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NONEQUILIBRIUM STATISTICAL THERMODYNAMICS

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ABSTRACT: This book is the first in world literature to examine the state of the art of nonequilibrium statistical thermodynamics from a single viewpoint. The book is intended for physicists and physical chemists working in the fields of theoretical physics, molecular physics, physical chemistry, and chemical physics.

Statistical thermodynamics of irreversible processes involves study of nonequilibrium processes - transfer of energy, momentum, mass and charge - in the various physical systems (gases, liquids, solids) by means of statistical mechanics methods.

The book is the first in world literature to examine the state of the art of nonequilibrium statistical thermodynamics as the natural extension of equilibrium statistical thermodynamics from a single viewpoint. In the book are presented: basic ideas of equilibrium and nonequilibrium statistical thermodynamics of classical and quantum systems; the effect on statistical ensembles of various mechanical and thermal perturbations which upset equilibrium; fluctuation-dissipation theorems, a method based on original investigations by the author of developing nonequilibrium distribution functions and statistical operators which permit development of thermodynamic equations of irreversible processes; and the application of these methods to various problems. Examined are the statistical derivation of thermal conductivity and diffusion equations and the Navier-Stokes equation for a multicomponent liquid or gas. Also investigated are the connection between kinetic coefficients and correlation functions; the statistical theory of relaxation processes and chemical reactions both in linear and in nonlinear (with respect to attractive thermodynamic forces) approximations; relativistic statistical hydrodynamics; the derivation of generalized kinetic equations; and the derivation of the Kramers and Fokker-Planck type equations for small subsystems which interact with larger ones; and the extremal properties of a nonequilibrium statistical operator.

The book is intended for physicists and physical chemists (scientific personnel, graduate students and advanced undergraduates) working in the fields of theoretical physics, molecular physics, physical chemistry, and chemical physics.

Two illustrations, 392 bibliographical entries.

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PREFACE

In this book an attempt is made to present from a unified point of view the current state of nonequilibrium statistical thermodynamics as a natural generalization of equilibrium statistical thermodynamics.

From a logical point of view it would be desirable to present the statistical theory of nonequilibrium processes first and to consider the theory of equilibrium processes as a limiting case. However, such a presentation is at the present time scarcely feasible, as nonequilibrium and equilibrium statistical thermodynamics are at very different levels of development. Therefore, in Chapters I and II we give a brief account of the basic ideas of classical and quantum statistical mechanics of equilibrium systems to the extent that these ideas are necessary to derive the basic thermodynamic relationships for the case of statistical equilibrium.

The purpose of these introductory chapters is to recall the general method of statistical ensembles, due to Gibbs, because later in Chapters III and IV attempts are made to apply the ideas of statistical ensembles to nonequilibrium statistical thermodynamics.

A separate chapter is devoted to classical statistical mechanics, although classical statistical mechanics can be regarded as the limiting case of quantum statistical mechanics for those situations in which it is permissible to neglect quantum corrections. We shall not follow such a course, because classical statistical mechanics is interesting in itself and is completely adequate for many problems. The methods of classical and quantum statistics have much in common as regards the theoretical formulation of problems. Very similar difficulties are encountered in attempts to justify both methods. The limiting transition from quantum to classical statistics will be considered later, at the end of Chapter II.

In Chapter III we consider nonequilibrium processes and study the reaction of statistical ensembles to external, mechanical perturbations. By this is meant a perturbation which arises from switching on an external field when the perturbation energy can be represented by an additional term in the

Hamiltonian. A state of statistical equilibrium is used as the initial condition. A discussion is given of the fluctuation-dissipation theorems, dispersion relations, and sum rules and their application, in particular for systems of charged particles.

Chapter IV is dedicated to thermal perturbations, which cannot, generally speaking, be represented by any perturbation energy; for example, perturbations arising from a change of temperature, pressure, or the concentration of particles in space and time are considered. This case requires a more explicit construction of statistical ensembles than does the case of mechanical perturbations.

Using the idea of "quasi-integrals of motion" for a compact description of the system, a nonequilibrium statistical operator is constructed and then applied to various problems, such as a derivation of a system of equations for the translation of energy, momentum and number of particles into a multicomponent system, or a derivation of relaxation equations, kinetic equations and equations of the Kramers-Fokker-Planck type. It is shown that this nonequilibrium statistical operator may be obtained from an extremum of the information entropy when the fixed quantities defining the nonequilibrium state are specified not only at a given moment, but also for all past times. This chapter is to a large degree based on the work of the author.

It is assumed that the reader is acquainted with the fundamentals of quantum and classical equilibrium statistical mechanics to the extent given in the usual university courses.

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D. Zubarev

INTRODUCTION

Nonequilibrium statistical thermodynamics forms the theoretical basis for nonequilibrium thermodynamics [1], just as the usual statistical thermodynamics is the basis for equilibrium thermodynamics. In nonequilibrium statistical thermodynamics one studies the processes of transfer of energy, momentum and particles in various physical systems (gases, liquids, solids) on the basis of statistical mechanics. The problem is to derive the equations of nonequilibrium thermodynamics by the methods of statistical mechanics (to the extent that this is possible) "from first principles," i.e., to find from the equations of quantum or classical mechanics expressions for the kinetic coefficients in terms of microscopic characteristics, to justify the symmetry properties of the coefficients, and to prove fluctuation-dissipation theorems.

The most highly developed method in the theory of irreversible processes is the method of the kinetic equation for the distribution function; the method was proposed already by Boltzmann and justified and further developed by N. N. Bogolyubov [2], Kirkwood [3], Born and Green [4], Van Hove [5], and others [6,7]. This method allows one to derive the equations of nonequilibrium thermodynamics, and to calculate explicitly the kinetic coefficients. The method has great practical importance, but it can be applied only to sufficiently dilute gases or to sufficiently weakly interacting gases. Thus there arises the problem of constructing the equations of irreversible thermodynamics on the basis of statistical mechanics for more general systems.

The usual linear phenomenological nonequilibrium thermodynamics can be applied to any system provided that the system is in a weakly nonequilibrium state, i.e., it is close to complete statistical equilibrium. We note that this theory does not employ a consistently macroscopic point of view. Besides the axiomatic thermodynamic method, it uses in an essential way an argument at a microscopic level, namely, that the particles obey the equations of mechanics. As an example, one can derive the Onsager reciprocity relations from the invariance of the equations of motion with respect to time reversal. In this, however, one uses only the fact that the equations of motion exist, not their specific form, which is associated with the form of the Hamiltonian. Nonequilibrium thermodynamics goes further in this direction, starting with a system described by a specific Hamiltonian and making explicit use of the equations of motion.

Nonequilibrium statistical thermodynamics is an outgrowth of the equilibrium theory, but the equilibrium theory is relatively well-developed, its foundations having been laid by Gibbs [8] around the turn of the century. On the other hand, the nonequilibrium theory is still in a state of development and is far from completion.

Until recently the opinion was widespread (it is held by many people even today) that there was no universal method, like the Gibbs method, which could be applied to the analysis of irreversible processes in an arbitrary system. It was thought that an exact formulation of the problem was possible only in the limiting cases of systems for which a kinetic equation could be constructed.

The development of the theory of irreversible processes during the past ten years (see the reviews [9-13]) shows that important steps have been taken toward the construction of the statistical thermodynamics of irreversible processes for arbitrary systems, and the theory has already begun to produce its own techniques. This confirms the idea of Callen and Welton expressed in 1951 in a work on the general theory of fluctuations and generalized noise [14]: "We believe that determination of the connection between equilibrium fluctuations and irreversibility opens up the path to the construction of a general theory of irreversibility using the methods of statistical ensembles." In this book an attempt is made to sum up the preliminary results which one encounters on this path.

We shall study nonequilibrium processes in macroscopic thermodynamic systems, for example, gases, liquids, and solids, by the methods of statistical mechanics. Therefore we shall assume in all that follows that the system under consideration is made up of a large number of particles and that it obeys the laws of quantum (or classical) mechanics and that Hamiltonian of the system is known. (An account of equilibrium statistical mechanics can be found in the references [15-19].)

Any state of a thermodynamic system which differs from a state of complete statistical equilibrium we shall call a nonequilibrium state. A process will be called a nonequilibrium process if it includes nonequilibrium states.

Processes accompanied by a production of entropy in the system (i.e., the formation of entropy, but not its redistribution) will be called irreversible. Examples are diffusion, viscous motion, thermal conduction, and electrical conduction in normal metals. Irreversible processes are also called dissipative.

CHAPTER I

EQUILIBRIUM STATISTICAL THERMODYNAMICS OF CLASSICAL SYSTEMS

Statistical thermodynamics of both equilibrium and nonequilibrium processes begins with the equations of mechanics (quantum or classical) for the collection of particles making up the system. The solution of this system of equations is impossible in practice because of the huge number of variables, but even if a solution were possible, we could not set up the initial conditions for such a large number of equations - this is far beyond experimental capabilities. Therefore, to study such systems the methods of statistical mechanics are used; these methods are based upon the introduction of distribution functions in classical statistical mechanics or of statistical operators in quantum statistical mechanics.

In this chapter we shall consider the basic concepts of classical statistical mechanics of equilibrium systems, i.e., the Gibbs method of statistical ensembles for systems of particles obeying classical mechanics.

§ 1. Distribution Functions

1.1 Distribution Functions for Systems of Interacting Particles.

Let us consider a system of N identical, interacting particles contained in a finite, but macroscopically large volume V. For simplicity we shall assume that the particles have no internal degrees of freedom.

In classical mechanics the dynamical state of each particle is defined by giving its coordinates q and momentum p, where q and p denote the set of three Cartesian coordinates and three components of momentum q^α, p^α ($\alpha=1,2,3$). The state of the whole system is defined by giving the set of coordinates $q_1,\dots,q_N$ and momenta $p_1,\dots,p_N$ of all particles, or by giving the location of a point in the 6N-dimensional phase space $(p_1,\dots,p_N; q_1,\dots,q_N)$.

The dynamical evolution of the system is defined by Hamilton's equations:

$$\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k}, \qquad \frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k} \qquad (k = 1, 2, \dots, N), \tag{1.1}$$

where

$$H = H(p_1, \dots, p_N; q_1, \dots, q_N; t)$$

is the total Hamiltonian of the system; the Hamiltonian is assumed to be known. For example, for a system of N particles with a two-particle, centrally-symmetric interaction, described by the potential $\phi(|q_i - q_k|)$, the Hamiltonian has the form

$$H = \sum_{k} \frac{p_k^2}{2m} + \frac{1}{2} \sum_{i \neq k} \phi(|q_i - q_k|). \tag{1.2}$$

The corresponding equations of motion are

$$\dot{q}_k = \frac{p_k}{m}, \quad \dot{p}_k = -\sum_{i \neq k} \frac{\partial \phi(|q_i - q_k|)}{\partial q_k} = F_k \quad (k = 1, 2, \ldots, N), \tag{1.3}$$

where F_k is the force produced on the kth particle by all the other particles. The fact that the volume is finite can be taken into account by adding to (1.2) an additional potential function $U_V(q_1,\ldots,q_N)$ which depends on the coordinates of the particles: U_V is constant within the volume V and rapidly approaches infinity upon the approach of any particle toward the boundary of the volume.

A probabilistic treatment of dynamical processes is applied in statistical mechanics. Following Gibbs, a given system is not considered by itself, but rather, a large number (in the limit - an infinite number) of copies of the system are considered; these copies are in macroscopically identical conditions. I.e., a statistical ensemble "representing" the macroscopic state of the system is introduced.

The identity of external conditions in a macroscopic sense means that all ensembles are characterized by identical values of the macroscopic parameters (to within the accuracy of possible fluctuations) and by identical types of contacts with the surrounding objects: reservoirs of energy or particles, or movable pistons. This puts restrictions on the coordinates and momenta of the particles; otherwise these variables are arbitrary.

A point in phase space $(p_1,\ldots,p_N; q_1,\ldots,q_N)$ or briefly, (p,q), corresponds to each system in the ensemble. With the passage of time each phase point moves along its characteristic trajectory in phase space in accordance with equations (1.1) or (1.3).

The statistical is defined by the distribution function

$$f(p,q,t)$$

which is the probability density for the distribution of systems in phase space. It is defined such that

$$dw = f(p,q,t)\, dp\, dq \tag{1.4}$$

is the probability of finding the system at an instant t in the element of phase volume dpdq near the point (p,q), i.e., $(p_1,\ldots,p_N; q_1,\ldots,q_N)$.

1.2 Normalization.

The distribution function (1.4) must satisfy the normalization condition

$$\int f(p,q,t)\,dpdq = 1, \tag{1.4a}$$

since the sum of the probabilities of all possible states must equal one.

However such a normalization of the distribution function is inconvenient. Classical statistics is the limiting case of quantum statistics for temperatures which are high enough such that quantum effects can be neglected. But the normalization (1.4a) does not correspond to the limiting transition from quantum to classical statistics. Thus, it is more convenient to use a distribution function with a different normalization.

From quantum mechanics it is known that the classical concepts of the position and momentum of a particle can be introduced without contradicting quantum mechanics only within the scope of the quasiclassical approximation. The smallest cell in phase space corresponding to one-dimensional motion of the i^{th} particle in the quasiclassical approximation has the magnitude $h = 2\pi\hbar$ (Planck's constant),

$$\Delta q_i^x \Delta p_i^x \geqslant h.$$

Consequently, the "volume" of the smallest cell in the phase space of a single particle is h^3; in the phase space of N particles it is h^{3N}. Thus, the quantity h^{3N} is the natural unit of phase-space (or simply, phase) volume. Therefore it is convenient to introduce a distribution function which is normalized to unity on the dimensionless phase volume $dpdq/h^{3N}$.

In addition, one must take into account that a quantum-mechanical state is unchanged by the interchange of the identical particles, and this property must be retained in classical statistics, if this is to be regarded as the limiting case of quantum statistics. Since the number of permutations of N identical particles is N!, the element of phase volume must be divided by N!, as it is necessary to take into account only distinct states.

From the above it is seen to be convenient to introduce a dimensionless distribution function, referred to an element of phase volume expressed in units of h^{3N} and taking into account the identity of the particles, i.e., $dpdq/N!h^{3N}$. Consequently, it is more convenient to define the distribution function f(p,q,t) by

$$dw = f(p, q, t)\frac{dp\,dq}{N!\,h^{3N}}. \tag{1.5}$$

rather than by (1.4). In this case the normalization condition for the distribution function is

$$\int f(p, q, t)\, d\Gamma = 1, \tag{1.5a}$$

where

$$d\Gamma = \frac{dp\, dq}{N!\, h^{3N}} \tag{1.5b}$$

is the dimensionless element of phase volume. Now the integration in (1.5a) corresponds to a summation over all distinct states. It can be shown that if classical mechanics is regarded as the limiting case of quantum mechanics, then this is precisely the normalization condition which is obtained (see §14).

We remark that the factor 1/N! in the phase volume was introduced by Gibbs [1] before the creation of quantum mechanics in order to avoid the paradox which bears his name - the increase of entropy upon mixing identical gases at the same temperature and pressure. He distinguished "specific" phases p,q and "generic" phases, for which the phase volume was divided by N!, and he normalized the distribution functions with respect to the generic phases.

Knowledge of the distribution function f(p,q,t) allows one to calculate the mean value of any dynamical variable A(p,q), i.e.,

$$\langle A\rangle = \int A(p, q)\, f(p, q, t)\, d\Gamma, \tag{1.6}$$

where the normalization (1.5a) is assumed.

§ 2. The Liouville Equation

2.1 The Liouville Theorem on the Invariance of the Phase Volume.

The possibility of introducing a distribution function as a probability density is based upon a theorem of Liouville - a theorem of pure mechanics, not drawing at all on probabilistic considerations. According to the Liouville theorem the phase volume is constant for the motion of systems obeying Hamilton's equations (1.1). That is, if at an initial time the phase points (p^0, q^0) continuously fill up some initial region G_0 in phase space, and at time t they occupy a region G_t, then the corresponding phase volumes are equal:

$$\int_{G_0} dp^0\, dq^0 = \int_{G_t} dp\, dq, \tag{2.1}$$

or for infinitesimal elements of phase volume

$$dp^0 dq^0 = dpdq \tag{2.2}$$

In other words the motion of phase points representing systems in phase space is similar to the motion of an incompressible fluid.

To prove the Liouville theorem we change the variables of integration on the right hand side of (2.1) from p,q to p^0,q^0. Then

$$\int\limits_{G_t} dp\, dq = \int\limits_{G_0} \frac{\partial (p, q)}{\partial (p^0, q^0)}\, dp^0\, dq^0,$$

where $\frac{\partial(p,q)}{\partial(p^0,q^0)}$ is the Jacobian of the transformation from the variables p,q to p^0,q^0. It is a determinant with elements $\partial x_i/\partial x_k^0$ where x_i is the set of momenta and coordinates p_i,q_i, and x_k^0 is the set p_k^0,q_k^0.

We shall now show that this Jacobian is equal to one on the basis of Hamilton's equations, i.e.,

$$\frac{\partial(p,q)}{\partial(p^0,q^0)} = 1 \tag{2.3}$$

One can prove equation (2.3) directly by differentiating the Jacobian with respect to time [2]. It is simpler, following Gibbs [1], to make use from the beginning of the property of functional determinants

$$\frac{\partial (p, q)}{\partial (p^0, q^0)} = \frac{\partial (p', q')}{\partial (p^0, q^0)} \cdot \frac{\partial (p, q)}{\partial (p', q')},$$

where p', q' are the values of momenta and coordinates corresponding to an arbitrary time t'. We differentiate this identity with respect to t, keeping t_0 and t' constant:

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

As t' is arbitrary, we put $t' = t$ after differentiating. In this case the only non-zero terms of the Jacobian are the elements along the main diagonal,

$$\frac{d}{dt} \frac{\partial (p, q)}{\partial (p^0, q^0)} = \frac{\partial (p, q)}{\partial (p^0, q^0)} \sum_i \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right) \tag{2.4}$$

(see [2,20]). But from the equations of motion (1.1)

$$\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} = 0, \tag{2.5}$$

and, consequently,

$$\frac{d}{dt}\frac{\partial(p,q)}{\partial(p^0,q^0)} = 0, \tag{2.6}$$

i.e., the Jacobian is independent of time.

Using the initial condition

$$\left.\frac{\partial (p, q)}{\partial (p^0, q^0)}\right|_{t=t_0} = 1,$$

we verify that the Jacobian (2.3) indeed equals one; thus, the theorem of Liouville is proved.

2.2 Liouville's Equation.

Until now in the derivation and formulation of Liouville's theorem we have nowhere made use of the concept of a distribution function; this is reasonable in that we have been discussing a theorem of mechanics. If now the distribution functions are introduced, as in § 1, then different formulations of Liouville's theorem can be given.

From Liouville's theorem it follows that the distribution function is constant along phase trajectories; this can be considered as one statement of the theorem.

In fact, for motion in phase space of points representing systems, the number of phase points does not change; all the phase points found at time t in the element of volume dpdq go into the element dp´dq´ at the time t´. Thus,

$$f(p,q,t)\,dp\,dq = f(p',q',t')\,dp'dq',$$

and since, by Liouville's theorem, dpdq = dp´dq´, we obtain

$$f(p,q,t) = f(p',q',t'), \tag{2.7}$$

i.e., f is constant along phase trajectories, which was to be shown.

We give one more very convenient formulation of Liouville's theorem which is most often used in practical problems - we derive Liouville's equation for the distribution function.

Putting the time t infinitesimally close to t´ = t + dt, we have from (2.7)

$$f(p,q,t) = f(p+\dot{p}dt, q+\dot{q}dt, t+dt).$$

Assuming further that the function f is differentiable, we obtain the differential equation for f:

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \sum_k \left(\frac{\partial f}{\partial p_k} \cdot \dot{p}_k + \frac{\partial f}{\partial q_k} \cdot \dot{q}_k \right) = 0. \tag{2.8}$$

Equation (2.8), combined with Hamilton's equations, is Liouville's equation:

$$\frac{\partial f}{\partial t} = \sum_k \left(\frac{\partial H}{\partial q_k} \cdot \frac{\partial f}{\partial p_k} - \frac{\partial H}{\partial p_k} \cdot \frac{\partial f}{\partial q_k} \right). \tag{2.9}$$

The sum on the right hand side of (2.9) is called the Poisson bracket for the functions H and f:

$$\{H, f\} = \sum_k \left(\frac{\partial H}{\partial q_k} \cdot \frac{\partial f}{\partial p_k} - \frac{\partial H}{\partial p_k} \cdot \frac{\partial f}{\partial q_k} \right) \equiv \frac{\partial H}{\partial q} \frac{\partial f}{\partial p} - \frac{\partial H}{\partial p} \frac{\partial f}{\partial q}; \tag{2.10}$$

thus, Liouville's equation can be written in the form

$$\frac{\partial f}{\partial t} = \{H, f\}. \tag{2.11}$$

This equation is fundamental for the construction of statistical ensembles in both equilibrium and nonequilibrium situations. Using this equation one can calculate f at any time t, if it is known at the time $t = t_0$. The equation allows one to study the reaction of statistical systems to external perturbations (see Chapter III).

Liouville's equation has the form of a continuity equation for the motion of phase points in phase space. One can obtain a simple, intuitive interpretation of this equation by considering the motion of points in the 6N-dimensional phase space as the motion of a "liquid" with density f. The velocity of flow is represented by a vector in this space $\dot{p}_1, \ldots, \dot{p}_N; \dot{q}_1, \ldots, \dot{q}_N$. Thus, the condition of the conservation of phase points, i.e., the equation of continuity in phase space has the form

$$\frac{\partial f}{\partial t} + \sum_k \left[\frac{\partial}{\partial p_k} \cdot (f \dot{p}_k) + \frac{\partial}{\partial q_k} \cdot (f \dot{q}_k) \right] = 0, \tag{2.12}$$

where the quantity in brackets is the 6N-dimensional divergence of the current vector. Carrying out the differentiation under the summation sign and using (2.5) (which came from Hamilton's equations) we verify that equation (2.12) is of the form of (2.8), i.e., it is Liouville's equation. From (2.5) it follows that the motion of the "liquid" is incompressible.

In statistical equilibrium f and H do not depend explicitly on time, and the Liouville equation is

$$\{H,f\} = 0, \tag{2.13}$$

i.e., in this case the distribution function is an integral of the motion.

In fact, Liouville's equation is a linear partial differential equation, while Hamilton's equations form the corresponding system of differential equations in the total derivatives. Therefore, the general solution of equation (2.9) is an arbitrary function of all the solutions of the system (1.1).

2.3 Time Evolution of the Distribution Function.

To study the time evolution of the distribution functions it is convenient to write the Liouville equation as

$$i\frac{\partial f}{\partial t} = -Lf, \tag{2.14}$$

where L is a linear operator defined by the relation

$$iLf = \{H,f\}; \tag{2.14a}$$

it is called the *Liouville operator*.

The representation of the Liouville equation in the form (2.14) is convenient, because the operator L is Hermitian, and the properties of Hermitian operators are well known. The Hermiticity of L is easy to verify. Indeed, for arbitrary functions $\varphi_m(p,q)$, $\varphi_n(p,q)$, which vanish on the boundaries of the phase volume, a partial integration of the Poisson brackets gives

$$\int \varphi_m^*(L\varphi_n)\,dp\,dq = \int \varphi_n(L^*\varphi_m^*)\,dp\,dq. \tag{2.15}$$

The relationship (2.15) is just the condition for the Hermiticity of L.

There exists a formal analogy between the Liouville equation (2.14) and the Schroedinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi,$$

as L and H are both linear Hermitian operators. This analogy was widely used by Prigogine [3] to transfer the methods of quantum mechanics into classical statistical mechanics.

For the Hamiltonian (1.2) the Liouville operator has the form

$$L = i \sum_k \left[\frac{p_k}{m} \cdot \frac{\partial}{\partial q_k} + F_k \cdot \frac{\partial}{\partial p_k} \right] \tag{2.16}$$

and does not depend explicitly on time.

Using the Liouville operator (2.14a) a formal solution of the Liouville equation can be written, if the initial value (at t = 0) of the distribution is known. The solution has the form

$$f(p,\, q,\, t) = e^{iLt} f(p,\, q,\, 0), \tag{2.17}$$

if L does not depend explicitly on time.

Differentiating (2.17) with respect to t, we verify that this function indeed satisfies the Liouville equation

$$\frac{\partial f(p,\, q,\, t)}{\partial t} = iL\, e^{iLt} f(p,\, q,\, 0) = iL\, f(p,\, q,\, t)$$

and the initial condition

$$f(p,\, q,\, t)\big|_{t=0} = f(p,\, q,\, 0).$$

We shall often make use of such a formal solution of the Liouville equation.

Let us derive the equation of motion for a dynamical variable A(p,q,t), where the last argument indicates the explicit time dependence. To do this we differentiate A(p,q,t) with respect to time, considering p and q to have the time dependence given by Hamilton's equations. We have

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A,\, H\}. \tag{2.18}$$

We show that in this case the mean value of the time derivative of A is equal to the derivative of the mean value. The mean value of A(p,q,t) at time t is

$$\langle A\rangle = \int A(p, q, t) f(p, q, t)\, d\Gamma, \tag{2.19}$$

where f(p,q,t) satisfies the Liouville equation (2.11). Differentiating (2.19) with respect to time, using the Liouville equation for f, and integrating the Poisson brackets by parts, we obtain

$$\frac{d}{dt}\langle A\rangle = \int \left(\frac{\partial A}{\partial t} + \{A, H\}\right) f\, d\Gamma,$$

i.e.,

$$\frac{d}{dt}\langle A\rangle = \left\langle\frac{dA}{dt}\right\rangle, \tag{2.19a}$$

which was to be shown.

If A does not depend explicitly on time, then

$$\frac{dA}{dt} = \{A, H\} = -iLA, \tag{2.20}$$

i.e., the dynamical variable satisfies an equation similar to the Liouville equation, but with the opposite sign in front of the Poisson bracket.

If the value of the dynamical variable A(0) is known for t=0, then, if L does not depend explicitly on time, (2.20) has the formal solution

$$A(t) = e^{-iLt} A(0), \tag{2.21}$$

i.e., the time evolution of dynamical variables can be expressed using the Liouville operator.

The operator e^{-iLt} is called the evolution operator. It acts on an arbitrary function $\varphi(p(0),q(0))$ to translate it into $\varphi(p(t),q(t))$, i.e.,

$$e^{-iLt}\varphi(p(0), q(0)) = \varphi(p(t), q(t)), \qquad (2.21a)$$

where p(t),q(t) are solutions of Hamilton's equations in which H has no explicit time dependence, and with the initial conditions $p(t)|_{t=0} = p(0)$, $q(t)|_{t=0} = q(0)$.

The relation (2.21a) is easily shown directly.

The relation (2.21a) follows from the properties of the Liouville operator, as

$$-iLq = \frac{dq}{dt}, \quad -iLp = \frac{dp}{dt}$$

and

$$(-iL)^n q = \left(\frac{d}{dt}\right)^n q, \quad (-iL)^n p = \left(\frac{d}{dt}\right)^n p,$$

from which we obtain

$$e^{-iLt} q(0) = \sum_n \frac{t^n}{n!}\left(\frac{d^n q}{dt^n}\right)_{t=0} = q(t), \qquad e^{-iLt} p(0) = p(t),$$

because these are Taylor series with the derivatives defined from the equations of motion. Very similar properties hold also for powers of the coordinates and momenta; for example, $-iLq^2 = \frac{dq^2}{dt}$. The relation (2.21a) for the evolution operator can be demonstrated using these properties by expanding φ in a Taylor series in p,q.

2.4 Entropy.

The negative of the logarithm of the distribution function plays a special role in statistical mechanics:

$$\eta = -\ln f(p,q,t) \qquad (2.22)$$

(Gibbs calls $-\eta$ the phase index). The quantity η is convenient because it is additive for multiplicative distribution functions, and, as we shall see in what follows, it is connected with the entropy of the system.

It is easy to see that η satisfies the Liouville equation

$$\frac{\partial \eta}{\partial t} = \{H, \eta\}. \qquad (2.23)$$

just as does f. This equation, obtained already by Gibbs, turns out to be very useful in the theory of irreversible processes, although it receives much less attention than the Liouville equation. The convenience of equation (2.23) lies in the fact that the properties of H are much closer to η than to f(p,q).

The mean value of the negative of the logarithm of the distribution function, i.e., the mean value of η, is called the Gibbs entropy. Using the dimensionless normalization of the distribution function (1.5a) the entropy is equal to

$$S = \langle \eta \rangle = -\int f(p, q, t) \ln f(p, q, t) \frac{dp\, dq}{N!\, h^{3N}}. \qquad (2.24)$$

Formula (2.24) is the Gibbs definition of entropy.

For a dilute gas the states of the different particles can be regarded as statistically independent; therefore, the total distribution function equals the product of the distribution functions for the individual particles:

$$f(p, q, t) = \frac{N!}{N^N} \prod_{i=1}^{N} f_1(p_i, q_i, t) \qquad \left(\ln N! \simeq N \ln \frac{N}{e}\right), \qquad (2.25)$$

where the single particle distribution functions have the normalization

$$\int f_1(p_i, q_i, t) \frac{dp_i\, dq_i}{h^3} = N. \qquad (2.26)$$

The factor $N!/N^N$ is in (2.25) in order to coordinate the normalization (1.5a) with (2.26). In fact,

$$\int f(p, q, t)\, d\Gamma = \left\{ \frac{1}{N} \int f_1(p_i, q_i, t) \frac{dp_i\, dq_i}{h^3} \right\}^N = 1.$$

For the distribution function (2.25) the entropy (2.24) equals

$$S = S_B, \tag{2.27}$$

where

$$S_B = - \int f_1(p_1, q_1, t) \ln \frac{f_1(p_1, q_1, t)}{e} \frac{dp_1 \, dq_1}{h^3} \tag{2.28}$$

is the Boltzmann entropy.

In the general case, when the multiplicative property (2.25) does not hold, the Boltzmann entropy can still be defined by the formula (2.28), where $f_1(p_1,q_1,t)$ is the single particle distribution function, obtained from $f(p,q,t)$ by integrating over all coordinates and momenta except p_1,q_1:

$$f_1(p_1, q_1, t) = \int f(p_1, q_1, \ldots, p_N, q_N; t) \frac{dp_2 \, dq_2 \ldots dp_N \, dq_N}{(N-1)! \, h^{3N-3}}. \tag{2.29}$$

The function $f_1(p_1,q_1,t)$ has the normalization (2.26).

From thermodynamics it is well known that the entropy of an isolated system increases, or in thermodynamic equilibrium, is a constant. If $f_1(p_1,q_1,t)$ satisfies Boltzmann's kinetic equation [4], then the Boltzmann entropy increases, but it is constant in the case of statistical equilibrium. However, the Boltzmann definition for the entropy (2.28) gives the correct expression for the entropy as a thermodynamic function in equilibrium states only for an ideal gas. Therefore S_B cannot be identified with the entropy of the system, and in the general case the Boltzmann definition of entropy is unsuitable.

The Gibbs definition of entropy (2.24) is notably better than the Boltzmann definition, since in the equilibrium case it gives the correct expression for entropy as a thermodynamic function (see §§ 3 and 5).

For an equilibrium situation there is no problem with the Gibbs definition of entropy. It is a different matter if f is time dependent. In that case the Gibbs definition of entropy has an essential defect and must be made more accurate (see Chapter IV).

It is easily seen that for an isolated system the Gibbs entropy is time independent and therefore cannot increase.

In fact, let the distribution function equal $f(p^0,q^0,0)$ at t=0 and $f(p,q,t)$ at time t, where (p,q) lies on the phase trajectory passing through (p^0,q^0) and defined by the equations of motion. By the Liouville theorem (2.7) we have

$$f(p^0,q^0,0) = f(p,q,t).$$

The Gibbs entropy at time t is equal to

$$S = -\int f(p, q, t) \ln f(p, q, t) \frac{dp\, dq}{N!\, h^{3N}} = -\int f(p^0, q^0, 0) \ln f(p^0, q^0, 0) \frac{dp^0\, dq^0}{N!\, h^{3N}},$$

since by the Liouville theorem (2.2)

$$dp dq = dp^0 dq^0.$$

Thus, the Gibbs entropy (2.24) for an isolated system does not change with time.

Gibbs tried to show that the entropy of an isolated system can in some sense increase. P. and T. Ehrenfest [5,6] showed in what sense this is possible. They proposed to "coarsen" the Gibbs definition of entropy and in place of the actual distribution function f(p,q,t), which might be called the fine-structure distribution density, to introduce the roughened coarse-structure density [1]

$$\bar{f}(p, q, t) = \frac{1}{\omega} \int_{\omega} f(p, q, t)\, dp\, dq, \tag{2.30}$$

where the integration is carried out over a small, fixed cell ω in phase space. From a physical point of view the operation of coarse-structure averaging (2.30) corresponds to the fact that observed quantities are always averages over some region. Quantum mechanics establishes a lower bound for the cell ω; it cannot be smaller than h^{3N}.

The Gibbs entropy constructed using the coarsened density is, generally speaking, not constant in time and can increase; this is true for arbitrarily small coarsenings.

Let us compare the values of the Gibbs entropy calculated for the coarse-structure distribution function (2.30) at times t and t=0; we assume that initially the actual and coarsened densities are the same:

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[1] In Russian literature the terms "coarse grained" and "fine grained" are sometimes used; such terminology does not seem very felicitous to us.

$$f(p^o,q^o,0) = \tilde{f}(p^o,q^o,0). \qquad (2.31)$$

We have

$$\begin{aligned} S_t - S_0 = & -\int \tilde{f}(p, q, t) \ln \tilde{f}(p, q, t)\, d\Gamma + \\ & + \int f(p^0, q^0, 0) \ln f(p^0, q^0, 0)\, d\Gamma_0 = \\ = & -\int \{f(p, q, t) \ln \tilde{f}(p, q, t) - f(p, q, t) \ln f(p, q, t)\}\, d\Gamma \end{aligned} \qquad (2.31a)$$

(we have used the Liouville theorem and removed the tilde from the distribution function which is not in the argument of a logarithm; this can always be done inside an integral).

For any two normalized distribution functions f and f′, defined on the same phase space, there exists the inequality

$$\int f \ln\left(\frac{f}{f'}\right) d\Gamma \geq 0. \qquad (2.32)$$

The equality holds only if f=f′. Using (2.32) we obtain

$$S_t \geq S_0.$$

The inequality (2.32) is a consequence of the obvious inequality

$$\ln\left(\frac{f}{f'}\right) \geq 1 - \frac{f'}{f} \qquad (f' > 0,\ f > 0), \qquad (2.32a)$$

the equality holding only for f=f′. Inequality (2.32a) is easily verified by noting that ln x - 1 + 1/x is a positive function, equal to zero only for x=1, and then putting x=f/f′.

We obtain inequality (2.32) by multiplying (2.32a) by f and integrating over all phase space. Thus,

$$\int f \ln\left(\frac{f}{\tilde{f}}\right) d\Gamma \geqslant \int f\left(1 - \frac{\tilde{f}}{f}\right) d\Gamma = 0,$$

which was to be shown.

Let us suppose that $f(p^o,q^o,0)$ does not correspond to an ensemble in statistical equilibrium; then at time t

$$f(p,q,t) \neq \tilde{f}(p,q,t), \qquad (2.33)$$

because although $f(p,q,t)$ does not change along phases trajectories, phase points will be interchanged between the given cell ω and other cells, and, in general, the number of points entering and leaving ω will not be identical. A "mixing" of phase points among the phase cells will take place. Using (2.33) we obtain

$$S_t > S_o, \qquad (2.34)$$

i.e., the entropy for the coarse-structure distribution function can increase.

The introduction of the coarse-structure averaging does not, however, resolve the question of the increase of the entropy; it must be verified that mixing in fact takes place. The smaller the scale of coarseness, the smaller becomes the growth of the entropy S_t, and in the limit $\omega \to 0$ it approaches zero. But the growth of the physical entropy cannot depend on the scale of the coarseness.

In answer to this objection we note that in applying the operation of coarse-structure averaging, we are effecting two limiting processes: the usual limiting transition of statistical mechanics $V \to \infty$ $(N/V = \text{const.})$ and the approach to zero of the cell ω. There is no basis for supposing that the result will not depend on the order in which the limits are taken. Ehrenfest's coarsening of the distribution function can be effective only if the limit $V \to \infty$ is taken first and then the limit $\omega \to 0$, and if there are no discontinuities in the limiting transitions.

It is interesting to recall that Gibbs, in constructing the analogy between the approach of a system toward equilibrium and mixing in an incompressible liquid, essentially introduced the procedure for the coarsening of the density of the distribution and noted the absence of discontinuities in the limiting transitions (see [1], chapter 12, pages 143-147).

Ehrenfest's coarse-structure averaging thus does not solve the problems of the increase of entropy, but the idea of averaging the distribution functions is clearly of interest.

The smoothing of the distribution functions is possible not only in phase space, but also in time. Actually, all observed quantities are averages taken over a time interval T of the order of the observation time. Therefore, the distribution function can be averaged over a time interval T

$$\widetilde{f(p,\, q,\, t)} = \frac{1}{T}\int_0^T f(p(t+t_1),\ q(t+t_1))\,dt_1 \tag{2.35}$$

The dynamical variables can be averaged in an analogous way.

This smoothing of the distribution functions with respect to time has been widely used by Kirkwood [7], and it is evidently more effective than Ehrenfest's coarse-structure smoothing. It is analogous to the averaging of the equations of motion in nonlinear mechanics, which smoothes the rapid oscillations about the mean trajectory and helps to define the average motion [8]. There is in general a deep relationship between the methods of nonlinear mechanics and statistical mechanics. A statistical system tends toward a state of statistical equilibrium regardless of the initial conditions, which are rapidly "forgotten"; this is similar to the approach of a nonlinear system toward a limit cycle. The methods of eliminating secular terms in constructing kinetic equations are the same as those used to solve the equations of nonlinear mechanics [9].

There is another possible method for time smoothing the distribution functions:

$$\widetilde{f(p,\, q,\, t)} = \varepsilon\int_{-\infty}^{0} e^{\varepsilon t_1} f(p(t+t_1),\ q(t+t_1))\,dt_1; \tag{2.36}$$

This method is applied to wave functions in collision theory in formulating the boundary conditions to select retarded solutions of the Schroedinger equation [10] (see Appendixes I and III). Later (Chapter IV) we shall use exactly this method of "causal" smoothing of dynamical variables, and we shall find that it is most convenient. It is necessary to take the limit $\varepsilon \to 0$ after the usual limiting transition of statistical mechanics $V \to \infty$ $(V/N = \text{const.})$.

§ 3. Gibbs Statistical Ensembles

In order to construct statistical equilibrium ensembles it must be decided on which integrals of motion the distribution function depends and what form it has for the various external conditions which macroscopically define the ensemble. This problem was solved by Gibbs, although rigorous justification of the resulting distributions is a complicated problem which up to the present time is not completely solved. It is not even clear to what extent a rigorous justification is possible.

For nonequilibrium states the construction of statistical ensembles is significantly more complicated, and tentative progress has been made in this direction only in the last few years. Here the more urgent problem is the actual construction of the ensembles, rather than their rigorous formal justification. We shall consider these questions in Chapters III and IV.

According to Gibbs the distribution function f in states of statistical equilibrium depends only on the single valued, additive integrals of motion.

The additive property of the integrals of motion means that the integrals of motion of the total system are obtained simply by adding the integrals of motion of the subsystems.

Three such integrals of motion are known: the energy H, the total momentum **P**, and the total angular momentum **M**. Consequently,

$$f = f(H,\mathbf{P},\mathbf{M}). \tag{3.1}$$

Neglecting the interaction with the container walls, **P** and **M** are exactly additive. H is additive to within a factor of the energy surface on the interface between subsystems; this energy surface arises from the interaction between particles in the different subsystems.

If the total number N of particles in each system in the ensemble is not specified, then N must be regarded as a fourth integral of motion, as N does not change with the evolution of the systems. Thus, in this case

$$f = f(H,N,\mathbf{P},\mathbf{M}). \tag{3.1a}$$

The integral of motion **M** must be taken into account if the system is rotating as a whole with constant angular velocity, and the integral of motion **P** must be considered for superconducting systems in quantum statistics.

The number of essential integrals of motion is decreased if the system is analyzed in a motionless container. Then the total momentum **P** and angular momentum **M** are zero in states of statistical equilibrium, and the additive integrals of motion **P** and **M** need not be considered. Thus, for systems with a fixed number of particles

$$f = f(H) \tag{3.2}$$

or if the number of particles is not fixed

$$f = f(H,N). \tag{3.2a}$$

The function f also depends on the macroscopic parameters defining the ensemble; these parameters are considered to be constant for all copies of the system in the ensemble. Examples are the total volume and the total number of particles N (for systems in which this parameter is fixed).

3.1 The Microcanonical Distribution.

Let us consider a statistical ensemble of closed, energetically isolated systems in a constant volume V, i.e., an ensemble of systems with constant particle number N in an adiabatic jacket and having identical energy E to within an accuracy ΔE<<E. Following Gibbs, we assume that the distribution function f(p,q) for such an ensemble is constant within a layer ΔE and equal to zero outside this layer:

$$f(p, q) = \begin{cases} [\Omega(E, N, V)]^{-1} & \text{for } E \leqslant H(p, q) \leqslant E + \Delta E, \\ 0 & \text{outside this layer} \end{cases} \tag{3.3}$$

Such a distribution is called microcanonical, and the corresponding ensemble is called the microcanonical ensemble. The macroscopic state of systems in such an ensemble is defined by three extensive parameters E, V, N. The constant Ω(E,N,V), called the statistical weight, is defined from the normalization condition (1.5a) and has the meaning of a dimensionless phase volume - the number of states in the layer ΔE:

$$\Omega(E, N, V) = \frac{1}{N!\, h^{3N}} \int\limits_{E \leqslant H(p, q) \leqslant E + \Delta E} dp\, dq. \tag{3.3a}$$

In classical mechanics the limit ΔE→0 can be taken and f can be written in the form

$$f = \Omega^{-1}(E, N, V)\, \delta(H(p, q) - E), \tag{3.4}$$

where

$$\Omega(E, N, V) = \frac{1}{N!\, h^{3N}} \int \delta(H(p, q) - E)\, dp\, dq,$$

$$\Omega^{-1}(E, N, V) = [\Omega(E, N, V)]^{-1}. \tag{3.4a}$$

(In formulas (3.3) and (3.4a) the number of states in the layer ΔE and the density of states on the constant-energy surface are denoted by the same symbol $\Omega(E,N,V)$.)

A similar limiting transition in quantum mechanics is forbidden by the uncertainty relation between observation time t and energy, $\Delta E \cdot t \sim \hbar$; the approach of ΔE toward zero would correspond to an infinite observation time. Therefore we shall make use of the representation (3.3) for f and only occasionally use (3.4) in order to simplify calculations.

Let us calculate the entropy (2.24) for the microcanonical distribution:

$$S = \langle \eta \rangle = -\frac{1}{N!\,h^{3N}} \int f(p,q) \ln f(p,q)\, dp\, dq. \tag{3.5}$$

Substituting into this expression the expression (3.3) and using (3.3a), we obtain

$$S(E,N,V) = \ln \Omega(E,N,V). \tag{3.5a}$$

Thus, for the microcanonical ensemble the entropy is equal to the logarithm of the statistical weight (3.3a). It can be shown that the entropy defined in this way indeed has the properties of the thermodynamic entropy. We shall return to this question in § 5.

The hypothesis that the microcanonical ensemble actually represents the macroscopic state of a closed, energetically-isolated system, i.e., that microcanonical averages coincide with the observed values of physical quantities, is one of the basic postulates of statistical mechanics.

