}, \quad \Phi = \ln Z = \ln Sp e^{-\beta(H - \mu N)} \quad (\text{C.17})$$

where $\Phi = -\Omega/T$.

²If index m is discrete, functional derivatives in (C.19) are replaced by the usual partial derivatives.

However, quasiequilibrium statistical operator, defined as in Eq. (C.10), *does not* satisfy Liouville equation and does not describe nonequilibrium processes. At the same time, we shall see below, that it can be used as a proper initial condition to Liouville equation, to find the general form of nonequilibrium statistical operator.

C.2 Nonequilibrium statistical operators and quasi-averages.

Both classical (C.1) and quantum Liouville equations (C.2) are symmetric with respect to time inversion (in classical case this corresponds to $t \rightarrow -t$, reversal of momenta (velocities) of all particles and direction of magnetic field). However, the solution of Liouville equation is unstable to small perturbations, breaking this symmetry.

Let us introduce into Liouville equation an infinitesimal “source”, which satisfies the following requirements:

1. the source is breaking time reversion invariance of Liouville equation and goes to zero for $\varepsilon \rightarrow 0$ (after thermodynamic limit);
2. the source selects *retarded* solutions of Liouville equation. This requirement determines the sign of $\varepsilon > 0, \varepsilon \rightarrow +0$. Advanced solutions, corresponding to the opposite sign, will lead to decrease of entropy with time;
3. the source becomes zero for ρ equal to quasiequilibrium statistical operator ρ_l (C.10). For the equilibrium state the source is just absent.

We may consider two ways to introduce the source into Liouville equation. First one is to introduce this infinitesimal source directly to the r.h.s. of Liouville equation:

$$\frac{\partial \rho_\varepsilon}{\partial t} + \frac{1}{i\hbar}[\rho_\varepsilon, H] = -\varepsilon(\rho_\varepsilon - \rho_l) \quad (\text{C.20})$$

where $\rho \rightarrow +0$, after thermodynamic limit (during calculations of statistical averages). This infinitesimal source breaks time reversion invariance of Liouville equation, as the l.h.s. changes sign under this reversion, while the r.h.s. does not change.

Let us rewrite Eq. (C.20) in the following form:

$$\frac{d}{dt}(e^{\varepsilon t} \rho_\varepsilon(t, t)) = \varepsilon e^{\varepsilon t} \rho_l(t, t) \quad (\text{C.21})$$

where

$$\begin{aligned} \rho_\varepsilon(t, t) &= U^+(t, 0)\rho_\varepsilon(t, 0)U(t, 0) \\ \rho_l(t, t) &= U^+(t, 0)\rho_l(t, 0)U(t, 0) \\ U(t, 0) &= \exp\left\{-i\frac{Ht}{\hbar}\right\} \end{aligned} \quad (\text{C.22})$$

(H is assumed to be time independent) and we introduced the notations:

$$\rho_\varepsilon = \rho_\varepsilon(t, 0), \quad \rho_l = \rho(t, 0) \quad (\text{C.23})$$

Integrating Eq. (C.21) from $-\infty$ to t and assuming that $\lim_{t \rightarrow -\infty} \rho(t, t) = 0$, we get:

$$\rho_\varepsilon(t, t) = \varepsilon \int_{-\infty}^t e^{\varepsilon(t_1-t)} \rho_l(t_1, t_1) dt_1 = \varepsilon \int_{-\infty}^t e^{\varepsilon t'} \rho_l(t+t', t+t') dt' \quad (\text{C.24})$$

Finally, the solution of Liouville equation (C.20) gives the *nonequilibrium statistical operator* in the following form:

$$\rho_\varepsilon = \rho_\varepsilon(t, 0) = \widetilde{\rho_l(t, 0)} = \varepsilon \int_{-\infty}^t e^{\varepsilon t'} \rho_l(t+t', t') dt' \quad (\text{C.25})$$

Integrating by parts, we can rewrite Eq. (C.25) as:

$$\rho_\varepsilon = \rho_l + \int_{-\infty}^0 dt' e^{\varepsilon t'} \int_0^1 d\tau e^{-\tau S(t+t', t')} S(t+t', t') e^{(\tau-1)S(t+t', t')} \quad (\text{C.26})$$

where

$$\begin{aligned} \dot{S}(t, 0) &= \frac{\partial S(t, 0)}{\partial t} + \frac{1}{i\hbar} [S(t, 0), H] \\ \dot{S}(t, t') &= U^+(t, 0) \dot{S}(t, 0) U(t', 0) \end{aligned} \quad (\text{C.27})$$

defines the operator of entropy production, which can be proven to be positive definite [38].