The observed values of physical quantities A(p,q) are always average values over some interval of observation time τ. The problem of justifying the replacement of time averages with microcanonical averages it the so-called ergodic problem. The problem is to demonstrate for closed, energetically isolated systems the equality

$$\frac{1}{\tau}\int_0^\tau A(p(t),q(t))\,dt = \frac{1}{N!\,h^{3N}} \int f(p,q)\,A(p,q)\, dp\, dq, \tag{3.6}$$

where f is the microcanonical distribution. This problem is very complex, and, despite the many important results which have been obtained, it is still not resolved. Therefore, we shall not consider the problem, and we refer the reader to the literature [6, 11, 12].

The microcanonical distribution is sometimes useful for general investigations, because of all the Gibbs distributions it is the one most directly connected with mechanics (all the parameters E,N,V have meaning in mechanics), but this distribution is not convenient for practical application to specific systems, because the calculation of $\Omega(E,N,V)$ is difficult.

It is much more convenient to consider systems in thermal contact with their surroundings, rather than to consider energetically isolated systems.

3.2 *The Gibbs Canonical Distribution.*

Let us now consider closed systems in thermal contact with a thermostat. We shall call a thermostat any system with a large number of degrees of freedom which is capable of exchanging energy with a given system and which is sufficiently large such that its state is practically unchanged by this exchange.

A statistical ensemble of systems with a fixed number of particles N and volume V in contact with a thermostat is called a *Gibbs canonical ensemble.*

Such an ensemble is described by the *Gibbs canonical distribution*

$$f(p,q) = Q^{-1}(\theta, V, N)\exp\left(-\frac{H(p,q)}{\theta}\right), \tag{3.7}$$

where θ is the modulus of the canonical distribution, which plays the role of the temperature, as will be shown below, and $Q(\theta,V,N)$ is the *statistical integral* defined by the normalization condition (1.5a):

$$Q(\theta, V, N) = \int \exp\left(-\frac{H(p,q)}{\theta}\right) d\Gamma, \text{ where } d\Gamma = \frac{dp\,dq}{N!\,h^{3N}}. \tag{3.8}$$

The statistical integral (3.8), constructed on the basis of the Gibbs canonical distribution, is a function of the macroscopic parameters θ,V,N which define the ensemble. Two of them, V and N, are extensive parameters, i.e., they are proportional to V when V/N = const., but the third, θ, is intensive, i.e., it has a finite value as $V\to\infty$, V/N = const. The statistical integral $Q(\theta,V,N)$ is a fundamental quantity which determines the thermodynamic properties of the system.

The logarithm of the statistical integral (3.8) defines the *free energy* of the system:

$$F(\theta,V,N) = -\theta \ln Q(\theta,V,N). \tag{3.8a}$$

For real systems in which N is very large we do not need the exact value of the function F(θ,V,N); it is sufficient to know the thermodynamic limit

$$\lim_{\substack{N\to\infty \\ V/N=v=\mathrm{const}}} \frac{F(\theta, V, N)}{N} = f(\theta, v),$$

i.e., the free energy per particle as the number of particles increases without limit for fixed density. This function defines all thermodynamic properties of the system.

Proof of the existence of the thermodynamic limit for the canonical ensemble is given by Van Hove [13] and N. N. Bogolyubov and B. I. Khatset [34] under fairly mild restrictions on the interaction potential between particles. Their proof was further refined for a large ensemble by Lee and Yang [14], Ruelle [15], R. L. Dobrushin [16] and others [17 a,b,c,d]. These works can be regarded as the start of a new branch of mathematical physics - mathematical statistical physics.

Differentiating (3.8) with respect to θ and taking (2.19) into account, we obtain the expression for the mean energy:

$$\langle H\rangle = \theta^2 \frac{\partial}{\partial\theta} \ln Q(\theta, V, N) = -\theta^2 \frac{\partial}{\partial\theta}\left(\frac{F}{\theta}\right)_{V,N}. \tag{3.8b}$$

The entropy (2.24) of the Gibbs canonical ensemble is

$$S = \langle\eta\rangle = -\int f \ln f \, d\Gamma = \frac{\langle H\rangle - F}{\theta} = -\left(\frac{\partial F}{\partial\theta}\right)_{V,N} \tag{3.8c}$$

(here relations (3.8a) and (3.8b) were used).

The relations (3.8b) and (3.8c) have the form of thermodynamic equalities, showing that F and S are indeed the free energy and entropy. We obtain a more complete thermodynamic analogy if we consider the canonical ensemble with a slowly changing volume (see section 5.4).

Fluctuations can also be calculated using the canonical distribution (3.7). Differentiating (3.8) twice with respect to 1/θ and using (3.8b), we find the expression for energy fluctuations in the Gibbs ensemble:

$$\langle H^2\rangle - \langle H\rangle^2 = \langle (H - \langle H\rangle)^2\rangle = \frac{\partial^2 \ln Q}{\partial (1/\theta)^2} = \theta^2 \frac{\partial \langle H\rangle}{\partial\theta} = \theta^2 C_V, \tag{3.8d}$$

where C_V is the specific heat at constant volume.

The quantity $\langle H \rangle$ is proportional to the number of particles N, while θ is independent of N; thus, for large systems the relative mean square energy fluctuations are proportional to 1/N, i.e., they are very small. Therefore, the canonical and microcanonical ensembles differ very little from each other. (More detail on the thermodynamic equivalence of ensembles is given in § 13.)

We have assumed until now that the system is not moving as a whole, and we have considered a single integral of the motion - the total energy H. If in addition to the energy there exist other additive integrals of the motion $\mathcal{P}_1, \ldots, \mathcal{P}_s$, the Gibbs distribution has the form

$$f(p, q) = Q^{-1}(\theta, \mathcal{F}_1, \ldots, \mathcal{F}_s) \exp\left\{-\frac{H(p, q)}{\theta} - \sum_{1 \leqslant k \leqslant s} \mathcal{F}_k \mathcal{P}_k(p, q)\right\}, \tag{3.9}$$

where $\mathcal{F}_k$ are the new thermodynamic parameters. We shall not indicate explicitly the dependence of Q on V and N.

In the particular case in which the total momentum **P** and the total angular momentum **M** are considered, the distribution (3.9) has the form

$$f(p, q) = Q^{-1} \exp\left\{-\frac{1}{\theta}[H(p, q) - v \cdot P(p) - \omega \cdot M(p, q)]\right\}, \tag{3.9a}$$

where **v** is the velocity of the system as a whole, and ω is its rotational angular velocity.

It is convenient to put expression (3.9) in a more symmetric form:

$$f(p, q) = \exp\left\{-\Phi(\mathcal{F}_0, \ldots, \mathcal{F}_s) - \sum_{0 \leqslant k \leqslant s} \mathcal{F}_k \mathcal{P}_k(p, q)\right\}, \tag{3.10}$$

where the notation

$$\mathcal{P}_0(p, q) = H(p, q), \quad \mathcal{F}_0 = 1/\theta, \quad \Phi(\mathcal{F}_0, \ldots, \mathcal{F}_s) = \ln Q. \tag{3.10a}$$

has been introduced.

The thermodynamic potential $\Phi(\mathcal{F}_0,\ldots,\mathcal{F}_s)$ is called the Mas'ye-Planck thermodynamic function.

For distribution functions in the form (3.10) the thermodynamic equalities and expressions for the fluctuations assume the especially simple form:

$$\begin{gathered}\langle\mathcal{P}_k\rangle = -\frac{\partial\Phi}{\partial\mathcal{F}_k}, \quad \mathcal{F}_k = \frac{\partial S}{\partial\langle\mathcal{P}_k\rangle}, \\ S = \Phi + \sum_k \mathcal{F}_k\langle\mathcal{P}_k\rangle = \Phi - \sum_k \mathcal{F}_k\frac{\partial\Phi}{\partial\mathcal{F}_k}, \\ \langle\mathcal{P}_k^2\rangle - \langle\mathcal{P}_k\rangle^2 = \frac{\partial^2\Phi}{\partial\mathcal{F}_k^2},\end{gathered} \tag{3.10b}$$

where S is the entropy.

3.3 Gibbs Theorem on the Canonical Distribution.

The postulates concerning the microcanonical distribution (3.3) and those concerning the canonical distribution (3.7) are not independent. We shall now prove a theorem of Gibbs on the canonical distribution according to which a small part of a microcanonical ensemble of systems with many degrees of freedom is distributed canonically.

The combination of the given system and the thermostat, which is supposed to be significantly larger than the given system (with respect to the number of degrees of freedom), can always be regarded as one large, closed, isolated system. If a microcanonical distribution is assumed for this total system, then it follows from the Gibbs theorem that the system in the thermostat has a canonical distribution.

Let us turn now to a proof of the theorem of Gibbs.

Let a large system with Hamiltonian H consist of two subsystems (1) and (2) with Hamiltonians $H_1(p,q)$ and $H_2(p',q')$, where p,q and p',q' are the sets of coordinates and momenta of the subsystems. The interaction between the subsystems will be considered negligible; then

$$H = H_1(p,q) + H_2(p',q'). \tag{3.11}$$

We suppose that subsystem (1) is significantly smaller than subsystem (2), which we shall call the thermostat. We assume further that the total system is distributed microcanonically. By (3.3) the distribution function of the total system has the form

$$f(p, q; p', q') = \begin{cases} \Omega^{-1}(E) & \text{in the layer } E \leqslant H \leqslant E + \Delta E, \\ 0 & \text{outside this layer} \end{cases} \tag{3.12}$$

where the statistical weight $\Omega^{-1}(E)$ may also depend on the total particle number N and on the volume V, but for brevity we shall omit such dependence.

In order to obtain the distribution function for the subsystem (1), i.e., for the small subsystem, the total distribution function must be integrated over all variables of the second subsystem (the thermostat), taking into account the normalization factors introduced in (1.5a), i.e.,

$$f_1(p, q) = \frac{1}{N_2!\, h^{3N_2}} \int f(p, q; p', q')\, dp'\, dq' =$$
$$= \Omega^{-1}(E) \frac{1}{N_2!\, h^{3N_2}} \int\limits_{E-H_1 \leqslant H_2 \leqslant E-H_1+\Delta E} dp'\, dq',$$

where the integration is carried out over variables p′,q′ falling in the layer

$$E - H_1(p, q) \leqslant H_2(p', q') \leqslant E - H_1(p, q) + \Delta E.$$

Taking into account the definition of statistical weight (3.3a), we notice that the distribution function of the first subsystem is equal to the ratio of the statistical weight of the second subsystem with energy E-H_1 to the statistical weight of the entire system:

$$f_1(p, q) = \frac{\Omega_2(E - H_1(p, q))}{\Omega(E)}. \tag{3.13}$$

To calculate f_1 we must obtain the asymptotic limit of the ratio of the statistical weights of the thermostat and the entire system, with the assumption that the thermostat is large.

Let us first give a very simple but nonrigorous derivation of the canonical distribution (3.7) from equation (3.13).

We introduce the entropy of the thermostat $S_2(E)$ and the entropy of the entire system $S(E)$ using the relation (3.5a):

$$S_2(E) = \ln\Omega_2(E), \quad S(E) = \ln\Omega(E) \tag{3.14}$$

and rewrite (3.13) in the form

$$f_1(p,q) = \exp\{S_2(E-H_1(p,q))-S(E)\}.$$

Because of the small size of subsystem (1) in comparison with the thermostat ($H_1 \ll E$), the function $S_2(E-H_1)$ can be expanded in a series in H_1, keeping only the first two terms:

$$S_2(E-H_1(p,q)) \cong S_2(E) - \frac{\partial S_2}{\partial E} H_1(p,q). \tag{3.14a}$$

Using this expansion, we write f_1 in the form

$$f_1(p,q) = Q^{-1}\exp\left(-\frac{H_1(p,q)}{\theta}\right), \tag{3.15}$$

where Q is the normalizing term (3.8), i.e., the statistical integral, and the quantity

$$\frac{1}{\theta} = \frac{\partial S_2(E)}{\partial E} = \frac{\partial \ln\Omega_2(E)}{\partial E} \tag{3.16}$$

plays the role of the inverse temperature. Thus, a system in the thermostat has a canonical distribution, which was to be shown.

In order to elucidate the character of the asymptotic approach of (3.13) to the Gibbs distribution upon increasing the size of the thermostat, we present a beautiful and more rigorous derivation of the Gibbs theorem due to Yu. A. Krutkov [18].

Let us write the expression (3.13) for f_1 in the form

$$f_1(p, q) = \frac{\omega_2(E - H_1(p, q))}{\omega(E)}, \tag{3.17}$$

where

$$\omega_2(E) = \frac{\Omega_2(E)}{\Delta E}, \qquad \omega(E) = \frac{\Omega(E)}{\Delta E} \tag{3.18}$$

are the densities of states of the thermostat and of the total system respectively.

Since $H_1(p,q)$ and $H_2(p',q')$ depend only on variables referring to the different subsystems, the statistical weight of the total system can be put into the form of successive integrations first over the coordinates of the second subsystem with fixed $H_1(p,q)=E_1$, and then over the coordinates of the first subsystem with $0 \leqslant E_1 \leqslant E$, i.e.,

$$\Omega(E) = \frac{1}{N_1!\, h^{3N_1}} \int\limits_{0 \leqslant H_1(p,q)=E_1 \leqslant E} dp\, dq \times \frac{1}{N_2!\, h^{3N_2}} \int\limits_{E-E_1 \leqslant H_2(p',q') \leqslant E-E_1+\Delta E} dp'\, dq'. \tag{3.18a}$$

We take into account separately the identity of particles in the thermostat and the system, because we do not allow the possibility of exchange of particles between them. It follows from (3.18a) that the density of states of the total system ω is related to the densities of states of the first and second subsystems ω_1 and ω_2 by a convolution integral:

$$\omega(E) = \int_0^E \omega_1(E - E_2)\, \omega_2(E_2)\, dE_2. \tag{3.19}$$

The relationship (3.19) can be considered as an integral equation defining $\omega_2(E)$. We solve it using Laplace transforms. Multiplying (3.19) by $e^{-\lambda E}$, integrating over E from zero to infinity, and going over to the variables $E_1 = E-E_2$, E_2 we obtain

$$Q(\lambda) = Q_1(\lambda) Q_2(\lambda), \tag{3.20}$$

where

$$Q(\lambda) = \int_0^\infty e^{-\lambda E}\,\omega(E)\,dE,$$

$$Q_k(\lambda) = \int_0^\infty e^{-\lambda E}\,\omega_k(E)\,dE \qquad (k = 1,\ 2) \tag{3.21}$$

are the Laplace transforms of the densities of states (3.18). We find the densities of states by inverting the Laplace transformations (3.21):

$$\omega_k(E) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} e^{\lambda E}\,Q_k(\lambda)\,d\lambda \qquad (k = 1,\ 2),$$

$$\omega(E) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} e^{\lambda E}\,Q(\lambda)\,d\lambda, \tag{3.22}$$

where $\alpha>0$ is a real positive constant.

Let us now assume that the second subsystem (the thermostat) consists of n-1 identical weakly interacting parts, each of which is identical with the first subsystem. Then from (3.20)

$$Q(\lambda) = [Q_1(\lambda)]^n, \quad Q_2(\lambda) = [Q_1(\lambda)]^{n-1}, \tag{3.23}$$

and the solutions of (3.22) have the form

$$\omega_2(E) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} e^{\lambda E}\,[Q_1(\lambda)]^{n-1}\,d\lambda,$$

$$\omega(E) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} e^{\lambda E}\,[Q_1(\lambda)]^{n}\,d\lambda. \tag{3.24}$$

We obtain an asymptotic estimate of expressions (3.24) for the densities of states as $n\to\infty$ by the method of steepest descents (or saddle point method) [19]. We write the second integral in (3.24) in the form

$$\omega(E) = \frac{1}{2\pi i} \int_{a-i\infty}^{a+i\infty} e^{n\chi(\lambda)}\, d\lambda, \tag{3.25}$$

where the function

$$\chi(\lambda) = \lambda \frac{E}{n} + \ln Q_1(\lambda). \tag{3.25a}$$

was introduced. The function X(λ) is assumed to be analytic in the region Reλ>0 in the complex λ plane. From the properties of analytic functions the function X(λ) can have neither a maximum nor a minimum; its extremum corresponds to a saddle point. A saddle point λ_1 is defined from the conditions

$$\chi'(\lambda_1) = \frac{E}{n} + \frac{Q_1'(\lambda_1)}{Q_1(\lambda_1)} = 0, \tag{3.26}$$

$$\chi''(\lambda_1) = \frac{d^2}{d\lambda^2} \ln Q_1(\lambda)_{\lambda=\lambda_1} > 0, \tag{3.26a}$$

where λ_1 is the single real root of equation (3.26). We assume that the conditions for applicability of the saddle-point method are fulfilled. We shall verify below that the condition (3.26a) is satisfied.

We introduce a new real variable ξ,

$$\lambda = \lambda_1 + i\xi,$$

and expand X(λ) at the saddle point in a Taylor series, keeping quadratic terms in ξ:

$$\chi(\lambda_1 + i\xi) \cong \chi(\lambda_1) - \frac{\chi''(\lambda_1)}{2} \xi^2;$$

thus,

$$\omega(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left\{ n\chi(\lambda_1) - \frac{n\chi''(\lambda_1)}{2} \xi^2 \right\} d\xi = \frac{1}{2\pi} e^{n\chi(\lambda_1)} \sqrt{\frac{2\pi}{n\chi''(\lambda_1)}}$$

$$(\lambda_1 > 0),$$

and finally

$$\omega(E) = e^{\lambda_1 E} [Q_1(\lambda_1)]^n \frac{1}{\sqrt{2\pi n\chi''(\lambda_1)}}. \tag{3.27}$$

Completely analogously, we obtain for ω_2

$$\omega_2(E) = e^{\lambda_1 E}[Q_1(\lambda_1)]^{n-1} \frac{1}{\sqrt{2\pi(n-1)\chi''(\lambda_1)}}. \qquad (3.27a)$$

Substituting (3.27) and (3.27a) into (3.17), we find

$$f_1(p,q) = Q_1^{-1}(\lambda_1)\exp(-\lambda_1 H_1(p,q)), \qquad (3.28)$$

which is the same as the canonical distribution (3.7) with the modulus

$$\Theta = \frac{1}{\lambda_1}. \qquad (3.29)$$

The condition (3.26) at the saddle point is the same as the thermodynamic equality (3.8b), and the inequality (3.26a) implies that energy fluctuations are positive, as is easily seen using (3.8d), and this is also satisfied. Thus, the Gibbs theorem is proved.

In the derivation of the canonical distribution presented above the system and the thermostat were considered to be identical in character. This assumption need not be made. The thermostat and the system can be described by different Hamiltonians, provided that the thermostat is sufficiently large and that its interaction with the system is sufficiently weak. That the Gibbs theorem remains valid in this case follows from a simple investigation (see (3.13) - (3.16)).

The Gibbs theorem can be shown in other ways, for example by the method of Khinchin [20,21], which is based on an application of the central limit theorem of probability theory.

Still another approach is possible in constructing distribution functions for statistical ensembles [22,23]; the approach is based on information theory, and we shall discuss it later in § 4.

3.4 The Gibbs Grand Canonical Distribution.

Earlier we considered closed systems in contact with a thermostat. A more general type of contact of a system with its surroundings is also possible. We consider an open system in a thermostat; the system can exchange both energy and particles with its surroundings. For example, there might be permeable walls between the system and the reservoir. Then the energy and the number of particles in the system are not constant, but the volume is assumed to be specified. A statistical ensemble corresponding to a collection of such systems in thermal and material contact with their surroundings is called the <u>Gibbs grand canonical ensemble</u>.

Such an ensemble is described by the Gibbs grand canonical distribution

$$f_N(p, q) = Q^{-1}(\theta, \mu, V)\exp\left\{-\frac{H(p, q) - \mu N}{\theta}\right\}, \tag{3.30}$$

where μ is the chemical potential, Q(θ,μ,V) is the statistical integral for the grand ensemble, defined by the normalization condition

$$\sum_{N\geqslant 0}\frac{1}{N!\,h^{3N}}\int f_N(p, q)\,dp_1\,dq_1\ldots dp_N\,dq_N = 1, \tag{3.30a}$$

which is the natural generalization of the normalization (1.5a) for a system with a variable particle number. Thus,

$$Q(\theta, \mu, V) = \sum_{N\geqslant 0}\int \exp\left(-\frac{H(p, q) - \mu N}{\theta}\right) d\Gamma_N, \tag{3.31}$$

where

$$d\Gamma_N = \frac{dp_1\,dq_1\ldots dp_N\,dq_N}{N!\,h^{3N}}.$$

The statistical integral for the grand canonical ensemble is a function of the macroscopic parameters θ, μ, V defining the ensemble. One of them, V, is an extensive parameter, and two of them, θ and μ, are intensive. We have denoted the statistical integral for the grand ensemble by the same letter Q as was used for the statistical integral of the canonical ensemble, but no confusion is possible, as they are functions of different variables.[1]

Using (3.30) the average value of any dynamical variable can be found:

$$\langle A\rangle = \sum_{N\geqslant 0}\int A(p, q)\,f_N(p, q)\,d\Gamma_N. \tag{3.32}$$

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[1] The statistical integral for the grand ensemble is sometimes denoted by Ξ(θ,μ,V). We shall use the same designation Q for the statistical integrals (and sums) of all the Gibbs ensembles, distinguishing by the arguments to which ensemble we refer.

The logarithm of the statistical integral (3.31) defines the thermodynamic potential $\Omega(\theta,\mu,V)$ for systems with variable particle number:

$$\Omega(\theta,\mu,V) = -\theta \ln Q(\theta,\mu,V). \tag{3.33}$$

The existence of the thermodynamic limit

$$\lim_{\substack{V\to\infty \\ V/\langle N\rangle = \mathrm{const}}} \frac{\Omega(\theta,\mu,V)}{V}$$

was demonstrated by Lee and Yang [14] for restricted forms of the interaction potential (see also [15-17d]).

Differentiating (3.31) with respect to θ and μ we obtain expressions for the mean energy and mean particle number:

$$\begin{aligned} \langle H\rangle - \mu\langle N\rangle &= \theta^2 \frac{\partial}{\partial\theta} \ln Q(\theta,\mu,V) = -\theta^2 \frac{\partial}{\partial\theta}\left(\frac{\Omega}{\theta}\right)_{\mu,V}, \\ \langle N\rangle &= \theta \frac{\partial}{\partial\mu} \ln Q(\theta,\mu,V) = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{\theta,V}. \end{aligned} \tag{3.33a}$$

The average of the negative of the logarithm of the distribution function (3.30) is the entropy of the Gibbs grand canonical ensemble:

$$S = \langle\eta\rangle = -\sum_N \int f_N \ln f_N \, d\Gamma_N = \frac{\langle H\rangle - \Omega - \mu\langle N\rangle}{\theta} = -\left(\frac{\partial\Omega}{\partial\theta}\right)_{V,\mu} \tag{3.34}$$

(the relations (3.33) and (3.33a) have been used).

Using the Gibbs grand canonical distribution the fluctuations in energy and particle number in the Gibbs grand ensemble can be calculated. Differentiating (3.31) twice with respect to θ and μ, we find

$$\begin{aligned} \langle N^2\rangle - \langle N\rangle^2 &= \theta \frac{\partial\langle N\rangle}{\partial\mu}, \\ \langle (H-\mu N)^2\rangle - \langle H-\mu N\rangle^2 &= \theta^2 \frac{\partial}{\partial\theta}(\langle H\rangle - \mu\langle N\rangle). \end{aligned} \tag{3.35}$$

The relative smallness of these fluctuations shows that the grand canonical ensemble differs very little from the canonical and microcanonical ensembles, but the grand ensemble is much more convenient for calculations, because the constancy of particle number and the constancy of energy do not have to be taken into account as auxiliary conditions.

For systems with variable particle number there exists also a theorem, due to Gibbs, according to which a small part of a microcanonical ensemble of systems with many degrees of freedom has a grand canonical distribution if the particle number is not constant for this part of the ensemble.

The combination of the given system and the thermostat, which is also a particle reservoir, can be regarded as one large, closed, isolated system. If a microcanonical distribution is assumed for the total system, then from the Gibbs theorem it follows that the open system in the thermostat has a Gibbs grand canonical distribution.

Let the large system with Hamiltonian H and particle number N consist of two subsystems (1) and (2) with Hamiltonians H_1 and H_2 and with particle numbers N_1 and N_2. We neglect the interaction between the subsystems; then

$$H = H_1+H_2, \quad N = N_1+N_2.$$

We assume that the subsystem (1) is significantly smaller than subsystem (2), which we shall call, as before, the thermostat.

Let us assume that the total system has a microcanonical distribution:

$$f_N = \begin{cases} \Omega^{-1}(E, N) \text{ in the layer } E \leqslant H \leqslant E+\Delta E, \\ 0 \text{ outside this layer.} \end{cases} \tag{3.36}$$

We find the distribution function of subsystem (1) by integrating f over the variables of the second subsystem:

$$f_{N_1} = \int\limits_{E-H_1 \leqslant H_2 \leqslant E-H_1+\Delta E} f_{N_1+N_2}\, d\Gamma_{N_2}, \tag{3.37}$$

where

$$d\Gamma_{N_2} = \frac{dp_1'\, dq_1' \ldots dp_{N_2}'\, dq_{N_2}'}{N_2!\, h^{3N_2}}.$$

Using (3.36) we find that the distribution function of the first subsystem is equal to the ratio of the statistical weight of the second subsystem with $E-H_1$

and $N-N_1$, to the statistical weight of the total system:

$$f_{N_1}(p, q) = \frac{\Omega_2(E - H_1(p, q), N - N_1)}{\Omega(E, N)}. \tag{3.38}$$

Using (3.5a) we introduce the entropy of the thermostat S_2 and of the total system S

$$S_2(E, N) = \ln \Omega_2(E, N), \qquad S(E, N) = \ln \Omega(E, N)$$

and write (3.38) in the form

$$f_{N_1}(p, q) = \exp\{S_2(E - H_1(p, q), N - N_1) - S(E, N)\}.$$

Taking into account the smallness of the first subsystem in comparison to the thermostat ($H_1 \ll E$, $N_1 \ll N$), we expand the function $S_2(E-H_1, N-N_1)$ in a series in H_1 and N_1, keeping only two terms:

$$S_2(E - H_1, N - N_1) \cong S_2(E, N) - \frac{\partial S_2}{\partial E} H_1 - \frac{\partial S_2}{\partial N} N_1.$$

Making use of this expansion, we write f_N in the form

$$f_N(p, q) = Q_1^{-1} \exp\left\{-\frac{H_1(p, q) - \mu N_1}{\theta}\right\}, \tag{3.39}$$

where

$$\frac{1}{\theta} = \frac{\partial S_2}{\partial E}, \qquad \frac{\mu}{\theta} = -\frac{\partial S_2}{\partial N}, \tag{3.39a}$$

i.e., θ is the temperature, and μ is the chemical potential.

A more rigorous proof of the Gibbs theorem can be given for the grand canonical ensemble [24]; the proof is analogous to the proof given in the preceding section for the canonical ensemble. Instead of the integral relationship (3.19) we have a similar expression in which besides an integration over the energy there is a summation over the number of particles N, where N is a variable which takes on only positive, integer values. The problem is thus reduced to the solution of a convolution-type integral equation in a

continuous and a discrete variable and to obtaining an asymptotic estimate of the resulting solution. We shall not carry out the derivation here; we refer the interested reader to the work of S. Shubin [24]. Later in § 9 of Chapter II we shall carry out a similar proof of the Gibbs theorem for the case of quantum statistics.

3.5 The Gibbs Distribution for an Isobaric-Isothermal Ensemble.

Until now we have considered the volume of the systems as fixed. We shall now allow it to vary, but we shall take pressure and particle number as fixed. This can be realized by using a movable piston to maintain the constant pressure.

An ensemble of systems with constant particle number and fixed pressure in contact with a thermostat is called a Gibbs isobaric-isothermal ensemble. We shall discuss briefly the properties of this ensemble.

The system together with the surroundings can be considered as one large, closed system with constant energy and volume. Let E_1, E_2 be the energies of the first and second subsystems, i.e., the given system and the thermostat, and let V_1, V_2 be their volumes; then

$$E = E_1 + E_2, \quad V = V_1 + V_2 \qquad (E_1 \ll E_2, \ V_1 \ll V_2) \tag{3.40}$$

are considered constant. The microcanonical distribution can be applied to the total system, and then the distribution function of the first subsystem can be found by integrating over the coordinates of the particles in the second subsystem.

Repeating the arguments of section 3.3, we obtain the distribution function of the first subsystem:

$$f_1(p, q) = \frac{\Omega_2(E - H_1, V - V_1)}{\Omega(E, V)} = \exp\{S_2(E - H_1, V - V_1) - S(E, V)\}. \tag{3.41}$$

Expanding S_2 in a series and using the fact that the first subsystem is small, we obtain

$$f_1(p, q) = Q^{-1}(\theta, p, N) \exp\left\{-\frac{H_1(p, q) + pV_1}{\theta}\right\}, \tag{3.42}$$

where

$$\frac{1}{\theta} = \frac{\partial S_2(E, V)}{\partial E}, \qquad \frac{p}{\theta} = \frac{\partial S_2(E, V)}{\partial V}. \tag{3.42a}$$

The parameter p plays the role of the pressure, as will be verified below.

Thus, we have shown that the Gibbs distribution for an isobaric-isothermal ensemble has the form

$$f_V(p, q) = Q^{-1}(\theta, p, N) \exp\left\{ -\frac{H(p, q) + pV}{\theta} \right\}, \tag{3.43}$$

where we have omitted the index 1.

Here Q(θ,p,N) is the statistical integral for an isobaric ensemble, defined from the normalization condition, which can be taken to be, for example

$$\int f_V(p, q)\, d\Gamma\, dV = 1; \tag{3.43a}$$

thus,

$$Q(\theta, p, N) = \int \exp\left\{ -\frac{H(p, q) + pV}{\theta} \right\} d\Gamma\, dV. \tag{3.43b}$$

With this normalization f_V has the dimension of inverse volume. A dimensionless normalization of f_V is also possible.

The statistical integral for the isobaric-isothermal ensemble is a function of the macroscopic parameters θ, p, N defining the ensemble. Two of these parameters, θ and p, are intensive, and one, N, is extensive. One should not confuse Q(θ,p,N) with Q(θ,V,N) and Q(θ,μ,V) which were introduced earlier.

Using (3.43) the mean value of any dynamical variable A(p,q) can be calculated:

$$\langle A \rangle = \int A(p, q) f_V(p, q)\, d\Gamma\, dV. \tag{3.44}$$

The logarithm of the statistical integral (3.43b) defines the thermodynamic potential $\Phi(\theta,p,N)$ for an isobaric-isothermal system, or simply the thermodynamic potential[1]

$$\Phi(\theta,\, p,\, N) = -\,\theta \ln Q(\theta,\, p,\, N). \tag{3.45}$$

Differentiating (3.43b) with respect to θ and p, we obtain the expressions for the average energy and average volume:

$$\begin{aligned} \langle H\rangle + p\langle V\rangle &= \theta^2 \frac{\partial}{\partial\theta} \ln Q(\theta,\, p,\, N) = -\,\theta^2 \frac{\partial}{\partial\theta}\left(\frac{\Phi}{\theta}\right)_{p,\,N}, \\ \langle V\rangle &= -\,\theta \frac{\partial}{\partial p} \ln Q(\theta,\, p,\, N) = \left(\frac{\partial\Phi}{\partial p}\right)_{\theta,\,N}. \end{aligned} \tag{3.46}$$

The average of the negative of the logarithm of the distribution function (3.43) is the entropy of the isobaric-isothermal Gibbs ensemble:

$$S = -\int f_V \ln f_V \, d\Gamma\, dV = \frac{\langle H\rangle + p\langle V\rangle - \Phi}{\theta} = -\left(\frac{\partial\Phi}{\partial\theta}\right)_{p,\,N}. \tag{3.47}$$

The relations (3.46), (3.47) show that Φ plays the role of the thermodynamic potential and the parameter p is the pressure. The second derivative of Φ with respect to p defines the volume fluctuations:

$$\langle V^2\rangle - \langle V\rangle^2 = -\,\theta \frac{\partial^2\Phi}{\partial p^2} = -\,\theta \frac{\partial\langle V\rangle}{\partial p}. \tag{3.48}$$

Sometimes a generalized Gibbs ensemble is introduced for systems in the thermostat with variable volume and variable particle number [25,26]. Then the ensemble is characterized by three intensive parameters θ,μ,p, i.e.,

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[1] The function $\Phi(\theta,p,N)$ should not be confused with the Mas'ye-Planck function (3.10a), as they depend on different variables.

the temperature, the chemical potential, and the pressure. This is inconvenient, because the parameters θ, μ, and p are not independent, but are related by $\mu=\mu(p,\theta)$. Therefore we shall not use this generalized ensemble, which has no advantages over the other ensembles. To describe an ensemble of systems it is always convenient to have at least one extensive parameter, as was the case in the Gibbs ensembles introduced previously.

The various Gibbs ensembles are equivalent in a thermodynamic respect, i.e., thermodynamic functions calculated with the different ensembles are the same for large systems in the limit $V\to\infty$, $N\to\infty$, $V/N=\mathrm{const}$. Therefore the question of which ensemble to use is a question of practical convenience only. As we have said already the most convenient is the Gibbs grand canonical ensemble, because with this ensemble no additional conditions need be considered. For the calculation of fluctuations the various Gibbs ensembles are not equivalent, and lead generally speaking to different results. The reason for the thermodynamic equivalence of the statistical ensembles is the small size of the fluctuations in energy, particle number, and volume (3.8d), (3.35), (3.48). A more rigorous proof of the thermodynamic equivalence of the statistical ensembles can be given by comparing the thermodynamic functions calculated with the different ensembles [26,27]. We shall return to this question in § 13.

§ 4. Connection Between Gibbs Distributions and the Information Entropy Maximum

The concept of entropy in statistical mechanics is intimately connected with information theory. We discuss this connection in the present paragraph.

4.1. Information Entropy.

The information entropy or simply the entropy is a measure of the uncertainty in the information corresponding to the statistical distribution [22, 23,28,29].

Let p_k be the discrete probability distribution of events. The quantity

$$H = -\sum_{k=1}^{n} p_k \ln p_k, \tag{4.1}$$

where

$$\sum_{k=1}^{n} p_k = 1. \tag{4.2}$$

is called the information entropy. It is also called the Shannon entropy.

In fact, the quantity H is equal to 0 if any of the p_k is equal to one and the remaining p_k are equal to 0, i.e., when the result of the experiment can be predicted with certainty and there is no uncertainty in the information. The quantity H takes on its largest value when all of the p_k are mutually equal, i.e., $p_k=1/n$. It is clear that this limiting case has the largest uncertainty. The entropy H is additive for a collection of independent events with probabilities u_i and v_k, because if $p_{ik}=u_i v_k$, then

$$-\sum_{i,k} p_{ik} \ln p_{ik} = -\sum_i u_i \ln u_i - \sum_k v_k \ln v_k, \qquad (4.3)$$

$$\sum_k u_k = \sum_k v_k = 1.$$

The uniqueness of the definition of the information entropy (4.1) with the required properties of continuity and additivity to within a constant factor was shown by Shannon [28,29].

For the probability distribution of the continuous quantity x with density f(x) the information entropy is equal to

$$S_u = -\int f(x) \ln f(x)\, dx, \qquad (4.4)$$

where

$$\int f(x)\, dx = 1.$$

The information entropy (4.4) is additive for independent events just as was (4.1); i.e., if

$$f(x,y) = f_1(x) f_2(y),$$

then

$$-\int\int f(x, y) \ln f(x, y)\, dx\, dy = -\int f_1(x) \ln f_1(x)\, dx - \int f_2(y) \ln f_2(y)\, dy.$$

For the distribution function f(p,q) in phase space the Gibbs entropy (2.24) is also an information entropy, i.e.

$$S_u = \langle \eta \rangle = -\int f \ln f\, d\Gamma \qquad (4.5)$$

with the normalization

$$\int f\, d\Gamma = 1 \tag{4.6}$$

for ensembles with fixed particle number, or

$$S_d = -\sum_{N\geqslant 0}\int f_N \ln f_N \, d\Gamma_N \tag{4.7}$$

with normalization

$$\sum_{N\geqslant 0}\int f_N \, d\Gamma_N = 1 \tag{4.8}$$

for ensembles with variable particle number.

It is completely natural to consider the entropy in statistical mechanics as an information entropy, because statistical mechanics must not go outside the limits of the restricted possibilities of measurements on macroscopic systems. In the language of information theory it might be said that the maximum integrity of information contained in the distribution function must be satisfied. The distribution for the Gibbs ensembles as we shall verify below satisfies this requirement.

The definition of entropy in the form (4.5) obviously makes sense only in the domain of applicability of classical statistics; it can be regarded as the limiting case of a quantum mechanical expression. Thus, in classical mechanics the concept of a probability density with an invariant measure dΓ is introduced, just as in quantum mechanics the concept of probability and its measure are naturally introduced.

Let us consider the extremal properties of the Gibbs distributions which were established by him long before the creation of information theory [1]. They are easily obtained from the auxiliary inequality (2.32)

$$\int f' \ln\left(\frac{f'}{f}\right) d\Gamma \geqslant 0, \tag{4.9}$$

where f and f′ are any two normalized distributions defined in the same phase space. The equal sign in (4.9) holds only for f=f′. In formula (4.9) and hereafter we shall omit the index N from dΓ.

4.2 Extremal Property of the Microcanonical Distribution.

Let us now show that the microcanonical distribution (3.3) corresponds to the maximum value of the information entropy (4.5) for all distributions with the same particle number and with energy falling within the same energy layer [1].

Let f be the distribution function of the microcanonical ensemble and f′ an arbitrary distribution function defined in the same phase space and within the same energy layer; for these functions

$$\int f'\,d\Gamma = \int f\,d\Gamma = 1.$$

Substituting f and f′ in the inequality (4.9), we obtain

$$-\int f'\ln f'\,d\Gamma \leqslant -\int f'\ln f\,d\Gamma = -\ln f\int f'\,d\Gamma = -\int f\ln f\,d\Gamma,$$

where we have used the fact that f is constant in the energy layer, and we have used the normalizations of f′ and f.

Thus it is shown that of all distributions with a given particle number and a given energy layer the microcanonical distribution corresponds to the maximum of the information entropy. The other Gibbs ensembles have similar extremal properties but with different conditions.

4.3. Extremal Property of the Gibbs Canonical Distribution.

The fact that systems described by the Gibbs canonical ensemble are in contact with the thermostat means that they are characterized by a fixed value of the average energy.

Let us show that the Gibbs canonical distribution (3.7) corresponds to the maximum of the information entropy (4.5) for fixed average energy

$$\langle H\rangle = \int Hf\,d\Gamma \tag{4.10}$$

with the condition that the normalization

$$\int f \, d\Gamma = 1. \tag{4.11}$$

be preserved. Let us find the extremum of the functional (4.1) with the auxiliary conditions (4.10) and (4.11). Following the usual procedure, we look for the absolute extremum of the functional

$$-\int f \ln f \, d\Gamma - \beta \int f H \, d\Gamma - \lambda \int f \, d\Gamma,$$

where β and λ are Lagrange multipliers defined by the conditions (4.10), (4.11). Setting the first variation of this functional equal to zero we find

$$f = Q^{-1}(\theta, V, N)\exp(-\beta H),$$

where

$$Q(\theta, V, N) = \int \exp(-\beta H) \, d\Gamma, \tag{4.12}$$

which is the same as the Gibbs canonical distribution (3.7).

We have verified that (4.12) corresponds to an extremum of the functional (4.5). Let us now show that this extremum is a maximum.

Let f′ be a normalized statistical distribution corresponding to the same average energy as the canonical distribution f,

$$\int f' H \, d\Gamma = \int f H \, d\Gamma,$$

with f′ being otherwise arbitrary. Substituting (4.12) into the inequality (4.9), we obtain

$$-\int f' \ln f' \, d\Gamma \leqslant -\int f' \ln f \, d\Gamma = \ln Q + \beta \int f' H \, d\Gamma = \ln Q + \beta \int f H \, d\Gamma,$$

i.e.,

$$-\int f' \ln f' \, d\Gamma \leqslant -\int f \ln f \, d\Gamma.$$

Thus, the Gibbs canonical distribution corresponds to a maximum of the information entropy for fixed average energy.

If the average values of any n quantities $\mathcal{P}_k$ are specified, possibly including the energy,

$$\langle \mathcal{P}_k \rangle = \int f \mathcal{P}_k \, d\Gamma \qquad (k = 0, 1, \ldots, n-1), \tag{4.13}$$

then from the extremal condition of the information entropy (4.5) we obtain immediately by the same technique as before the distribution

$$f = Q^{-1} \exp\left\{ - \sum_{k=0}^{n-1} \mathcal{F}_k \mathcal{P}_k \right\}, \tag{4.14}$$

which is the same as (3.9), if $\mathcal{P}_k$ are integrals of motion. If the $\mathcal{P}_k$ are not integrals of motion, then (4.14) does not satisfy the Liouville equation and cannot describe a statistical equilibrium ensemble. We shall consider similar distributions in Chapter IV.

4.4. Extremal Property of the Grand Canonical Distribution.

The fact that systems described by the Gibbs grand canonical ensemble are in contact with the thermostat and the reservoir of particles means that they are characterized by fixed average energy and average particle number. We shall show that the grand canonical distribution (3.30) corresponds to the maximum of the information entropy (4.7) with fixed average energy

$$\langle H \rangle = \sum_N \int H f_N \, d\Gamma,$$

with fixed average particle number

$$\langle N \rangle = \sum_N \int N f_N \, d\Gamma$$

and with the preservation of the normalization

$$\sum_N \int f_N \, d\Gamma = 1.$$

Just as before, we look for the absolute extremum of the functional

$$-\sum_N \int f_N \ln f_N \, d\Gamma - \beta \sum_N \int f_N H \, d\Gamma + \nu \sum_N \int f_N N \, d\Gamma - \lambda \sum_N \int f_N \, d\Gamma,$$

where β, ν, λ are Lagrange multipliers. From the extermum condition we find

$$f_N = Q^{-1} \exp\left\{-\frac{H-\mu N}{\theta}\right\}, \tag{4.18}$$

where

$$Q(\theta, \mu, V) = \sum_N \int \exp\left\{-\frac{H-\mu N}{\theta}\right\} d\Gamma,$$

which is the same as the Gibbs grand canonical ensemble (3.30).

From the inequality (4.9) it follows that the extremum is a maximum. In fact, we have

$$\sum_N \int f'_N \ln \frac{f'_N}{f_N} \, d\Gamma \geqslant 0.$$

Substituting for f_N the expression (4.18), we obtain

$$\begin{aligned} -\sum_N \int f'_N \ln f'_N \, d\Gamma \leqslant -\sum_N \int f'_N \ln f_N \, d\Gamma = \\ = -\sum_N \int f'_N \left(-\ln Q - \frac{H}{\theta} + \frac{\mu N}{\theta}\right) d\Gamma = \\ = -\sum_N \int f_N \left(-\ln Q - \frac{H-\mu N}{\theta}\right) d\Gamma, \end{aligned}$$

where the conditions (4.15), (4.16), (4.17) have been used. Consequently,

$$-\sum_N \int f'_N \ln f'_N \, d\Gamma \leqslant -\sum_N \int f_N \ln f_N \, d\Gamma,$$

i.e., the grand canonical distribution (4.18) indeed corresponds to the maximum of the information entropy for fixed average energy and fixed average particle number.

Finally, it is easily verified by the same method that the Gibbs distribution for the isobaric-isothermal ensemble (3.43) corresponds to the maximum of the information entropy

$$S_u = -\int f_V \ln f_V \, d\Gamma \, dV \tag{4.19}$$

with the auxiliary conditions of constant average energy and constant volume

$$\langle H\rangle = \int H f_V \, d\Gamma_V \, dV, \quad \langle V\rangle = \int V f_V \, d\Gamma \, dV. \tag{4.20}$$

Proof of this assertion is in no way different from the previous proofs.

The extremal properties of the Gibbs ensembles considered in this paragraph allow these ensembles to be introduced somewhat differently. Information theory borrowed many of its ideas from statistical mechanics. Now that information theory has become a well-developed theory in its own right, it is possible, following Jaynes [22,23], to consider its concepts as primary and to make use of them in statistical mechanics. The existence of the invariant probability measure (1.5b) can be postulated, and then, regarding statistical mechanics as information theory, one can obtain all the Gibbs distributions from the condition of maximum information entropy [22,23]. In this case all the calculations presented so far are still valid.

Such a method of deriving the statistical distributions must not, however, be regarded as a rigorous justification of statistical mechanics; in this method questions of justification are simply not considered. But in any case the use of the extremal properties of the information entropy is a very convenient heuristic method for finding the various distribution functions. This method is applicable both in classical and in quantum statistical mechanics. It is especially convenient for the nonequilibrium case, and we shall often make use of it (see Chapter IV).

§ 5. Thermodynamic Equalities

5.1. Quasistatic Process.

Until this time we have obtained thermodynamic relationships simply by differentiating the statistical integrals for the various ensembles with respect to the variables on which they depend. To construct a complete system of thermodynamic equalities it is necessary to consider the process of an infinitely slow change of the external parameters which define the given ensemble, i.e., a quasistatic process, because it is exactly these processes which are studied in equilibrium thermodynamics. For the present time we accept without proof the existence of quasistatic processes. In Chapter IV we shall consider the influence on statistical ensembles of a change of the external parameters, and we shall make more precise the concept of a quasistatic process.

Let the external parameters $\alpha_1, \alpha_2, \ldots, \alpha_s$ characterize in a macroscopic sense the state of statistical equilibrium of the dynamic systems under consideration. Such parameters might be the volume of the container, the strength of an external electric or magnetic field, and so on.

Let us suppose that the ensemble is in a state of statistical equilibrium. If the external parameters are changed, then in general the distribution function of the ensemble will also be changed. Let us imagine that the external parameters $\alpha_1, \alpha_2, \ldots, \alpha_s$ are changed so slowly that during a time on the order of the relaxation time of the system to an equilibrium distribution they can be considered practically constant. Then the system can be considered to be in a state of statistical equilibrium at each moment of time. Such a process of change of the external parameters we shall call quasistatic.

If the parameters $\alpha_1, \ldots, \alpha_s$ are considered to be generalized coordinates, then the corresponding generalized forces are equal to

$$A_i = -\frac{\partial H}{\partial a_i}. \tag{5.1}$$

For a quasistatic process the observed value of a generalized force is equal to the average value over an equilibrium statistical ensemble:

$$\langle A_i \rangle = -\left\langle \frac{\partial H}{\partial a_i} \right\rangle = -\int f(p, q) \frac{\partial H(p, q)}{\partial a_i} \, d\Gamma. \tag{5.2}$$

If the volume of the system V is chosen, for example, as one of the external parameters, then the corresponding generalized force is the pressure,

$$p = -\left\langle \frac{\partial H(p, q)}{\partial V} \right\rangle. \tag{5.3}$$

Later we shall define precisely the explicit form of the dynamical variable $\partial H(p,q)/\partial V$.

5.2. Thermodynamic Equalities for a Microcanonical Ensemble.

In systems described by a microcanonical distribution (3.3) the pressure can be obtained by differentiating the statistical weight (3.3a) with respect to volume, i.e., by differentiating the corresponding phase integral with respect to the variable limit of integration. To do this it is convenient to write the statistical weight using a δ-function (3.4a):

$$\Omega(E, N, V) = \int \delta(H(p, q) - E) \frac{dp\, dq}{N!\, h^{3N}}. \tag{5.4}$$

Here we considered that H(p,q) depends on V through the potential $U_V(q)$, which represents the action of the walls and which rises sharply near the boundaries of the volume V; the limits of integration are taken to be infinite. Differentiating (5.4) with respect to V, we obtain

$$\frac{\partial\Omega}{\partial V} = \int \frac{\partial}{\partial V} \delta(H(p, q) - E)\, d\Gamma = - \int \frac{\partial}{\partial E} \delta(H(p, q) - E) \frac{\partial H(p, q)}{\partial V}\, d\Gamma$$

or, since $\partial H(p,q)/\partial V$ is independent of E,

$$\frac{\partial\Omega}{\partial V} = - \frac{\partial}{\partial E} \int \delta(H(p, q) - E) \frac{\partial H(p, q)}{\partial V}\, d\Gamma.$$

Using (3.4) this equation can be rewritten in the form

$$\frac{\partial\Omega(E, N, V)}{\partial V} = - \frac{\partial}{\partial E} \left(\Omega(E, N, V) \left\langle \frac{\partial H(p, q)}{\partial V} \right\rangle \right), \tag{5.5}$$

from which it follows that

$$\frac{\partial}{\partial V} \ln \Omega(E, N, V) = - \left\langle \frac{\partial H(p, q)}{\partial V} \right\rangle \frac{\partial}{\partial E} \ln \Omega(E, N, V) - \frac{\partial}{\partial E} \left\langle \frac{\partial H(p, q)}{\partial V} \right\rangle. \tag{5.5a}$$

The first term on the right hand side of (5.5a) is finite as $N \to \infty$ ($V/N = \text{const.}$), because the entropy $S = \ln\Omega$ is proportional to the volume, but the second term falls off as $1/N$, and can therefore be dropped. Thus,

$$\frac{\partial}{\partial V} \ln \Omega(E, N, V) = -\left\langle \frac{\partial H(p\ q)}{\partial V} \right\rangle \frac{\partial}{\partial E} \ln \Omega(E, N, V), \qquad (5.5b)$$

which can be written using (5.3) in the form

$$\frac{p}{\theta} = \frac{\partial}{\partial V} \ln \Omega(E, N, V) = \frac{\partial S(E, N, V)}{\partial V}, \qquad (5.6)$$

or the quantity

$$\frac{1}{\theta} = \frac{\partial}{\partial E} \ln \Omega(E, N, V) = \frac{\partial S(E, N, V)}{\partial E} \qquad (5.6a)$$

plays the role of the inverse temperature.

From the relations (5.6), (5.6a) one can obtain a complete system of thermodynamic equalities for the microcanonical ensemble.

The differential of the entropy

$$S(E, N, V) = \ln \Omega(E, N, V)$$

is equal to

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial N} dN \qquad (5.7)$$

or using (5.6) and (5.6a)

$$\theta\, dS = dE + p\, dV - \mu\, dN \qquad (5.8)$$

where

$$-\frac{\mu}{\theta} = \frac{\partial S(E, N, V)}{\partial N}, \qquad (5.8a)$$

μ is the chemical potential.

Thus, $1/\theta$ is an integrating factor for the left hand side of (5.8); therefore, in accordance with macroscopic thermodynamics the quantity $\theta = kT$, where k is Boltzmann's constant, can be identified with the absolute temperature, and S can be identified with the entropy. Equation (5.8) has the form of the usual thermodynamic equality which expresses the first and second laws of thermodynamics. Thus, all thermodynamic relations can be derived from the microcanonical distribution.

5.3. Virial Theorem.

We have defined the pressure as the average value of the generalized force $\partial H(p,q)/\partial V$, which represents a dynamical variable, i.e., a function of the momenta and coordinates of all particles. Let us make more precise the explicit form of this dynamical variable. We shall proceed as before from the microcanonical ensemble, although all derivations can be carried out completely analogously for any of the Gibbs ensembles.

Let us write the statistical weight (5.4) in the form

$$\Omega(E, N, V) = \int_{\{\dots V \dots\}} \delta(H(p, q) - E) \frac{dp\,dq}{N!\,h^{3N}}, \tag{5.9}$$

where we consider that $H(p,q)$ does not depend explicitly on V, and the term $U_V(q)$, describing the action of the walls, is taken into account by restricting the region of integration such that each q_i lies in the volume V (this is denoted by the symbol $\{\dots V \dots\}$).

The variability of the volume is conveniently described by introducing a parameter λ^3 in front of V:

$$\Omega(E, N, \lambda^3 V) = \int_{\{\dots \lambda^3 V \dots\}} \delta(H(p, q) - E) \frac{dp\,dq}{N!\,h^{3N}}. \tag{5.9a}$$

We carry out a change of the variables of integration, a change of scale by the factor λ:

$$q = \lambda q', \quad p = \lambda^{-1} p'. \tag{5.9b}$$

This is a canonical transformation which leaves the phase volume $dpdq$ unchanged and renders the limits of integration independent of λ:

$$\Omega(E, N, \lambda^3 V) = \int_{\{\dots V \dots\}} \delta\left(H\left(\frac{p}{\lambda}, \lambda q\right) - E\right) \frac{dp\,dq}{N!\,h^{3N}}.$$

Differentiating this expression with respect to λ, we obtain

$$\frac{\partial\Omega}{\partial\lambda} = -\int\limits_{(\ldots V\ldots)} \frac{\partial}{\partial E}\,\delta\left(H\left(\frac{p}{\lambda},\lambda q\right) - E\right)\frac{\partial H\left(\frac{p}{\lambda},\lambda q\right)}{\partial\lambda}\,d\Gamma,$$

or, setting λ=1,

$$\left(\frac{\partial\Omega}{\partial\lambda}\right)_{\lambda=1} = -\frac{\partial}{\partial E}\,\Omega\left\langle\frac{\partial}{\partial\lambda}\,H\left(\frac{p}{\lambda},\lambda q\right)\right\rangle_{\lambda=1}. \tag{5.10}$$

On the other hand,

$$\left(\frac{\partial\Omega}{\partial\lambda}\right)_{\lambda=1} = \frac{\partial\Omega}{\partial V}\,3V, \tag{5.10a}$$

thus,

$$\left(\frac{\partial\Omega}{\partial V}\right)_{\lambda=1} = -\frac{\partial}{\partial E}\,\Omega\frac{1}{3V}\left\langle\frac{\partial}{\partial\lambda}\,H\left(\frac{p}{\lambda},\lambda q\right)\right\rangle_{\lambda=1}. \tag{5.11}$$

Comparing (5.11) with (5.5), we find the explicit expression for the dynamical variable corresponding to the pressure ∂H(p,q)/∂V:

$$-\frac{\partial H(p,q)}{\partial V} = -\frac{1}{3V}\,\frac{\partial}{\partial\lambda}\,H\left(\frac{p}{\lambda},\lambda q\right)_{\lambda=1}. \tag{5.12}$$

For example, if H is the Hamiltonian of the system of particles with the two-particle interaction (1.2), from (5.12) we obtain directly

$$-\frac{\partial H(p,q)}{\partial V} = \frac{2}{3V}\sum_i \frac{p_i^2}{2m} + \frac{1}{6V}\sum_{i\neq j}(q_i - q_j)\cdot F_{ij}, \tag{5.13}$$

where

$$F_{ij} = -\frac{\partial\Phi(q_i - q_j)}{\partial q_i}$$

is the two-particle interaction force between the ith and the jth particles.

Formula (5.13) is the required explicit expression for the dynamical variable describing the pressure.

The average value of the dynamical variable (5.13) leads to an expression for the pressure

$$p = \frac{2}{3V}\sum_{i}\frac{\langle p_i^2\rangle}{2m} + \frac{1}{6V}\sum_{i\neq j}\langle(\boldsymbol{q}_i - \boldsymbol{q}_j)\cdot\boldsymbol{F}_{ij}\rangle, \tag{5.14}$$

which is called the *virial theorem*. The quantity

$$\frac{1}{2}\sum_{i\neq j}\langle(\boldsymbol{q}_i - \boldsymbol{q}_j)\cdot\boldsymbol{F}_{ij}\rangle$$

is called the *virial force.*

Thus according to the virial theorem the pressure is equal to 2/3 of the average kinetic energy density plus 1/3 of the virial force density. This theorem remains valid, if by <...> is understood an averaging over any of the Gibbs ensembles, not just over the microcanonical ensemble. It is valid also in quantum statistics, if by <...> is understood an averaging over a quantum ensemble (see section 11.3, Chapter II). For the classical Gibbs canonical ensemble the average kinetic energy is easily calculated:

$$\sum_{i}\frac{\langle p_i^2\rangle}{2m} = \frac{3N}{2}\theta, \tag{5.14a}$$

and the virial theorem gives

$$p = \frac{N\theta}{V} + \frac{1}{6V}\sum_{i\neq j}\langle(\boldsymbol{q}_i - \boldsymbol{q}_j)\cdot\boldsymbol{F}_{ij}\rangle. \tag{5.14b}$$

This form of the virial theorem is valid only in classical statistics.

The relation (5.14a) can be written in the form

$$\frac{\langle p_i^2\rangle}{2m} = \frac{3}{2}\theta = \frac{3}{2}kT, \tag{5.14c}$$

i.e., in classical statistics the average kinetic energy per degree of freedom is the same for all degrees of freedom and is equal to

$$\frac{\theta}{2}=\frac{kT}{2}.$$

For the harmonic oscillator in classical statistics the potential energy is also uniformly distributed over the degrees of freedom, and each degree of freedom again has θ/2.

5.4. Thermodynamic Equalities for the Gibbs Canonical Ensemble.

In the case in which the ensemble is described by the Gibbs canonical distribution (3.7), the average value of the derivative of the Hamiltonian with respect to the parameter α_i is equal to

$$\left\langle\frac{\partial H}{\partial \alpha_i}\right\rangle = e^{F/\theta}\int e^{-H/\theta}\frac{\partial H}{\partial \alpha_i}\,d\Gamma = -\theta e^{F/\theta}\frac{\partial}{\partial \alpha_i}\int e^{-H/\theta}\,d\Gamma =$$
$$= -\theta e^{F/\theta}\frac{\partial}{\partial \alpha_i}e^{-F/\theta} = \left(\frac{\partial F}{\partial \alpha_i}\right)_{\theta,N}.$$

Thus, the observed value of the average of the generalized force, which corresponds to a change of the parameter α_i in a quasistatic process with constant θ and N, is equal to

$$\langle A_i\rangle = -\left(\frac{\partial F}{\partial \alpha_i}\right)_{\theta,N}, \tag{5.15}$$

or in the particular case when $\alpha_i = V$,

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\theta,N}. \tag{5.16}$$

Now all thermodynamic relations for the canonical ensemble can be easily obtained. The free energy of the system F is a function of $\theta,\alpha_1,\ldots,\alpha_s,N$. Thus,

$$dF = \left(\frac{\partial F}{\partial \theta}\right)_{\alpha_i,N}d\theta + \sum_{i=1}^{s}\left(\frac{\partial F}{\partial \alpha_i}\right)_{\theta,N}d\alpha_i + \left(\frac{\partial F}{\partial N}\right)_{\theta,\alpha_i}dN, \tag{5.17}$$

or

$$dF = -S\,d\theta - \sum_{i=1}^{s} \langle A_i \rangle\, da_i + \mu\, dN; \tag{5.17a}$$

here we have made use of the relations (3.8c), (5.15) and have introduced the chemical potential

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{a_i,\, \theta}. \tag{5.18}$$

In § 13 it will shown that the values of μ calculated from (5.18) and from (5.8a) coincide in the thermodynamic limit.

Using (3.8c) the relationship (5.17) can be written in the form

$$d\langle H \rangle = d(F + \theta S) = \theta\, dS - \sum_{i=1}^{s} \langle A_i \rangle\, da_i + \mu\, dN. \tag{5.19}$$

Thus, $1/\theta$ is an integrating factor for

$$d\langle H \rangle + \sum_i \langle A_i \rangle\, da_i - \mu\, dN,$$

therefore $\theta = kT$ can be identified with the absolute temperature of the thermostat and S with the entropy.

The equation (5.17a) comprises a complete system of thermodynamic relations, which can be expressed not only in terms of the free energy F, but also in terms of the other thermodynamic potentials.

A thermodynamic equality (5.17a) can be rewritten in the form

$$d\left(F + \sum_i \langle A_i \rangle a_i\right) = d\Phi = -S\,d\theta + \sum_i a_i\, d\langle A_i \rangle + \mu\, dN, \tag{5.20}$$

where

$$\Phi = F + \sum_i \langle A_i \rangle a_i \tag{5.21}$$

is the thermodynamic potential for the isobaric-isothermal systems (a function of the variables θ, $\langle A_i\rangle$, N), which we introduced earlier for the particular case α_1=V, $\langle A_1\rangle$=p. In that case

$$\Phi = F + pV. \tag{5.22}$$

A thermodynamic potential Φ is often simply called the thermodynamic potential (in the narrow sense of the word) or the Gibbs potential and is denoted by G(θ,p,N). The transition from F to Φ is a Legendre transformation for the thermodynamic functions.

From (5.20) it follows that $\mu=\partial\Phi/\partial N$. On the other hand, the function Φ depends on only one extensive variable N, and therefore the thermodynamic limit

$$\lim_{\substack{N\to\infty \\ \langle V\rangle/N=\mathrm{const}}} \frac{\Phi}{N}$$

must be finite; Φ must be proportional to N and have the form Φ=Nf(θ,p). Thus,

$$\mu=\Phi/N. \tag{5.23}$$

The thermodynamic equality (5.17a) can also be written in the form

$$d(F-\mu N) = d\Omega = -S\,d\theta - \sum_i \langle A_i\rangle\, da_i - N\,d\mu, \tag{5.24}$$

where

$$\Omega = F - \mu N \tag{5.25}$$

is the thermodynamic potential in the variables θ,α_i,μ.[1] The transition from F to Ω is also a Legendre transformation.

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[1] Do not confuse (5.25) with the statistical weight (3.3a) which is denoted by the same letter.

Using (5.21) and (5.23) we obtain for Ω the expression

$$\Omega = F - \Phi = -\sum_i \langle A_i \rangle a_i. \tag{5.26}$$

In the particular case when there is only one external parameter V,

$$\Omega = -pV. \tag{5.27}$$

Thus, after the introduction of quasistatic processes all thermodynamic functions can be obtained on the basis of the canonical distribution alone.

5.5. Thermodynamic Equalities for the Gibbs Grand Canonical Ensemble.

A similar derivation of the thermodynamic equalities can be carried out also for the other ensembles, for example, for the Gibbs grand canonical ensemble. In that case

$$\left\langle \frac{\partial H}{\partial a_i} \right\rangle = e^{\Omega/\theta} \sum_N \int e^{-(H-\mu N)/\theta} \frac{\partial H}{\partial a_i} \, d\Gamma = \left(\frac{\partial \Omega}{\partial a_i} \right)_{\theta,\mu}.$$

Thus, the average generalized force is equal to

$$\langle A_i \rangle = -\left(\frac{\partial \Omega}{\partial a_i} \right)_{\theta,\mu}, \tag{5.28}$$

or, in a particular case,

$$p = -\left(\frac{\partial \Omega}{\partial V} \right)_{\theta,\mu}. \tag{5.29}$$

The thermodynamic potential Ω is a function of $\theta, \mu, \alpha_1, \ldots, \alpha_s$. Therefore

$$d\Omega = \left(\frac{\partial \Omega}{\partial \theta} \right)_{a_i,\mu} d\theta + \sum_i \left(\frac{\partial \Omega}{\partial a_i} \right)_{\theta,\mu} da_i + \left(\frac{\partial \Omega}{\partial \mu} \right)_{a_i,\theta} d\mu, \tag{5.30}$$

or, using the relations (3.33a), (3.34) and (5.28),

$$d\Omega = - S\,d\theta - \sum_i \langle A_i \rangle\, da_i - \langle N \rangle\, d\mu. \tag{5.31}$$

Thus, we have obtained a thermodynamic relationship, which is the same as (5.24) if one puts <N>=N.

§ 6. Fluctuations

6.1. Quasithermodynamic Fluctuation Theory.

The Gibbs statistical ensembles make it possible to calculate fluctuations of any dynamical variable in a statistical equilibrium state. We have already considered fluctuations of several quantities, for example, energy fluctuations in the Gibbs canonical ensemble (3.8d), fluctuations of particle number and energy in the Gibbs grand canonical ensemble (3.35), volume fluctuations in the Gibbs isobaric-isothermal ensemble (3.48). In all these cases we were interested in fluctuations in quantities on which the ensemble distribution function depends explicitly. In the microcanonical ensemble energy and particle number are specified and, thus, do not fluctuate, but in this ensemble there exist pressure fluctuations.

The calculation of fluctuations for an arbitrary dynamical variable is no less complicated than the calculation of its average value; therefore the problem must be restricted. One might be interested in the probability distribution of the fluctuations of various quantities, assuming the thermodynamic functions of the system to be known. This is how the problem is posed in the quasithermodynamic theory of fluctuations; we are proceeding toward an exposition of this theory in which we shall follow the work of R. Green and H. B. Callen [30]. The simplifying feature in the theory of fluctuations is their relative smallness.

Let $\xi_1, \xi_2, \ldots, \xi_s$ be physical quantities characterizing the system, but not necessarily integrals of motion.[1] We shall assume, however, that the average values $\langle \xi_k \rangle$ can characterize some state of partial statistical equilibrium. It is necessary to determine the thermodynamic functions of this state.

We define, following Leontovich [2], the free energy of the nonequilibrium state, characterized by giving the average values $\langle \xi_k \rangle$, as the free energy of an equilibrium state in auxiliary fields which produce an equilibrium system with fixed values $\langle \xi_k \rangle$. We shall repeatedly use this approach

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[1] In [30] the quantities ξ_k are considered to be integrals of motion.

in what follows.

We shall consider the most general possible equilibrium with fixed values $\langle\xi_k\rangle$. This means that a statistical ensemble must be used in which is specified the average values of the quantities ξ_k

$$\langle\xi_k\rangle = \int \xi_k f(p, q)\, d\Gamma \tag{6.1}$$

and in which the information entropy (4.5) is a maximum. For ensembles with variable N in (6.1) a summation over N is assumed in addition to the integration.

The condition (6.1) must be added to the usual conditions of constant average energy (4.15), average particle number (4.16), and preservation of the normalization.

Repeating the arguments of § 4, we obtain

$$f = Q^{-1}\exp\left\{-\beta\left(H - \mu N - \sum_k \alpha_k \xi_k\right)\right\}, \tag{6.2}$$

where α_k are the parameters thermodynamically conjugate to $\langle\xi_k\rangle$ and are defined by equation (6.1).

The statistical integral Q, defined by the condition of normalization of the distribution function (6.2), is a function of θ, μ, α_k or $\theta, \mu, \langle\xi_k\rangle$ and defines the thermodynamic functions in a state of partial statistical equilibrium with fixed $\langle\xi_k\rangle$ as a function of $\theta, \mu, \langle\xi_k\rangle$. From now on we shall not stipulate the possible dependence of Q on the volume V.

The distribution function (6.2) in general does not satisfy the Liouville equation, if the ξ_k are not integrals of motion, but it turns out to be useful for calculation of fluctuations.

The physical meaning of the distribution function for systems in partial statistical equilibrium (6.2) consists of regarding such a state as a statistical equilibrium state, but in some auxiliary field α_k, which makes it an equilibrium state [2].

It is convenient to rewrite the distribution function (6.2) in a more symmetric form, similar to (4.14):

$$f = \exp\left\{-\Phi(\mathcal{F}_0, \ldots, \mathcal{F}_n) - \sum_{k=1}^{n} \mathcal{F}_k \mathcal{P}_k\right\}. \tag{6.3}$$

where

$$\mathcal{F}_0=\beta, \qquad \mathcal{P}_0=H,$$
$$\mathcal{F}_1=-\beta\mu, \qquad \mathcal{P}_1=N,$$
$$\mathcal{F}_k=-\beta a_{k-1}, \qquad \mathcal{P}_k=\xi_{k-1} \qquad (k=2,\ 3,\ \ldots,\ n). \tag{6.3a}$$

The function

$$\Phi(\mathcal{F}_0,\ \ldots,\ \mathcal{F}_n)=\ln Q(\mathcal{F}_0,\ \ldots,\ \mathcal{F}_n). \tag{6.4}$$

defined from the normalization condition (6.3)

$$e^{\Phi}=\sum_N\int\exp\left\{-\sum_k\mathcal{F}_k\mathcal{P}_k\right\}d\Gamma, \tag{6.5}$$

is called the Mas'ye-Planck thermodynamic function. It is related to the entropy (4.4) by the relation

$$S=\Phi+\sum_{k=0}^{n}\mathcal{F}_k\langle\mathcal{P}_k\rangle \tag{6.6}$$

and it allows one to represent all thermodynamic relations in an especially symmetric form.

For example, the average values and fluctuations of the quantities $\mathcal{P}_k$ are equal to

$$\langle\mathcal{P}_k\rangle=-\frac{\partial\Phi}{\partial\mathcal{F}_k},$$
$$\langle\mathcal{P}_i\mathcal{P}_k\rangle-\langle\mathcal{P}_i\rangle\langle\mathcal{P}_k\rangle=\frac{\partial^2\Phi}{\partial\mathcal{F}_i\,\partial\mathcal{F}_k}=-\frac{\partial\langle\mathcal{P}_i\rangle}{\partial\mathcal{F}_k}=-\frac{\partial\langle\mathcal{P}_k\rangle}{\partial\mathcal{F}_i} \tag{6.7}$$

Higher correlations are easily calculated in an analogous fashion [30].

Using the entropy (6.6) the distribution function (6.3) can be written in the form

$$f=\exp\left\{-S-\sum_{k=0}^{n}\mathcal{F}_k(\mathcal{P}_k-\langle\mathcal{P}_k\rangle)\right\}, \tag{6.8}$$

where

$$e^{S}=\sum_N\int\exp\left\{-\sum_k\mathcal{F}_k(\mathcal{P}_k-\langle\mathcal{P}_k\rangle)\right\}d\Gamma. \tag{6.9}$$

Differentiating (6.9) with respect to $\langle\mathcal{P}_k\rangle$, we obtain another form of the thermodynamic equalities

$$\frac{\partial S}{\partial \langle \mathcal{P}_k \rangle} = \mathcal{F}_k, \tag{6.10}$$

because the terms which appear upon differentiating $\mathcal{F}_i$ with respect to $\langle \mathcal{P}_k \rangle$ are zero. Formulas (6.7)-(6.10) serve as a basis for calculating the probability distribution of the fluctuations of the quantities $\mathcal{P}_k$.

6.2. Gaussian Distribution for Fluctuation Probability.

Let us proceed to the calculation of the probability of the fluctuation of the quantity $\mathcal{P}_k$. In the formulas (6.3) and (6.8) the quantity $\mathcal{P}_k$ is a dynamical variable, i.e., a function of the momenta and coordinates of all particles p,q.

Following Einstein [31], we construct a macroscopic distribution function on the basis of (6.3), assuming that $\mathcal{P}_k$ have some fixed values.

We introduce the macroscopic distribution function W:

$$W\,d\mathcal{P}_0 \ldots d\mathcal{P}_n = \\ = \Omega\,d\mathcal{P}_0 \ldots d\mathcal{P}_n \exp\Big\{-\Phi(\mathcal{F}_0, \ldots, \mathcal{F}_n) - \sum_k \mathcal{F}_k \mathcal{P}_k\Big\}, \tag{6.11}$$

which gives the probability that the parameters $\mathcal{P}_0,\ldots\mathcal{P}_n$ lie in a region $d\mathcal{P}_0,\ldots,d\mathcal{P}_n$ around the values $\mathcal{P}_0,\ldots\mathcal{P}_n$. Now we regard $\mathcal{P}_k$ not as dynamical variables, but as ordinary quantities; we continue to use the previous notation however. The quantity Ω is the number of states in the region $d\mathcal{P}_0,\ldots,d\mathcal{P}_n$ around $\mathcal{P}_0,\ldots\mathcal{P}_n$. The function W must be normalized not in phase space, but in the space of the values of $\mathcal{P}_0,\ldots,\mathcal{P}_n$:

$$\int W(\mathcal{P}_0, \ldots, \mathcal{P}_n)\,d\mathcal{P}_0 \ldots d\mathcal{P}_n = 1. \tag{6.12}$$

The quantity Ω can be estimated using the entropy s of the microcanonical ensemble in which the parameters $\mathcal{P}_0,\ldots,\mathcal{P}_n$ are given in a region $d\mathcal{P}_0,\ldots,d\mathcal{P}_n$ around the values $\mathcal{P}_0,\ldots,\mathcal{P}_n$:

$$s = \ln \Omega/\Omega_v, \tag{6.13}$$

where Ω_0 is a normalization constant which is unimportant for us right now and which will be defined later.

Using (6.6) and (6.13) we write the macroscopic distribution function (6.11) in the form

$$W = \Omega_0 \exp\left\{ s - S - \sum_k \mathcal{F}_k (\mathcal{P}_k - \langle \mathcal{P}_k \rangle) \right\}, \tag{6.14}$$

where S is the entropy in the quasiequilibrium grand canonical ensemble (6.3).

Let us note something which will be essential in what follows. As a consequence of the thermodynamic equivalence of the statistical ensembles the entropy in the ensemble (6.3) is the same function of $\langle\mathcal{P}_0\rangle, \ldots, \mathcal{P}_n\rangle$ as the entropy in the corresponding microcanonical ensemble is of the variables $\mathcal{P}_0, \ldots \mathcal{P}_n$, i.e., S and s are identical functions, but of different variables. Therefore s - S can be expanded in a series in $\mathcal{P}_k - \langle\mathcal{P}_k\rangle$; because of the small size of the fluctuations the series may be terminated with terms of the second order. Using (6.10) we obtain

$$\begin{gathered} s - S = \sum_k \mathcal{F}_k \Delta\mathcal{P}_k + \frac{1}{2} \sum_{i,\,k} \frac{\partial^2 S}{\partial\langle\mathcal{P}_i\rangle\, \partial\langle\mathcal{P}_k\rangle} \Delta\mathcal{P}_i \Delta\mathcal{P}_k, \\ \Delta\mathcal{P}_k = \mathcal{P}_k - \langle\mathcal{P}_k\rangle. \end{gathered} \tag{6.15}$$

Substituting (6.15) in (6.14) and using the fact that the linear terms cancel, we obtain the distribution function for fluctuations:

$$W = A \exp\left\{ \frac{1}{2} \sum_{i,\,k} \frac{\partial^2 S}{\partial\langle\mathcal{P}_i\rangle\, \partial\langle\mathcal{P}_k\rangle} \Delta\mathcal{P}_i \Delta\mathcal{P}_k \right\} \tag{6.16}$$

(the constant A is defined by the normalization condition (6.12)). Thus, the probability of fluctuations of the quantities $\mathcal{P}_k$ is defined by the <u>Gaussian distribution</u> (6.16).

We write the Gaussian distribution (6.16) in the form

$$W = A \exp\left\{ -\frac{1}{2} \sum_{i,\,k} \lambda_{ik} x_i x_k \right\}, \tag{6.17}$$

where

$$\lambda_{ik} = \lambda_{ki} = - \frac{\partial^2 S}{\partial\langle\mathcal{P}_i\rangle\, \partial\langle\mathcal{P}_k\rangle}, \qquad x_i = \Delta\mathcal{P}_i = \mathcal{P}_i - \langle\mathcal{P}_i\rangle. \tag{6.17a}$$

or, after calculation of the normalization constant A,

$$W = \frac{\sqrt{\lambda}}{(2\pi)^{(n+1)/2}} \exp\left\{ -\frac{1}{2} \sum_{i,\,k} \lambda_{ik} x_i x_k \right\}, \tag{6.18}$$

where λ is a determinant with elements λ_{ik}, which are assumed positive and non-zero, and n+1 is the number of variables x_i.

All fluctuations can be calculated using the Gaussian distribution function (6.18). We write (6.18) in the form

$$W = Ae^{-K(x_0,\,\ldots,\,x_n)}, \tag{6.18a}$$

where

$$K(x_0,\ \ldots,\ x_n) = \frac{1}{2} \sum_{i,\,k} \lambda_{ik} x_i x_k = \frac{1}{2} \boldsymbol{\lambda} : \boldsymbol{xx} \tag{6.18b}$$

is a quadratic form, λ is a tensor with elements λ_{ik}, x is a vector with components x_i; the symbol : between tensors denotes their complete contraction.

We calculate the average value with respect to the Gaussian distribution of the product of x_i and X_k,

$$X_k = \frac{\partial K}{\partial x_k}. \tag{6.19}$$

Carrying out an integration by parts, we obtain

$$A \int e^{-K} x_i \frac{\partial K}{\partial x_k} dx_0 \ldots dx_n = -A \int x_i \frac{\partial}{\partial x_k} e^{-K} dx_0 \ldots dx_n = \delta_{ik}. \tag{6.20}$$

Thus,

$$\left\langle x_i \frac{\partial K}{\partial x_k} \right\rangle = \langle x_i X_k \rangle = \delta_{ik},$$

or

$$\sum_m \langle x_i x_m \rangle \lambda_{mk} = \delta_{ik}, \tag{6.21}$$

i.e., the product of the matrix $\langle x_i x_k \rangle$ with λ_{mk} is equal to the unit matrix.

Thus, the mean square fluctuations are defined by the matrix which is inverse to λ_{mk}:

$$\langle x_i x_m \rangle = (\lambda^{-1})_{im}. \tag{6.22}$$

Let us show that λ is a positive definite matrix. We convert (6.21) to diagonal form using a canonical transformation from x to x′; then

$$\langle (x'_i)^2 \rangle = \frac{1}{\lambda_{ii}}; \tag{6.22a}$$

thus, $\lambda_{ii} > 0$, as was assumed earlier.

Formula (6.22) is the quadratic fluctuations calculated using the Gaussian distribution. On the other hand, the formula (6.7) gives the exact value of the fluctuations calculated using the Gibbs distribution (6.3):

$$\langle x_i x_k \rangle = \frac{\partial^2 \Phi}{\partial \mathcal{F}_i \partial \mathcal{F}_k}. \tag{6.23}$$

It is easy to see that these values are the same. In fact the matrices

$$\frac{\partial^2 \Phi}{\partial \mathcal{F}_i \partial \mathcal{F}_k} \text{ and } -\frac{\partial^2 S}{\partial \langle \mathcal{P}_i \rangle \partial \langle \mathcal{P}_k \rangle}$$

are mutual inverses. Using (6.7) and (6.10) we obtain

$$-\sum_k \frac{\partial^2 \Phi}{\partial \mathcal{F}_i \partial \mathcal{F}_k} \frac{\partial^2 S}{\partial \langle \mathcal{P}_m \rangle \partial \langle \mathcal{P}_k \rangle} = \sum_k \frac{\partial \langle \mathcal{P}_i \rangle}{\partial \mathcal{F}_k} \frac{\partial \mathcal{F}_k}{\partial \langle \mathcal{P}_m \rangle} = \frac{\partial \langle \mathcal{P}_i \rangle}{\partial \langle \mathcal{P}_m \rangle} = \delta_{im}. \tag{6.24}$$

This means that the Gaussian distribution (6.18) gives the exact value of the quadratic fluctuations of the quantities x_i. For higher order fluctuations this is not true, and higher order terms in the expansion (6.15) of the entropy must be considered.

In this chapter we shall not consider further the theory of fluctuations, referring the interested reader to the literature [2, 26, 32, 33]. We shall return again and again to the question of fluctuations, because they are intimately connected with irreversible processes.

We end this paragraph with a short review of the basic concepts of classical statistical mechanics.

Classical statistical mechanics is applicable only for temperatures sufficiently high that quantum effects can be neglected. Otherwise it can lead to incorrect results. For example, the uniform distribution of energy over the degrees of freedom, which follows from classical statistics, is not valid for low temperatures. But even in the region of its applicability classical statistical mechanics, as we have seen in § 1, borrows some of its concepts from quantum statistics. For example, the assumption of the existence of a smallest cell in phase space h^{3N} and the factor $1/N!$, which takes into account the identity of states, differing only by a permutation of the particles, are introduced into classical statistics from without. These effects are taken into account completely naturally in quantum statistical mechanics, the basic principles of which we discuss in Chapter II.

CHAPTER II

EQUILIBRIUM STATISTICAL MECHANICS OF QUANTUM SYSTEMS

We give a short review of the basic propositions of statistical mechanics of quantum systems for the equilibrium case to the extent that this is necessary for what follows (see [1-4]).

§ 7. Statistical Operator

7.1. Pure Ensemble.

Until now we have considered classical statistical mechanics, in which the state of the system was described by a point (p,q) in a 6N-dimensional phase space, and the time evolution of the state was described by Hamilton's equations (1.1). The dynamical variables, for example the energy (1.2), and the total momentum, were functions of the coordinates and momenta p,q, i.e., functions of the state of the dynamical system.

Quantum statistical mechanics proceeds from the basic representations of quantum mechanics, where the situation is entirely different. In quantum mechanics the state of a dynamical system is described by a wave function $\Psi(x_1,\ldots,x_N,t)$ or, more briefly, $\Psi(x,t)$, depending on time and the coordinates of the particles $x_1,\ldots,x_N$ or on some other system of simultaneously measurable quantities.

The time evolution of the state is described by the Schroedinger equation

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi, \tag{7.1}$$

where H is a self-adjoint operator acting on the wave function Ψ, and $\hbar$ is Planck's constant.

For example, for a system of N identical particles of mass m, having no internal degrees of freedom and interacting among themselves with the potential $\phi(|x|)$, the Schroedinger equation has the form

$$i\hbar\frac{\partial\Psi}{\partial t} = \left\{-\frac{\hbar^2}{2m}\sum_{1\le j\le N}\nabla_j^2 + \frac{1}{2}\sum_{j\ne k}\phi(|x_j-x_k|)\right\}\Psi, \tag{7.2}$$

where

$$\nabla_j^2 = \sum_{1 \leq \alpha \leq 3} \frac{\partial^2}{\partial (x_j^\alpha)^2}$$

is the Laplacian.

The Schroedinger equation completely determines Ψ at any moment of time t, if it is known at an initial time t=0. For example, for an isolated system, when H has no explicit time dependence,

$$\Psi(t) = e^{\frac{1}{i\hbar}Ht}\,\Psi(0) \tag{7.3}$$

is a formal solution of the Schroedinger equation.

The dynamical variables in quantum mechanics are not functions of the state of the dynamical system, but are represented by linear self-adjoint operators acting in the space of the wave functions. Their spectrum defines the possible observable values of the physical quantities. Therefore a specification of the state of the system, i.e., Ψ, does not imply an exact knowledge of the dynamical variables. The wave function Ψ allows calculation only of the average value of any dynamical variable represented by the operator A in the state Ψ:

$$\bar{A} = (\Psi^*, A\Psi), \tag{7.4}$$

where the wave functions are normalized to unity

$$(\Psi^*, \Psi) = 1, \tag{7.5}$$

and the brackets denote the scalar product of functions in Hilbert space, i.e.,

$$(\Psi^*, \Phi) = \int \Psi^*(x)\,\Phi(x)\,dx; \tag{7.6}$$

x is the collection of coordinates $x_1, x_2, \ldots, x_N$.

In general the function $\Psi(x)$ depends also on time t, i.e., one must write $\Psi(x,t)$, but we shall omit the argument t. If the state is characterized also by spin variables $\sigma_1, \ldots, \sigma_N$, then in (7.6) a summation over spin variables must be carried out in addition to the integration.

The formula (7.4) gives only the probabilities of prediction of the observed values of any physical quantities. Only in the particular case in which Ψ is an eigenfunction of the operator A does formula (7.4) give the exact value of the quantity A in the state Ψ.

A state which can be described by a wave function is called a pure state. The corresponding statistical ensemble, i.e., a large number of non-interacting "copies" of the given system, in the given quantum state and with the stipulation that averages are calculated according to formula (7.4), is called a pure ensemble. A pure state is usually called simply a quantum mechanical state. It represents the maximum possible information about a quantum mechanical system. All of quantum mechanics, with the exception of some questions in the theory of measurement [2, 5-9], is founded on applications of pure ensembles.

It is convenient to use a projection operator to represent the average values of dynamical quantities in a pure ensemble.

We write the linear operator A in a matrix x-representation, defining it through the matrix elements,

$$A\Psi(x) = \int A(x, x')\Psi(x')\,dx'. \tag{7.7}$$

Substituting (7.7) into (7.4), we obtain

$$\bar{A} = \int A(x, x')\mathcal{P}(x', x)\,dx\,dx' = \mathrm{Sp}(A\mathcal{P}), \tag{7.8}$$

where

$$\mathcal{P}(x, x') = \Psi(x)\Psi^*(x') \tag{7.8a}$$

is called the projection operator, which thus represents a pure ensemble.

This name stems from the fact that the operation of the operator $\mathcal{P}$ on any function φ projects it in the Hilbert space onto the direction Ψ. In fact,

$$\mathcal{P}\varphi = \int \mathcal{P}(x, x')\varphi(x')\,dx' = (\Psi^*, \varphi)\,\Psi(x). \tag{7.9}$$

The function Ψ is assumed to be normalized.

That the projection operator is Hermitian follows from (7.8a):

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

Besides this, it has the property that

$$\mathcal{P}^2 = \mathcal{P}, \tag{7.10}$$

which follows from (7.9). This property is evident, because after one projection operation all subsequent projections onto the same direction no longer change the result.

In addition, it is always true that

$$\mathrm{Sp}\,\mathcal{P} = 1, \tag{7.11}$$

which follows from (7.8) after substituting for A the unit operator or from (7.8a) using the normalization (7.5).

Let us show that all eigenvalues of the projection operator are equal to zero, except one which is equal to unity.

The Hermitian operator $\mathcal{P}$ can always be converted to diagonal form. Then its eigenvalues will also satisfy equation (7.10), and, thus, are equal to zero or unity. But from the normalization condition (7.11) the projection operator can have in this case only one eigenvalue equal to unity. Therefore all eigenvalues of the projection operator are equal to zero, except one which is equal to unity.

Condition (7.10) together with the Hermiticity condition can be regarded as the definition of the projection operator, and thus of a pure state.

Knowledge of the wave function $\Psi_1(x,t)$ allows calculation of the probability of transition from the state $\Psi_1(x,t)$ to any state $\Psi_2(x,t)$ in the time t:

$$W_{12}(t) = |(\Psi_2^*(t), \Psi_1(t))|^2,$$

which can be written using projection operators:

$$W_{12}(t) = \int \mathscr{P}_1(x, x', t)\mathscr{P}_2(x', x, t)\,dx\,dx' = \mathrm{Sp}(\mathscr{P}_1(t)\mathscr{P}_2(t)),$$

where

$$\mathscr{P}_\alpha(x, x', t) = \Psi_\alpha(x, t)\Psi_\alpha^*(x', t) \qquad (\alpha = 1, 2)$$

are the projection operators corresponding to the states Ψ_1 and Ψ_2.

For a pure ensemble the negative of the average of the logarithm of ρ corresponds to the information entropy (4.1), and it is zero:

$$-\langle \ln \mathscr{P} \rangle = -\mathrm{Sp}(\mathscr{P} \ln \mathscr{P}) = 0.$$

In connection with this, if ρ is converted to diagonal form, then the product $\rho_{nn} \ln \rho_{nn}$ is equal to zero, because $\mathscr{P}_{nn}$ is either zero or one and x ln x for x=0 is taken to be zero. Thus, for a pure ensemble the measure of uncertainty in the information entropy is equal to zero; i.e., it corresponds to the maximum possible information about quantum mechanical systems.

Quantum statistical mechanics is in some sense simpler than classical, because it already contains the concept of probability, but a pure quantum mechanical ensemble turns out to be insufficient in quantum statistics, because as a rule we do not have available complete information about the systems we study, because of the large number of particles.

7.2. Mixed Ensemble and Statistical Operator.

Quantum statistical mechanics makes use of a statistical ensemble of a more general type than the "pure" ensemble considered above, namely a mixed ensemble (or "mixture"), which is based on an incomplete set of data about the system (see [1-10]).

Let us consider a large number of identical, non-interacting copies of the given system, which may be in different quantum states.

In a mixed ensemble only the probabilities $w_1, w_2, \ldots$ of finding the system in various quantum states $\Psi_1, \Psi_2, \ldots$ are defined. The average value of any physical quantity, represented by the operator A, is defined in a mixed state by the expression

$$\langle A\rangle = \sum_k w_k (\Psi_k^*, A\Psi_k), \tag{7.12}$$

for which

$$\sum_k w_k = 1, \quad w_k \geqslant 0. \tag{7.12a}$$

Here $(\Psi^*_k, A\Psi_k)$ is the quantum mechanical average of the operator A in the state Ψ_k. The auxiliary conditions (7.12a) mean that the total probability of all quantum states is equal to unity and that the probability cannot be negative.