Parameters $F_m(t)$, entering the expression for entropy operator are chosen so that the average values of P_m , calculated with nonequilibrium statistical operator (C.25), coincide with averages over quasiequilibrium statistical operator (C.10):

$$\langle P_m \rangle^t = \langle P_m \rangle_l^t \quad (\text{C.28})$$

where

$$\langle \dots \rangle^t = \lim_{\varepsilon \rightarrow +0} Sp(\rho_\varepsilon \dots) \quad (\text{C.29})$$

Then $\langle P_m \rangle^t$ and $F_m(t)$ become conjugate parameters, so that:

$$\frac{\delta \Phi}{\delta F_m(t)} = - \langle P_m \rangle_l^t = - \langle P_m \rangle^t \quad (\text{C.30})$$

Nonequilibrium statistical operator (C.25) can be used to calculate the average value of an arbitrary operator A as:

$$\langle A \rangle = \lim_{\varepsilon \rightarrow +0} Sp \rho_\varepsilon A \equiv \langle A \rangle \quad (\text{C.31})$$

which is a typical *quasiaverage*, as introduced by Bogolyubov (cf. discussion in Chapter 8). Applying (C.31) to operators \dot{P}_m and taking into account (C.28) we obtain transport equations:

$$\frac{\partial}{\partial t} \langle P_m \rangle_l^t = \langle \dot{P}_m \rangle^t = \lim_{\varepsilon \rightarrow +0} Sp \rho_\varepsilon \dot{P}_m = \langle \dot{P}_m \rangle \quad (\text{C.32})$$

The second way to introduce infinitesimal sources uses the fact, that logarithm of statistical operator, satisfying Liouville equation, also satisfies Liouville equation:

$$\frac{\partial \ln \rho}{\partial t} + \frac{1}{i\hbar} [\ln \rho, H] = 0 \quad (\text{C.33})$$

We may introduce infinitesimal source directly to Eq. (C.33) as:

$$\frac{\partial \ln \rho_\varepsilon}{\partial t} + \frac{1}{i\hbar} [\ln \rho_\varepsilon, H] = -\varepsilon (\ln \rho_\varepsilon - \ln \rho_l) \quad (\text{C.34})$$

where $\varepsilon \rightarrow +0$ is again performed after the thermodynamic limit. Once again we see, that this extra source breaks time reversion symmetry of Eq. (C.33).

Let us rewrite Eq. (C.34) as:

$$\frac{d}{dt} (e^{\varepsilon t} \ln \rho_\varepsilon(t, t)) = \varepsilon e^{\varepsilon t} \ln \rho_l(t, t) \quad (\text{C.35})$$

Integrating Eq. (C.35) from $-\infty$ to t , we obtain:

$$\ln \rho_\varepsilon(t, t) = \varepsilon \int_{-\infty}^t e^{\varepsilon(t_1-t)} \ln \rho_l(t_1, t_1) dt_1 = \varepsilon \int_{-\infty}^0 e^{\varepsilon t'} \ln \rho_l(t+t', t+t') dt' \quad (\text{C.36})$$

so that this version of nonequilibrium statistical operator is written as:

$$\rho_\varepsilon = \rho_\varepsilon(t, 0) = \exp\{\widetilde{\ln \rho_l(t, 0)}\} = \exp\left\{-\varepsilon \int_{-\infty}^0 dt' e^{\varepsilon t'} \ln \rho_l(t+t', t')\right\} \quad (\text{C.37})$$

where again $\varepsilon \rightarrow +0$ after the thermodynamic limit. After partial integration, we can rewrite (C.37) as:

$$\rho_\varepsilon = \exp\{-\widetilde{S(t, 0)}\} = \exp\left\{-S(t, 0) + \int_{-\infty}^0 dt' e^{\varepsilon t'} \dot{S}(t+t', t')\right\} \quad (\text{C.38})$$

Parameters $F_m(t)$, entering expression for $S(t, 0)$ and entropy production $\dot{S}(t, 0)$, are defined as above by Eqs. (C.28).

It can be shown that nonequilibrium statistical operator (C.38) corresponds to the extremum of information entropy (C.5) under additional conditions of fixing of $\langle P_m(t') \rangle = Sp \rho P_m(t')$ for any previous moment of time $-\infty \leq t' \leq 0$ and usual normalization condition.

Nonequilibrium statistical operators (C.25), (C.38) was used by different authors to derive equations of hydrodynamics, relaxation equations and kinetic equations [38]. It can be shown that in lowest orders over interactions, or in case of small thermodynamic perturbations, both (C.25) and (C.38) lead to the same transport equations (C.32). However, the question of equivalence or nonequivalence of these forms of nonequilibrium statistical operators is still open. Detailed discussion of nonequilibrium statistical operators and applications to various physical problems can be found in Ref. [38].

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