A pure ensemble is a particular case of a mixed ensemble in which all probabilities w_k are equal to zero except one, which is equal to unity. Then (7.12) goes over into (7.4).

In a mixed ensemble, as distinguished from a pure ensemble, the different quantum states do not interfere among themselves, because in the definition of averages for the mixture (7.12) it is average values rather than wave functions which are added. If the system were described by a wave function in the form of a superposition of the states Ψ_k, then in the expression for averages (7.4) there would also be cross terms (interference terms) connecting the different quantum states; this is not the case in (7.12).

To study mixed ensembles it is convenient to introduce a statistical operator proposed by von Neumann [2,3], and also for a particular case by L. D. Landau [11]. We write the linear operator A in the matrix x-representation (7.7). Substituting (7.7) into (7.12), we obtain

$$\langle A\rangle = \int A(x, x')\rho(x', x)\,dx\,dx', \tag{7.13}$$

or

$$\langle A\rangle = \mathrm{Sp}(A\rho), \tag{7.14}$$

where

$$\rho(x, x') = \sum_k w_k \Psi_k(x)\Psi_k^*(x') \tag{7.15}$$

is the statistical operator in the matrix x-representation or <u>density matrix.</u> The statistical operator (7.15) depends on the 2N variables $x_1, \ldots, x_N$; $x'_1, \ldots, x'_N$, i.e., on exactly the same variables as does the distribution function in classical statistical mechanics, which depends on the 2N coordinates and momenta $q_1, \ldots, q_N; p_1, \ldots, p_N$.

The statistical operator (7.15) satisfies the normalization condition

$$\mathrm{Sp}\,\rho = 1, \tag{7.16}$$

because

$$\mathrm{Sp}\,\rho = \int \rho(x, x)\,dx = \sum_k w_k(\Psi_k^*, \Psi_k),$$

and from the normalization conditions of the wave functions and the probabilities w_k it follows that

$$(\Psi_k^*, \Psi_k) = 1, \quad \sum_k w_k = 1.$$

The normalization condition (7.16) follows also from (7.14) if the unit operator is substituted into it in place of A. This normalization condition is the quantum analog of the normalization condition of the distribution function (1.5a).

Formula (7.14) is convenient because the spur (or trace) of a matrix is invariant with respect to unitary transformations of the operators. Therefore the formula (7.14) does not depend on the representation of the operators A and ρ; it is valid for any representation, not just for the matrix x-representation of the operators. Other more convenient representations for the operators are usually used in practical problems.

For example, in the discrete matrix n-representation

$$\langle A\rangle = \sum_{m,n} A_{mn}\rho_{nm},$$

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

The statistical operator (7.15) is Hermitian:

$$\rho^*(x, x') = \rho(x', x), \tag{7.17}$$

which follows immediately from its definition (7.15).

Using the projection operator (7.8a) the statistical operator (7.15) can be written in the form

$$\rho = \sum_k w_k \mathcal{P}_{\Psi_k}, \quad \sum_k w_k = 1, \quad w_k \geqslant 0, \tag{7.18}$$

where $\mathcal{P}_{\Psi_k}$ is the projection operator onto the state Ψ_k. In the particular case in which all the w_k are equal to zero except one, which is equal to unity, the statistical operator (7.18) coincides with the projection operator (7.8a).

Let us show that the statistical operator is positive definite, i.e., that it has no negative eigenvalues. This property follows from (7.18), because the sum of positive definite matrices is also positive definite, and the projection operator, as we have verified earlier, is positive definite. In any case, it is easy to prove directly that the eigenvalues of ρ are positive.

Because ρ is Hermitian, the condition that its eigenvalues be positive definite can be written in the form

$$\langle A^2 \rangle = \mathrm{Sp}(\rho A^2) \geqslant 0, \tag{7.19}$$

where A^2 is an arbitrary Hermitian operator. Indeed, taking ρ to diagonal form, which is possible because it is Hermitian, we can write (7.19) in the form

$$\sum_{n,k} \rho_{nn} A_{nk} A_{kn} = \sum_{n,k} \rho_{nn} | A_{nk} |^2 \geqslant 0,$$

from which it followx that $\rho_{nn} \geqslant 0$. For the statistical operator (7.15) the property (7.19) is satisfied, because

$$\langle A^2 \rangle = \sum_k w_k (A^2)_{kk} = \sum_{k,m} w_k A_{km} A_{mk} = \sum_{k,m} w_k | A_{km} |^2 \geqslant 0, \tag{7.19a}$$

and thus, the statistical operator is positive definite.

It is not difficult to verify that any positive definite Hermitian operator satisfying the normalization condition (7.16) can be represented in the form (7.18). To do this it is necessary to reduce the operator to diagonal form; after this it is represented as a sum of matrices in which all the diagonal elements except one are equal to zero. The positive eigenvalues of the operator, the sum of which is equal to unity by the normalization condition, play the role of the w_k, and the remaining matrices will be the projections.

Let us show that all matrix elements of the statistical operator are bounded. The spur of the square of the statistical operator is equal to

$$\operatorname{Sp} \rho^2 = \sum_{m,n} |\rho_{mn}|^2.$$

Let us note that in the diagonal representation this quantity is less than one, because in that case from the positivity of the eigenvalues ρ_{nn} of the statistical operators

$$\sum_n \rho_{nn}^2 \leqslant \Big(\sum_n \rho_{nn}\Big)^2 = 1.$$

Keeping in mind that the spur is invariant with respect to the representation, we obtain

$$\operatorname{Sp} \rho^2 = \sum_{m,n} |\rho_{mn}|^2 \leqslant 1.$$

This inequality shows that all matrix elements of the statistical operator are bounded.

§ 8. Liouville's Quantum Equation

8.1. Liouville Equation in the Quantum Case.

Let us consider the time evolution of the statistical operator for an ensemble of systems with a Hamiltonian H, which may be time dependent. The statistical operator at the instant t has the form (7.15), but now the Ψ_k depend on time:

$$\rho(x, x', t) = \sum_k w_k \Psi_k(x, t) \Psi_k^*(x', t), \tag{8.1}$$

where the w_k do not depend on t, because they correspond to the probability distribution at t=0. The functions $\Psi_k(x,t)$ are solutions of the Schroedinger equation, satisfying the initial condition

$$\Psi_k(x, t)|_{t=0} = \Psi_k(x),$$

where $\Psi_k(x)$ is some system of wave functions defining the statistical operator at t=0:

$$\rho(x, x') = \sum_k w_k \Psi_k(x) \Psi_k^*(x').$$

Because of this initial condition the non-stationary solutions of the Schroedinger equation depend on the quantum number k.

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

The change of the state $\Psi_k(x,t)$ in time is defined by the Schroedinger equation (7.1)

$$i\hbar \frac{\partial \Psi_k(x, t)}{\partial t} = H\Psi_k(x, t), \tag{8.2}$$

which can be written using (7.7) in the matrix form

$$i\hbar \frac{\partial \Psi_k(x, t)}{\partial t} = \int H(x, x') \Psi_k(x', t)\, dx'. \tag{8.3}$$

Thus, the statistical operator (8.1) satisfies the equation

$$\begin{aligned} i\hbar \frac{\partial \rho(x, x', t)}{\partial t} &= \int \sum_k (H(x, x'') w_k \Psi_k(x'', t) \Psi_k^*(x', t) - \\ &\quad - w_k \Psi_k(x, t) \Psi_k^*(x'', t) H(x'', x'))\, dx'' = \\ &= \int (H(x, x'') \rho(x'', x', t) - \rho(x, x'', t) H(x'', x'))\, dx'', \end{aligned} \tag{8.4}$$

where the hermiticity of the Hamiltonian has been used

$$H^{*}(x, x') = H(x', x). \tag{8.5}$$

Thus, we have obtained the equation of motion of the statistical operator - the quantum Liouville equation in matrix form (8.4). It is convenient to write it in operator form

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho], \tag{8.6}$$

where

$$\frac{1}{i\hbar}[H, \rho] = \frac{1}{i\hbar}(H\rho - \rho H) \tag{8.7}$$

are the quantum Poisson brackets.

The quantum Liouville equation (8.6) is analogous to the classical Liouville equation (2.11) for the distribution function $f(p,q,t)$. Instead of the classical Poisson brackets (2.10), it contains the quantum Poisson brackets (8.7). There exists, however, also an essential difference. The statistical operator $\rho(x,x',t)$ is a complex function of the collection of coordinates of the particles $x_1,\ldots,x_N$ and $x'_1,\ldots,x'_N$, but $f(p,q,t)$ is a real function of the collection of coordinates and momenta. A closer analogy, shown by Wigner [12], exists between the statistical operator in the mixed coordinate-momentum representation $\rho(x,p,t)$ and the classical distribution function (see § 14).

In the case of statistical equilibrium ρ and H do not depend explicitly on time, and the quantum Liouville equation has the form

$$[H,\rho] = 0, \tag{8.8}$$

i.e., in this case the statistical operator ρ commutes with the Hamiltonian and, consequently, is an integral of motion. In classical statistical mechanics the equilibrium distribution function, as we verified in § 2, is also an integral of motion, which is evident from (2.13).

The facts that the operators ρ and H commute and are both hermitian show that they have a common system of eigenfunctions. Therefore the statistical operator in the case of statistical equilibrium can be represented in the form

$$\rho(x, x') = \sum_k w_k \Psi_k(x) \Psi_k^*(x'), \tag{8.9}$$

where $\Psi_k(x)$ are the eigenfunctions of the Hamiltonian

$$H\Psi_k = E_k\Psi_k. \tag{8.10}$$

In quantum mechanics not all eigenfunctions are admissible wave functions of the system; only those wave functions which have the necessary symmetry properties are permissible.

For a system of particles with spin equal to zero or an integer multiple of $\hbar$ only wave functions which are symmetric with respect to simultaneous permutation of the coordinates and spins of the particles are admitted. In this case it is said that the particles obey Bose statistics.

For a system of particles with half-integer (in units of $\hbar$) spin only wave functions which are anti-symmetric with respect to permutation of coordinates and spins are admissible. In this case it is said that the particles obey Fermi statistics.

In the expression (8.9) for the statistical operator it is assumed that the summation is carried out not over all wave functions, but only over those functions which are admissible in the quantum states of the system.

The Liouville equation (8.6) allows one to find the statistical operator at any moment of time, if it is known at the initial time.

Let the statistical operator at t=0, $\rho(0)$, be given. Then at time t the statistical operator has the form

$$\rho(t) = e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}, \tag{8.11}$$

if the Hamiltonian H does not depend on t. Indeed, differentiating (8.11) with respect to time, we verify that $\rho(t)$ satisfies the Liouville equation (8.6). In addition, $\rho(t)$ satisfies the initial condition

$$\rho(t)|_{t=0} = \rho(0). \tag{8.11a}$$

The expression (8.11) is a formal solution of the Liouville equation (8.6). It is analogous to the expression (2.17) in classical statistical mechanics. In what follows we shall often make use of a similar method of formal solution of the Liouville equation.

If the Hamiltonian H_t is explicitly time dependent, then the Liouville equation can be formally integrated using the evolution operator U(t,0) - a unitary operator satisfying the equation

$$i\hbar \frac{\partial U(t,0)}{\partial t} = H_t U(t,0), \text{ где } U^{+}(t_1,t_2) = U^{-1}(t_1,t_2), \qquad (8.12)$$

and the initial condition

$$U(0,0) = 1. \qquad (8.12a)$$

The statistical operator at time t has the form

$$\rho(t) = U(t,0)\rho(0)U^{-1}(t,0). \qquad (8.13)$$

In this connection, $\rho(t)$ satisfies the Liouville equation

$$\frac{\partial\rho(t)}{\partial t} = \frac{1}{i\hbar}[H_t, \rho(t)] \qquad (8.14)$$

and the initial condition (8.11a).

8.2. Schroedinger and Heisenberg Representations for Statistical Operators.

Up to now we have made use of a representation in which the statistical operator ρ is time dependent, but the dynamical variables have no time dependence (through the coordinates and momenta); they can depend on time only through an external field. This corresponds to the Schroedinger representation in quantum mechanics.

Sometimes it is more convenient to use the Heisenberg representation, in which ρ is time independent, but the dynamical variables depend on time through the coordinates and momenta, in addition to the possible parametric dependence on time through an external field.

The average value of any dynamical variable is equal to

$$\langle A\rangle = \mathrm{Sp}(\rho(t)A). \tag{8.15}$$

Substituting ρ(t) from (8.11) (or (8.13)) into this expression and using the permutability of operators under the spur (trace) sign, we obtain

$$\langle A\rangle = \mathrm{Sp}\,(\rho(0)\,A(t)), \tag{8.16}$$

where

$$A(t) = e^{iHt/\hbar} A\, e^{-iHt/\hbar} \tag{8.17}$$

or

$$A(t) = U^{-1}(t, 0)\, AU(t, 0) \tag{8.17a}$$

is the operator A in the Heisenberg representation, and U(t,0) is the evolution operator (8.12). Formula (8.15) corresponds to the Schroedinger representation, while (8.17) and (8.17a) correspond to the Heisenberg representation for the operator A.

Let us obtain an expression for the time derivative of a dynamical variable in the Heisenberg representation in the general case.

Differentiating the identity (8.15) with respect to time, we find

$$\frac{d}{dt}\langle A\rangle = \mathrm{Sp}\left(\frac{\partial\rho}{\partial t} A + \rho\,\frac{\partial A}{\partial t}\right).$$

Substituting here ∂ρ/∂t from the Liouville equation (8.6), we obtain

$$\frac{d}{dt}\langle A\rangle = \mathrm{Sp}\left\{\left(\frac{\partial A}{\partial t} + \frac{1}{i\hbar}[A, H]\right)\rho\right\}$$

or

$$\frac{d}{dt}\langle A\rangle = \mathrm{Sp}\left(\frac{dA}{dt}\rho\right) = \left\langle\frac{dA}{dt}\right\rangle, \tag{8.18}$$

where

$$\frac{dA}{dt} = \frac{\partial A}{\partial t} + \frac{1}{i\hbar}[A, H] \tag{8.19}$$

is the derivative of the dynamical variable A with respect to time. The same relationship can be obtained by differentiating (8.17) or (8.17a) with respect to time. Formulas (8.18) and (8.19) are analogous to the formulas (2.19a) and (2.18) in classical statistical mechanics.

If the dynamical variable A is not explicitly time dependent, then its derivative is equal to

$$\frac{dA}{dt} = \frac{1}{i\hbar}[A, H]. \tag{8.20}$$

In what follows we shall make wide use of the equation of motion for dynamical variables.

8.3. Entropy Operator.

In classical statistical mechanics one can introduce the entropy operator

$$\eta = - \ln \rho, \tag{8.21}$$

which is analogous to the phase index (2.22) of classical statistical mechanics.

As we showed earlier, the statistical operator ρ is Hermitian and positive definite. Thus, its logarithm is Hermitian, and the entropy operator η is positive definite. In fact, if $w_1, w_2, \ldots$ are the eigenvalues of the operator ρ, for which $0 \leqslant w_k \leqslant 1$, then $-\ln w_1, -\ln w_2$ are the eigenvalues of η, because the eigenvalues of a function of an operator are equal to the same functions of the eigenvalues.

From the inequality $w_k \leqslant 1$ it follows that $-\ln w_k \geqslant 0$, i.e., that the eigenvalues of η are positive, but not necessarily bounded, although is always bounded.

The entropy operator η has the property of additivity, i.e., if the operator ρ is the direct product[1] of the operators ρ_1 and ρ_2

$$\rho = \rho_1 \times \rho_2, \tag{8.22}$$

which denotes the direct product of the corresponding matrices, then

$$\eta = \eta_1 + \eta_2, \tag{8.23}$$

---

[1] A square matrix C is the direct product of A and B, if $C = \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix}$.

where $\eta=-\ln\rho, \eta_1=-\ln\rho_1, \eta_2=-\ln\rho_2$.

The entropy operator η satisfies the Liouville equation, just as does ρ,

$$i\hbar\frac{\partial\eta}{\partial t}=[H,\eta], \tag{8.24}$$

which can easily be shown directly. For example, if ρ satisfies the equation (8.6), then ρ^2 satisfies the same equation

$$i\hbar\frac{\partial}{\partial t}\rho\rho=[H,\rho\rho], \tag{8.25}$$

because the Poisson brackets have the property

$$[H,\rho\rho]=[H,\rho]\rho+\rho[H,\rho].$$

The equation (8.24) sometimes turns out to be very convenient, because H and η are additive Hermitian operators.

8.4. Entropy.

The average value of the negative of the logarithm of the statistical operator, i.e., the average value of the entropy operator, is called the Gibbs entropy,

$$S=\langle\eta\rangle=-\langle\ln\rho\rangle=-\mathrm{Sp}(\rho\ln\rho). \tag{8.26}$$

This definition corresponds to the Gibbs definition of the entropy (2.24) in classical statistical mechanics and is its quantum generalization.

From the properties of the statistical operator which were considered in section 7.2, it follows that the entropy (8.26) is a positive definite quantity. In fact, in the diagonal representation it has the form

$$S=-\sum_n\rho_{nn}\ln\rho_{nn}\geq 0, \tag{8.27}$$

because in accordance with (7.19) the eigenvalues of the statistical operator cannot be negative, $\rho_{nn}\geq 0$.

Only in the particular case in which the statistical operator describes a pure state does S=0.

The entropy (8.26) has the additivity property. If ρ describes statistically independent ensembles and is the direct product of ρ_1 and ρ_2 (8.22), then

$$S = S_1 + S_2, \qquad (8.28)$$

where

$$S = -\langle \ln \rho \rangle, \quad S_1 = -\langle \ln \rho_1 \rangle, \quad S_2 = -\langle \ln \rho_2 \rangle.$$

The entropy defined using formula (8.26) is time independent for an isolated system.

In fact, the statistical operator at time t is connected with its value at t=0 by the unitary transformation (8.13):

$$\rho(t) = U(t, 0)\rho(0)U^{-1}(t, 0). \qquad (8.29)$$

For example, $U(t,0)=e^{-iHt/\hbar}$ if the Hamiltonian is time independent.

Then we have

$$S(t) = -\operatorname{Sp}\{U(t, 0)\rho(0)U^{-1}(t, 0)\ln(U(t, 0)\rho(0)U^{-1}(t, 0))\} =$$
$$= -\operatorname{Sp}\{U(t, 0)\rho(0)U^{-1}(t, 0)U(t, 0)\ln(\rho(0))U^{-1}(t, 0)\},$$

because

$$\ln(U(t, 0)\rho(0)U^{-1}(t, 0)) = U(t, 0)\ln(\rho(0))U^{-1}(t, 0),$$

which holds in general for any function of an operator and can be demonstrated by expansion in a Taylor series. Using the fact that

$$U(t, 0)U^{-1}(t, 0) = 1$$

and that operators under the spur sign can be cyclically permuted, we obtain

$$S(t) = -\operatorname{Sp}\{\rho(0)\ln\rho(0)\} = S(0). \qquad (8.30)$$

On the other hand, it is well known from thermodynamics that the entropy of an isolated system can increase. Therefore for nonequilibrium processes it is sometimes suggested [14] that the thermodynamic entropy should be associated not with (8.26), but rather with the entropy calculated using a "coarsened" statistical operator $\tilde{\rho}$, averaged over a small range of the quantum mechanical states $\Delta\Gamma$ - a coarse-structure statistical operator

$$\tilde{\rho} = \frac{1}{\Delta\Gamma}\,\mathrm{Sp}_{\Delta\Gamma}\,\rho. \tag{8.31}$$

The operation of coarsening the statistical operator (8.31) is analogous to the operation of coarsening the distribution function in classical statistical mechanics (2.30). For the coarse-structure statistical operator (8.31) the entropy

$$S_t = -\,\mathrm{Sp}(\tilde{\rho}(t)\ln\tilde{\rho}(t)) \tag{8.32}$$

can increase.

Suppose that at t=0 the state is described by the coarse-structure statistical operator

$$\rho(0) = \tilde{\rho}(0).$$

The corresponding entropy is equal to

$$S_0 = -\,\mathrm{Sp}(\tilde{\rho}(0)\ln\rho(0)). \tag{8.33}$$

At time t the entropy calculated using the coarsened statistical operator is equal to (8.32), which gives

$$\begin{aligned} S_t - S_0 &= -\,\mathrm{Sp}(\tilde{\rho}(t)\ln\tilde{\rho}(t)) + \mathrm{Sp}(\rho(0)\ln\tilde{\rho}(0)) = \\ &= -\,\mathrm{Sp}(\rho(t)\ln\tilde{\rho}(t)) + \mathrm{Sp}(\rho(t)\ln\rho(t)) \end{aligned} \tag{8.34}$$

(cf. (2.31a)), because in accordance with the Liouville theorem

$$\mathrm{Sp}(\rho(t)\ln\rho(t)) = \mathrm{Sp}(\rho(0)\ln\rho(0)).$$

For any two statistical operators there exists the inequality

$$\mathrm{Sp}(\rho\ln\rho) \geq \mathrm{Sp}(\rho\ln\rho_1), \tag{8.35}$$

and equality is achieved only in the case $\rho=\rho_1$. The inequality (8.35) follows from the obvious inequality

$$\ln x \geqslant 1-\frac{1}{x}, \qquad x>0, \tag{8.36}$$

where equality holds only for x=1.

Substituting in (8.36) $x=\rho\rho_1^{-1}$ (ρ and ρ_1 are positive definite operators) and averaging the equality over ρ, we obtain

$$\mathrm{Sp}\{\rho\ln(\rho\rho_1^{-1})\} \geq \mathrm{Sp}\,\rho(1-\rho_1\rho^{-1}) = 0, \tag{8.37}$$

because both operators are normalized (the operators under the spur sign have been permuted). The inequality (8.37) coincides with (8.35), which was to be demonstrated.

Putting $\rho = \rho(t), \rho_1=\tilde{\rho}(t)$ it follows from (8.34) and (8.35) that

$$S_t \geqslant S_0.$$

Let us assume that $\rho(t)$ does not describe a state of statistical equilibrium; then, in general,

$$\rho(t) \neq \tilde{\rho}(t), \tag{8.38}$$

and

$$S_t > S_0, \tag{8.39}$$

i.e., the entropy S_t can increase.

In quantum statistical mechanics, as in classical, besides smoothing of the statistical operator over the states, a smoothing in time is also possible

$$\widetilde{\rho(t)} = \frac{1}{T}\int_0^T \rho(t+t_1)\,dt_1, \tag{8.40}$$

or

$$\widetilde{\rho(t)} = \varepsilon\int_{-\infty}^0 e^{\varepsilon t_1}\,\rho(t+t_1)\,dt_1, \tag{8.41}$$

analogous to the corresponding averaging of the distribution function (2.35) and (2.36) in classical statistical mechanics.

Most convenient is the smoothing in the form (8.41), for which $\varepsilon \to 0$ after the limiting transition $V \to \infty$ ($V/N = \text{const}$), because it corresponds (as was noted earlier at the end of § 2) to the application of the causality condition for choosing the retarded solutions of the Schroedinger equat[illegible]e formal theory of scattering (see appendices I and III).

The remarks made earlier about the coarsening of the statistical operator do not resolve the question of the definition of the entropy of a nonequilibrium state. The concept of the entropy of a nonequilibrium state will be considered in Chapter IV.

§ 9. Gibbs Statistical Ensembles in the Quantum Case

The basic ideas of the theory of Gibbs statistical ensembles, discussed in § 3, carry over directly into quantum statistical mechanics [1-3].

In states of statistical equilibrium the statistical operator can depend only on the additive integrals of motion of the quantum Liouville equation (8.6). Three such integrals of motion are known: the total energy, represented by the Hamiltonian operator H (time independent), the total momentum **P** and the total angular momentum **M**. All of these quantities are dynamical variables in the sense of quantum mechanics, i.e., Hermitian operators acting in the space of the wave functions.

Consequently, in accordance with the basic ideas of Gibbs ensembles, ρ is a function of $H, \mathbf{P}, \mathbf{M}$:

$$\rho = \rho(H, \mathbf{P}, \mathbf{M}). \tag{9.1}$$

If the number of particles N in the ensemble is not specified, then it must be considered as a fourth integral of motion:

$$[N, H] = 0,$$

where N is an operator taking on positive integer values 0, 1, 2,.... Then

$$\rho = \rho(H,N,P,M). \tag{9.2}$$

If we further consider systems in a motionless container, then P=M=0, and these integrals of motion need not be considered. Thus, for systems with a specified particle number

$$\rho = \rho(H), \tag{9.3}$$

and for systems with an unspecified particle number

$$\rho = \rho(H,N). \tag{9.4}$$

In addition, the statistical operator can depend parametrically on the quantities which are specified for systems in the ensemble, for example, on the volume V and particle number N in the case (9.3), or on V in the case (9.4).

9.1. The Gibbs Microcanonical Distribution.

The microcanonical distribution can be introduced in exactly the same way in quantum statistical mechanics as in classical (see section 3.1). For this let us consider an ensemble of closed, energetically isolated systems with constant volume V and total particle number N, having identical energy E to within the accuracy $\Delta E \ll E$. Let us assume that for such systems all quantum mechanical states in the layer $E, E+\Delta E$ are equally probable. Such a distribution, for which

$$w(E_k) = \begin{cases} \Omega^{-1}(E,N,V) & \text{for } E \le E_k \le E+\Delta E, \\ 0 & \text{outside this layer} \end{cases} \tag{9.5}$$

is called the microcanonical distribution, and the corresponding ensemble is called the microcanonical ensemble of quantum statistics.

Microcanonical distribution (9.5) is the quantum generalization of the distribution (3.3) of classical statistical mechanics. The difference is that the statistical weight $\Omega(E,N,V)$ is now not simply equal to the phase volume (3.3a), but is the number of quantum mechanical states in the layer $E, E+\Delta E$ for a system with particle number N and volume V. This follows from the fact that the probability $w(E_k)$ must be normalized to unity:

$$\sum_k w(E_k) = 1. \tag{9.6}$$

We assume, as in Chapter I, that the quantity ΔE is small but finite, because in quantum mechanics an exact specification of the energy would require an infinite observation time, in accordance with the uncertainty principle between time and energy. For ΔE one might choose, for example, the average value of the energy fluctuation of the system.

Theoretically one can consider as an idealized limiting case an ensemble of completely isolated systems. Such a model is convenient in the respect that all arguments about the properties of isolated systems, introduced in section 8.1 and in the beginning of this paragraph, are exactly applicable. For completely isolated systems $\Omega(E,N,V)$ is equal to the degree of degeneracy of the energy level E of a system with particle number N and volume V. If N is large, the number $\Omega(E,N,V)$ is very large.

The statistical operator (8.9) corresponds to the microcanonical distribution (9.5). It has the matrix form

$$\rho(x, x') = \Omega^{-1}(E, N, V) \sum_{1 \leqslant k \leqslant \Omega} \Psi_k(x)\, \Psi_k^*(x'), \tag{9.7}$$

where x is the set of coordinates (and spins) of the N particles, and $\Psi_1, \ldots, \Psi_\Omega$ are the eigenfunctions of the Hamiltonian operator H, corresponding to the energy E. In operator form we have:

$$\rho = \Omega^{-1}(E,N,V)\Delta(H-E), \tag{9.7a}$$

where H is the Hamiltonian of the system, and $\Delta(x)$ is a function which is nonzero only in a thin energy layer $0 \leqslant x \leqslant \Delta E$, where it is equal to one; outside of this layer it is equal to zero.

From the quantum Liouville theorem (8.6) it follows that the microcanonical distribution is stationary. It must be stressed, however, that the assumption about the equal probability of the quantum mechanical states with the same energy for a closed, isolated system is the simplest assumption, but it is in no way a self-evident assumption. The problem of justifying this hypothesis is called the quantum mechanical ergodic problem. We shall not discuss these questions here, referring the reader to the literature [13,14].

The extremal property of the microcanonical distribution can serve as an argument in its favor. The microcanonical distribution corresponds to the maximum entropy among all distributions in the same energy layer (see section

10.1). The extremal property of the microcanonical distribution in classical statistical mechanics has already been discussed in § 4.

Let us calculate the entropy for the microcanonical distribution. In a diagonal representation

$$S = \langle \eta \rangle = -\mathrm{Sp}(\rho \ln \rho) = -\sum w_k \ln w_k, \tag{9.8}$$

or, since all w_k in the layer $E, E+\Delta E$ are identical and equal to $\Omega^{-1}(E,N,V)$, we obtain

$$S = \ln\Omega(E,N,V), \tag{9.9}$$

i.e., the entropy for the microcanonical ensemble is equal to the logarithm of the statistical weight. Formula (9.9) corresponds to the Planck definition of the entropy, which is valid in general only for the equilibrium case and for the microcanonical ensemble.

The microcanonical distribution is inconvenient for practical applications, because in order to calculate the statistical weight, one must investigate the distribution of eigenvalues of the Hamiltonian H, which is a very complex problem. Rather than to consider energetically isolated systems, it is more convenient to consider systems in thermal contact with their surroundings.

9.2. The Gibbs Canonical Distribution.

Let us consider quantum mechanical systems with constant particle number and constant volume in contact with a thermostat. The thermostat is assumed to be sufficiently large such that upon interchange of energy with the systems of the ensemble the state of the thermostat is practically unchanged. The statistical ensemble of quantum mechanical systems with fixed particle number N and constant volume V in contact with a thermostat is called the Gibbs canonical ensemble in quantum statistics. Such an ensemble is described by the Gibbs canonical distribution

$$w(E_k) = Q^{-1}(\theta,V,N)\exp(-E_k/\theta), \tag{9.10}$$

where θ is the modulus of the canonical distribution, which plays the role of the temperature, and $Q(\theta,V,N)$ is the statistical sum, defined from the normalization condition (7.12a):

$$Q(\theta, V, N) = \sum_k \exp(-E_k/\theta). \tag{9.11}$$

In the statistical sum (9.11) the summation is carried out over all quantum mechanical states allowed by the symmetry principle; states belonging to a degenerate level are considered distinct.

The logarithm of the statistical integral (9.11) defines the free energy

$$F(\theta,V,N) = -\theta \ln Q(\theta,V,N) \tag{9.12}$$

as a function of the parameters θ,V,N.

The Gibbs canonical distribution (9.10) is significantly more convenient than the microcanonical distribution, because the sum (9.11) over the eigenvalues can sometimes be calculated without knowing the eigenvalues themselves. In calculating the statistical sum it is necessary to consider only the auxiliary condition of constant particle number, rather than particle number and energy, as in calculating the statistical weight in the microcanonical distribution; therefore it is much simpler to work with the canonical distribution rather than the microcanonical.

The statistical operator

$$\rho(x, x') = Q^{-1}(\theta, V, N) \sum_k e^{-E_k/\theta} \Psi_k(x) \Psi_k^*(x'), \tag{9.13}$$

corresponds to the Gibbs canonical distribution (9.10), where x is the set of coordinates (and possibly spins) of the particles $x_1,\dots,x_N$; $\Psi_k(x)$ are the eigenfunctions of the Hamiltonian H.

Let us introduce the operator $e^{-H/\theta}$ and stipulate that it acts not in the entire space of the wave functions, but only in the space of the wave functions allowed by the symmetry principle. Then (9.13) and (9.11) can be written in a more compact operator form:

$$\rho = Q^{-1}(\theta, V, N) e^{-H/\theta} = e^{(F-H)/\theta}, \tag{9.14}$$

$$Q(\theta, V, N) = \operatorname{Sp} e^{-H/\theta} = \sum_k \int \Psi_k^*(x) e^{-H/\theta} \Psi_k(x)\, dx. \tag{9.15}$$

The expression (9.15) for the statistical sum is very convenient, because by the invariance of the spur (trace) operation with respect to the representation of the matrix it is independent of the choice of functions $\Psi_k(x)$, which need not even be eigenfunctions of H.

Up to now we have assumed that the system does not move as a whole and has a single additive integral, the energy H. In the case in which besides the total energy H there exist integrals of motion $\mathcal{P}_1, \ldots, \mathcal{P}_s$, the statistical operator has the form

$$\rho = Q^{-1}(\theta, \mathcal{F}_1, \ldots, \mathcal{F}_s) \exp\left\{ -\frac{H}{\theta} - \sum_{1 \leq k \leq s} \mathcal{F}_k \mathcal{P}_k \right\}, \tag{9.16}$$

where $\mathcal{F}_1, \ldots, \mathcal{F}_s$ are new thermodynamic parameters defined from the conditions

$$\langle \mathcal{P}_k \rangle = \mathrm{Sp}\,(\rho \mathcal{P}_k). \tag{9.16a}$$

9.3. Gibbs Theorem on the Canonical Distribution.

In quantum statistical mechanics, as in classical, the postulates about the microcanonical distribution (9.5) and about the canonical distribution (9.10) are not independent. Here also there is a Gibbs theorem about the canonical distribution, according to which a small part of a microcanonical ensemble of quantum systems is distributed canonically. Proof of this theorem is very similar to the corresponding proof of the Gibbs theorem in the classical case, which was presented in section 3.3.

The combination of the given system and the thermostat will be regarded as a single, closed, energetically isolated system with the Hamiltonian

$$H = H_1 + H_2, \tag{9.17}$$

where H_1 is the Hamiltonian of the original system, and H_2 is the Hamiltonian of the thermostat, which is assumed to be significantly larger than the original system, i.e., having a much greater number of degrees of freedom. The interaction between the system and the thermostat is assumed to be very small but non-zero, because it must insure that the energy of the total system remains constant. In fact, thermal contact with the thermostat is effected through the walls of the container and is therefore a small surface effect.

The wave function of the Hamiltonian of the total system (9.17) splits into a product of wave functions of the thermostat (system (2)) and the system under consideration (1):

$$\Psi_{ik}(x,y) = \Psi_k(x)\Psi_i(y), \tag{9.18}$$

where $\Psi_k(x)$ are the eigenfunctions of H_1, and $\Psi_i(y)$ are the eigenfunctions of H_2; x and y are the sets of coordinates of the system being considered and the thermostat, respectively.

The energy levels of the total system are equal to the sum of the levels of system (1) and (2):

$$E_{ik} = E_i + E_k, \tag{9.18a}$$

where E_k are the energy levels of the system (1), and E_i are the energy levels of the thermostat.

In accordance with (7.15) the statistical operator of the total system has the form

$$\rho(xy, x'y') = \sum_{i,k} w_{ik} \Psi_{ik}(x, y) \Psi^*_{ik}(x', y'), \tag{9.19}$$

where w_{ik} is defined by the expression (9.5).

By calculating the spur of the total statistical operator over the coordinates of the thermostat we obtain the statistical operator of the system(1):

$$\rho(x, x') = \mathrm{Sp}_{(2)}\rho(xy, x'y') = \sum_{i,k} w_{ik} \int \Psi_{ik}(x, y) \Psi^*_{ik}(x', y)\, dy,$$

from which, using (9.18) and assuming that the eigenfunctions are normalized, we obtain

$$\rho(x, x') = \sum_k w_k \Psi_k(x) \Psi^*_k(x'), \tag{9.20}$$

where

$$w_k = \sum_i w_{ik}. \tag{9.20a}$$

Thus, to find the probability distribution over the states in the system (1), it is necessary to sum the probability distribution in the total system over all states of the thermostat:

$$w(E_k) = \sum_{\substack{i \\ (E_i+E_k=E)}} w(E_i+E_k) = \frac{1}{\Omega(E)} \sum_{\substack{i \\ (E_i=E-E_k)}} 1. \tag{9.21}$$

(to shorten the notation we shall omit the arguments N and V from $\Omega(E)$). This expression for the probability distribution of states in the original system can be written in the form

$$w(E_k) = \frac{\Omega_2(E-E_k)}{\Omega(E)}, \tag{9.21a}$$

where $\Omega_2(E-E_k)$ is the number of quantum mechanical states of the thermostat corresponding to the level $E-E_k$, and $\Omega(E)$ is the number of states of the total system corresponding to the level E.

In order to calculate $w(E_k)$ it is necessary to obtain asymptotic estimate for the ratio of the statistical weights of the thermostat to the weights of the entire system, assuming that the thermostat is large, just as this was done in the case of classical statistics for the ratio (3.13).

We shall present first a simple, but non-rigorous, derivation of the canonical distribution.

Introducing the entropy of the thermostat $S_2(E)$ and the entropy of the entire system $S(E)$ using the relation (9.9), we write (9.21a) in the form

$$w(E_k) = \exp\{S_2(E-E_k)-S(E)\}. \tag{9.22}$$

Taking into account that the system (1) is small compared to the thermostat, i.e., $E_k \ll E$, we expand $S_2(E-E_k)$ in a series in E_k and keep only two terms:

$$S_2(E-E_k) \simeq S_2(E) - \frac{\partial S_2}{\partial E} E_k.$$

Using this expression we rewrite (9.22) in the form

$$w(E_k) = Q^{-1} \exp\left(-\frac{E_k}{\theta}\right), \tag{9.23}$$

where Q is the statistical sum (9.11) and

[illegible] (9.23a)

is the inverse temperature. Thus, a small part of the microcanonical ensemble is distributed canonically.

We shall present now a more rigorous proof of the Gibbs theorem, analogous to the proof of Yu. A. Krutkov given in section 3.3.

Let us calculate the number of eigenfunctions of the total system with energy E. Each eigenfunction of the system (1) with energy E_1 can be combined with any of the eigenfunctions of the system (2) (thermostat) with energy $E-E_1$. $\Omega_1(E_1)$ eigenfunctions of the system (1) correspond to the energy level E_1. $\Omega_2(E-E_1)$ eigenfunctions of the system (2) correspond to the energy level $E-E_1$. Thus, the total number $\Omega(E)$ of eigenfunctions of the system, corresponding to the energy E, is equal to

$$\Omega(E) = \sum_{E_1 \le E} \Omega_1(E_1)\,\Omega_2(E-E_1). \tag{9.24}$$

The relationship (9.24) can be considered as a defining equation for Ω_2, if Ω and Ω_1 are considered to be known. This equation is the quantum analog of the integral equation (3.19).

Multiplying (9.24) by $e^{-\lambda E}$ and summing over all E, we obtain

$$\sum_{0\le E<\infty} e^{-\lambda E}\,\Omega(E) = \sum_{0\le E<\infty} e^{-\lambda E} \sum_{0\le E_2\le E} \Omega_2(E_2)\,\Omega_1(E-E_2).$$

Changing the order of the summations on the right hand side of the equation, we have

$$\sum_{0\le E<\infty} e^{-\lambda E}\,\Omega(E) = \sum_{0\le E_2<\infty}\ \sum_{E_2\le E<\infty} e^{-\lambda E}\,\Omega_2(E_2)\,\Omega_1(E-E_2).$$

Making a change of variables $E_1=E-E_2$, we obtain

$$Q(\lambda) = Q_1(\lambda)\,Q_2(\lambda), \tag{9.25}$$

where

$$Q(\lambda) = \sum_{0\le E<\infty} e^{-\lambda E}\,\Omega(E), \qquad Q_\alpha(\lambda) = \sum_{0\le E<\infty} e^{-\lambda E}\,\Omega_\alpha(E) \qquad (\alpha = 1,\ 2). \tag{9.26}$$

To estimate the statistical weights it is necessary to invert equation (9.26).

Let us show that for the discrete spectrum the number of eigenvalues with energy in the interval from 0 to E is equal to

$$\Gamma(E) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} e^{\lambda E} Q(\lambda)\frac{d\lambda}{\lambda}, \qquad (9.27)$$

where α is a positive constant

$$Q(\lambda) = \sum_{0\leqslant E<\infty} e^{-\lambda E}\Omega(E) = \sum_{k} e^{-\lambda E_k}. \qquad (9.28)$$

Formula (9.27) expresses the theorem on the inversion of a statistical sum.

Substituting (9.28) into (9.27), we obtain

$$\Gamma(E) = \sum_{k}\mathcal{F}(E - E_k), \qquad (9.29)$$

where $\mathcal{F}(x)$ is the discontinuous function:

$$\mathcal{F}(x) = \frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty}\frac{e^{\lambda x}}{\lambda}\,d\lambda = \begin{cases} 0 & \text{for } x<0, \\ 1/2 & \text{for } x=0, \\ 1 & \text{for } x>0. \end{cases} \qquad (9.29a)$$

Thus, Γ(E) gives with very good accuracy the total number of eigenvalues less than E, because the lowest eigenvalue can always be chosen to begin the calculation of the energy. In applying (9.29) to the calculation of the eigenvalues, the error introduced by the value of $\mathcal{F}(x)$ near x=0 can clearly be neglected, because the number of eigenvalues is very large.

The number of eigenvalues in the interval of energy (E,E+ΔE) is evidently equal to

$$\Omega(E) = \Gamma(E+\Delta E) - \Gamma(E), \qquad (9.30)$$

and, thus, using the expression (9.27) for $\Gamma(E)$, we obtain

$$\Omega(E) = \frac{1}{2\pi i} \int\limits_{a-i\infty}^{a+i\infty} \{e^{\lambda(E+\Delta E)} - e^{\lambda E}\} Q(\lambda) \frac{d\lambda}{\lambda}. \tag{9.31}$$

Formula (9.31) gives the required inversion of the series (9.28).

Using (9.31) we obtain an inversion of the series (9.26):

$$\begin{aligned} \Omega(E) &= \frac{1}{2\pi i} \int\limits_{a-i\infty}^{a+i\infty} e^{\lambda E} \frac{e^{\lambda \Delta E} - 1}{\lambda} Q(\lambda)\, d\lambda, \\ \Omega_2(E) &= \frac{1}{2\pi i} \int\limits_{a-i\infty}^{a+i\infty} e^{\lambda E} \frac{e^{\lambda \Delta E} - 1}{\lambda} \frac{Q(\lambda)}{Q_1(\lambda)}\, d\lambda. \end{aligned} \tag{9.32}$$

In accordance with the basic ideas of the Gibbs ensembles we assume now that the system (2) (thermostat) consists of n-1 identical, weakly interacting parts, each of which coincides with the system (1). The total system consists of n such systems where n is assumed to be very large, and in the limit $n \to \infty$. Let us recall that the system (1) itself consists of a very large number of particles.

From (9.25) it follows that $Q(\lambda)$ splits into a product of n identical factors equal to $Q_1(\lambda)$:

$$Q(\lambda) = [Q_1(\lambda)]^n, \tag{9.33}$$

and analogously for the thermostat

$$Q_2(\lambda) = [Q_1(\lambda)]^{n-1}. \tag{9.33a}$$

Thus, the expression (9.32) for the statistical weights takes on the form

$$\begin{aligned} \Omega(E) &= \frac{1}{2\pi i} \int\limits_{a-i\infty}^{a+i\infty} e^{\lambda E} \frac{e^{\lambda \Delta E} - 1}{\lambda} [Q_1(\lambda)]^n\, d\lambda, \\ \Omega_2(E) &= \frac{1}{2\pi i} \int\limits_{a-i\infty}^{a+i\infty} e^{\lambda E} \frac{e^{\lambda \Delta E} - 1}{\lambda} [Q_1(\lambda)]^{n-1}\, d\lambda. \end{aligned} \tag{9.34}$$

We shall obtain an asymptotic estimate of these expressions for the case n→∞ by the saddle-point method. It is convenient to write the first integral in (9.34) in the form

$$\Omega(E)=\frac{1}{2\pi i}\int_{a-i\infty}^{a+i\infty} e^{n\chi(\lambda)}\frac{e^{\lambda\,\Delta E}-1}{\lambda}\,d\lambda, \qquad (9.35)$$

where

$$\chi(\lambda)=\lambda\frac{E}{n}+\ln Q_1(\lambda). \qquad (9.35a)$$

Repeating the same arguments as in the classical case (see (3.25)), we find the asymptotic estimates of the statistical weights:

$$\begin{aligned}\Omega(E)&=\frac{e^{\lambda_1\Delta E}-1}{\lambda_1\sqrt{2\pi n\chi''(\lambda_1)}}\,e^{\lambda_1 E}[Q_1(\lambda_1)]^n,\\ \Omega_{-}(E)&=\frac{e^{\lambda_1\Delta E}-1}{\lambda_1\sqrt{2\pi(n-1)\chi''(\lambda_1)}}\,e^{\lambda_1 E}[Q_1(\lambda_1)]^{n-1},\end{aligned} \qquad (9.36)$$

where the parameter λ_1 is defined from the condition of the existence of the saddle-point (3.26).

Substituting the resulting estimates (9.36) into (9.21a), we verify that the expression for $w(E_k)$ is independent of the quantity ΔE and has the form

$$w(E_k)=Q^{-1}(\theta,V,N)\,e^{-E_k/\theta}, \qquad (9.37)$$

where

$$\theta=\frac{1}{\lambda_1} \qquad (9.37a)$$

is the temperature, and

$$Q(\theta,V,N)=\sum_E e^{-E/\theta}\,\Omega_1(E)=\sum_k e^{-E_k/\theta} \qquad (9.37b)$$

is the statistical sum.

Thus, if the total system has a microcanonical distribution, then a small subsystem is distributed according to the Gibbs canonical distribution.

9.4. The Gibbs Grand Canonical Distribution

Let us consider quantum mechanical systems with constant volume in contact with a thermostat which serves also as a reservoir of particles. The thermostat is assumed to be large enough such that upon interchange of energy and particles with systems of the ensemble its state is practically unchanged. A statistical ensemble of quantum mechanical systems with fixed volume V in contact with a thermostat and a reservoir of particles is called the Gibbs grand canonical ensemble in quantum statistics. Such an ensemble is described by the Gibbs grand canonical distribution

$$w_N(E_k) = Q^{-1}(\theta, \mu, V)\exp\left(-\frac{E_k - \mu N}{\theta}\right), \tag{9.38}$$

where θ is the absolute temperature, and $Q(\theta,\mu,V)$ is the statistical sum for the grand ensemble, defined by the normalization condition

$$\sum_{k,N} w_N(E_k) = 1 \tag{9.38a}$$

and equal to

$$Q(\theta, \mu, V) = \sum_{N,k} \exp\left(-\frac{E_k - \mu N}{\theta}\right). \tag{9.39}$$

We assume throughout the discussion that E_k depends on N, i.e., $E_k = E_{k,N}$, but we shall not indicate this explicitly.

In the statistical sum (9.39) the summation is carried out over all admissible quantum mechanical states and over all positive integers $N \geq 0$. We shall denote by the same letter Q the statistical sum for the grand ensemble (9.39) and for the canonical ensemble (9.11), but we shall distinguish them through the variables on which they depend[1].

The logarithm of the statistical sum (9.39) defines the thermodynamic potential $\Omega(\theta,\mu,V)$:

$$\Omega(\theta,\mu,V) = -\theta \ln Q(\theta,\mu,V). \tag{9.40}$$

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[1] The statistical sum of the grand ensemble is sometimes denoted by $\Xi(\theta,\mu,V)$.

The statistical operator

$$\rho(x, x') = \sum_{N, k} \exp\left(\frac{\Omega - E_k + \mu N}{\theta}\right) \Psi_k(x)\, \Psi_k^*(x'), \tag{9.41}$$

corresponds to the Gibbs grand canonical distribution (9.38) where x is the collection of coordinates and spins of the particles, and $\Psi_k(x)$ are the eigenfunctions of the Hamiltonian H and the operator N, i.e., $\Psi_k(x) = \Psi_{k,N}(x)$. Since the operator H commutes with the total number operator N, the functions $\Psi_k(x)$ can simultaneously be eigenfunctions of the operator N.

Let us introduce the operator $e^{-(H-\mu N)/\theta}$, which acts in the space of admissible wave functions of the system; here we consider N as an operator, although we retain the previous notation for it. Then the formulas (9.41) and (9.39) can be written in a more compact operator form:

$$\rho = e^{(\Omega - H + \mu N)/\theta}, \tag{9.42}$$

$$e^{-\Omega/\theta} = \mathrm{Sp}\, e^{-(H - \mu N)/\theta} = \sum_{k, N} \int \Psi_k^*(x)\, e^{-(H - \mu N)/\theta}\, \Psi_k(x)\, dx, \tag{9.42a}$$

where $\Psi_k(x)$ is a complete set of functions satisfying the symmetry or antisymmetry property, but not necessarily satisfying the Schroedinger equation. Formula (9.42a) is convenient because of the invariance of the spur (trace) with respect to the representation of the operators.

Until now we have considered systems consisting only of one type of particle. It is easy to generalize the Gibbs grand canonical distribution to systems consisting of several types of particles. It can be imagined that the system is found in thermal and material contact with s large reservoirs of particles and of energy using semi-permeable membranes, which transmit only one type of molecule. The statistical operator of such an ensemble will have the form

$$\rho = \exp\left\{\frac{\Omega + \sum\limits_{1 \leq \alpha \leq s} \mu_\alpha N_\alpha - H}{\theta}\right\}, \tag{9.43}$$

where μ_α is the chemical potential for particles of type α.

9.5. The Gibbs Theorem on the Grand Canonical Distribution.

For an ensemble of quantum mechanical systems with variable particle number there exists a Gibbs theorem analogous to the corresponding theorem in classical statistics: consider a small part of a microcanonical ensemble of quantum mechanical systems with many degrees of freedom. If in this small part of the ensemble the particle number is not constant, this part of the ensemble has a Gibbs grand canonical distribution (9.42).

Let us prove the theorem.

Let the system with energy E and particle number N consist of two weakly interacting subsystems with energies E_1, E_2 and particle numbers N_1, N_2, respectively; then

$$E = E_1 + E_2, \quad N = N_1 + N_2. \tag{9.44}$$

Let us assume that the second subsystem (thermostat and particle reservoir) is significantly larger than the first

$$E_1 \ll E_2, \quad N_1 \ll N_2.$$

As the total system is closed and isolated, the microcanonical distribution (9.5) can be applied to it. Repeating the arguments which were made in deriving the canonical distribution in section 3.3, we find the probability distribution in the first, small subsystem $w_{N1}(E_1)$ by summing the microcanonical distribution of the total system over all states of the second subsystem. We thus obtain, in complete analogy with formula (9.21a):

$$w_{N_1}(E_1) = \frac{\Omega_2(E - E_1, N - N_1)}{\Omega(E, N)}, \tag{9.45}$$

where Ω_2 is the statistical weight of the second subsystem, and Ω is the statistical weight of the entire system. An elementary proof of the Gibbs theorem follows from this immediately. Expressing the statistical weights in (9.45) through the entropy of the second subsystem and of the total system according to the relationship (9.9) and expanding the argument of the exponent with $E_1 \ll E, N_1 \ll N$, we obtain immediately the Gibbs grand canonical distribution (9.38). A similar derivation for the classical case was carried out in section 3.4.

We shall give below a more rigorous proof of the Gibbs theorem based on inversion of the statistical sums.

The statistical weight of the total system Ω is connected with the statistical weights of the subsystems Ω_1 and Ω_2 by the relationship

$$\Omega(E,\ N)=\sum_{\substack{0\leqslant N_1\leqslant N\\ 0\leqslant E_1\leqslant E}}\Omega_1(E_1,\ N_1)\,\Omega_2(E-E_1,\ N-N_1), \tag{9.46}$$

which is analogous to the relation (9.24), but which takes into account the possibility of the various distributions of particles between the subsystems (1) and (2).

The relation (9.46) can be considered as a defining equation for Ω_2, if Ω and Ω_1 are considered to be known. It has the form of a finite-difference equation with respect to the variables E and N. In the case of classical statistics it goes over into an integral equation in the variable E and a difference equation in the variable N; this equation was studied by Shubin [15].

Let us solve the equation (9.46) for Ω_2. To do this we multiply both sides of the equation by $e^{-\lambda E+\nu N}$ and sum it over all values of E and N from 0 to ∞:

$$\sum_{\substack{0\leqslant N<\infty\\ 0\leqslant E<\infty}} e^{-\lambda E+\nu N}\,\Omega(E,\ N)=$$

$$=\sum_{\substack{0\leqslant N<\infty\\ 0\leqslant E<\infty}}\ \sum_{\substack{0\leqslant N_1\leqslant N\\ 0\leqslant E_1\leqslant E}} e^{-\lambda E+\nu N}\,\Omega_1(E_1,\ N_1)\,\Omega_2(E-E_1,\ N-N_1).$$

Changing the order of summation on the right hand side of this equation and making the changes of variables $E-E_1=E_2, N-N_1=N_2$, we convert this equation to the form

$$Q(\lambda,\ \nu)=Q_1(\lambda,\ \nu)\,Q_2(\lambda,\ \nu), \tag{9.47}$$

where

$$Q(\lambda,\ \nu)=\sum_{\substack{0\leqslant N<\infty\\ 0\leqslant E<\infty}} e^{-\lambda E+\nu N}\,\Omega(E,\ N),$$

$$Q_a(\lambda,\ \nu)=\sum_{\substack{0\leqslant N<\infty\\ 0\leqslant E<\infty}} e^{-\lambda E+\nu N}\,\Omega_a(E,\ N)\qquad (a=1,\ 2). \tag{9.48}$$

Let us note that if ν is purely imaginary, then the right hand sides of (9.48) become Fourier series in the variable ν.

Inverting the relations (9.48) to find the statistical weights, just as

was done for the relations (9.26), we obtain

$$\begin{aligned}
&\Omega_2(E,\ N) = \\
&= \frac{1}{(2\pi i)^2} \int\limits_{c-2\pi i}^{c+2\pi i} d\nu \int\limits_{a-i\infty}^{a+i\infty} \frac{Q(\lambda,\ \nu)}{Q_1(\lambda,\ \nu)}\, e^{\lambda E-\nu N}\left(e^{\lambda\,\Delta E-\nu\,\Delta N}-1\right)\frac{d\lambda}{\lambda}, \\
&\Omega(E,\ N) = \\
&= \frac{1}{(2\pi i)^2} \int\limits_{c-2\pi i}^{c+2\pi i} d\nu \int\limits_{a-i\infty}^{a+i\infty} Q(\lambda,\ \nu)\, e^{\lambda E-\nu N}\left(e^{\lambda\,\Delta E-\nu\,\Delta N}-1\right)\frac{d\lambda}{\lambda},
\end{aligned} \tag{9.49}$$

where $a>0, c>0$. Thus, (9.49) is a solution of the equation (9.46).

Let the second subsystem, i.e., the reservoir of energy and particles, consist of n-1 subsystems identical with the first subsystem. Then the total system consists of n such subsystems. On the basis of (9.47) we have

$$Q_2(\lambda,\nu)=[Q_1(\lambda,\nu)]^{n-1}, \quad Q(\lambda,\nu)=[Q_1(\lambda,\nu)]^{n}. \tag{9.50}$$

Using these relations, we write (9.49) in the form

$$\begin{aligned}
&\Omega_2(E,\ N) = \\
&= \frac{1}{(2\pi i)^2} \int\limits_{c-2\pi i}^{c+2\pi i} d\nu \int\limits_{a-i\infty}^{a+i\infty} [Q_1(\lambda,\ \nu)]^{n-1} e^{\lambda E-\nu N}\left(e^{\lambda\,\Delta E-\nu\,\Delta N}-1\right)\frac{d\lambda}{\lambda}, \\
&\Omega(E,\ N) = \\
&= \frac{1}{(2\pi i)^2} \int\limits_{c-2\pi i}^{c+2\pi i} d\nu \int\limits_{a-i\infty}^{a+i\infty} [Q_1(\lambda,\ \nu)]^{n} e^{\lambda E-\nu N}\left(e^{\lambda\,\Delta E-\nu\,\Delta N}-1\right)\frac{d\lambda}{\lambda}.
\end{aligned} \tag{9.51}$$

Substituting (9.51) into (9.45) we obtain

$$\begin{aligned}
&w_{N_1}(E_1) = \\
&= \frac{\displaystyle\int\limits_{c-2\pi i}^{c+2\pi i} d\nu \int\limits_{a-i\infty}^{a+i\infty} [Q_1(\lambda,\ \nu)]^{n-1} e^{\lambda(E-E_1)-\nu(N-N_1)}\left(e^{\lambda\,\Delta E-\nu\,\Delta N}-1\right)\frac{d\lambda}{\lambda}}{\displaystyle\int\limits_{c-2\pi i}^{c+2\pi i} d\nu \int\limits_{a-i\infty}^{a+i\infty} [Q_1(\lambda,\ \nu)]^{n} e^{\lambda E-\nu N}\left(e^{\lambda\,\Delta E-\nu\,\Delta N}-1\right)\frac{d\lambda}{\lambda}}.
\end{aligned} \tag{9.52}$$

The integrals in formula (9.52) can be estimated by the saddle-point method, using the fact that n is large, just as we did in section 9.3.

The saddle point for the integrand in the denominator of (9.52) corresponds to the minimum of the function $x(\lambda,\nu)$ (see (9.35) and (9.35a)) for real values of the variables λ and ν:

$$\chi(\lambda,\nu)=\lambda\frac{E}{n}-\nu\frac{N}{n}+\ln Q_1(\lambda,\nu).$$

Thus, on the basis of the properties of functions of a complex variable, the function $x(\lambda,\nu)$ has a sharp maximum in the direction parallel to the imaginary axis, because n is large ($E/n=\text{const}$, $N/n=\text{const}$).

The minimum of $x(\lambda,\nu)$ is found from the equations

$$\begin{aligned}\frac{E}{n}+\frac{\partial}{\partial\lambda}\ln Q_1(\lambda,\nu)&=0,\\ -\frac{N}{n}+\frac{\partial}{\partial\nu}\ln Q_1(\lambda,\nu)&=0.\end{aligned}\qquad(9.53)$$

Let the roots of the equations (9.53) be equal to λ_1 and ν_1. The path of integration in (9.52) is taken through these points. Let us note that the asymptotic expression for $w_{N_1}(E_1)$ as $n\to\infty$ can be written immediately if the slowly varying function

$$Q_1^{-1}(\lambda,\nu)e^{-\lambda E_1+\nu N_1}$$

is taken out from under the integral sign in the numerator at the saddle point $\lambda=\lambda_1,\nu=\nu_1$. Then the remaining integral cancels with the integral in the denominator, and we thus obtain

$$w_{N_1}(E_1)=Q_1^{-1}(\lambda_1,\nu_1)e^{-\lambda_1E_1+\nu_1N_1},\qquad(9.54)$$

which is the same as (9.38), if one puts

$$\frac{1}{\theta}=\lambda_1,\quad\frac{\mu}{\theta}=\nu_1.\qquad(9.55)$$

Thus, the probabilities of states in the small subsystem are distributed according to the Gibbs grand canonical ensemble.

9.6. The Gibbs Distribution for an Isobaric-Isothermal Ensemble.

Let us consider quantum mechanical systems with constant particle number, but variable volume in contact with a thermostat. A statistical ensemble of quantum mechanical systems with fixed particle number N and pressure p in contact with a thermostat is called the Gibbs isobaric-isothermal ensemble.

Let the system with energy E and volume V consist of two weakly interacting parts with energies E_1, E_2 and volumes V_1, V_2:

$$E = E_1 + E_2, \quad V = V_1 + V_2, \tag{9.56}$$

in which the first subsystem is significantly smaller than the second (the thermostat),

$$E_1 << E_2, \quad V_1 << V_2.$$

Let us assume that the total system has a microcanonical distribution. Then, repeating the arguments of the preceding section, we find the probability distribution in the first subsystem:

$$w_{V_1}(E_1) = \frac{\Omega_2(E - E_1, V - V_1)}{\Omega(E, V)} = \\ = \exp\{S_2(E - E_1, V - V_1) - S(E, V)\}, \tag{9.57}$$

where $\Omega_2(E,V)$ and $\Omega(E,V)$ are the numbers of quantum mechanical states for E and V for the thermostat and the entire system, respectively; S_2 and S are the entropies of the thermostat and of the entire system.

Taking into account the smallest of the first subsystem, we expand the entropy in (9.57) in powers of E_1 and V_1. Terminating the series with the linear terms, we obtain

$$w_V(E_k) = Q^{-1}(\theta, p, N) \exp\left\{-\frac{E_k + pV}{\theta}\right\} = \exp\left\{\frac{\Phi - pV - E_k}{\theta}\right\}, \tag{9.58}$$

where $$\frac{1}{\theta} = \frac{\partial S_2(E, V)}{\partial E}, \quad \frac{p}{\theta} = \frac{\partial S_2(E, V)}{\partial V}, \tag{9.58a}$$

and θ is the temperature, p is the pressure, and $\phi(\theta,p,N)$ is the Gibbs thermodynamic potential, in complete analogy with the corresponding formulas (3.42)-(3.43) of classical statistical mechanics.

The statistical operator

$$\rho = \exp\left\{\frac{\Phi - pV - H}{\theta}\right\}. \tag{9.59}$$

corresponds to the distribution (9.58).

We have considered four types of Gibbs statistical ensembles: the microcanonical, the canonical, the grand canonical, and the isobaric-isothermal ensembles. Sometimes a generalized Gibbs ensemble is introduced in which the energy, particle number, and volume are variables [16, 17]. But such an ensemble is inconvenient, as we have already noted in Chapter I, because in this ensemble it is necessary to introduce the intensive variables θ,μ,p, which are not independent. In constructing statistical ensembles it is convenient to keep at least one extensive thermodynamic variable.

§ 10. Connection Between the Gibbs Distribution and the Maximum Information Entropy (Quantum Case)

In § 4 we considered the connection between the Gibbs distribution of classical statistical mechanics and the maximum of the information entropy. There exists a completely analogous relationship in quantum statistical mechanics.

The information entropy (4.1) is defined for a discrete probability distribution. Quantum statistics studies distributions over discrete, quantum states; therefore, the analogy between the information entropy (4.1) and the entropy in quantum statistical mechanics (8.26) is closer than in classical statistical mechanics. The difficulty in choosing an invariant probability measure, which arises for continuous distributions, does not exist in quantum statistics.

We have already introduced the entropy for quantum ensembles in section 8.4:

$$S_u = -\langle \ln \rho \rangle = -\operatorname{Sp}(\rho \ln \rho), \tag{10.1}$$

or, if the statistical operator is represented in diagonal form,

$$S_u = -\sum_k w_k \ln w_k. \tag{10.1a}$$

We have denoted the entropy not by S but by S_u, in order to emphasize that we are considering the information entropy as a functional of an arbitrary statistical operator ρ.

Let us consider the extremal properties of the Gibbs quantum statistical ensembles. The extremal properties of all of the Gibbs ensembles can be obtained from the inequality (8.35):

$$\mathrm{Sp}(\rho' \ln\rho') \geqslant \mathrm{Sp}(\rho' \ln\rho), \qquad (10.2)$$

where ρ and ρ' are arbitrary statistical operators. We have already made use of this inequality in section 8.4.

10.1. Extremal Property of the Microcanonical Distribution.

Let us show that of all distributions with the same particle number and energy falling in the same energy layer the microcanonical distribution (9.7a) corresponds to the maximum value of the information entropy.

Let ρ be the statistical operator of the microcanonical distribution (9.7a), and let ρ' be an arbitrary statistical operator acting in the same space and non-zero in the same energy layer as ρ. From the normalization condition of the statistical operators it follows that

$$\mathrm{Sp}\rho = \mathrm{Sp}\rho' = 1.$$

Substituting ρ and ρ' into the inequality (10.2), we obtain

$$-\mathrm{Sp}(\rho' \ln\rho') \leqslant -\mathrm{Sp}(\rho' \ln\rho) = \mathrm{Sp}\rho' \ln\Omega = \ln\Omega(E,N,V),$$

i.e., using (9.8) and (9.9)

$$-\mathrm{Sp}(\rho' \ln\rho') \leqslant -\mathrm{SP}(\rho \ln\rho). \qquad (10.3)$$

Thus it is shown that the microcanonical distribution (9.7a) corresponds to the maximum of the information entropy among all distributions in a given energy layer.

10.2. Extremal Property of the Gibbs Canonical Distribution.

Let us show that the Gibbs canonical distribution corresponds to the maximum of the information entropy (10.1) for fixed average energy

$$\langle H \rangle = \mathrm{Sp}(\rho H) \tag{10.4}$$

and with the normalization

$$\mathrm{Sp}\rho = 1. \tag{10.5}$$

We shall seek an extremum of the functional (10.1) with the auxiliary conditions (10.4) and (10.5). For this it is necessary to find the absolute extremum of the functional

$$-\mathrm{Sp}(\rho \ln \rho) - \beta \mathrm{Sp}(\rho H) - \lambda \mathrm{Sp}\rho,$$

where β and λ are Lagrange multipliers, defined from the conditions (10.4), (10.5). Setting the first variation of this functional to zero, we find

$$\rho = Q^{-1} \exp(-\beta H), \tag{10.6}$$

where

$$Q(\theta, V, N) = \mathrm{Sp}\exp(-\beta H), \quad \beta = \frac{1}{\theta}, \tag{10.6a}$$

which coincides with the canonical distribution (9.14). Thus, (10.6) corresponds to the extremum (10.1).

Let us now show that (10.6) corresponds to the maximum of (10.1).

Let ρ' be a normalized statistical operator, corresponding to the same average energy as (10.6),

$$\mathrm{Sp}(\rho' H) = \mathrm{Sp}(\rho H),$$

but otherwise arbitrary. Substituting (10.6) into the inequality (10.2), we obtain

$$-\operatorname{Sp}(\rho'\ln\rho')\leqslant-\operatorname{Sp}(\rho'\ln\rho)=$$
$$=\operatorname{Sp}\rho'\ln Q+\beta\operatorname{Sp}(\rho'H)=\ln Q+\beta\operatorname{Sp}(\rho H),$$

i.e.,

$$-\operatorname{Sp}(\rho'\ln\rho')\leqslant-\operatorname{Sp}(\rho\ln\rho),$$

where ρ is the Gibbs canonical distribution (10.6).

Thus, the Gibbs canonical distribution corresponds to the maximum of the information entropy among distributions with the same average energy.

In the case in which the average values of any n quantities are given

$$\langle\mathcal{P}_k\rangle=\operatorname{Sp}(\rho\mathcal{P}_k)\qquad(k=0,\ 1,\ 2,\ \ldots,\ n-1), \tag{10.7}$$

from the extremum condition of the information entropy (10.1) we obtain

$$\rho=\exp\left\{-\Phi(\mathcal{F}_0,\ \ldots,\ \mathcal{F}_{n-1})-\sum_{k=0}^{n-1}\mathcal{F}_k\mathcal{P}_k\right\}, \tag{10.8}$$

which corresponds to its maximum.

10.3. Extremal Property of the Gibbs Grand Canonical Distribution.

Let us show that the Gibbs grand canonical distribution (9.42) corresponds to the maximum of the information entropy (10.1) for fixed average energy

$$\langle H\rangle = \operatorname{Sp}(\rho H) \tag{10.9}$$

and average particle number

$$\langle N\rangle = \operatorname{Sp}(\rho N) \tag{10.10}$$

and with the normalization

$$\mathrm{Sp}\rho = 1. \tag{10.11}$$

We look for the absolute extremum of the functional

$$-\mathrm{Sp}(\rho \ln\rho) - \beta\,\mathrm{Sp}(\rho H) + \nu\,\mathrm{Sp}(\rho N) - \lambda\,\mathrm{Sp}\rho,$$

where β, ν, λ are Lagrange multipliers. From the extremum of the functional we find

$$\rho = \exp\left\{\frac{\Omega - H + \mu N}{\theta}\right\}, \tag{10.12}$$

where

$$e^{-\Omega/\theta} = \mathrm{Sp}\exp\left\{-\frac{H - \mu N}{\theta}\right\}, \quad \beta = \frac{1}{\theta}, \quad \nu = \frac{\mu}{\theta}, \tag{10.12a}$$

which is the same as the statistical operator of the Gibbs grand canonical distribution (9.42).

From the inequality (10.2) it follows that the extremum corresponds to a maximum:

$$\begin{aligned} -\mathrm{Sp}(\rho' \ln \rho') &\leqslant -\mathrm{Sp}(\rho' \ln \rho) = \\ &= -\mathrm{Sp}\left\{\rho'\left(\frac{\Omega}{\theta} - \frac{H}{\theta} + \frac{\mu N}{\theta}\right)\right\} = -\mathrm{Sp}(\rho \ln \rho), \end{aligned} \tag{10.13}$$

where the conditions (10.9)-(10.11) have been used for ρ and ρ', i.e.,

$$\mathrm{Sp}(\rho' H) = \mathrm{Sp}(\rho H), \qquad \mathrm{Sp}(\rho' N) = \mathrm{Sp}(\rho N).$$

Thus, the statistical operator (10.12) corresponds to the maximum of the information entropy for fixed average energy and average particle number.

It is easily verified by an analogous method that the statistical operator for the isobaric-isothermal Gibbs ensemble (9.59) corresponds to the maximum of the information entropy

$$S_u = -\int \mathrm{Sp}(\rho \ln \rho)\, dV, \tag{10.14}$$

with the auxiliary conditions of constant average energy and average volume

$$\langle H \rangle = \int \mathrm{Sp}(\rho H)\, dV, \quad \langle V \rangle = \int \mathrm{Sp}(\rho V)\, dV. \tag{10.15}$$

The extremal properties of the Gibbs quantum ensembles were noticed long ago [2, 3, 9]. In generalizing the Gibbs ensembles to the case of quantum statistics, von Neumann proceeded from exactly these extremal properties of the entropy [2, 3].

The extremal properties of the Gibbs statistical ensembles which have been considered above can be used as a basis for their definition; this is done by Jaynes [18, 19]. In what follows we shall often make use of the extremal properties of the entropy to construct ensembles in nonequilibrium statistical thermodynamics (see Chapter IV).

§ 11. Thermodynamic Equalities

11.1. Quasistatic Process.

To obtain thermodynamic equalities in quantum statistical mechanics, as in classical, it is necessary to consider a quasistatic process of infinitely slow change of the external parameters defining the ensemble. We shall assume that in a quasistatic process the external parameters $\alpha_1, \alpha_2, \ldots, \alpha_s$ are changed so slowly that the ensemble of quantum mechanical systems can be considered at each moment of time to be in statistical equilibrium. The generalized forces $\alpha_1, \ldots, \alpha_s$ correspond to the parameters

$$A_i = -\frac{\partial H}{\partial a_i}. \tag{11.1}$$

Their observed values in a quasistatic process are equal to averages calculated using the equilibrium statistical operator:

$$\langle A_i \rangle = \mathrm{Sp}(\rho A_i) = -\left\langle \frac{\partial H}{\partial a_i} \right\rangle. \tag{11.2}$$

In the particular case in which the volume V is chosen as the generalized parameter, the generalized force is the pressure

$$p = -\left\langle \frac{\partial H}{\partial V} \right\rangle. \tag{11.3}$$

The quantity $\partial H/\partial V$ is a dynamical variable whose form we shall define more precisely below.

11.2. Thermodynamic Equalities for a Microcanonical Ensemble.

In accordance with (9.9) the entropy for the Gibbs microcanonical ensemble is equal to the logarithm of the statistical weight:

$$S(E,N,V) = \ln\Omega(E,N,V). \tag{11.4}$$

The total increase of the entropy for a change of the energy, the number of particles, and the volume is equal to

$$dS = \frac{\partial \ln \Omega}{\partial E}\, dE + \frac{\partial \ln \Omega}{\partial V}\, dV + \frac{\partial \ln \Omega}{\partial N}\, dN, \tag{11.5}$$

which can be written in the form of the usual thermodynamic equality

$$dS = \frac{1}{\theta}\, dE + \frac{p}{\theta}\, dV - \frac{\mu}{\theta}\, dN, \tag{11.6}$$

where

$$\frac{1}{\theta} = \frac{\partial \ln \Omega}{\partial E}, \quad \frac{p}{\theta} = \frac{\partial \ln \Omega}{\partial V}, \quad \frac{\mu}{\theta} = -\frac{\partial \ln \Omega}{\partial N}, \tag{11.7}$$

and θ is the temperature, p is the pressure, and μ is the chemical potential.

It is easily verified that the pressure defined by formula (11.7) is indeed the average value of the generalized force $\partial H/\partial V$. In fact, the statistical weight of the microcanonical distribution (9.7a) can be written in the form

$$\Omega(E,N,V) = \mathrm{Sp}(\Delta(H-E)). \tag{11.8}$$

For convenience of calculation it can be considered that Δ is a continuous function approximating the step function. Let us calculate the partial derivative with respect to V of the identity (11.8):

$$\frac{\partial\Omega}{\partial V} = \mathrm{Sp}\left(\frac{\partial}{\partial V}\Delta(H-E)\right) = -\,\mathrm{Sp}\left\{\frac{\partial}{\partial E}\Delta(H-E)\frac{\partial H}{\partial V}\right\} =$$

$$= -\frac{\partial}{\partial E}\,\mathrm{Sp}\left\{\Delta(H-E)\frac{\partial H}{\partial V}\right\},$$

or

$$\frac{\partial\Omega}{\partial V} = -\frac{\partial}{\partial E}\,\Omega\left\langle\frac{\partial H}{\partial V}\right\rangle \simeq -\frac{\partial\Omega}{\partial E}\left\langle\frac{\partial H}{\partial V}\right\rangle \tag{11.9}$$

(we have discarded the small terms of the order of the fluctuations, which is permissible in the thermodynamic limit). Thus,

$$\frac{\partial \ln\Omega(E,N,V)}{\partial V} = -\frac{\partial \ln\Omega(E,N,V)}{\partial E}\left\langle\frac{\partial H}{\partial V}\right\rangle, \tag{11.9a}$$

and p, defined by equation (11.7), coincides with the average value of the generalized force $\partial H/\partial V$, which was to be shown.

The physical interpretation of θ as the temperature is evident from the fact that this quantity is an integrating factor for $dE+pdV-\mu dN$.

11.3. Virial Theorem for Quantum Systems.

Let us consider the virial theorem for the case of quantum statistics; it is analogous to the classical virial theorem considered in section 5.3.

Earlier we defined the pressure as the average value of the operator of the generalized force $\partial H(p,x)/\partial V$, which is a function of the momentum and position operators p,x. Let us determine the explicit form of this operator.

We shall begin with the statistical distribution (9.7a). We write the statistical weight (11.8) in the form

$$\Omega(E,N,V) = \mathrm{Sp}_V\{\Delta(H(p,x)-E)\}, \tag{11.10}$$

where we consider that H(p,x) is independent of the volume V; a volume dependence enters only through the dimensions of the basic region $V=L^3$ of normalization of the wave functions which are used to calculate the spur (trace) in (11.10). We indicate this by the subscript V on the spur. We shall describe the variation of the volume by introducing the parameter λ^3 in front of V:

$$\Omega(E, N, \lambda^3 V) = \mathrm{Sp}_{\lambda^3 V}\{\Delta(H(p, x) - E)\}. \tag{11.10a}$$

We make the change of variables

$$x = \lambda x', \qquad p = \lambda^{-1} p', \tag{11.10b}$$

i.e., we carry out a canonical transformation, which does not change the phase of the wave functions

$$(xp) = (x'p')$$

and which makes the basic region of normalization independent of λ:

$$\Omega(E, N, \lambda^3 V) = \mathrm{Sp}_V\left\{\Delta\left(H\left(\frac{p}{\lambda}, \lambda x\right) - E\right)\right\}. \tag{11.11}$$

Differentiating Ω with respect to λ, we obtain

$$\frac{\partial\Omega}{\partial\lambda} = -\,\mathrm{Sp}_V\left\{\frac{\partial}{\partial E}\Delta\left(H\left(\frac{p}{\lambda}, \lambda x\right) - E\right)\frac{\partial H\left(\frac{p}{\lambda}, \lambda x\right)}{\partial\lambda}\right\}$$

or, putting λ=1,

$$\left(\frac{\partial\Omega}{\partial\lambda}\right)_{\lambda=1} = -\frac{\partial}{\partial E}\left(\Omega\left\langle\frac{\partial}{\partial\lambda} H\left(\frac{p}{\lambda}, \lambda x\right)\right\rangle\right)_{\lambda=1}. \tag{11.12}$$

Using (5.10a), we obtain

$$\frac{\partial\Omega}{\partial V} = -\frac{\partial}{\partial E}\Omega\frac{1}{3V}\left\langle\frac{\partial}{\partial\lambda} H\left(\frac{p}{\lambda}, \lambda x\right)\right\rangle_{\lambda=1}. \tag{11.12a}$$

Comparing (11.12a) with (11.9), we find the explicit form of the operator ∂H(p,x)/∂V, which corresponds to the pressure:

$$-\frac{\partial H(p, x)}{\partial V} = -\frac{1}{3V}\frac{\partial}{\partial \lambda} H\left(\frac{p}{\lambda}, \lambda x\right)_{\lambda=1}. \tag{11.13}$$

The formula thus obtained differs from (5.12) only in that p and x are now non-commuting operators. Otherwise it has an identical form.

In the particular case of a Hamiltonian for particles with a two-body interaction we obtain

$$-\frac{\partial H(p, x)}{\partial V} = \frac{2}{3V}\sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \frac{1}{6V}\sum_{i\neq j}(x_i - x_j)\cdot\frac{\partial \phi(x_i - x_j)}{\partial x_i}. \tag{11.14}$$

This formula gives the required representation for the pressure operator. The average value of the operator (11.14) gives an expression for the pressure:

$$p = \frac{2}{3V}\sum_i \frac{1}{2m}\langle \hbar^2 \nabla_i^2\rangle + \frac{1}{6V}\sum_{i\neq j}\langle (x_i - x_j)\cdot F_{ij}\rangle,$$

$$F_{ij} = -\frac{\partial \phi(x_i - x_j)}{\partial x_i}, \tag{11.15}$$

i.e., a generalization of the virial theorem for the case of quantum statistics. Thus, in quantum statistics the pressure is equal to 2/3 of the average kinetic energy density plus 1/3 of the virial forces, as in classical statistics.

The difference from the classical case lies in the fact that the operators appearing in (11.15) for the kinetic energy and the virial forces do not commute among themselves. Therefore the formula (5.14c), expressing the law of uniform distribution of energy over the degrees of freedom, is not valid in the quantum case.

11.4. Thermodynamic Equalities for the Gibbs Canonical Ensemble.

The entropy for the Gibbs canonical ensemble (9.14) is equal to

$$S = -\operatorname{Sp}(\rho \ln \rho) = \frac{\langle H\rangle - F}{\theta}. \tag{11.16}$$

Differentiating the identity (9.15)

$$e^{-F/\theta} = \mathrm{Sp}\, e^{-H/\theta}$$

with respect to θ, we find an expression for the average energy:

$$\langle H\rangle = -\theta^2 \frac{\partial}{\partial\theta}\left(\frac{F}{\theta}\right)_{a_i,\, N}. \qquad (11.17)$$

Substituting (11.17) into (11.16), we obtain another expression for the entropy:

$$S = -\left(\frac{\partial F}{\partial\theta}\right)_{a_i,\, N}. \qquad (11.18)$$

The average value over the Gibbs canonical distribution of the generalized force (11.1) is equal to

$$\langle A_i\rangle = -\left\langle\frac{\partial H}{\partial a_i}\right\rangle = -e^{F/\theta}\,\mathrm{Sp}\left(e^{-H/\theta}\frac{\partial H}{\partial a_i}\right), \qquad (11.19)$$

or

$$\langle A_i\rangle = \theta\, e^{F/\theta}\frac{\partial}{\partial a_i}\,\mathrm{Sp}\, e^{-H/\theta} = -\theta\, e^{F/\theta}\frac{\partial}{\partial a_i}\, e^{-F/\theta}.$$

Thus, the observed value of the average of the generalized force, corresponding to a change of the parameter α_i, is equal to

$$\langle A_i\rangle = -\left(\frac{\partial F}{\partial a_i}\right)_{\theta,\, N} \qquad (11.20)$$

or, in the particular case in which $\alpha_i = V$,

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\theta,\, N}. \qquad (11.20a)$$

We write the system of thermodynamic equalities thus obtained in the form of one relationship giving the change of the free energy F upon variation of the parameters θ, $a_1,\ldots,a_s$, N:

$$dF=\left(\frac{\partial F}{\partial\theta}\right)_{a_i,\,N}d\theta+\sum_{i=1}^{s}\left(\frac{\partial F}{\partial a_i}\right)_{\theta,\,N}da_i+\left(\frac{\partial F}{\partial N}\right)_{\theta,\,a_i}dN, \tag{11.21}$$

or using (11.18) and (11.20)

$$dF=-S\,d\theta-\sum_{i=1}^{s}\langle A_i\rangle\,da_i+\mu\,dN, \tag{11.22}$$

where

$$\mu=\left(\frac{\partial F}{\partial N}\right)_{\theta,\,a_i}. \tag{11.23}$$

Equation (11.22) comprises a complete system of thermodynamic relations, which can be expressed not only through F, but also through the other thermodynamic functions, as in section 5.4.

11.5. Thermodynamic Equalities for the Gibbs Grand Canonical Ensemble.

The thermodynamic equalities for the Gibbs grand canonical ensemble are obtained in exactly the same way as for the canonical ensemble.

The entropy for the Gibbs grand canonical ensemble (9.42) is equal to

$$S=-\mathrm{Sp}(\rho\ln\rho)=\frac{\langle H\rangle-\Omega-\mu\langle N\rangle}{\theta}. \tag{11.24}$$

Differentiating the identity (9.42a) with respect to θ and μ, we obtain an expression for the average energy and average particle number:

$$\langle H\rangle-\mu\langle N\rangle=-\theta^2\frac{\partial}{\partial\theta}\left(\frac{\Omega}{\theta}\right)_{\mu,\,a_i},\qquad \langle N\rangle=-\left(\frac{\partial\Omega}{\partial\mu}\right)_{\theta,\,a_i}. \tag{11.25}$$

Substituting (11.25) into (11.24), we write the entropy in the form

$$S = -\left(\frac{\partial\Omega}{\partial\theta}\right)_{a_i,\,\mu}. \tag{11.26}$$

The average of the generalized force (11.1) over the grand canonical ensemble is equal to

$$\langle A_i\rangle = -\left\langle\frac{\partial H}{\partial a_i}\right\rangle = -e^{\Omega/\theta}\,\mathrm{Sp}\left(e^{-(H-\mu N)/\theta}\frac{\partial H}{\partial a_i}\right) =$$

$$= \theta\, e^{\Omega/\theta}\frac{\partial}{\partial a_i}\,\mathrm{Sp}\, e^{-(H-\mu N)/\theta} = \theta\, e^{\Omega/\theta}\frac{\partial}{\partial a_i}e^{-\Omega/\theta}.$$

Thus,

$$\langle A_i\rangle = -\left(\frac{\partial\Omega}{\partial a_i}\right)_{\theta,\,N}. \tag{11.27}$$

In the particular case in which $\alpha_i = V$

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{\theta,\,N}. \tag{11.27a}$$

To obtain a complete system of thermodynamic equalities we calculate the change of the thermodynamic potential $\Omega(\theta,\mu,\alpha_1,\dots,\alpha_s)$ upon variation of the parameters θ, μ, $\alpha_1,\dots,\alpha_s$:

$$d\Omega = \left(\frac{\partial\Omega}{\partial\theta}\right)_{\mu,\,a_i} d\theta + \sum_{i=1}^{s}\left(\frac{\partial\Omega}{\partial a_i}\right)_{\theta,\,a_l} da_i + \frac{\partial\Omega}{\partial\mu}\,d\mu, \tag{11.28}$$

or using (11.26), (11.27), and (11.25)

$$d\Omega = -S\,d\theta - \sum_{i=1}^{s}\langle A_i\rangle\,da_i - \langle N\rangle\,d\mu. \tag{11.29}$$

Equation (11.29) comprises a complete system of thermodynamic relationships.

11.6. *Nernst Theorem.*

In the preceding sections of this paragraph, we obtained thermodynamic equalities expressing the first and second laws of thermodynamics on the basis of the various Gibbs ensembles. We discuss now the *Nernst theorem*, or the *third law of thermodynamics*.

The Nernst theorem establishes the behavior of the thermodynamic functions upon the approach of the temperature to zero and is connected with the quantum properties of the systems at low temperatures. Nernst established experimentally that upon the approach of the temperature to zero for all substances the difference of their entropies $S(\theta,\alpha_i)$ (which is the only measurable quantity) approaches zero together with its derivative with respect to external parameters, i.e.,

$$S(0, \alpha_i) = S(0, \alpha_i'), \qquad \left(\frac{\partial S}{\partial \alpha_i}\right)_{\theta \to 0} = 0 \tag{11.30}$$

for all values of the parameters α_i, α'_i. For example, if the volume is the external parameter, then

$$S(0, V_1) = S(0, V_2), \qquad \left(\frac{\partial S}{\partial V}\right)_{\theta \to 0} = 0. \tag{11.30a}$$

Since the limiting value of the entropy is independent of the parameters defining the system, it is convenient, following Planck, to put it equal to zero and to obtain an absolute normalization of the entropy of any substance:

$$S(0,\alpha_i) = 0. \tag{11.30b}$$

These distinctive features of the behavior of the entropy at low temperatures constitute the theorem of Nernst [20-22].

The Nernst theorem is not applicable to substances which are not in statistical equilibrium, for example, amorphous bodies or disordered alloys, which can exist even at very low temperatures as "frozen" metastable states with very long relaxation times. Because of the illegitimate application of the Nernst theorem to such substances the validity of the theorem was formerly doubted.

Unlike the first and second laws of thermodynamics, which follow directly from the Gibbs distributions, there does not exist a general statistical proof of the Nernst theorem, although for all known, physically reasonable models the Nernst theorem can be shown to be satisfied by the use of quantum statistical mechanics.

Let us consider the limit of the Gibbs distribution

$$w_k = e^{(F-E_k)/\theta} \tag{11.31}$$

as the temperature approaches zero.

It is convenient to express the free energy in (11.31) through the entropy using the relationship (11.16)

$$w_k = \exp\left\{-S + \frac{\langle H\rangle - E_k}{\theta}\right\},$$

or

$$w_k = \exp\left\{-S + \frac{\langle H\rangle - E_0}{\theta} + \frac{E_0 - E_k}{\theta}\right\}, \tag{11.31a}$$

where E_0 is the energy of the ground state, for which $E_k > E_0$ for $k \neq 0$, because the degenerate levels lie above the ground state. As $\theta \to 0$ the average energy $\langle H\rangle$ approaches E_0. Calculating the limit of the expression (11.31a) as $\theta \to 0$ using l'Hopital's rule, we obtain

$$\lim_{\theta \to 0} w_k = w_k(0) = \exp(-S(0) + C_V(0))\,\delta_{E_k - E_0},$$

where

$$\delta_{E_k - E_0} = \begin{cases} 1 & \text{при} \quad E_k = E_0, \\ 0 & \text{при} \quad E_k \neq E_0, \end{cases} \tag{11.32}$$

and is the specific heat at constant volume for $\theta = 0$. From the normalization condition for the probability (11.32) it follows that

$$w_k(0) = \frac{1}{\Omega_0}\,\delta_{E_k - E_0}, \tag{11.33}$$

where Ω_0 is the multiplicity of the ground state E_0. But from the expression

$$S = \frac{\langle H \rangle - F}{\theta}$$

it follows from l'Hopital's rule that

$$S(0) = C_V(0) + S(0),$$

i.e., that

$$C_V(0) = 0.$$

Thus, the limiting value of the entropy as $\theta \to 0$ is equal to

$$S(0) = \ln\Omega_0. \qquad (11.34)$$

From the formula (11.33) it follows that as $\theta \to 0$ the Gibbs canonical ensemble goes over into the microcanonical ensemble with entropy (11.34).

For all known systems (crystal lattices, quantum gases, etc.) the ground state is non-degenerate, i.e.,

$$\Omega_0 = 1,$$

and, consequently, for these systems the entropy approaches zero as $\theta \to 0$. Even if $\Omega_0 >> 1$, but the thermodynamic limit

$$\lim_{N \to \infty} \frac{\ln \Omega_0}{N} = 0,$$

it can be considered that

$$S(0) = 0. \qquad (11.35)$$

Sometimes in textbooks the Nernst theorem is incorrectly associated only with the absence of degeneracy in the ground state. In reality the main point of the Nernst theorem does not lie in that; rather it lies in the distinctive features of the energy spectrum for small degeneracies.

If the Nernst theorem is associated only with the absence of degeneracy of the ground state, then the distinctive features of the behavior of the thermodynamic functions which follow from the Nernst theorem would begin to appear only at very low temperatures θ_1, of the order of the difference of the energy of the first excited level and the ground state,

$$\theta_1 = E_1 - E_0,$$

but since the spectrum of macroscopic bodies is practically continuous, these are very low, unobservable temperatures. For example, for an ideal gas of atoms with mass m in volume $V=L^3$

$$E_1 - E_0 = \frac{\hbar^2}{2m} k_{\min}^2 = \frac{\hbar^2}{2mV^{2/3}},$$

where $k_{\min}=2\pi/L$ is the minimum value of the wave vector. For a crystal lattice

$$E_1 - E_0 = \hbar s k_{\min} = \frac{\hbar s}{V^{1/3}},$$

where s is the speed of sound.

In reality the behavior of the entropy required by the Nernst theorem begins to appear at much higher temperatures. For example, for ideal quantum gases the Nernst theorem follows from the degeneracy effects. For an ideal Bose gas the behavior of the entropy corresponding to the Nernst theorem begins to appear at temperatures of the order of the degeneracy temperature θ_0

$$\theta_0 \approx \frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3}, \qquad (11.36)$$

and for an ideal Fermi gas it begins to appear at temperatures lower than that corresponding to the Fermi energy. The order of magnitude of this temperature is given by the same expression (11.36), but for electrons in a metal this can be very large because of the smallness of their masses.

The degeneracy temperature of ideal gases is significantly higher than θ_1, which is defined by the position of the first excited level. For crystal lattices the Nernst theorem begins to appear at temperatures of the order of the Debye temperature θ_D, defined by the energy of the elementary excitations for maximum wave vector k_D:

$$\theta_D = \hbar s k_D = \hbar s \left(\frac{6\pi^2 N}{V}\right)^{1/3}.$$

The fact that the degeneracy temperature and the Debye temperature are both proportional to Planck's constant $\hbar$ shows that the Nernst theorem is connected with the quantum properties of the system. To prove the Nernst theorem for the general case it would be necessary to study the distribution of the eigenvalues E_k near the ground state, i.e., to study the function $\Omega(E,N,V)$ near $E=E_0$. Up to the present time this has been done only for specific models. For all models of physical interest which have been studied, the distribution of eigenvalues near the ground state is such that the Nernst theorem is satisfied. It can be said that in all cases when the lower part of the spectrum of the system can be represented in the form of an ideal gas of quasi particles (Fermi or Bose types), the Nernst theorem turns out to be satisfied.

§ 12. Fluctuations in Quantum Systems

We shall consider fluctuations for the quantum Gibbs statistical ensembles. It is particularly simple to calculate fluctuations of quantities on which the statistical operator which describes the ensemble depends, for example energy fluctuations in the Gibbs canonical ensemble.

12.1. Fluctuations in the Gibbs Canonical Ensemble.

The average value of the energy for the Gibbs canonical ensemble is equal to

$$\langle H \rangle = \mathrm{Sp}\,(e^{(F-H)/\theta} H). \tag{12.1}$$

Differentiating this identity with respect to θ for constant V and N, and using (11.17), we obtain an expression for the energy fluctuations in the Gibbs canonical ensemble

$$\langle H^2 \rangle - \langle H \rangle^2 = \theta^2 \frac{\partial \langle H \rangle}{\partial \theta}, \tag{12.2}$$

which has the same form as in the classical case (3.8d), but with the difference that the averaging is carried out not with the classical distribution function, but with the statistical operator.

The relative smallness of the energy fluctuations in the Gibbs canonical ensemble follows from (12.2), because the average energy is proportional to the number of particles N, while θ is independent of N.

12.2. Fluctuations in the Gibbs Grand Canonical Ensemble.

In an analogous way we calculate the fluctuations of energy and particle number in the Gibbs grand canonical ensemble. Differentiating the expressions

$$\begin{gathered}\langle H-\mu N\rangle = \operatorname{Sp}\left(e^{(\Omega-H+\mu N)/\theta}(H-\mu N)\right),\\ \langle N\rangle = \operatorname{Sp}\left(e^{(\Omega-H+\mu N)/\theta} N\right)\end{gathered} \qquad (12.3)$$

with respect to θ and μ with the remaining parameters being constant, and using (11.25), we obtain expressions for the fluctuations of energy and particle numbers in the Gibbs grand canonical ensemble:

$$\begin{gathered}\langle (H-\mu N)^2\rangle - \langle H-\mu N\rangle^2 = \theta^2\frac{\partial}{\partial\theta}\left(\langle H\rangle - \mu\langle N\rangle\right),\\ \langle N^2\rangle - \langle N\rangle^2 = \theta\frac{\partial\langle N\rangle}{\partial\mu},\end{gathered} \qquad (12.4)$$

i.e., the same expressions as in the classical case (3.35).

The relative smallness of the fluctuations in energy and particle number in the Gibbs grand canonical ensemble follows from (12.4).

12.3. Fluctuations in the Gibbs Generalized Ensemble.

Let us consider fluctuations for the distribution which is described by the statistical operator (10.8)

$$\rho = \exp\left\{-\Phi(\mathcal{F}_0, \ldots, \mathcal{F}_n) - \sum_{k=0}^{n}\mathcal{F}_k\mathcal{P}_k\right\}, \qquad (12.5)$$

in which are given the average values

$$\langle \mathcal{P}_k \rangle = \mathrm{Sp}\,(\rho \mathcal{P}_k) \qquad (k = 0,\ 1,\ \ldots,\ n). \tag{12.6}$$

In (12.5) $\Phi(\mathcal{F}_0,\ldots,\mathcal{F}_n)$ is the Mas'ye-Planck function, defined by the normalization of the spur (trace) to unity:

$$e^{\Phi} = \mathrm{Sp}\, e^{-\sum \mathcal{F}_k \mathcal{P}_k}. \tag{12.7}$$

Differentiating this identity with respect to $\mathcal{F}_k$, we obtain the average value of $\mathcal{P}_k$:

$$\langle \mathcal{P}_k \rangle = \mathrm{Sp}\left(e^{-\Phi - \sum \mathcal{F}_k \mathcal{P}_k} \mathcal{P}_k\right) = -\frac{\partial \Phi}{\partial \mathcal{F}_k}. \tag{12.8}$$

To calculate fluctuations it is necessary to distinguish two cases: when all of the $\mathcal{P}_k$ are integrals of motion and when not all of the $\mathcal{P}_k$ are integrals of motion.

Let us consider the first case. Since it is assumed that all of the $\mathcal{P}_k$ commute the exponential of the sum of operators can be differentiated like an ordinary function, even outside the spur sign. Differentiating the identity (12.8) with respect to $\mathcal{F}_i$, we obtain an expression for fluctuations of the quantities

$$\langle \mathcal{P}_k \mathcal{P}_i \rangle - \langle \mathcal{P}_k \rangle \langle \mathcal{P}_i \rangle = -\frac{\partial \langle \mathcal{P}_k \rangle}{\partial \mathcal{F}_i} = -\frac{\partial \langle \mathcal{P}_i \rangle}{\partial \mathcal{F}_k} = \frac{\partial^2 \Phi}{\partial \mathcal{F}_i \partial \mathcal{F}_k}, \tag{12.9}$$

analogous to the classical expression (6.7).

In the second case when not all of the $\mathcal{P}_k$ are integrals of motion and may not commute among themselves, care must be taken in differentiating the exponential, which contains a sum of non-commuting operators.

Let us derive a formula for differentiating the exponential $e^{A(\alpha)}$ with respect to the parameter α. To do this it is necessary to expand the exponential e^{A+B} in a series in B, where $B=\delta A$ and does not commute with A. It is convenient to introduce the auxiliary operator $\mathcal{H}(\tau)$

$$e^{(A+B)\tau} = \mathcal{H}(\tau)\, e^{A\tau}, \tag{12.10}$$

satisfying the condition

$$\mathcal{H}(0) = 1. \tag{12.10a}$$

The expression (12.10) can be simply differentiated with respect to τ, because A+B is independent of τ, and the increment $(A+B)\delta\tau$ commutes with A+B. The relationship (12.10) is equivalent to the differential equation for $\mathcal{H}$

$$\frac{\partial \mathcal{H}}{\partial \tau} = \mathcal{H} e^{A\tau} B e^{-A\tau} \tag{12.11}$$

with the initial condition (12.10a), because in differentiating (12.10) with respect to τ the terms $\mathcal{H} e^{A\tau} A$ on the left and right sides cancel. The differential equation (12.11) and the initial condition (12.10a) are equivalent to the operator integral equation for $\mathcal{H}$:

$$\mathcal{H}(\tau) = 1 + \int_0^\tau \mathcal{H}(\tau_1) e^{A\tau_1} B e^{-A\tau_1} d\tau_1. \tag{12.12}$$

Iteration of the equation (12.12) gives an expansion of $\mathcal{H}$ in powers of B. Keeping only the first order term in B, we obtain

$$\mathcal{H}(\tau) \cong 1 + \int_0^\tau e^{A\tau_1} B e^{-A\tau_1} d\tau_1. \tag{12.12a}$$

Setting τ=1 in (12.12a) and substituting this expression into (12.10), we obtain

$$e^{A+B} \cong \left(1 + \int_0^1 e^{A\tau} B e^{-A\tau} d\tau\right) e^A,$$

i.e.,

$$\delta e^A = \int_0^1 e^{A\tau} \delta A \, e^{-A\tau} e^A d\tau, \tag{12.13}$$

or

$$\frac{d}{d\alpha} e^{A(\alpha)} = \int_0^1 e^{A\tau} \frac{dA}{d\alpha} e^{-A\tau} e^A d\tau. \tag{12.14}$$

Formula (12.14) gives the rule for differentiating the exponential of an operator in the general case. In the particular case where A is proportional

to α, the usual rule of differentiating an exponential follows from (12.14).

To calculate the fluctuations of the quantities $\mathcal{P}_k$ we differentiate the formula (12.8) with respect to $\mathcal{F}_i$ according to the rule (12.14). We obtain

$$\frac{\partial\langle\mathcal{P}_k\rangle}{\partial\mathcal{F}_i} = \langle\mathcal{P}_i\rangle\langle\mathcal{P}_k\rangle - \int_0^1 \langle\mathcal{P}_k\mathcal{P}_i(\tau)\rangle\, d\tau, \tag{12.15}$$

where

$$\mathcal{P}_i(\tau) = e^{-\tau\sum\mathcal{F}_k\mathcal{P}_k}\,\mathcal{P}_i\, e^{\tau\sum\mathcal{F}_k\mathcal{P}_k}; \tag{12.16}$$

thus,

$$\frac{\partial\langle\mathcal{P}_k\rangle}{\partial\mathcal{F}_i} = -\int_0^1 \langle(\mathcal{P}_k-\langle\mathcal{P}_k\rangle)(\mathcal{P}_i(\tau)-\langle\mathcal{P}_i\rangle)\rangle\, d\tau. \tag{12.17}$$

It is convenient to introduce a more compact notation for the quantities on the right hand side of (12.17), which we shall often encounter.

$$(\mathcal{P}_k, \mathcal{P}_i) = \int_0^1 \langle(\mathcal{P}_k-\langle\mathcal{P}_k\rangle)(\mathcal{P}_i(\tau)-\langle\mathcal{P}_i\rangle)\rangle\, d\tau, \tag{12.18}$$

Therefore, (12.17) can be rewritten in the form

$$(\mathcal{P}_k, \mathcal{P}_i) = -\frac{\partial\langle\mathcal{P}_k\rangle}{\partial\mathcal{F}_i} = -\frac{\partial\langle\mathcal{P}_i\rangle}{\partial\mathcal{F}_k} = \frac{\partial^2\Phi}{\partial\mathcal{F}_i\,\partial\mathcal{F}_k}. \tag{12.19}$$

Thus, if the quantities $\mathcal{P}_i (i=0, 1, \ldots, n)$ do not commute among themselves, the second derivative of Φ with respect to the parameters $\mathcal{F}_i$ and $\mathcal{F}_k$ does not simply give the relative fluctuations of $\mathcal{P}_i$ and $\mathcal{P}_k$, but rather the average with respect to τ of the value of the fluctuations of $\mathcal{P}_k$ and $\mathcal{P}_i(\tau)$.

Only in the particular case in which the operators $\mathcal{P}_i$ commute or in which their non-commutativity can be neglected do we obtain the formula (12.9) for the fluctuations. In that case the macroscopic distribution function (6.11), introduced in § 6, can be constructed.

§ 13. Thermodynamic Equivalence of Gibbs Statistical Ensembles

As was shown in §§ 3 and 9, all of the ensembles of statistical mechanics are defined by specifying the external conditions in which the systems making up the ensembles are found. For example, the microcanonical ensemble is defined by constant energy, constant particle number, and constant volume; the canonical is defined by constant particle number, constant volume, and contact with a thermostat; the grand canonical is defined by constant volume and by contact with a thermostat and a reservoir of particles; the isobaric-isothermal is defined by constant particle number, constant pressure, and by contact with a thermostat.

The application of statistical ensembles to concrete problems is usually not restricted by the conditions for which the ensembles are defined. In the choice of an ensemble one is guided by the convenience of calculation, and not by the conditions in which the system is found.

As justification for replacing one ensemble by another, it is usually pointed out that the different ensembles differ very little from one another, because of the small fluctuations in the quantities which are not specified for the ensembles. Indeed, as we verified in § 12, the fluctuations in energy in the Gibbs canonical ensemble and the fluctuations in particle number in the Gibbs grand canonical ensemble are small. These physical considerations cannot, of course, be considered as a proof of the equivalence of the statistical ensembles in a thermodynamic sense. To prove this equivalence it is necessary to show that in replacing one ensemble by another that the thermodynamic functions calculated with each ensemble differ little from each other and coincide in the thermodynamic limit $V\to\infty$, $N/V=\text{const}$.

The question of the thermodynamic equivalence of the statistical ensembles was considered in [17], where it was shown, for example, that if one retains only the maximum term in the statistical sum of the Gibbs grand canonical ensemble, then the thermodynamic functions obtained in this approximation coincide in the thermodynamic limit with the thermodynamic functions calculated on the basis of the canonical ensemble with particle number equal to the average particle number in the Gibbs grand ensemble. However, this is still not a complete proof of the thermodynamic equivalence of the ensembles, because in the method used to separate out the maximum term in the statistical sums there is no way to estimate the discarded terms.

In this paragraph we shall give, following [23], a proof of the thermodynamic equivalence of the statistical ensembles using the saddle-point method.

13.1. Thermodynamic Equivalence of Gibbs Canonical and Microcanonical Ensemble.

Let the system be in a thermostat and described by the Gibbs canonical distribution (9.10). We shall find an approximate microcanonical distribution for the system, with which all thermodynamic functions could be calculated.

The statistical sum $Q(\theta,V,N)$ is connected with the statistical weight $\Omega(E,N,V)$ by the relationship

$$Q(0, V, N) = \sum_{E} e^{-E\theta}\Omega(E, N, V), \qquad (13.1)$$

where the summation is carried out over all allowed values of the energy, and $\Omega(E,N,V)$ is the number of states for systems with energy E, particle number N, and volume V. If the summatior is carried out over a layer of energy ΔE, as we shall assume from now on, then $\Omega(E,N,V)$ is the number of states in that layer.

Using the theorem on the inversion of the statistical sum (9.27), we obtain for the statistical weight the expression

$$\Omega(E, N, V) = \Gamma(E + \Delta E, N, V) - \Gamma(E, N, V) = \\ = \frac{1}{2\pi i}\int\limits_{a-i\infty}^{a+i\infty} e^{\lambda E} Q(\lambda^{-1}, V, N)\frac{e^{\lambda\Delta E} - 1}{\lambda}\,d\lambda; \qquad (13.2)$$

$Q(\lambda^{-1},V,N) \equiv Q(\lambda)$ in the previous notation, and α is a real positive number. Thus, (13.2) gives the inversion of the statistical sum (13.1). It is convenient to rewrite formula (13.2) in the form

$$\Omega(E, N, V) = \frac{1}{2\pi i}\int\limits_{a-i\infty}^{a+i\infty} e^{N\chi(\lambda)}\frac{e^{\lambda\Delta E} - 1}{\lambda}\,d\lambda, \qquad (13.3)$$

where

$$\chi(\lambda) = \frac{E}{N}\lambda - \lambda\frac{F(\lambda^{-1}, V, N)}{N}, \qquad (13.3a)$$

and $F(\theta,V,N)$ is the free energy. In writing the exponential in formula (13.3) the large magnitude of the term (N_x) is explicitly taken into account, because x is finite as $N\to\infty$.

We shall assume that the thermodynamic limit

$$\lim_{N\to\infty}\frac{F}{N} \qquad (V/N = \text{const}).$$

exists for our system. Then as $N\to\infty$ the function (13.3a) approaches a finite limit; therefore, for large N the integral (13.3) can be estimated by the saddle-point method, assuming that $x^{(\lambda)}$ is an analytic function for $\mathrm{Re}\lambda > \alpha$. We shall see below that the necessary conditions for the applicability of the saddle-point method are indeed satisfied.

As the saddle point we select λ_1, the real positive root of the equation

$$\frac{\partial\chi}{\partial\lambda}(\lambda_1)=0 \tag{13.4}$$

and we put in (13.3) $\alpha=\lambda_1=1/\theta$. Then, repeating the calculations of section 3.3, we obtain

$$\Omega(E,\ N,\ V)=e^{N\chi(\lambda_1)}\frac{e^{\lambda_1\Delta E}-1}{\lambda_1\sqrt{2\pi N\chi''(\lambda_1)}}=Q(\theta,\ V,\ N)\,e^{E/\theta}\,\frac{e^{\Delta E/\theta}-1}{\sqrt{2\pi C_V}}, \tag{13.5}$$

where

$$C_V=\frac{\partial\bar{E}}{\partial\theta},\qquad \bar{E}=-\theta^2\frac{\partial}{\partial\theta}\left(\frac{F(\theta,\ V,\ N)}{\theta}\right). \tag{13.5a}$$

The condition (13.4) for the saddle point takes on the form

$$E=\bar{E}=\langle H\rangle=-\theta^2\frac{\partial}{\partial\theta}\left(\frac{F(\theta,\ V,\ N)}{\theta}\right), \tag{13.6}$$

i.e., E must be taken equal to the average energy (11.17) in the canonical ensemble.

In order that the saddle-point method be applicable it is necessary that the point λ_1 be a maximum as one moves parallel to the imaginary axis, i.e., that $x''(\lambda_1)$ be positive, or that

$$C_V>0, \tag{13.7}$$

which is one of the conditions of thermodynamic stability of the system, which is satisfied for ordinary systems as a result of the relationship (12.2)

$$\langle(H-\langle H\rangle)^2\rangle=\theta^2C_V>0. \tag{13.8}$$

Let us construct an approximate microcanonical distribution

$$w(E_k)=\begin{cases}\Omega^{-1}(E,\ N,\ V) & \text{for } E\leqslant E_k\leqslant E+\Delta E,\\ 0 & \text{outside this interval}\end{cases} \tag{13.9}$$

where $\Omega(E,N,V)$ is defined by the formula (13.5), $E=\bar{E}$, and ΔE is equal to the average energy fluctuation (13.8). The relation (13.5) can be rewritten in the form

$$\Omega(E,\ N,\ V) = e^{E/\theta} Q(\theta,\ N,\ V) \frac{e^{\sqrt{C_V}}}{\sqrt{2\pi C_V}}. \tag{13.10}$$

The expression (13.10), where θ is defined from the equation (13.6), gives the statistical weight as a function of E, N, V for the required approximate microcanonical distribution (13.9). The entropy of the approximate microcanonical ensemble is equal to

$$\begin{aligned}\ln\Omega(E,\ N,\ V) &= \frac{E-F(\theta,\ V,\ N)}{\theta} + \frac{1}{\theta}\sqrt{\langle (H-\langle H\rangle)^2\rangle} = \\ &= S(\theta,\ V,\ N) + \sqrt{C_V},\end{aligned} \tag{13.11}$$

where only the leading term in N is kept, and $S(\theta,V,N)$ is the entropy of the canonical ensemble.

Thus, the difference in the entropies calculated with the approximate microcanonical distribution (13.9) and with the canonical distribution is equal to $\sqrt{C_V}$. If the fluctuations are normal, i.e., $\sqrt{C_V}\sim\sqrt{N}$, then the last term in (13.11) gives a correction which vanishes for the limiting transition

$$\lim_{N\to\infty} \ln \frac{\Omega(E,\ N,\ V)}{N} \qquad \left(\frac{V}{N} = \mathrm{const}\right).$$

The temperature θ is connected to the statistical weight by the relation

$$\frac{1}{\theta} = \frac{\partial}{\partial E}\ln\Omega(E,\ N,\ V) - \frac{1}{C_V}\left(\frac{\partial\sqrt{C_V}}{\partial\theta}\right)_{V,\,N}, \tag{13.12}$$

which is obtained by substituting F from (13.11) into (13.6). From (13.12) it follows that in the thermodynamic limit the inverse temperature is equal to the derivative of the entropy of the approximate microcanonical ensemble with respect to energy.

The relations (13.11) and (13.6) allow one to calculate all thermodynamic quantities for the approximate microcanonical distribution, if they are known for the canonical distribution. For example, for the pressure and chemical potential we obtain

$$\left.\begin{aligned} \frac{p}{\theta} &= \frac{\partial}{\partial V}\ln\Omega(E, N, V) - \left(\frac{\partial\sqrt{C_V}}{\partial V}\right)_{\theta, N} + \frac{1}{C_V}\left(\frac{\partial\sqrt{C_V}}{\partial\theta}\right)_{V, N}\left(\frac{\partial\bar{E}}{\partial V}\right)_{\theta, N}, \\ \frac{\mu}{\theta} &= -\frac{\partial}{\partial N}\ln\Omega(E, N, V) + \left(\frac{\partial\sqrt{C_V}}{\partial N}\right)_{\theta, V} - \frac{1}{C_V}\left(\frac{\partial\sqrt{C_V}}{\partial\theta}\right)_{V, N}\left(\frac{\partial\bar{E}}{\partial N}\right)_{V, \theta}. \end{aligned}\right\} \qquad (13.13)$$

The second and third terms on the right hand sides of equations (13.13) represent the difference in the pressure and the chemical potential (divided by θ) calculated using the canonical and microcanonical distributions (13.9). This difference is small, of the order of $1/\sqrt{N}$, and disappears in the limit $N\to\infty$.

We must turn our attention to a special case. For a system composed of a liquid in equilibrium with a saturated vapor at constant pressure, the temperature is constant independent of the energy imparted to the system. In this case, as was noted already by Gibbs [24], the specific heat is infinite. For such a system our derivation of the equivalence of the canonical and microcanonical distributions is invalid.

Let us note, however, that systems with such properties can be obtained only after the transition to the thermodynamic limit $N\to\infty$, $V\to\infty$ (V/N=const). Therefore it is impossible to substitute $C_V=\infty$ into the formula (13.11); but rather it is necessary to estimate the order of magnitude of the approach of C_V to infinity and to carry out the transition to the thermodynamic limit.

As at the present time there exists no satisfactory theory of condensation, we cannot generalize the theorem on the equivalence of statistical ensembles to the case of systems consisting of several phases in equilibrium.

We shall make an observation on the meaning of the thermodynamic limit for the case in which there exists surface energy. It is well known that the thermodynamic method can be successfully applied to surface phenomena and there exists a statistical thermodynamics of surface phenomena [25]. In the thermodynamic limit for the free energy it is necessary to consider in addition to the volume terms also terms of a higher order of smallness, proportional to the surface of the system, i.e., in the expression for the free energy it is necessary to keep terms of the order of

$$F \cong Vf + Sf_S,$$

where f and f_s are the densities of volume and surface energy, and S is the surface of the system. In order that this be possible it is necessary that the energy fluctuations be significantly smaller than the surface energy, i.e.,

$$\theta\sqrt{C_V} \ll Sf_S.$$

Since $C_V \sim N$, $S \sim N^{2/3}$, then we have

$$\lim_{N\to\infty} \frac{\sqrt{C_V}}{S} = \lim_{N\to\infty} \frac{1}{N^{1/6}} = 0,$$

i.e., the energy fluctuations are small compared to the surface energy. Thus, one can take the surface energy into account while neglecting fluctuations. This estimate shows that statistical thermodynamics of surface phenomena is possible, despite fluctuations of extensive quantities.

13.2. Thermodynamic Equivalence of Gibbs Grand Canonical and Canonical Ensemble.

Let systems with variable particle number in a thermostat be described by the Gibbs grand canonical distribution (9.38). Their thermodynamic properties are defined by the statistical sum (9.39), which is related to the statistical sum of the canonical ensemble (13.1) by the relation

$$Q(\theta, \mu, V) = \sum_{N \geqslant 0} \lambda^N Q(\theta, V, N) \equiv Q(\lambda), \tag{13.14}$$

where

$$\lambda = e^{\mu/\theta} \tag{13.14a}$$

is the absolute activity. Here, as earlier, we are using the same letter Q for the statistical sum of the Gibbs grand canonical and canonical ensembles, distinguishing them only by the arguments on which they depend.

Considering λ as a complex quantity, we obtain the analytic continuation of the function Q(λ) into the complex region.

The inverse of formula (13.14) has the form

$$Q(0, V, N) = \frac{1}{2\pi i} \oint Q(\lambda) \frac{d\lambda}{\lambda^{N+1}}, \tag{13.15}$$

where the contour of integration encloses the point $\lambda=0$. Indeed, substituting (13.14) into (3.15), we verify that only one term in the sum, $N_1=N$, is non-zero, and the contour integral is equal to the residue at the point $\lambda=0$. The method of Darwin and Fowler [16] is based on an application of the inversion formula (13.15).

We introduce in place of Q(λ) the function (9.40)

$$\Omega(\lambda) = -\theta \ln Q(\lambda), \tag{13.16}$$

which plays the role of the thermodynamic potential for the Gibbs grand ensemble (Ω=-pV), and we rewrite (13.15) in the form

$$Q(\theta, V, N) = \frac{1}{2\pi i} \oint \exp\left\{ -\frac{Nv\Omega(\lambda)}{\theta V} \right\} \frac{d\lambda}{\lambda^{N+1}} = \frac{1}{2\pi i} \oint e^{N\varphi(\lambda)} \frac{d\lambda}{\lambda}, \tag{13.17}$$

where

$$\varphi(\lambda) = -\frac{v\Omega(\lambda)}{\theta V} - \ln \lambda, \qquad v = \frac{V}{N}. \tag{13.17a}$$

The function φ(λ) approaches a finite limit as N→∞,v=const, because the ratio Ω(λ)/V is finite in the thermodynamic limit. In addition, φ(λ) is assumed to be analytic in the region Reλ>0 of the complex λ plane. Therefore the integral (13.17) can be estimated by the saddle-point method, as in the preceding paragraph. As a result we obtain

$$Q(\theta, V, N) = \frac{\exp(N\varphi(\lambda_0))}{\lambda_0 \sqrt{2\pi N\varphi''(\lambda_0)}}, \tag{13.18}$$

where λ_0 is the real positive root of the equation

$$\frac{\partial \varphi(\lambda_0)}{\partial \lambda} = 0, \tag{13.19}$$

which can be rewritten using (13.17a) in the form

$$\frac{1}{v} = -\frac{1}{V\theta} \lambda_0 \frac{\partial \Omega(\lambda_0)}{\partial \lambda}, \tag{13.19a}$$

or

$$N = -\frac{\partial \Omega}{\partial \mu} = \overline{N}, \text{ where } \mu_0 = \theta \ln \lambda_0. \tag{13.19b}$$

The expression (13.18) can be considered as a statistical sum of the approximate canonical ensemble with particle number equal, in accordance with (13.19b), to the average particle number in the grand canonical ensemble.

In order to apply the saddle-point method it is necessary that for motion parallel to the imaginary axis and through the point λ_0 (see section 3.3) a true maximum exists at that point, i.e., satisfication of the condition

$$\frac{\partial^2\varphi(\lambda_0)}{\partial\lambda^2} > 0, \qquad (13.20)$$

which can be written in the form

$$\frac{\partial\bar{N}}{\partial\mu} > 0. \qquad (13.20a)$$

In general this condition is satisfied, because using (12.4) we have

$$\frac{\partial\bar{N}}{\partial\mu} = \frac{1}{\theta}\overline{(N-\bar{N})^2} > 0. \qquad (13.21)$$

We write the expression (13.18) for the statistical sum in the form

$$Q(\theta, V, N) = Q(\theta, \mu, V)\frac{\exp(-N\mu/\theta)}{\sqrt{2\pi\frac{\partial\bar{N}}{\partial\mu}\theta}} = \frac{Q(\theta, \mu, V)\exp(-N\mu/\theta)}{\sqrt{2\pi(\bar{N^2}-(\bar{N})^2)}} \qquad (13.22)$$

$$(\mu = \mu_0).$$

If the fluctuation in particle number is small, then in (13.22) only the leading terms need be kept, and we obtain

$$Q(\theta, V, N) \cong Q(\theta, \mu, V)\exp(-N\mu/\theta), \qquad (13.23)$$

because the discarded term gives no contribution in the thermodynamic limit.

As is well known, in a region of coexisting phases the absolute activity λ is independent of specific volume, i.e.,

$$\frac{\partial\lambda}{\partial v} = 0, \quad \textbf{or} \quad \frac{1}{V}\frac{\partial\bar{N}}{\partial\lambda} = \infty, \quad \textbf{as} \quad v = V/\bar{N}.$$

In this case we cannot make any conclusion from formula (13.22) about the thermodynamic equivalence of the grand canonical and canonical ensembles. However it must be noted that in formula (13.22) one cannot substitute $1/V\ \partial\bar{N}/\partial\lambda = \infty$, because, as we have already noted in the previous paragraph, systems with such properties can be obtained only after the transition to the thermodynamic limit, but because of the absence of a consistent theory of condensation, we cannot estimate the order of magnitude of the growth of $\partial\bar{N}/\partial\lambda$.

Using (13.22) and (13.20) all thermodynamic functions can be calculated. For the free energy we obtain

$$F(\theta,\ V,\ \bar{N}) = \Omega(\theta,\ \mu,\ V) + \mu\bar{N} + \frac{\theta}{2}\ln\left(2\pi\theta\frac{\partial\bar{N}}{\partial\mu}\right), \tag{13.24}$$

where μ is defined from the equation (13.19b). Substituting (13.24) into (13.19b), but we shall have for the chemical potential the expression

$$\mu = \left(\frac{\partial F}{\partial\bar{N}}\right)_{V,\theta} - \frac{\theta}{2}\frac{\partial^2\bar{N}}{\partial\mu^2}\left(\frac{\partial\bar{N}}{\partial\mu}\right)^{-2}. \tag{13.25}$$

Differentiating (13.24) with respect to V and θ, and using (13.19b) and (13.25), we obtain for the pressure and the entropy, respectively,

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{\theta,\mu} = -\left(\frac{\partial F}{\partial V}\right)_{\theta,\bar{N}} - \frac{\theta}{2}\frac{\partial}{\partial\mu}\left\{\frac{\partial\bar{N}}{\partial V}\left(\frac{\partial\bar{N}}{\partial\mu}\right)^{-1}\right\}, \tag{13.26}$$

$$\begin{aligned} S &= -\left(\frac{\partial\Omega}{\partial\theta}\right)_{V,\mu} = \\ &= -\left(\frac{\partial F}{\partial\theta}\right)_{V,\bar{N}} - \frac{\theta}{2}\left(\frac{\partial^2\bar{N}}{\partial\mu^2}\right)\left(\frac{\partial\bar{N}}{\partial\theta}\right)\left(\frac{\partial\bar{N}}{\partial\mu}\right)^{-2} + \frac{1}{2}\frac{\partial}{\partial\theta}\left\{\theta\ln\left(2\pi\theta\frac{\partial\bar{N}}{\partial\mu}\right)\right\}. \end{aligned} \tag{13.27}$$

In the expressions (13.25)-(13.27) the dominant contribution is given by the first terms on the right hand sides, and the remaining terms are negligibly small in the thermodynamic limit. Neglecting these small terms, we obtain the well-known relations (11.23), (11.20a), (11.18), i.e., the chemical potential, pressure, and the entropy are the same whether calculated with the statistical sum (13.14) of the Gibbs grand ensemble or with the statistical sum (13.23). Thus, the Gibbs grand ensemble is equivalent to the canonical ensemble in the thermodynamic respect.

§ 14. Limiting Transition from Quantum Statistics to Classical Statistics

For sufficiently high temperatures and sufficiently low densities, when quantum effects can be neglected, the Gibbs quantum mechanical ensemble goes over into the classical ensemble, and the statistical sum of the quantum ensemble (9.11) goes over into the statistical integral of the classical ensemble (3.8). This problem was considered by Wigner [12], Uhlenbeck and Gropper [26], and Kirkwood [27]. We shall follow the last work.

14.1. Limiting Transition for Statistical Sums.

Let us restrict ourserves for simplicity to a system composed of N monatomic molecules with mass m in a volume V, interacting by means of the potential

$$v(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \frac{1}{2} \sum_{i \neq j} \phi(\boldsymbol{x}_i - \boldsymbol{x}_j).$$

For the Gibbs canonical ensemble the statistical sum for the system has the form

$$Q = \sum_k \int \Psi_k^*(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)\, e^{-\beta H}\, \Psi_k(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)\, d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_N, \tag{14.1}$$

where

$$H = -\sum_j \frac{\hbar^2}{2m} \nabla_j^2 + v(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N). \tag{14.2}$$

Ψ_k is a complete set of functions with the required symmetry. Here and in what follows we shall not explicitly write out the arguments θ,V,N, on which Q depends.

Since Q does not depend on the choice of the functions Ψ_k, any complete orthonormal set of functions can be chosen, symmetric in the case of Bose systems and antisymmetric in the case of Fermi systems. We shall choose for the Ψ_k a symmetrized or antisymmetrized product of plane waves, normalized in a volume V:

$$\Psi_p = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}} (\pm 1)^{\mathcal{P}} \mathcal{P} \varphi_{p_1}(\boldsymbol{x}_1) \ldots \varphi_{p_N}(\boldsymbol{x}_N),$$
$$\varphi_{p_j}(\boldsymbol{x}_j) = V^{-1/2} e^{\frac{i}{\hbar}(p_j x_j)}, \qquad p = (p_1, \ldots, p_N). \tag{14.3}$$

The plus sign corresponds to Bose statistics, and the minus sign corresponds to Fermi statistics (for simplicity we do not consider the spin of the particles). The operator $\mathcal{P}$ denotes a permutation of the quantities $x_1, \ldots, x_N$ or what is the same thing, of the quantities $p_1, \ldots, p_N$; $(\pm 1)^{\mathcal{P}} = 1$ for a Bose gas and +1 or -1, depending on the sign of the permutation, for a Fermi gas. The factor $1/\sqrt{N!}$ guarantees the normalization of the functions Ψ_p to unity. In this regard,

$$\int \Psi_p^* \Psi_p \, dx_1 \ldots dx_N = \\ = \frac{1}{V^N N!} \sum_{\mathcal{P}, \mathcal{P}'} (\pm 1)^{\mathcal{P} + \mathcal{P}'} \int \exp\left\{-\frac{i\mathcal{P}}{\hbar} \sum (p_j x_j)\right\} \exp\left\{\frac{i\mathcal{P}'}{\hbar} \sum (p_j x_j)\right\} \times \\ \times dx_1 \ldots dx_N = \frac{1}{V^N N!} \sum_{\mathcal{P}} \int dx_1 \ldots dx_N = \frac{1}{N!} \sum_{\mathcal{P}} 1 = 1,$$

because for $\mathcal{P} \neq \mathcal{P}'$ the integral is equal to zero, and $\sum_{\mathcal{P}} 1$ is equal to the number of permutations of N elements.

We choose the single particle wave functions $\varphi_{p_j}(x_j)$ in such a way that they are periodic in a cube with side $L = V^{1/3}$, i.e.,

$$\varphi_{p_j}(x_j^\alpha + L) = \varphi_{p_j}(x_j^\alpha),$$

in which case the quantum numbers p_j can take on only the values

$$p_j^\alpha = \frac{2\pi\hbar}{L} n_{p_j^\alpha},$$

where $n_{p_j^\alpha}$ are whole numbers 0, ±1, ±2, ... Thus, there are $V \, dp_j/(2\pi\hbar)^3$ quantum states in the element of phase volume of each particle

The summation over the quantum states p_j^α in (14.1) can be replaced by integration over momentum, because the number of particles is very large, and the spectrum is practically continuous:

$$\sum_{p_1, \ldots, p_N} \rightarrow \frac{1}{N!} \frac{V^N}{(2\pi\hbar)^{3N}} \int \ldots \int dp_1 \ldots dp_N, \qquad (14.4)$$

where the sum over the momenta denotes a summation over all distinct states. The factor 1/N! compensates for the fact that a permutation of particles does not change the state; cf. (1.5b)[1]. In going over from sums to integrals we are neglecting the possible case of a degenerate Bose gas for which in the ground state there can be a macroscopically large number of particles. This case must be considered separately.

Using (14.3) and (14.4) we write the statistical sum (14.1) in the form

$$Q = \frac{1}{(N!)^2}\frac{1}{(2\pi\hbar)^{3N}}\int\ldots\int\sum_{\mathcal{P},\mathcal{P}'}(\pm 1)^{\mathcal{P}+\mathcal{P}'}\exp\left\{-\frac{i\mathcal{P}}{\hbar}\sum_j(p_jx_j)\right\}\times$$
$$\times e^{-\beta H}\exp\left\{\frac{i\mathcal{P}'}{\hbar}\sum_j(p_jx_j)\right\}dx\,dp, \qquad (14.5)$$

where $$dx\,dp = dx_1\ldots dx_N\,dp_1\ldots dp_N.$$

Since the integral in (14.5) is unchanged upon a permutation of the variables of integration, which is only a change in notation, the double sum over the permutations can be replaced by a single sum. Using the fact that

$$\sum_{\mathcal{P},\mathcal{P}'}\to N!\sum_{\mathcal{P}},$$

we obtain

$$Q = \int\ldots\int\sum_{\mathcal{P}}(\pm 1)^{\mathcal{P}}\exp\left\{-\frac{i\mathcal{P}}{\hbar}\sum_j(p_jx_j)\right\}e^{-\beta H}\exp\left\{\frac{i}{\hbar}\sum_j(p_jx_j)\right\}d\Gamma, \qquad (14.6)$$

where

$$d\Gamma = \frac{dp\,dx}{N!\,(2\pi\hbar)^{3N}}. \qquad (14.7)$$

Now the statistical sum is represented in the form of an integral over the entire phase space of N particles, which is similar to the statistical integral of classical statistical mechanics (3.8). The element of integration (14.7) has precisely the same form as (1.5b), which was assumed earlier in classical statistical mechanics without rigorous proof. To calculate the integral (14.6) it is necessary to determine explicitly the results of the action of the operator $e^{-\beta H}$ on the function $\exp\left\{\frac{i}{\hbar}\sum_j(p_jx_j)\right\}$

---

[1] This factor was at first mistakenly omitted by Kirkwood [27], but was noticed by him and corrected [27a]. However, this mistake has passed into textbooks [17].

i.e., to find the function

$$u = e^{-\beta H} e^{\frac{i}{\hbar}(px)}, \qquad (px) = \sum_j (p_j x_j). \tag{14.8}$$

Below we shall calculate functions of a somewhat more general type:

$$u(\mathscr{P}) = e^{-\beta H} e^{\frac{i\mathscr{P}}{\hbar}(px)}, \tag{14.9}$$

where $\mathscr{P}$ is the permutation operator for the coordinates of the particles. For $\mathscr{P}=1$ (14.9) coincides with (14.8). We shall need these functions later at the end of this paragraph in order to calculate the statistical operators in the quasi-classical approximation, i.e., when quantum effects can be considered as small corrections to the classical. The functions (14.9) satisfy the equation

$$\frac{\partial u}{\partial \beta} = -Hu \qquad \left(\beta = \frac{1}{\theta}\right) \tag{14.10}$$

with the initial condition

$$u\big|_{\beta=0} = e^{\frac{i\mathscr{P}}{\hbar}(px)}. \tag{14.10a}$$

Equation (14.10) is called the Bloch equation and plays an important role in quantum statistics. It is applied not only with the initial condition (10.10a), but also with different initial conditions. For example, the operator

$$U = e^{-\beta H}$$

also satisfies equation (14.10), but with the initial condition

$$U\big|_{\beta=0} = 1.$$

If in the Bloch equation the replacement $\beta \to it/\hbar$ is made, then it has the same form as the Schroedinger equation. This formal analogy is convenient for transferring the methods developed in quantum mechanics and in the quantum theory of fields into quantum statistics. In particular, following this analogy, to find the solution of equation (14.10) we shall later make use of the method of expansion in powers of Planck's constant $\hbar$, i.e., a quasi-classical approximation, an analog of the well-known method of Wentzel-Kramers-

-Brillouin in quantum mechanics.

Let us replace in equation (14.10) the unknown function u by w:

$$u(\mathscr{P}) = e^{-\beta H(p,x)} e^{\frac{i\mathscr{P}}{\hbar}(p,x)} w(p, x, \beta), \tag{14.11}$$

where w(p,x,β) is a function of the variables p, x, β, and H(p,x) is a function of p, x and not an operator. Then the equation (14.10) is brought to the form

$$\frac{\partial w}{\partial \beta} = e^{\beta H(p,x)} \left\{ \frac{\hbar^2}{2m} \nabla^2 (e^{-\beta H(p,x)} w) + \frac{i\hbar}{m} \mathscr{P}(p\nabla) e^{-\beta H(p,x)} w \right\}, \tag{14.12}$$

where

$$\nabla = \left\{ \frac{\partial}{\partial x_1} \cdots \frac{\partial}{\partial x_N} \right\},$$

with the initial condition

$$w|_{\beta=0} = 1, \tag{14.12a}$$

or, since

$$H(p, x) = \sum_j \frac{p_j^2}{2m} + v(x_1, \ldots, x_N) = T(p) + v(x),$$

to the form

$$\frac{\partial w}{\partial \beta} = e^{\beta v(x)} \left\{ \frac{i\hbar}{m} \mathscr{P}(p\nabla) e^{-\beta v(x)} w + \frac{\hbar^2}{2m} \nabla^2 (e^{-\beta v(x)} w) \right\}. \tag{14.13}$$

The small parameter ħ is contained on the right hand side of this equation. In fact, as we shall verify later, the role of the small parameter is played not by ħ itself, but by the dimensionless ratio of the deBroglie wave length, corresonding to the average thermal speed, to the average distance between molecules.

Equation (14.13) can be solved using an expansion in powers of ħ:

$$w = \sum_{n \geqslant 0} \hbar^n w_n. \tag{14.14}$$

To do this it is convenient to write it in the form of an integral equation

$$w = 1 + \frac{i\hbar}{m} \int_0^\beta e^{v(x)\tau} [\mathcal{P}(p\nabla) e^{-v(x)\tau} w] \, d\tau + \\ + \frac{\hbar^2}{2m} \int_0^\beta e^{v(x)\tau} \nabla^2 (e^{-v(x)\tau} w) \, d\tau,$$

from which it is easy to find the coefficients $w_0, w_1, \ldots$ by the method of successive approximations:

$$\begin{aligned} w_0 &= 1; \\ w_1 &= \frac{i}{m} \int_0^\beta e^{v(x)\tau} \mathcal{P}(p\nabla) e^{-v(x)\tau} d\tau = \frac{-i\beta^2}{2m} \mathcal{P}(p\nabla) v(x); \\ w_2 &= \frac{1}{2m^2} \int_0^\beta e^{v(x)\tau} \mathcal{P}(p\nabla) e^{-v(x)\tau} \mathcal{P}(p\nabla) v(x) \tau^2 d\tau + \\ &\quad + \frac{1}{2m} \int_0^\beta e^{v(x)\tau} \nabla^2 e^{-v(x)\tau} d\tau = \\ &= -\frac{1}{2m} \left\{ \frac{\beta^2}{2} \nabla^2 v - \frac{\beta^3}{3} (\nabla v)^2 - \frac{\beta^3}{3m} (\mathcal{P}(p\nabla))^2 v + \frac{\beta^4}{4m} (\mathcal{P}(p\nabla) v)^2 \right\} \end{aligned}$$

etc. (14.15)

Using the resulting expressions and setting $\mathcal{P}=1$, we write the statistical sum (14.6) in the form

$$Q = \int e^{-\beta H(p,x)} [1 + w_1 h + w_2 h^2 + \ldots] \, d\Gamma + \\ + \sum_{\mathcal{P} \neq 1} (\pm 1)^{\mathcal{P}} \int \left[\mathcal{P} e^{-\frac{i}{h}(px)} \right] e^{\frac{i}{h}(px)} e^{-\beta H(p,x)} \times \\ \times [1 + w_1 h + w_2 h^2 + \ldots] \, d\Gamma, \qquad (14.16)$$

where $x=(x_1, \ldots, x_N)$, $p=(p_1, \ldots, p_N)$, and w_i are calculated with $\mathcal{P}=1$. We have written out separately the first integral, corresponding to the identity permutation.

Carrying out the operation of permutation of the particle coordinates and retaining only pairwise permutations, we transform (14.16) to the form

$$
\begin{aligned}
Q = \int e^{-\beta H(p,x)}\left[1 + w_1\hbar + w_2\hbar^2 + \ldots\right] d\Gamma \pm \\
\pm \sum_{k \neq l} \int e^{-\beta H(p,x)} e^{\frac{i}{\hbar}(p_k - p_l,\, x_k - x_l)} \times \\
\times \left[1 + w_1\hbar + w_2\hbar^2 + \ldots\right] d\Gamma.
\end{aligned}
\qquad (14.17)
$$

It is easy to carry out the integration over $p_1, \ldots, p_N$ in formula (14.17), if use is made of the relation

$$
\int_{-\infty}^{\infty} e^{-\alpha x^2 + i\gamma x}\, x\, dx = \frac{1}{i}\frac{\partial}{\partial\gamma} \int_{-\infty}^{\infty} e^{-\alpha x^2 + i\gamma x}\, dx = \frac{1}{i}\sqrt{\frac{\pi}{\alpha}}\,\frac{\partial}{\partial\gamma} e^{-\frac{\gamma^2}{4\alpha}}.
$$

Finally for the statistical sum we obtain the expression

$$
\begin{aligned}
Q = \frac{(2\pi m\theta)^{3N/2}}{(2\pi\hbar)^{3N}\, N!} \int e^{-\beta v} \Big\{ 1 - \frac{\hbar^2\beta^2}{12m} \sum_{i} \Big(\nabla_j^2 v - \frac{\beta}{2}(\nabla_j v)^2\Big) \pm \\
\pm \sum_{i \neq k} \exp\Big\{ -\frac{m|\boldsymbol{x}_{ik}|^2}{\beta\hbar^2} \Big\} \Big[1 + \frac{\beta}{2}\boldsymbol{x}_{ik} \cdot (\nabla_i v - \nabla_k v) + \ldots \Big] \Big\} d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_N,
\end{aligned}
\qquad (14.18)
$$

$$
\boldsymbol{x}_{ik} = \boldsymbol{x}_i - \boldsymbol{x}_k.
$$

The first two terms in formula (14.18) corresponding to the identity permutation, were first obtained by Wigner [12], and the remaining two terms taking into account pairwise permutations, were obtained by Uhlenbeck and Gropper [26].

If only the first term is kept in (14.18), then the statistical sum goes over into the statistical integral of classical statistical mechanics (3.8):

$$
Q_{\mathrm{cl}} = \frac{(2\pi m\theta)^{3N/2}}{(2\pi\hbar)^{3N}\, N!} \int e^{-\beta v(\boldsymbol{x}_1 \ldots \boldsymbol{x}_N)}\, d\boldsymbol{x}_1 \ldots d\boldsymbol{x}_N = \int e^{-\beta H(p,x)}\, d\Gamma. \qquad (14.19)
$$

Thus, if classical statistical mechanics is regarded as the limiting case of quantum statistical mechanics, then we obtain the correct expression for the statistical integral (3.8), which corresponds to the normalization of the classical distribution functions (1.5a). This is a good definition in that it does not lead to the Gibbs paradox.

The second term in (14.18) gives the quantum corrections connected with the interaction, but without taking into account exchange effects. The third term is caused by quantum exchange and is non-zero even in the absence of interaction, i.e., for an ideal quantum gas. The last term is connected both with exchange and with the interaction.

The terms connected with exchange contain the exponential factor

$$\exp\left\{-\frac{|x_{ik}|^2 m}{\beta\hbar^2}\right\},$$

and therefore they are small if the density is not too large, in which case

$$\overline{|x^2|} \gg \frac{\beta\hbar^2}{m} = \frac{\hbar^2}{m\theta}, \tag{14.20}$$

where $\overline{|x^2|}$ is the mean square distance between particles, i.e., when the average distance between particles is significantly larger than the deBroglie wave length $\hbar/\sqrt{m\theta}$ corresponding to particle energy θ.

At low temperatures or at high densities, when condition (14.20) is not satisfied, the statistical sum and statistical integral can be quite different and degeneracy of quantum gases sets in.

14.2. Limiting Transition for Equilibrium Statistical Operators.

There is no difficulty in obtaining quasi-classical expansions, similar to (14.16), for equilibrium statistical operators.

Using the plane waves (14.3) the statistical operator in the coordinate x-representation can be written in the form

$$\begin{aligned}\rho(x_1, \ldots, x_N, x'_1, \ldots, x'_N) &= \\ &= \sum_p \Psi^*_p(x'_1, \ldots, x'_N)\, e^{-(H-F)/\theta}\, \Psi_p(x_1, \ldots, x_N).\end{aligned} \tag{14.21}$$

It is especially simple to find the statistical operator in a mixed coordinate-momentum representation:

$$\rho(x_1, \dots, x_N, p_1, \dots, p_N) = \\ = \frac{1}{(2\pi\hbar)^{3N}} \int \rho(x_1, \dots, x_N, x'_1, \dots, x'_N) \times \\ \times \exp\left\{-\frac{1}{i\hbar}\sum_j (p_j x'_j)\right\} dx'_1 \dots dx'_N. \tag{14.21a}$$

Substituting (14.21) into this expression and using the fact that

$$\frac{1}{(2\pi\hbar)^{3N}} \int \exp\left\{\frac{i}{\hbar}\sum_j (x'_j, p'_j - \mathscr{P}p_j)\right\} dx'_1 \dots dx'_N = \delta(p' - \mathscr{P}p),$$

we obtain

$$\rho(x_1, \dots, x_N, p_1, \dots, p_N) = \\ = \frac{1}{N!\,(2\pi\hbar)^{3N}} \sum_{\mathscr{P}} (\pm 1)^{\mathscr{P}} \int \delta(p' - \mathscr{P}p)\, e^{-(H-F)/\theta}\, e^{\frac{i}{\hbar}(p'x)}\, dp'_1 \dots dp'_N,$$

or

$$\rho(x_1, \dots, x_N, p_1, \dots, p_N) = \\ = \frac{1}{N!\,(2\pi\hbar)^{3N}} \sum_{\mathscr{P}} (\pm 1)^{\mathscr{P}}\, e^{-\frac{H-F}{\theta}}\, e^{\frac{i\mathscr{P}}{\hbar}(px)}. \tag{14.22}$$

Thus, to calculate the statistical operator in the mixed representation it is necessary to find the function (14.9), the calculation of which we considered in the previous paragraph.

Using the relations (14.9) and (14.11), we obtain

$$\rho(x_1, \dots, x_N, p_1, \dots, p_N) = \\ = \frac{1}{N!\,(2\pi\hbar)^{3N}}\, e^{-\frac{H(p,\,x)-F}{\theta}} \sum_{\mathscr{P}} (\pm 1)^{\mathscr{P}}\, e^{\frac{i\mathscr{P}}{\hbar}(px)} (1 + w_1\hbar + w_2\hbar^2 + \dots), \tag{14.22a}$$

where w_1, w_2 are given by formulas (14.15). Retaining only the first term in formula (14.22a), we obtain the classical distribution function except for an inessential phase factor:

$$\rho(x_1, \ldots, x_N, p_1, \ldots, p_N) = \\ = \frac{1}{N!\,(2\pi h)^{3N}} e^{-\frac{H(p,x)-F}{\theta}} e^{\frac{i(px)}{h}}, \tag{14.23}$$

$$|\rho(x, p)|\,dx\,dp = e^{-\frac{H(p,x)-F}{\theta}} d\Gamma.$$

In order to avoid such phased factors, Wigner [12] proposed a somewhat different definition for the operator in the mixed representation. Wigner introduced the function

$$f(x_1, \ldots, x_N, p_1, \ldots, p_N) = \\ = \frac{1}{(2\pi h)^{3N}} \int \rho\left(x_1 + \frac{\xi_1}{2}, \ldots, x_N + \frac{\xi_N}{2}, \; x_1 - \frac{\xi_1}{2}, \ldots, x_N - \frac{\xi_N}{2}\right) \times \\ \times \exp\left\{\frac{i}{h}\sum_j (p_j \xi_j)\right\} d\xi_1 \ldots d\xi_N. \tag{14.24}$$

The integrals of this function over all x and all p have the form of the diagonal elements of the density matrix in the x- and p-representations, respectively:

$$\int f(x, p)\,dp = \rho(x, x), \qquad \int f(x, p)\,dx = \rho(p, p), \tag{14.25}$$

where $x=(x_1,\ldots,x_N)$, $p=(p_1,\ldots,p_N)$. We obtain the relationship (14.25) by making the change of variables $x_i-(\xi_i/2)=x'_i$, $x_i+(\xi_i/2)=x''_i$.

The function f(x,p) cannot, of course, be considered as a distribution function for the coordinates and momenta. Its integrals give distribution functions for coordinates and momenta, but the function itself can be negative and does not have the meaning of a probability density.

The limiting transition to classical statistics can be discussed using the statistical operator in the mixed Wigner representation f(x,p), as was done by Wigner himself [12].

Thus, we have verified that the quantum mechanical Gibbs canonical ensemble goes over into the classical ensemble upon taking $\hbar \to 0$. One can also consider the more general question of the transition of the quantum Poisson brackets to the classical Poisson brackets and of the transition of the statistical operators into distribution functions, when the system is described by an equilibrium Gibbs ensemble. This question is discussed in reference [28], where it is shown that the quantum Poisson brackets go over into the classical Poisson brackets as $\hbar \to 0$, but the limiting transition for the statistical operators must be carried out with "classical symmetry." I.e., the statistical operators are symmetric only with respect to simultaneous permutation of both groups of variables $x_1, \ldots, x_N$ and $x'_1, \ldots, x'_N$, because the quantum symmetry property (with respect to permutations of only one group of the variables) has no classical analog.

This question is essentially related to the limiting transition from quantum mechanics to classical mechanics, and we shall not consider it here.

CHAPTER III

IRREVERSIBLE PROCESSES INITIATED BY MECHANICAL PERTURBATIONS

§ 15. Reaction of a System to External Mechanical Perturbations

Up to this time we have considered only equilibrium processes. Let us go now to a study of nonequilibrium, irreversible processes.

One of the fundamental problems of the theory of irreversible processes is the study of the influence on statistical ensembles of various perturbations which disturb the equilibrium. We have essentially already considered the influence of a change of the external parameters earlier in Chapters I and II, which were devoted to equilibrium statistical mechanics, when we derived the thermodynamic equalities in §§ 5 and 11. But in doing this we made an assumption about the infinitely slow, quasi-static character of the change of the parameters, according to which at each moment of time the system can be considered to be in statistical equilibrium. A change of the external parameters is also considered in the theory of irreversible processes, but the change need not be infinitely slow.

A nonequilibrium ensemble can arise, for example, from an equilibrium ensemble (described therefore by one of the Gibbs distributions) if some external processes begin to influence the ensemble, leading to a change of the parameters which define the ensemble (volume, particle number, temperature, chemical potential, etc.). The source of these perturbations might be work carried out on the system, through a change of its volume, or the interaction with different ensembles (having different temperature or chemical potential), or, finally, the switching on of external fields which act directly on the particles of the system. This last example of an irreversible process, initiated by a mechanical perturbation, will be considered in the present chapter. This is the easiest case in which to explain the mechanism of the appearance of irreversibility.

In general a change of the external parameters influences the distribution function (or statistical operator) indirectly; it creates a state of statistical nonequilibrium which then approaches an equilibrium state, if there are no effects which inhibit this approach. Only in the case in which the perturbation is caused by external fields does it have a direct influence on the distribution function; this is the reason for the relative simplicity of the study of such perturbations.

We shall make several comments about terminology. In macroscopic thermodynamics work carried out on the system, for example, in a change of the volume by a movable piston (mechanical contact), is called a mechanical effect. A perturbation caused by contact of the system with other thermodynamic systems having different temperatures (thermal contact) is called a thermal effect. This type of contact includes contact with a reservoir with which exchange of matter (material contact) is possible. In the statistical thermodynamics of irreversible processes a somewhat different terminology is customary. One calls mechanical perturbations only those perturbations which represent the action of external fields and which can be completely described by adding to the Hamiltonian the corresponding interaction energy of the system with the field. Perturbations which in general do not admit of such a representation are in the terminology of Kubo [1-4] called thermal perturbations. In what follows we shall follow this terminology. Work carried out on the system by a change of its volume (or other parameters, not linked to a real external field) will be referred to in what follows as thermal perturbations in accordance with accepted terminology.

Let us note that one can sometimes formally describe thermal perturbations as the result of several mechanical perturbations, if one introduces the corresponding fictitious fields [5-9]. For example, a diffusion current can be considered as a consequence of switching on an auxiliary gravitational or centrifugal field [5], a viscous current as a consequence of the motion of the walls of the container [5]. Depending on the character of this motion, one can obtain either sheer viscosity [5], or second viscosity [6]. To take into account an inhomogeneous temperature one can introduce an auxiliary gravitational field [7], because in accordance with the general theory of relativity the temperature in a gravitational field is nonhomogeneous even in a state of statistical equilibrium.

The arbitrariness of the replacement of thermal perturbations by mechanical perturbations should be noted. In reality the motion of the walls of the container cannot be instantaneously transferred to the molecules, and the influence of the motion is indirect. It creates a nonequilibrium state, which is propagated at the speed of sound and which cannot be exactly represented as the action of an external field. But in the case of sufficiently slow change of the parameters these analogies, not taken too literally, lead to reasonable results and are very useful. They are based on the fact that mechanical and thermal perturbations can give rise to identical transfer processes.

Let us go now to an exposition of the theory of the linear reaction of statistical systems to mechanical perturbations.

15.1. Linear Reaction of a System (Classical Statistics).

It is easy to analyze the reaction of a statistical ensemble to an external time dependent perturbation for either the classical or the quantum case [1-14]. It is closely connected with the theory of the retarded Green function [15, 12-14]. We discuss this problem first on the basis of classical statistical mechanics (we shall consider the quantum case in the following section).

We shall consider a statistical ensemble of systems with a Hamiltonian $H(p,q)$ which is not explicitly time dependent, and where p,q is the set of coordinates and momenta of all particles. The Hamiltonian includes all possible interactions between the particles. We shall study the reaction of the ensemble to the switching on of an external time dependent perturbation $H_t^1(p,q)$.

The dynamical variable $H_t^1(p,q)$ represents the energy of interaction of the system with the external field. The subscript t denotes only the explicit dependence of the perturbation on time. In addition it has a possible implicit time dependence through the coordinates and momenta of the particles $p(t),q(t)$ in accordance with the equations of motion.

The total Hamiltonian describing the system and its interaction with the field is equal to

$$H(p,q) + H_t^1(p,q). \tag{15.1}$$

The Hamiltonian of the external field which is causing the interaction $H_t^1(p,q)$ is not included here, because the external field is considered to be fixed.

We shall assume that at $t=-\infty$ there is no external perturbation, i.e.,

$$H_t^1(p,q)\big|_{t=-\infty} = 0. \tag{15.1a}$$

The perturbation $H_t^1(p,q)$ can often be represented in the form of a sum

$$H_t^1(p,q) = -\sum_j B_j(p,q)\,F_j(t), \tag{15.2}$$

where the $F_j(t)$ are functions of time but are independent of the coordinates and momenta of the particles - external driving forces, and $B_j(p,q)$ are dynamical variables, not explicitly time dependent, conjugate to the fields $F_j(t)$.

For an adiabatic switching on of a periodic perturbation

$$H_t^1(p,q) = \sum_\omega e^{\varepsilon t - i\omega t} B_\omega(p,q) \qquad (\varepsilon > 0), \tag{15.2a}$$

where ε is a positive infinitesimal quantity, and $B_\omega = B^*_{-\omega}$, because the energy H_t^1 is real. For an instantaneous switching on

[Note: two pages missing from original Russian text - pp.128-129]

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it is necessary to add the initial condition

$$f_1(t)\big|_{t=-\infty} = f_0, \tag{15.10}$$

which follows from (15.5) and (15.5a), because $e^{-itL}f_0 = f_0$, as f_0 is a solution of the Liouville equation. Equation (15.8) contains only the perturbation energy $H^1_t(t)$ on the right hand side, therefore it is convenient for a study of the behavior of the system when there are small perturbations.

It is convenient to write equation (15.8) and the initial condition (15.10) in the form of a single integral equation

$$f_1(t) = f_0 + \int_{-\infty}^{t} \{H^1_{t'}(t'),\ f_1(t')\}\, dt', \tag{15.11}$$

or

$$f(t) = f_0 + \int_{-\infty}^{t} e^{i(t-t')L} \{H^1_{t'},\ f(t')\}\, dt'. \tag{15.11a}$$

If the perturbation H^1_t is small, then the solution of equation (15.11a) can be obtained by the method of iteration, taking f_0 as the zero order approximation. In the first approximation we find

$$f(t) = f_0 + \int_{-\infty}^{t} \{H^1_{t'}(t'-t),\ f_0\}\, dt', \tag{15.12}$$

where the Poisson brackets are equal to

$$\{H^1_t,\ f_0\} = \frac{\partial H^1_t}{\partial q}\frac{\partial f_0}{\partial p} - \frac{\partial H^1_t}{\partial p}\frac{\partial f_0}{\partial q},$$

where a summation over all particles is understood on the right hand side. Noticing that

$$\{H^1_t,\ f_0\} = -\beta\{H^1_t,\ H\} f_0, \qquad \beta = \frac{1}{\theta}, \tag{15.13}$$

we write (15.12) in the form

$$f(t)=f_0\left(1-\beta\int\limits_{-\infty}^{t}\{H^1_{t'}(t'-t),\ H\}\,dt'\right). \tag{15.14}$$

Using (15.12) or (15.14) the average value of any dynamical variable A(p,q) can be calculated to an approximation linear in H^1_t:

$$\langle A\rangle=\int A(p,\ q)\,f(p,\ q,\ t)\,d\Gamma,\text{where}\quad d\Gamma=\frac{dp\,dq}{N!\,(2\pi\hbar)^{3N}}. \tag{15.15}$$

Substituting (15.12) into (15.15) and integrating by parts, we obtain

$$\langle A\rangle=\langle A\rangle_0+\int\limits_{-\infty}^{t}\langle\{A,\ H^1_{t'}(t'-t)\}\rangle_0\,dt', \tag{15.16}$$

where

$$\langle\ldots\rangle_0=\int\ldots f_0\,d\Gamma$$

is an averaging with the equilibrium distribution function.

In principle, formula (15.16) gives the solution to the problem of the reaction of a classical system to a mechanical perturbation. An actual calculation of the right hand side of (15.16) is far from simple however, because it contains the averages of dynamical variables at different moments of time and requires solution of a dynamical problem. In some cases this can be done for systems with a small parameter.

The expression (15.16) describes the retarded reaction of the average values of A to a variable perturbation $H^1_{t'}$. This reaction has a causal character, because the effect of the perturbations turns out to be significant only for $t'<t$, i.e., for perturbations taking place at past times.

It is convenient to extend formally the range of integration in formula (15.16) by introducing the discontinuous function $\theta(t-t')$:

$$\theta(t)=\begin{cases}1 & \text{for} \quad t>0,\\ 0 & \text{for} \quad t<0.\end{cases} \tag{15.17}$$

Then

$$\langle A\rangle=\langle A\rangle_0+\int_{-\infty}^{\infty}\langle\langle AH^{1}_{t'}(t'-t)\rangle\rangle\,dt', \tag{15.18}$$

where

$$\langle\langle AB(t'-t)\rangle\rangle=\theta(t-t')\langle\{A,\ B(t'-t)\}\rangle_0=\theta(t-t')\langle\{A(t),\ B(t')\}\rangle_0 \tag{15.19}$$

is the retarded doubletime Green function of classical statistical mechanics.

The last equality in (15.19) is connected with the fact that the average value of the product of dynamical variables $\langle A(t)B(t')\rangle_0$ (or of the corresponding Poisson brackets) in a statistical equilibrium state depends only on the difference of the time arguments. The dependence of the average of a product of dynamical variables, taken at different moments of time, on only the difference of the times is the stationarity condition, which is well known from the theory of random stationary processes [16, 17]. It implies that in a stationary case the time correlation functions cannot depend on the choice of the time origin, i.e.,

$$\langle A(t+\tau)B(t'+\tau)\rangle=\langle A(t)B(t')\rangle,$$

from which, putting $\tau=-t$, we obtain

$$\langle A(t)B(t')\rangle=\langle AB(t'-t)\rangle,$$

where the averaging is carried out over a stationary state.

This property is easy to demostrate for averaging over an equilibrium state. By definition we have

$$\langle A(t_1)B(t_2)\rangle_0=$$
$$=Q^{-1}\int e^{-\beta H(p,q)}A(p(t_1),\ q(t_1))\,B(p(t_2),\ q(t_2))\frac{dp(0)\,dq(0)}{N!\,h^{3N}},$$

where

$$p(t)=e^{-itL}p(0),\qquad q(t)=e^{-itL}q(0).$$

Using the Liouville theorem (2.2)

$$dp(0)\,dq(0) = dp(t_1)\,dq(t_1)$$

we transform the integral on the right hand side to

$$Q^{-1}\int e^{-\beta H(p,q)} A(p(t_1), q(t_1))\, B(p(t_2), q(t_2))\, \frac{dp(t_1)\,dq(t_1)}{N!\,h^{3N}}.$$

Introducing new variables of integration $p'=p(t_1)$, $q'=q(t_1)$, we obtain

$$\begin{aligned}\langle A(t_1)\,B(t_2)\rangle_0 &= \\ &= Q^{-1}\int e^{-\beta H(p',q')} A(p', q')\, B(p'(t_2-t_1), q'(t_2-t_1))\, \frac{dp'\,dq'}{N!\,h^{3N}} = \\ &= \langle AB(t_2-t_1)\rangle_0,\end{aligned}$$

because
$$\begin{aligned}p(t_2) &= e^{-i(t_2-t_1)L}\, p(t_1) = e^{-i(t_2-t_1)L}\, p', \\ q(t_2) &= e^{-i(t_2-t_1)L}\, q(t_1) = e^{-i(t_2-t_1)L}\, q',\end{aligned}$$

and $H(p,q)$ is an integral of motion. Thus, the required property is demonstrated.

Thus, we have verified that the effect of an external mechanical perturbation on the average value of a dynamical variable is described by the retarded Green function, which connects this variable with the perturbation.

The retarded Green functions (15.19) introduced by N. N. Bogolyubov and S. V. Tyablikov [15] for the case of quantum statistics, are very convenient to use in the statistical mechanics of equilibrium and nonequilibrium systems because of their transparent physical interpretation and simple analytic properties [12-15] (see further § 16). They are also useful in classical statistical mechanics [18-20].

The physical meaning of the retarded Green functions can be explained by considering the effect of the instantaneous δ-form perturbation

$$H_t^1 = B\,\delta(t-t_1) \tag{15.20}$$

on the average value of the dynamical quantity A. Substituting (15.20) into (15.18), we obtain

$$\langle A\rangle = \langle A\rangle_0 + \langle\langle AB(t_1 - t)\rangle\rangle = \langle A\rangle_0 + \langle\langle A(t)\,B(t_1)\rangle\rangle. \tag{15.21}$$

Thus, the retarded Green function is equal to the change of the average value of A at the time t because of the instantaneous switching on of the δ-form perturbation at the time t_1.

Using (15.14) another form for the relation (15.18) can be obtained:

$$\langle A\rangle = \langle A\rangle_0 - \frac{1}{\theta}\int_{-\infty}^{t} \langle A\dot{H}^1_{t'}(t'-t)\rangle_0\,dt' =$$

$$= \langle A\rangle_0 + \frac{1}{\theta}\int_{-\infty}^{t} \langle \dot{A}(t-t')\,H^1_{t'}\rangle_0\,dt' \qquad (\theta = \beta^{-1}), \tag{15.22}$$

where

$$A = \{A,\ H\}.$$

The last equality in (15.22) follows from the stationarity condition

$$\langle A\dot{H}^1_{t'}(t'-t)\rangle_0 = -\langle \dot{A}(t-t')\,H^1_{t'}\rangle_0. \tag{15.23}$$

In fact, the average value of the product of dynamical variables in a state of statistical equilibrium depends only on the time difference:

$$\langle AH^1_{t'}(t'-t)\rangle_0 = \langle A(t-t')\,H^1_{t'}\rangle_0,$$

from which we obtain the relationship (15.23) by differentiating with respect to t.

Thus, in the linear approximation the change of the average value of A under the influence of the perturbation H^1_t is defined by the time correlation function, relating A to $\dot{H}^1_t$ or $\dot{A}$ to H^1_t.

If the external perturbation has the form (15.2), then the formulas (15.18) and (15.22) can be written in the form

$$\langle A\rangle = \langle A\rangle_0 - \sum_j \int_{-\infty}^{\infty} \langle\langle A(t)\, B_j(t')\rangle\rangle\, F_j(t')\, dt', \tag{15.24}$$

$$\langle A\rangle = \langle A\rangle_0 + \sum_j \frac{1}{\theta} \int_{-\infty}^{t} \langle A(t)\, \dot{B}_j(t')\rangle_0\, F_j(t')\, dt'. \tag{15.24a}$$

These relationships for the linear reaction of a system are called the Kubo formulas.

Kubo has made a detailed study of the reaction of classical and quantum systems to the switching on of an external perturbation, proceeding from the Liouville equation and the equilibrium condition at $t=-\infty$ [1, 3, 4]. However, relationships similar to the Kubo formulas were obtained still earlier for a particular case by Kirkwood [21], who expressed the coefficient of friction of a Brownian particle for the classical case through the correlation function of the forces acting on the particle (see § 26), and also by Callen and Welton [22], who proved the generalized Nyquist theorem on the connection between susceptibilities (or kinetic coefficients) in linear dissipative processes and equilibrium fluctuations; we shall consider this theorem in § 17. The great merit of Kubo's work consists in the fact that he gave the most general proof of these formulas, widely applied them to the theory of linear dissipative processes, and drew the attention of physicists to them[1].

The remarkable property of the Kubo relations consists in the fact that they express nonequilibrium properties in the form of averages over a state of statistical equilibrium and have an extremely general character.

In the case of an adiabatic switching on of a periodic perturbation (15.2a) formula (15.18) takes on the form

$$\langle A\rangle = \langle A\rangle_0 + \sum_{\omega} e^{\varepsilon t - i\omega t} \langle\langle AB_\omega\rangle\rangle_\omega, \tag{15.25}$$

where

$$\langle\langle AB_\omega\rangle\rangle_\omega = \int_{-\infty}^{\infty} e^{\varepsilon t - i\omega t} \langle\langle AB_\omega(t)\rangle\rangle\, dt \tag{15.25a}$$

is the Fourier component of the retarded Green function[2].

If the external perturbation contains only one harmonic of frequency ω,

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[1] The method of Callen and Welton [22] proceeding from the Schroedinger equation and the theory of quantum transitions, as will be shown in section 17.5, has a more restricted region of applicability than the method of Kubo.

[2] The normalization of the Fourier component (15.25a) of the Green function differs from that used in [12] by a factor of 2π.

i.e.,

$$H_t^1 = -F\cos\omega t\, e^{\varepsilon t} B, \tag{15.26}$$

where F is the amplitude of the periodic force, which is independent of the coordinates and the momenta, and B is a dynamical variable, then the linear reaction has the form

$$\langle A\rangle = \langle A\rangle_0 + \mathrm{Re}\{\varkappa(\omega) F e^{-i\omega t+\varepsilon t}\}, \tag{15.27}$$

where Re denotes the real part of the expression, and $x(\omega)$ is the complex generalized susceptibility, equal to

$$\varkappa(\omega) = -\langle\langle AB\rangle\rangle_\omega, \text{ where } \langle\langle AB\rangle\rangle_\omega = \int_{-\infty}^{\infty} e^{-i\omega t+\varepsilon t} \langle\langle AB(t)\rangle\rangle\, dt. \tag{15.28}$$

This then is the Kubo formula for the susceptibility. The relations (15.27) and (15.28) show that the Fourier components of the retarded Green function have the meaning of the generalized complex susceptibility, which describes the influence of the perturbation (15.26) on the average value of A.

Let us note that in calculating the complex susceptibility (15.28) it is necessary to carry out two limiting transitions: the usual limiting transition of statistical mechanics $V\to\infty$ $(V/N=\text{const})$ for calculation of the statistical averages, and the limiting transition $\varepsilon\to 0$. The result depends on the order of carrying out these limiting transitions. The correct order is to take first $V\to\infty$ and then $\varepsilon\to 0$[1].

Just as in equilibrium statistical thermodynamics it is always assumed that the thermodynamic limit $V\to\infty$, $V/N=\text{const}$ exists, in nonequilibrium statistical thermodynamics it is assumed in addition that the limiting process described by first taking $V\to\infty$ and then $\varepsilon\to 0$ exists for the expressions (15.28). We shall call it the (V,ε)-limit. While the existence of the thermodynamic limit for specific restrictions on the interaction potential has been shown (see the literature [13-17d] for Chapter I), the existence of the (V,ε)-limit has not been rigorously proven mathematically. Later in sections 15.4 and 17.4 of this chapter, we shall again return to a consideration of the order of the limiting transitions.

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[1] In Appendix I it is shown by the example of the problem of quantum mechanical scattering (where the volume in which the wave functions are normalized plays the role of V) that such an order of limiting transitions corresponds to excluding advanced solutions of the Schroedinger equation.

15.2. Linear Reaction of a System (Quantum Statistics).

Let us consider the reaction of a quantum statistical ensemble of systems with a Hamiltonian H, which is independent of time, to the switching on of an external time dependent perturbation H_t^1.

The total Hamiltonian of the system including the external perturbation is equal to

$$H + H_t^1, \tag{15.29}$$

where H_t^1 is the operator for the interaction of the system of particles with the external field. The Hamiltonian of the external field itself, with which the particles interact, is not included in (15.29), because the field is considered to be fixed.

We shall assume that earlier at t=-∞ there was no external perturbation, i.e.,

$$H_t^1 \big|_{t=-\infty} = 0. \tag{15.29a}$$

The perturbation H_t^1 can often be represented in the form

$$H_t^1 = -\sum_j B_j F_j(t), \tag{15.30}$$

where the $F_j(t)$ are functions of time and are C-numbers[1], - the external driving forces, and the B_j are operators, which do not depend explicitly on time, linked to the fields $F_j(t)$. Expression (15.30) is analogous to the classical expression (15.2).

If a periodic perturbation is switched on adiabatically, then

$$H_t^1 = -\sum_j e^{\varepsilon t - i\omega t} B_j \qquad (\varepsilon > 0), \tag{15.30a}$$

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[1] In the terminology of quantum mechanics quantities which do not have an operator structure are called C-numbers.

where ε is a positive infinitesimal quantity, and B_ω is a quantum mechanical operator, which does not depend explicitly on time. From the hermiticity of (15.30a) it follows that $B_\omega^+ = B_{-\omega}$.

The statistical operator ρ satisfies the quantum Liouville equation (8.6)

$$i\hbar \frac{\partial \rho}{\partial t} = [H + H_t^1, \rho] \tag{15.31}$$

and the initial condition

$$\rho|_{t=-\infty} = \rho_0 = Q^{-1}(\theta, V, N) e^{-H/\theta}, \tag{15.32}$$

which implies that at $t=-\infty$ the system is in a state of statistical equilibrium and is described by the Gibbs canonical ensemble (9.14). The Gibbs grand canonical ensemble (9.42) can also be taken as the initial condition:

$$\rho|_{t=-\infty} = \rho_0 = Q^{-1}(\theta, \mu, V) e^{-(H-\mu N)/\theta}. \tag{15.32a}$$

We go from the statistical operator ρ to the operator ρ_1 by means of the canonical transformation

$$\rho_1 = e^{iHt/\hbar} \rho e^{-iHt/\hbar}. \tag{15.33}$$

Then the quantum Liouville equation is transformed to

$$i\hbar \frac{\partial \rho_1}{\partial t} = [H_t^1(t), \rho_1] \tag{15.34}$$

with the initial condition

$$\rho_1|_{t=-\infty} = \rho_0, \tag{15.35}$$

where

$$H_t^1(t) = e^{iHt/\hbar} H_t^1 e^{-iHt/\hbar} \tag{15.36}$$

is the perturbation operator in the Heisenberg representation with the Hamiltonian H; with respect to the total Hamiltonian (15.29) formula (15.36) gives the interaction representation.

Equation (15.34) and the initial condition (15.35) can be written in the form of a single integral equation

$$\rho_1(t) = \rho_0 + \int_{-\infty}^{t} \frac{1}{i\hbar}\left[H^1_{t'}(t'),\ \rho_1(t')\right]dt', \tag{15.37}$$

or

$$\rho(t) = \rho_0 + \int_{-\infty}^{t} e^{-iH(t-t')/\hbar}\,\frac{1}{i\hbar}\left[H^1_{t'},\ \rho\right]e^{iH(t-t')/\hbar}\,dt'; \tag{15.37a}$$

these equations are analogous to the classical equations (15.11) and (15.11a).

If the perturbation H^1_t is small, then the solution of equation (15.37) can be obtained by iteration, taking ρ_0 as the zero order approximation. In the first approximation we have

$$\rho = \rho_0 + \int_{-\infty}^{t} \frac{1}{i\hbar}\left[H^1_{t'}(t'-t),\ \rho_0\right]dt'. \tag{15.38}$$

Up to this point all relationships are valid if ρ_0 is the canonical or grand canonical distribution, but they are also valid for any equilibrium distribution, for example the Gibbs microcanonical distribution, because we have nowhere made use of the explicit form of ρ_0. Let us assume now that ρ_0 is the Gibbs canonical distribution (15.32).

Using the identity, which is valid for any operator A,

$$[A,\ e^{-\beta H}] = -e^{-\beta H}\int_{0}^{\beta} e^{\lambda H}[A,\ H]\,e^{-\lambda H}\,d\lambda, \tag{15.39}$$

usually called the Kubo identity, which we shall prove somewhat later (see formula (15.42) and below), we obtain

$$\rho = \rho_0\left(1 - \int_{0}^{\beta}\int_{-\infty}^{t} e^{\lambda H}\,\dot{H}^1_{t'}(t'-t)\,e^{-\lambda H}\,d\lambda\,dt'\right), \tag{15.40}$$

where

$$\dot{H}^1_{t'}(t'-t) = \frac{1}{i\hbar}\left[H^1_{t'}(t'-t),\ H\right]. \tag{15.41}$$

In the case in which ρ_0 is the Gibbs grand canonical distribution (15.32a), the formula (15.40) remains valid, but the replacement must be made

$$\dot{H}^1_{t'}(t'-t) = \frac{1}{i\hbar}\left[H^1_{t'}(t'-t),\ H-\mu N\right]. \tag{15.41a}$$

If H^1_t commutes with N, as is often the case, then (15.41a) coincides with (15.41). If ρ_0 is the microcanonical distribution, then formula (15.40) is not valid.

We shall now derive the Kubo identity (15.39). We put

$$[A, e^{-\beta H}] = e^{-\beta H}\, S(\beta), \tag{15.42}$$

where $S(\beta)$ is an unknown operator. Differentiating (15.42) with respect to β, we obtain a differential equation for $S(\beta)$:

$$\frac{\partial S}{\partial \beta} = -\, e^{\beta H}[A,\ H]\, e^{-\beta H}$$

with the initial condition $S|_{\beta=0}=0$. Integrating this equation and using the initial condition, we obtain the Kubo identity (15.39).

Formulas (15.37a) and (15.40) allow one to calculate in an approximation linear in H'_t the average value of any observable quantity, represented by an operator A:

$$\langle A\rangle = \mathrm{Sp}(\rho A). \tag{15.43}$$

Substituting (15.38) into (15.43) and using the invariance of the spur with respect to a cyclic permutation of operators, we obtain

$$\langle A\rangle = \langle A\rangle_0 + \int_{-\infty}^{t} \frac{1}{i\hbar}\langle [A(t),\ H^1_{t'}(t')]\rangle_0\, dt', \tag{15.44}$$

where

$$A(t) = e^{iHt/\hbar} A\, e^{-iHt/\hbar} \tag{15.45}$$

is the operator A in the Heisenberg representation, and

$$\langle \ldots \rangle_0 = \mathrm{Sp}(\rho_0 \ldots) \tag{15.46}$$

is an averaging with the equilibrium statistical operator (15.32) or (15.32a).

Equation (15.44) describes the retarded reaction of the average values of the operator A to the switching on of the perturbation H_t^1, for a quantum statistical ensemble. It has exactly the same form as equation (15.16) in classical statistical mechanics, except for the replacement of the classical Poisson brackets by the quantum brackets and the replacement of the classical averaging by the quantum averaging.

Extending the integration over time in (15.44) to +∞ by introducing the discontinuous function $\theta(t-t')$ (15.17), equation (15.44) can be conveniently written in the form

$$\langle A\rangle = \langle A\rangle_0 + \int_{-\infty}^{\infty} \langle\langle A(t)\, H_{t'}^1(t')\rangle\rangle\, dt', \tag{15.47}$$

where

$$\langle\langle A(t)\, B(t')\rangle\rangle = \theta(t-t')\frac{1}{i\hbar}\langle[A(t),\ B(t')]\rangle_0 \tag{15.48}$$

is the retarded doubletime Green function in quantum statistical mechanics, which was introduced by Bogolyubov and Tyablikov [12-15].

Formulas (15.47) and (15.48) are analogous to the formulas (15.18) and (15.19) of classical statistical mechanics. Thus, the effect of external perturbations on the average value of observable quantities in quantum statistics, as in classical statistics, is described by retarded quantum Green functions, which relate the observable quantity to the perturbation.

The Green functions (15.48) depend on the difference of the time arguments t-t´, just as do the time correlation functions

$$\langle A(t)\, B(t')\rangle_0 = \langle A(t-t')\, B\rangle_0 = \langle AB(t'-t)\rangle_0, \tag{15.48a}$$

because the averaging is carried out over an equilibrium ensemble. This is easily verified directly by making use of a cyclic permutation of the operators under the spur sign. Indeed,

$$\begin{aligned}\langle A(t)\, B(t')\rangle &= Q^{-1}\,\mathrm{Sp}\left\{e^{-\beta H} e^{\frac{iHt}{\hbar}} A e^{\frac{-iH(t-t')}{\hbar}} B e^{\frac{-iHt'}{\hbar}}\right\} = \\ &= Q^{-1}\,\mathrm{Sp}\left\{A e^{\frac{iH(t'-t)}{\hbar}} B e^{\frac{-iH(t'-t)}{\hbar}} e^{-\beta H}\right\} = \langle AB(t'-t)\rangle,\end{aligned}$$

which was to be shown. The same relationship is valid for averaging over the grand ensemble; in the proof it is necessary only to make the replacement $H \to H - \mu N$.

The physical meaning of the retarded quantum Green functions is the same as for the classical functions. The instantaneous δ-form perturbation of the type (15.20) effects the average value of the observable quantity A through the Green function

$$\langle A\rangle = \langle A\rangle_0 + \langle\langle A(t)\, B(t_1)\rangle\rangle. \qquad (15.49)$$

Just as in classical statistics, the effect of the perturbation on the average values can be expressed through the time correlation functions. To do this we make use of the expression (15.40) for the perturbed statistical operator. Then

$$\begin{aligned}\langle A\rangle &= \langle A\rangle_0 - \int_0^{\beta}\int_{-\infty}^{t} \langle e^{\lambda H} \dot{H}^1_{t'}(t')\, e^{-\lambda H} A(t)\rangle_0\, d\lambda\, dt' = \\ &= \langle A\rangle_0 + \int_0^{\beta}\int_{-\infty}^{t} \langle e^{\lambda H} H^1_{t'}(t')\, e^{-\lambda H} \dot{A}(t)\rangle_0\, d\lambda\, dt', \end{aligned} \qquad (15.50)$$

where use has been made of the stationarity condition (15.23), as in the derivation of (15.22). Formula (15.50) can also be written in the form

$$\begin{aligned}\langle A\rangle &= \langle A\rangle_0 - \int_0^{\beta}\int_{-\infty}^{t} \langle \dot{H}^1_{t'}(t' - i\hbar\lambda)\, A(t)\rangle_0\, d\lambda\, dt' = \\ &= \langle A\rangle_0 + \int_0^{\beta}\int_{-\infty}^{t} \langle H^1_{t'}(t' - i\hbar\lambda)\, \dot{A}(t)\rangle_0\, d\lambda\, dt'. \end{aligned} \qquad (15.51)$$

Comparing (15.51) with the classical expression (15.22) for the linear reaction, we notice that (15.51) goes over into (15.22), if one formally puts $\hbar=0$ and replaces the quantum averaging by classical averaging. This simple rule can be applied for obtaining classical formulas from quantum formulas.

Formulas (15.47) and (15.51) give expressions for the linear reaction to a mechanical perturbation of a quantum statistical ensemble through the Green function or the quantum time correlation functions. For an external perturbation in the form (15.30) the formulas can be written in the form

$$\langle A\rangle = \langle A\rangle_0 - \sum_j \int_{-\infty}^{\infty} \langle\langle A(t) B_j(t')\rangle\rangle F_j(t')\,dt',$$

$$\langle A\rangle = \langle A_0\rangle + \sum_j \int_{-\infty}^{t}\int_{0}^{\beta} \langle e^{\lambda H} \dot{B}_j(t') e^{-\lambda H} A(t)\rangle_0 F_j(t')\,dt'\,d\lambda, \qquad (15.51a)$$

which is similar to the formulas (15.24) and (15.24a) of classical statistical mechanics. These are the Kubo formulas for the linear reaction of a quantum system.

Formulas (15.51a) for the linear reaction of a system are sometimes represented in the form

$$\langle A\rangle = \langle A\rangle_0 + \sum_j \int_{-\infty}^{t} \varphi_{AB_j}(t-t') F_j(t')\,dt',$$

where

$$\varphi_{AB_j}(t-t') = \int_0^{\beta} \langle e^{\lambda H} \dot{B}_j(t') e^{-\lambda H} A(t)\rangle_0\,d\lambda = \beta(\dot{B}_j(t'), A(t))$$

is the reaction function, or aftereffect function, describing the effect of the perturbation B_j on the average value of A. Sometimes it is called the response. In the classical case it goes over into the time correlation function

$$\varphi_{AB_j}(t-t') = \beta\langle \dot{B}_j(t') A(t)\rangle_0.$$

The reaction function differs from the Green function only by the discontinuous factor θ(t-t′). Indeed, by comparison with (15.51a)

$$\langle\langle A(t) B(t')\rangle\rangle = -\theta(t-t')\varphi_{AB}(t-t').$$

Sometimes the relaxation function is introduced in addition to the reaction function

$$\Phi_{AB}(t) = \int_t^{\infty} \varphi_{AB}(t') e^{-\varepsilon t'}\,dt'.$$

The theory of the linear reaction can be presented using these functions, as is done by Kubo (see [1,3,4]). But since they are simply connected with retarded Green functions, which have a very simple physical interpretation it is evidently simpler to construct the theory of the linear reaction on the basis of the retarded Green functions, and this is the course we shall follow in this book.

15.3. Nonlinear Reaction of a System.

The nonlinear reaction of a statistical system to external mechanical perturbations can be studied by the same method as was used in sections 15.1 and 15.2 to analyze the linear reaction [1, 11]. In this section we shall consider only the quantum case, because the classical case can be treated analogously, by replacing the quantum Poisson brackets by the classical Poisson brackets and the quantum averaging by classical averaging.

Once again we proceed from the quantum Liouville equation (15.31) and the initial conditions (15.32) or (15.32a) and transform the Liouville equation to the integral form (15.37). Iterating the equation (15.37a), we obtain a perturbation series for the statistical operator [1]

$$\begin{aligned}\rho(t) = \rho_0 &+ \\ &+ \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_{n-1}} dt_n \, e^{-iHt/\hbar} [H^1_{t_1}(t_1) [H^1_{t_2}(t_2) \ldots \\ &\ldots [H^1_{t_n}(t_n), \rho_0] \ldots] e^{iHt/\hbar}\end{aligned} \tag{15.52}$$

and for the average value of the operator A

$$\begin{aligned}\langle A \rangle = \langle A \rangle_0 &+ \\ &+ \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n} \int_{-\infty}^{t} \int_{-\infty}^{t_1} \ldots \int_{-\infty}^{t_{n-1}} \mathrm{Sp} \{ A(t) [H^1_{t_1}(t_1) [H^1_{t_2}(t_2) \ldots \\ &\ldots [H^1_{t_n}(t_n), \rho_0] \ldots] \} dt_1 \ldots dt_n.\end{aligned} \tag{15.52a}$$

The series (15.52a) describes the nonlinear reaction of a statistical system to the switching on of the perturbation H^1_t.

A more compact formula for the nonlinear reaction of a system is easily obtained, if one proceeds from the equation of motion for the evolution operator U(t):

$$i\hbar \frac{\partial U(t)}{\partial t} = (H + H^1_t) U(t). \tag{15.53}$$

For $H_t^1=0$ the solution of equation (15.53) has the form

$$U(t) = e^{-iHt/\hbar},$$

because in this case the Heisenberg representation (8.17a) has the form (8.17). Thus, equation (15.53) must be supplemented by the initial condition

$$e^{iHt/\hbar} U(t)\,|_{t=-\infty} = 1. \tag{15.53a}$$

It is easily verified that if U(t) satisfies equation (15.53) and the initial condition (15.53a), then

$$\rho(t) = U(t)\,\rho_0\,U^+(t) \tag{15.53b}$$

satisfies the Liouville equation (15.31) and the initial condition (15.32) or (15.32a). Indeed, differentiating (15.53b) and using (15.53), we obtain (15.31). In addition, in accordance with (15.53a) as $t \to -\infty$ $\rho(t)$ approaches

$$e^{-iHt/\hbar}\,\rho_0\,e^{iHt/\hbar} = \rho_0,$$

i.e., $\rho(t)$ satisfies the initial condition (15.32) or (15.32a), as was to be shown.

It is convenient to multiply equation (15.53) from the left by $e^{iHt/\hbar}$ and to transform it to the form

$$i\hbar \frac{\partial}{\partial t}\left(e^{iHt/\hbar}\,U(t)\right) = H_t^1(t)\,e^{iHt/\hbar}\,U(t), \tag{15.54}$$

where

$$H_t^1(t) = e^{iHt/\hbar}\,H_t^1\,e^{-iHt/\hbar} \tag{15.55}$$

is the operator of the perturbation energy in the Heisenberg representation. Integration equation (15.54) with respect to t from $-\infty$ to t and using the initial condition (15.53a), we obtain an integral equation for U(t):

$$U(t) = e^{-iHt/\hbar}\left\{1 + \frac{1}{i\hbar}\int_{-\infty}^{t} H_{t_1}^1(t_1)\,e^{iHt_1/\hbar}\,U(t_1)\,dt_1\right\}. \tag{15.56}$$

It is convenient to transform to the operator

$$U_1(t) = e^{iHt/\hbar}\, U(t),$$

which satisfies a simpler integral equation

$$U_1(t) = 1 + \frac{1}{i\hbar}\int_{-\infty}^{t} H^1_{t_1}(t_1)\, U_1(t_1)\, dt_1$$

with the initial condition

$$U_1(t)\big|_{t=-\infty} = 1.$$

Solving this integral equation by iteration, we obtain a perturbation series for U(t):

$$= e^{-\frac{iHt}{\hbar}} \sum_{n=0}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_{n-1}} dt_n\, H^1_{t_1}(t_1)\, H^1_{t_2}(t_2) \ldots H^1_{t_n}(t_n). \tag{15.56a}$$

The operator U(t) can be written in a more compact form by using the chronological ordering operator P, which, acting on any product of time dependent operators, places them in chronological order of decreasing time, i.e.,

$$P\,[A(t_1)\, B(t_2) \ldots L(t_n)] = A(t_1)\, B(t_2) \ldots L(t_n),$$

where $t_1 > t_2 > .. > t_n$; A, B, ..., L are arbitrary operators depending on time, for example, through the Heisenberg representation or the interaction representation. By use of P the nth term of the series (15.56a) can be written in the form of a multiple integral with identical upper limits:

$$\frac{1}{(i\hbar)^n} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_{n-1}} dt_n\, H^1_{t_1}(t_1)\, H^1_{t_2}(t_2) \ldots H^1_{t_n}(t_n) =$$

$$= \frac{1}{n!}\, \frac{1}{(i\hbar)^n} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \ldots \int_{-\infty}^{t} dt_n\, P\left[H^1_{t_1}(t_1)\, H^1_{t_2}(t_2) \ldots H^1_{t_n}(t_n)\right],$$

because the integral on the right hand side of this equation is symmetric with respect to $t_1, \dots, t_n$ and there are n! possible permutations of the time arguments. Thus, the evolution operator (15.56a) can be written in the form of an ordered P-exponential

$$U(t) = e^{-iHt/\hbar} P \exp\left\{ \frac{1}{i\hbar} \int_{-\infty}^{t} H^1_{t_1}(t_1)\, dt_1 \right\}, \tag{15.56b}$$

as this is usually done in the quantum theory of fields [23-26].

The formula (15.53b) can be written in the explicit form:

$$\rho(t) = U(t) e^{-\beta(H-F)} U^+(t), \tag{15.57}$$

or

$$\rho(t) = U(t) e^{-\beta(H-\mu N-\Omega)} U^+(t) \tag{15.57a}$$

respectively for the Gibbs canonical and grand canonical ensembles.

We shall obtain one more formula for the statistical operators (15.57) and (15.57a). Let us note that for f(A) - an arbitrary function of the operator A - there exists the relationship

$$Uf(A)U^+ = f(U AU^+), \tag{15.58}$$

where U is an operator corresponding to an arbitrary unitary transformation ($U^+U=UU^+=1$), for example (15.56). The relation (15.58) is easily shown by expanding f(A) in a Taylor series and taking into account that

$$UA^nU^+ = UAU^+UA \dots UAU^+ = (UAU^+)^n,$$

because $U^+U=1$. Using (15.58) we obtain

$$\rho(t) = \exp\{-\beta[U(t) HU^+(t) - F]\} \tag{15.59}$$

or

$$\rho(t) = \exp\{-\beta[U(t)(H-\mu N)U^+(t) - \Omega]\} \tag{15.59a}$$

instead of (15.57) and (15.57a). These formulas together with (15.56b) give a compact description of the perturbation series (15.52) for the statistical operator.

We note, however, that the theory of the nonlinear reaction to mechanical perturbations, which was given above, is less well-founded than the theory of the linear reaction. We considered the contact with the thermostat as an initial condition at $t=-\infty$, and then studied the evolution of the system as if it were isolated from all external interactions, except the force field. In reality, almost every real system which receives energy from an external field can transfer it to its external surroundings. This is particularly evident if the system is understood to be only a mentally separated part of a large system.

Even if it is assumed that at the initial time the system was in equilibrium with the thermostat, this equilibrium is violated as a consequence of the mechanical perturbations, and this gives rise to thermal perturbations, which cannot be described by an external field. Only in the linear approximation are mechanical and thermal perturbations additive.

A system containing a large number of particles which is obtaining energy from an external field can distribute the energy among its particles, for example, in the form of liberation of Joule heat, and the system is characterized by a time dependent temperature. Many experiments on the behavior of magnetic materials which are found in a constant magnetic field and to which is applied a variable magnetic field can be interpreted if a time dependent spin temperature is introduced [27]. On the other hand, the theory of the nonlinear reaction presented above contains only the equilibrium values of the parameters $\beta=1/kT$ and μ, which appear because of the initial condition of statistical equilibrium at $t=-\infty$. This theory in the usual form is not very well adapted for the introduction of the concept of a time dependent temperature. This temperature dependence is usually obtained from the condition of balance of the energy and the work done by the external field on the system, taking into account the effect of the field adiabatically [27], but this procedure is rather artificial. In the references [28] it is shown that for spin systems the time dependence of the spin temperature can be discussed on the basis of the theory of the nonlinear reaction by means of a summation in the perturbation series (15.52a) of the terms which are significant at large times. An analogous procedure in nonlinear mechanics is the selection and summation of the secular terms. In Chapter IV it will be shown how to find the solution of the Liouville equation with time dependent parameters.

We note that in the theory of the nonlinear reaction there does not always exist a unique connection between the external perturbation H_t^1 and $\langle A\rangle-\langle A\rangle_0$ - the system reaction to the perturbation. This is most easily explained by an analogy with the theory of nonlinear automatic systems [29]. In the language of this theory the perturbation H_t^1 can be called the input signal, and $\langle A\rangle-\langle A\rangle_0$ the output signal. It is well known that for nonlinear automatic systems with feedback there cannot exist a unique connection between the input and output signals. Such (autonomous) systems are possible not only in cybernetics, but also in statistical mechanics, because in statistical mechanics there is also a possible feedback mechanism. For example, the self-oscillating regime is possible in turbulent flow[1], in nonlinear acoustics for thermal generation of sound [30], and in a quantum oscillator [31,32]. A self-oscillating regime is possible also in chemical kinetics (chemical oscillations) where the mechanism of feedback is created either by chemical autocatalysis (kinetic oscillations), or by heat, which is given off in a reaction and which accelerates the reaction (thermokinetic oscillations) [33]. Biological rhythms in a living organism can also be connected with periodic chemical processes [33].

In automatic systems small perturbations grow to some finite magnitude, which does not depend on the initial conditions. An analogous situation exists in nonlinear mechanics [34-36], where the oscillation tends toward a limit cycle, independently of the initial conditions.

We shall explain in somewhat more detail the analogy between the theory of the nonlinear reaction in statistical mechanics and the theory of nonlinear automatic systems.

In the theory of the linear reaction the connection between the driving force F(t) (input signal) and the reaction of the system $\Delta A=\langle A\rangle-\langle A\rangle_0$ (output signal) is given by the linear integral relationship (15.51a)

$$\Delta A(t)=\int_{-\infty}^{t} L(t-t')F(t')\,dt', \tag{15.60}$$

where

$$L(t-t')=-\langle\langle A(t)B(t')\rangle\rangle$$

is the retarded Green function. In the nonlinear theory of automatic systems with feedback the input signal F(t) and the output signal ΔA are related by the nonlinear integral relation [29]

$$\Delta A(t)=\int_{-\infty}^{\infty} L(t,t')f\left[F(t')-\int_{-\infty}^{\infty} K(t',t'')\Delta A(t'')\,dt''\right]dt', \tag{15.61}$$

where the function $L(t,t')$ defines the reaction ΔA (response) of the system, $K(t',t'')$ is the feedback reaction (the countereffect on the perturbation F

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[1] The mechanism of feedback was formally introduced by L. D. Landau in the theory of turbulence to describe the establishment of a limit to the growth of turbulent pulsations for hydrodynamically unstable motions [86].

of the response of the system), and f[...] is the noninertial nonlinear transformation to a direct circuit. In the linear theory without feedback

$$f[F(t)]=F(t), \quad L(t,t')=L(t-t'), \quad K(t',t'')=0,$$

and (15.61) goes over into (15.60). In the nonlinear theory of the reaction of a statistical ensemble without feedback $K(t',t'')=0$, and the transformation f has a nonlinear and retarded character, as can be seen from (15.52a) (every power of F gives one integral of the retarded type).

The nonlinear integral equation (15.61) for positive feedback defines, as is well known [29], the regime of automatic control. Analogous processes are possible also in nonequilibrium statistical mechanics, when an unstable state is excited and an oscillation appears. Equation (15.61) can be taken as a model of such a process.

For a nonlinear system with feedback it is impossible to obtain in explicit form the dependence between the input and output signals. In such a system small perturbations grow to some value, and then the system fluctuates about this value. In this case the statistical characteristics of the transformed signal are studied for fixed characteristics of the input signal. An analogous formulation of the problem is necessary for unstable statistical systems.

The theory of the nonlinear reaction, presented in this section, has nevertheless its own region of applicability, when the thermal perturbations arising from the mechanical perturbations can be neglected, and the medium is passive, i.e., there is no feedback and oscillation in the medium is impossible. These conditions can be realized, for example, in the theory of magnetic resonance [27,37], in nonlinear optics [38], and in nonlinear acoustics [30].

15.4. Effect of Variable Electrical Field; Electrical Conductivity.

In sections 15.1-15.3 we considered the linear and nonlinear reaction of a system to a perturbation H_t^1, not defining its nature any further, and assuming only that it is the result of the action of a real external field. This perturbation can be caused by a variable electric, magnetic, or in general electromagnetic field, and also by a gravitational field.

Let us consider the effect on a statistical ensemble of switching on a spatially homogeneous variable external electric field, which is periodic in time:

$$\boldsymbol{E}^{0}(t)=\boldsymbol{E}^{0}\cos\omega t\, e^{\varepsilon t}=\mathrm{Re}\{e^{-i\omega t+\varepsilon t}\boldsymbol{E}^{0}\}. \qquad (15.62)$$

The electric field E in a medium which contains charges is not the same as the external electric field because of the strong shielding of the charges; this is due to the Coulomb interaction between the charges. In deriving formulas for the theory of the linear reaction in an electric field sufficient attention is not always given to the difference between the external field and the field in the medium [1,4,5,11,12,39]. A more detailed discussion of this question is given in [3,40,41].

The electrical conductivity is defined as the coefficient of proportionality between the current density and the average field in the medium, or if there is dispersion, then it is defined as the coefficient of proportionality between the spatial and temporal Fourier components of the same fields (see § 18). To define the conductivity it is necessary to know the relation between the external field E^0 acting on the charges and the average field. Two cases must be distinguished:

1) The Coulomb interaction between the charges is taken into account by introducing a shielded field, as is often done in the electron theory of metals [42,43]. In this case it is not necessary to take the effect of shielding into account a second time, and the external field is equal to the average electric field in the medium $E^0=E$. The majority of authors studying the linear reaction of a system to an external electric field consider exactly this case [1,3,5,11,12,39], although this is not always stipulated. In this case to describe the electrons interacting with the lattice the Froehlich model is used [44-46], in which the Coulomb interaction is taken into account only indirectly, through a modification of the matrix elements of the interaction of the electrons with the lattice[1].

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[1] In the Froehlich model the electron-phonon interaction Hamiltonian, in second quantized notation, is

$$H_{\text{int}} = \frac{1}{\sqrt{V}} \sum_{\substack{k_1 k_2 q \\ k_1 - k_2 = q}} v_q \left(\frac{\hbar}{2\omega_q}\right)^{1/2} (b_q + b^+_{-q})\, a^+_{k_1\sigma} a_{k_2\sigma},$$

where ω_q is the phonon frequency, and $v_q \sim q$ is the shielded interaction energy of the electrons with the lattice potential, which has been deformed as a result of the motion of the atoms (the proportionality of v_q to the phonon wave number q arises as a result of the shielding of the Coulomb interaction between the electrons [44-46]). The quantity

$$\left(\frac{\hbar}{2\omega_q}\right)^{1/2} (b_q + b^+_{-q})$$

is the generalized coordinate for the normal oscillations of the lattice.

2) The Coulomb interaction between the electrons is taken into account explicitly. To describe the interaction of the electrons with the lattice it is necessary to use a model in which the matrix elements of the interaction do not include the Coulomb interaction between the electrons, which is taken into account separately[1].

If this model is assumed, then it is necessary to take into account the effect of shielding and of dielectric polarization of the medium [4,40,41]. In this case the external effective field $\mathbf{E}^0$ is equal to the displacement $\mathbf{E}^0=\mathbf{D}$.

Let us consider the reaction of the system to the external electric field. The operator

$$H_t^1 = -\sum_j e_j (\boldsymbol{E}^0 \boldsymbol{x}_j)\cos\omega t\, e^{\varepsilon t} = -(\boldsymbol{E}^0\boldsymbol{P})\cos\omega t\, e^{\varepsilon t}, \tag{15.63}$$

corresponds to the perturbation (15.62), where e_j is the charge of the particle, x_j is the radius vector to the position of the particle, and

$$\boldsymbol{P} = \sum_j e_j \boldsymbol{x}_j \tag{15.64}$$

is the polarization vector, considered as a quantum mechanical operator, or in the classical case, as a dynamical variable. In accordance with (15.47) the perturbation (15.63) gives rise to an electrical current in the system

$$\langle J_\alpha\rangle = \int_{-\infty}^{\infty} \langle\langle J_\alpha(t)\, H_{t'}^1(t')\rangle\rangle\, dt'. \tag{15.65}$$

In this formula there is no constant term, because in statistical equilibrium the average current is equal to zero, $\langle J_\alpha\rangle_0=0$. In formula (15.65)

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[1] For the electron-phonon interaction Hamiltonian in this case one must use an expression similar to H_{int} in the Froehlich model, but in this case $v_q=v_q^i$ - the "bare" interaction of the electrons with the phonons, for which $v_q^i \sim 1/q$, and which does not include the effects of Coulomb shielding. If the Coulomb interaction is taken into account through the shielding effect, then it can be excluded from the Hamiltonian, replacing v_q^i by $v_q \sim q$ (see [44-46]). We then arrive at the Froehlich model.

$$H_t^1(t) = -(E^0 P(t)) \cos \omega t \, e^{\varepsilon t}, \qquad J_\alpha(t) = \sum_j e_j \dot{x}_{j\alpha}(t) = \dot{P}_\alpha(t). \tag{15.65a}$$

J_α is the electric current operator, and $\dot{x}_{j\alpha}$ is the α component of the velocity operator of the j^{th} particle. In second quantized notation the electric current operator has the form

$$J_\alpha = \frac{e}{m} \sum_{p,\sigma} p_\alpha a^+_{p\sigma} a_{p\sigma}, \tag{15.65b}$$

where $a^+_{p\sigma}$ and $a_{p\sigma}$ are respectively the creation and annihilation operators for particles in a state with momentum p and spin σ (we assume that the charges of the particles are identical).

Using (15.65a) we write the expression (15.65) in the form

$$\langle J_\alpha \rangle = -\sum_\beta \int_{-\infty}^{\infty} \langle\langle J_\alpha(t) P_\beta(t') \rangle\rangle E^0_\beta \cos \omega t' \, e^{\varepsilon t'} \, dt'. \tag{15.65c}$$

All of the arguments up to now are valid both for the first case, where E^0=E, and for the second case, where E^0=D. In the following we shall consider first the first case, in which the applied field is equal to the average field in the medium. Formula (15.65c) can then be rewritten in the form

$$\langle J_\alpha \rangle = \sum_\beta \mathrm{Re} \{ \sigma_{\alpha\beta}(\omega) e^{-i\omega t + \varepsilon t} \} E_\beta, \tag{15.66}$$

where

$$\sigma_{\alpha\beta}(\omega) = -\int_{-\infty}^{\infty} e^{-i\omega t + \varepsilon t} \langle\langle J_\alpha P_\beta(t) \rangle\rangle \, dt \tag{15.66a}$$

is the electric conductivity tensor in a periodic field. The limiting transition $\varepsilon \to 0$ is carried out after passing to the thermodynamic limit $V \to 0$ (V/N= const).

Let us now consider the second case in which it is necessary to take into account the dielectric polarization of the medium[1], and the external field E^0

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[1] In the case of an inhomogeneous field (see § 18) it must be taken into account that only the longitudinal part is shielded, i.e., the part parallel to the wave vector.

corresponds not to the average electric field in the medium **E** but to the displacement **D**:

$$\boldsymbol{E}^0 = \boldsymbol{D} = \varepsilon(\omega)\cdot \boldsymbol{E}, \tag{15.67}$$

where $\varepsilon(\omega)$ is the dielectric permittivity tensor, for which we shall later obtain an explicit expression. We represent formula (15.65c) in the form

$$\langle J_\alpha\rangle = \sum_\beta \mathrm{Re}\{\varkappa_{\alpha\beta}(\omega)\, e^{-i\omega t+\varepsilon t}\}\, D_\beta, \tag{15.68}$$

where

$$\varkappa_{\alpha\beta}(\omega) = -\int_{-\infty}^{\infty} e^{-i\omega t+\varepsilon t}\,\langle\langle J_\alpha P_\beta(t)\rangle\rangle\, dt \tag{15.68a}$$

is the electric susceptibility tensor in a periodic field. Expressions (15.66a) and (15.68a) are identical in external form; the difference between them is in the meaning of the averaging operation <...>, and in particular, in the way the Coulomb interaction is taken into account in the Hamiltonian with which the averaging is carried out, as a shielded self-consistent field or in an explicit manner. In the first case the Hamiltonian does not contain the Coulomb interaction, but the matrix elements of the interaction of the electrons with the phonons are modified by the Coulomb interaction (see the footnote on page 176). In the second case the Hamiltonian contains both a term for the interaction with the phonons, and a term for the direct Coulomb interaction (see the footnote on page 177).

Using (15.66) formula (15.68) can be rewritten in the form

$$\langle J_\alpha\rangle = \sum_\beta \mathrm{Re}\{\sigma_{\alpha\beta}(\omega)\, e^{-i\omega t+\varepsilon t} E_\beta\} = \mathrm{Re}\{\sigma(\omega)\cdot \boldsymbol{E}\, e^{-i\omega t+\varepsilon t}\}_\alpha, \tag{15.69}$$

where

$$\sigma_{\alpha\beta}(\omega) = \sum_\gamma \varkappa_{\alpha\gamma}(\omega)\,\varepsilon_{\gamma\beta}(\omega), \tag{15.70}$$

$$\sigma(\omega) = \varkappa(\omega)\cdot\varepsilon(\omega)$$

is the electric conductivity tensor in a periodic field.

The dielectric permittivity tensor $\varepsilon(\omega)$ can be expressed through the susceptibility tensor $x(\omega)$, by making use of the relation [1]

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[1] In the case of an inhomogeneous field (see § 18) the relationship (15.71) is valid only for the longitudinal components of the field, because only they are shielded.

$$\boldsymbol{D} = \boldsymbol{E} + 4\pi \langle \boldsymbol{P} \rangle, \tag{15.71}$$

which in our case of a periodic field (15.62) in complex notation has the form

$$\boldsymbol{D} = E - \frac{4\pi}{i\omega} \langle \boldsymbol{J} \rangle,$$

because

$$\langle J \rangle = \langle \dot{P} \rangle$$

in accordance with (15.65a). Using this relation and (15.67)-(15.70), we obtain for ω≠0

$$\varepsilon^{-1}(\omega) = 1 + \frac{4\pi\varkappa(\omega)}{i\omega}, \qquad \sigma(\omega) = \varkappa(\omega)\left(1 + \frac{4\pi\varkappa(\omega)}{i\omega}\right)^{-1}. \tag{15.72}$$

Thus, the electric susceptibility tensor (15.68a) allows one to define the dielectric permittivity tensor ε(ω) and the electric conductivity tensor σ(ω) in a periodic field.

Thus, the adiabatic switching on of an electrical field leads to the formation of an electric current (15.66) in a system with finite electrical conductivity, i.e., it leads to an irreversible process. In general, the electrical conductivity remains finite even for a static electric field, for which ω=0. In this case from (15.66a) in the limit ω→0 we find the static conductivity:

$$\sigma_{\alpha\beta}(0) = -\lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} e^{\varepsilon t} \langle\langle J_\alpha P_\beta(t) \rangle\rangle \, dt. \tag{15.73}$$

Another expression for the tensor $x_{\alpha\beta}(\omega)$ can be obtained if (15.68a) is written in the form

$$\varkappa_{\alpha\beta}(\omega) = -\frac{1}{i\hbar} \int_{-\infty}^{0} e^{-i\omega t + \varepsilon t} \, \mathrm{Sp}\,\{[P_\beta(t), \rho_0]\, J_\alpha\}\, dt$$

and the Kubo identity (15.39) is used, according to which

$$[P_\beta(t),\ \rho_0] = -i\hbar\rho_0 \int_0^\beta e^{\lambda H}\dot{P}_\beta(t)e^{-\lambda H}\,d\lambda. \tag{15.74}$$

Then we obtain

$$\varkappa_{\alpha\beta}(\omega) = \int_0^\beta\int_0^\infty e^{i\omega t-\varepsilon t}\langle e^{\lambda H} J_\beta e^{-\lambda H} J_\alpha(t)\rangle\,d\lambda\,dt =$$

$$= \int_0^\beta\int_0^\infty e^{i\omega t-\varepsilon t}\langle J_\beta J_\alpha(t+i\hbar\lambda)\rangle\,d\lambda\,dt = \beta\int_0^\infty e^{i\omega t-\varepsilon t}(J_\beta,\ J_\alpha(t))\,dt. \tag{15.75}$$

The formula (15.66a) is reduced to the same form:

$$\sigma_{\alpha\beta}(\omega) = \int_0^\beta\int_0^\infty e^{i\omega t-\varepsilon t}\langle J_\beta J_\alpha(t+i\hbar\lambda)\rangle\,d\lambda\,dt, \tag{15.76}$$

which in the classical limit ħ→0 has the form

$$\sigma_{\alpha\beta}(\omega) = \beta\int_0^\infty e^{i\omega t-\varepsilon t}\langle J_\beta J_\alpha(t)\rangle\,dt. \tag{15.77}$$

This formula also follows directly from the classical formula for the linear reaction (15.22) by using (15.63).

In the case of a static field formula (15.76) becomes

$$\sigma_{\alpha\beta}(0) = \lim_{\varepsilon\to0}\int_0^\beta\int_0^\infty e^{-\varepsilon t}\langle J_\beta J_\alpha(t+i\hbar\lambda)\rangle\,d\lambda\,dt. \tag{15.78}$$

Expressions for the kinetic coefficients of the type (15.76)-(15.78) and the equivalent expression (15.73) are usually called Kubo formulas, although they were known earlier to other authors (see the footnotes on pages 160 and 161).

The order of the limiting transitions ε→0 and V→∞ in the Kubo formulas is very important, because there is no uniformity with respect to these two transitions, and the result depends on the order in which they are carried out. The limiting transition in which first V→∞ (for V/N=const), and then ε→0, i.e., the (V,ε)-limit, corresponds to imposing the condition of causality on the solution of the Liouville equation. It implies the exclusion of advanced solutions, which is evident from a consideration of the boundary conditions of the formal scattering theory of Gell-Mann and Goldberger [47] (see Appendix I). Only this order of the limiting transitions can give a finite value for the kinetic coefficients (15.66a), (15.68a).

A different order of the limiting transitions in which first $\varepsilon \to 0$ for finite volume, and then $V \to \infty$ (for $V/N = \text{const}$), is unsuitable, because for $\omega \to 0$ it leads to absurd expressions for the kinetic coefficients. We shall return again to this question in § 17.

Using the Kubo formula (15.78) the static electrical conductivity can be calculated [48-50], and the dynamic electrical conductivity can be calculated by means of (15.76) [41,49,51-56,103] without making use of the kinetic equation, but this is not a simple problem, because it requires calculation of the time correlation functions.

15.5. Effect of Variable Magnetic Field; Magnetic Susceptibility.

To conclude this paragraph we shall consider the effect on a statistical ensemble of switching on a spatially homogeneous external magnetic field H(t) with a periodic time dependence of frequency ω:

$$H(t) = H \cos \omega t \, e^{\varepsilon t} = \operatorname{Re} \{ e^{-i\omega t + \varepsilon t} H \}. \tag{15.79}$$

This problem is analogous to the problem considered earlier in section 15.4 of the effect of an electric field; therefore, we shall discuss it more briefly.

The operator

$$H_t^1 = -(M \cdot H(t)) = -(MH) \cos \omega t \, e^{\varepsilon t}, \tag{15.80}$$

corresponds to the perturbation (15.79), where M is the total magnetic moment operator of the system. Under the influence of the perturbation (15.80) the magnetic moment changes in time in accordance with (15.47) according to the formula

$$\langle M_\alpha \rangle = \langle M_\alpha \rangle_0 + \int_{-\infty}^{\infty} \langle\langle M_\alpha(t) H_{t'}^1(t') \rangle\rangle \, dt' \tag{15.81}$$

where $\langle M_\alpha \rangle_0$ is the average component of the magnetic moment on the α axis in a state of statistical equilibrium. If in the equilibrium state a magnetic field is present, then $\langle M_\alpha \rangle_0 \neq 0$. We write formula (15.81) in the form

$$\langle M_\alpha \rangle = \langle M_\alpha \rangle_0 + \sum_\beta \mathrm{Re}\,\{\chi_{\alpha\beta}(\omega)\, e^{-i\omega t+\varepsilon t}\}\, H_\beta, \tag{15.82}$$

where

$$\chi_{\alpha\beta}(\omega) = -\int_{-\infty}^{\infty} e^{-i\omega t+\varepsilon t} \langle\langle M_\alpha M_\beta(t) \rangle\rangle\, dt \tag{15.83}$$

is the magnetic susceptibility tensor in a periodic magnetic field. Using the Kubo identity (15.39) the magnetic susceptibility tensor (15.83) can be written also in the form

$$\chi_{\alpha\beta}(\omega) = \int_0^\beta \int_0^\infty e^{i\omega t-\varepsilon t} \langle \dot{M}_\beta M_\alpha(t + i\hbar\lambda) \rangle\, d\lambda\, dt, \tag{15.84}$$

which is analogous to formula (15.75). Application of the formulas (15.83) and (15.84) to the theory of magnetic resonance can be found in the articles [15-59] and in the monographs [13,14,27,37].

§ 16. Doubletime Green Functions

The reaction of a quantum system to an external mechanical perturbation, as was shown in the previous paragraph, is expressed through the retarded doubletime Green functions (15.48) and the reaction of a classical system is expressed through (15.19). We shall now discuss the basic properties of quantum doubletime Green functions, and we shall discuss the connection between Green functions of the various types, their spectral representations, dispersion relations, and their symmetry properties. This will allow us later in § 17 to obtain in an extremely simple fashion the fluctuation-dissipation theorems and all properties of the kinetic coefficients. The properties of Green functions (especially the retarded) will be widely used in what follows. We shall restrict ourselves to the case of quantum Green functions, because the classical case is easily obtained analogously, or by the limiting transition $\hbar \to 0$.

There are many papers in which Green functions are applied to the various problems of statistical mechanics, both equilibrium and nonequilibrium (see [12-15,60-64], where a more extensive list of references can be found).

Various types of Green functions are applied which differ according to:

the character of the averaging process, the arguments on which they depend explicitly, and their analytic properties. If the averaging is carried out over the ground state, then this is the field theoretic Green function, which is usually used in the quantum theory of fields. If the averaging is carried out over a statistical ensemble, then this is the thermodynamic Green function. If the Green functions depend on time variables, then they are called time dependent Green functions; if they depend explicitly on the temperature, then they are called temperature dependent or Matsubara Green functions, because they were first introduced by Matsubara [65].

The various Green functions have their advantages and disadvantages. The causal Green functions have a more complicated analytic structure, but they are closely connected with perturbation theory. The retarded Green functions have a simple analytic structure, and they are simply connected with the kinetic coefficients, but are more indirectly related to perturbation theory. In the theory of irreversible processes, evidently the most convenient are the retarded Green functions; therefore, we shall give primary consideration to them.

In this paragraph will be considered the spectral representations, dispersion relations, sum rules, symmetry properties, and several other properties of Green functions and of the correlation functions.

16.1. Retarded, Advanced, and Causal Green Functions.

Green functions in statistical mechanics are a convenient generalization of the concept of correlation functions. Like the correlation functions, the Green functions are closely related to the calculation of observable quantities, but they have advantages in constructing and solving their defining equations.

In statistical mechanics, as in the quantum theory of fields, one can consider retarded $G_r(t,t')$, advanced $G_\alpha(t,t')$, and causal $G_c(t,t')$ Green functions:

$$\begin{aligned} G_r(t,\ t') &= \langle\langle A(t)\,B(t')\rangle\rangle_r = \frac{1}{i\hbar}\,\theta(t-t')\,\langle [A(t),\ B(t')]\rangle, \\ G_a(t,\ t') &= \langle\langle A(t)\,B(t')\rangle\rangle_a = -\frac{1}{i\hbar}\,\theta(t'-t)\,\langle [A(t),\ B(t')]\rangle, \qquad (16.1) \\ G_c(t,\ t') &= \langle\langle A(t)\,B(t')\rangle\rangle_c = \frac{1}{i\hbar}\,\langle T A(t)\,B(t')\rangle. \end{aligned}$$

Here <...> denotes an averaging over the Gibbs grand canonical ensemble (9.42). We omit the index 0 on the brackets, denoting equilibrium averages, because in this paragraph we shall consider only averaging over an equilibrium ensemble;

$$\langle \ldots \rangle = Q^{-1}\,\mathrm{Sp}\,(e^{-\mathcal{H}/\theta}\ldots), \qquad Q = \mathrm{Sp}\, e^{-\mathcal{H}/\theta} = e^{-\Omega/\theta}; \tag{16.2}$$

Ω is the thermodynamic potential (9.40) in the variables θ, μ, V. The operator $\mathcal{H}$ included a term with the chemical potential μ:

$$\mathcal{H} = H - \mu N. \tag{16.3}$$

The time arguments of the operators $A(t), B(t')$ denote the Heisenberg representation:

$$A(t) = e^{i\mathcal{H}t/\hbar} A e^{-i\mathcal{H}t/\hbar}, \tag{16.4}$$

The symbol T denotes the chronological product of operators[1]:

$$TA(t)\,B(t') = \theta(t-t')\,A(t)\,B(t') + \eta\theta(t'-t)\,B(t')\,A(t), \tag{16.5}$$

where $\theta(t)$ is the discontinuous function (15.17). Finally $[A,B]$ is the commutator or anticommutator, depending on the sign of η:

$$[A,B] = AB - \eta BA, \tag{16.6}$$

i.e., for $\eta=1$ it is the commutator, and for $\eta=-1$ it is the anticommutator.

The sign of η in formulas (16.5) and (16.6) is chosen plus or minus on the basis of convenience in the problem. If A and B are Bose operators, the plus sign is usually taken. If they are Fermi operators, the minus sign is usually taken (for such a choice of η we have $[A,A^+]=1$) but another choice of the sign of η is possible. We have already introduced the Green functions $G_r(t,t')$ with $\eta=1$ (see formula (15.48)). Generally speaking, A and B are neither Fermi nor Bose, because the products of operators can satisfy more complicated commutation relations than the original operators. In quantum field theory the sign of η in the T-product is defined by the parity of the permutation of the Fermi operators making up the product upon transferring them to chronological order.

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[1] We made use of a particular case of this operation with $\eta=1$ in § 15 in writing the ordering of the P-exponential (15.56b).

Let us note that if t=t′, the Green functions are undefined because of the discontinuous factor θ(t-t′). This indefiniteness is well known in the quantum theory of fields [23-26].

From the definitions (16.1)-(16.6) it follows that the Green functions used in statistics differ from the field theoretic Green functions only in the method of averaging. Instead of averaging over the lowest, vacuum state of the system, the averaging is carried out over the Gibbs grand canonical ensemble (16.2). Thus, the Green functions which have been introduced here depend both on time and on temperature. Obviously, as the temperature approaches zero the Green functions (16.1) go over into the usual field theoretic Green functions, in which the averaging is carried out over the lowest energy state. Let us note that in contrast to quantum field theory, where the vacuum averages are infinite and are discarded as having no physical meaning, in statistical mechanics the averages over the ground state of the system in the thermodynamic limit (see section 3.2) give observable quantities.

The use of the Gibbs grand ensemble is not accidental. It is very convenient to work with this ensemble, because it is not necessary to impose an auxiliary condition of constant particle number, as for the Gibbs canonical ensemble (9.14), and the occupation numbers of the various states are independent.

For the case of statistical equilibrium the Green functions (16.1) depend only on t-t′; this follows because of the possibility of cyclic permutation under the spur sign (see (15.48a)).

Many problems of statistical mechanics can be limited to doubletime functions; it is not necessary to resort to multiple time functions. The doubletime functions are very convenient, because one can make use of simple spectral expansions for them, which greatly facilitates the solution of the equations for the Green functions. On the other hand, they contain a sufficiently great amount of information about the equilibrium and nonequilibrium properties of many particle systems. Of the doubletime Green functions the most convenient are the retarded and advanced Green functions G_r and G_a, because their Fourier components can be analytically continued into the complex energy plane.

We shall obtain a system of equations for the Green functions (16.1). The operators A(t) and B(t) satisfy equations of motion of the form

[illegible] (16.7)

where A is an operator in the Heisenberg representation (16.4). The right hand side of equation (16.7) can be expanded using the explicit form of the Hamiltonian and the commutation relations for the operators. Differentiating the Green functions (16.1) with respect to t, we obtain the equation

$$i\hbar \frac{dG(t-t')}{dt} = i\hbar \frac{d}{dt}\langle\langle A(t)\,B(t')\rangle\rangle =$$
$$= \frac{d\theta(t-t')}{dt}\langle [A(t),\ B(t')]\rangle + \langle\langle i\hbar \frac{dA(t)}{dt}\,B(t')\rangle\rangle,$$

which is identical for all three Green functions G_r, G_α, G_c because

$$\frac{d}{dt}\theta(-t) = -\frac{d}{dt}\theta(t).$$

Therefore we write simply G and <<...>> without subscripts denoting the type of Green function. Using the relation of the discontinuous function $\theta(t)$ to the δ-function of t,

$$\theta(t) = \int_{-\infty}^{t} \delta(t)\,dt, \tag{16.8}$$

and the equation of motion (16.7) for the operator A(t), we write the equation for the Green function in the form

$$i\hbar \frac{dG(t-t')}{dt} = \delta(t-t')\langle [A(0),\ B(0)]\rangle + \langle\langle (A(t)\mathcal{H} - \mathcal{H}A(t))\,B(t')\rangle\rangle, \tag{16.9}$$

where we have taken into account that in statistical equilibrium $\langle A(t)B(t')\rangle$ depends only on the difference $t-t'$, and thus

$$\langle A(t)\,B(t)\rangle = \langle A(0)\,B(0)\rangle, \qquad A(0) = A,\ B(0) = B.$$

In general, doubletime Green functions of a higher order than the original appear on the right hand side of equation (16.9). One can also set up for the higher order Green functions an equation of the type (16.9) and obtain a chain of coupled equations for the Green functions.

Chains of equations of the type (16.9) are simply equations of motion for the Green functions. These equations alone are insufficient, which is evident from the fact that they are identical for all Green functions G_r, G_α, G_c, if they are constructed from the same operators A and B. It is necessary to supplement them with boundary conditions. This will be done below, in section 16.3, using the spectral theorems.

Equations (16.9) are exact; therefore solution of this chain of equations is an immensely complicated problem. It is sometimes possible by using some sort of approximate method to uncouple the chain of equations of the type (16.9), i.e., to transform it to a finite system of equations and to solve them. Examples of such uncouplings can be found in [12-15,63,64,66]. If the system contains a small parameter, for example a small interaction or a small density, then such uncouplings can be justified.

16.2. Spectral Representation of Time Correlation Functions.

In solving equations (16.9) for the Green functions it is important to have spectral representations for them, which supplement the system of equations with the necessary boundary conditions. We shall obtain spectral representations for the Green functions (16.1) in the following section; here we do so for the corresponding correlation functions

$$F_{BA}(t'-t)=\langle B(t')\,A(t)\rangle, \qquad F_{AB}(t-t')=\langle A(t)\,B(t')\rangle. \tag{16.10}$$

Let C_ν and E_ν be the eigenfunctions and eigenvalues of the Hamiltonian (16.3):

$$\mathcal{H}C_\nu = E_\nu C_\nu. \tag{16.11}$$

We write out explicitly the operation of statistical averaging for the time correlation functions (16.10):

$$\langle B(t')\,A(t)\rangle = Q^{-1}\sum_\nu \left(C_\nu^* B(t')\,A(t)\,C_\nu\right) e^{-\frac{E_\nu}{\theta}}. \tag{16.12}$$

We make use of the usual method of the theory of dispersion relations, based on the completeness of the system of functions C_ν [23,25,67], and represent (16.12) in the form

$$\langle B(t')\,A(t)\rangle = Q^{-1}\sum_{\nu,\,\mu}\left(C_\nu^* B(t')\,C_\mu\right)\left(C_\mu^* A(t)\,C_\nu\right)e^{-\frac{E_\nu}{\theta}} =$$
$$= Q^{-1}\sum_{\nu,\,\mu}\left(C_\nu^* B(0)\,C_\mu\right)\left(C_\mu^* A(0)\,C_\nu\right)e^{-E_\nu/\theta}\exp\left\{\frac{i}{\hbar}(E_\mu - E_\nu)(t-t')\right\}, \qquad (16.13)$$

because
$$e^{-i\mathcal{H}t/\hbar}C_\nu = e^{-\frac{iE_\nu t}{\hbar}}C_\nu, \qquad C_\mu^* e^{\frac{i\mathcal{H}t}{\hbar}} = C_\mu^* e^{\frac{iE_\mu t}{\hbar}}.$$

On the other hand

$$\langle A(t)\,B(t')\rangle =$$
$$= Q^{-1}\sum_{\nu,\,\mu}\left(C_\nu^* A(0)\,C_\mu\right)\left(C_\mu^* B(0)\,C_\nu\right)e^{-E_\nu/\theta}\exp\left\{\frac{i}{\hbar}(E_\mu - E_\nu)(t'-t)\right\}. \qquad (16.14)$$

Interchanging the summation indices μ and ν in the last equation and comparing (16.13) and (16.14), we notice that they can be represented in the form

$$\langle B(t')\,A(t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} J_{BA}(\omega)\,e^{i\omega(t'-t)}\,d\omega, \qquad (16.15)$$
$$\langle A(t)\,B(t')\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} J_{BA}(\omega)\,e^{\frac{\hbar\omega}{\theta}}e^{i\omega(t'-t)}\,d\omega,$$

where the notation

$$J_{BA}(\omega) = 2\pi Q^{-1}\sum_{\nu,\,\mu}\left(C_\mu^* B(0)\,C_\nu\right)\left(C_\nu^* A(0)\,C_\mu\right)e^{-\frac{E_\mu}{\theta}}\,\delta\left(\frac{E_\mu - E_\nu}{\hbar} - \omega\right). \qquad (16.16)$$

has been introduced.

Relations (16.15) are the required spectral representations of the time correlation functions[1]: $J_{BA}(\omega)$ is the spectral intensity of the function $\langle B(t')A(t)\rangle$.

Comparing the first of relations (16.15) with the second, we obtain an important property of the spectral intensity:

$$J_{AB}(-\omega) = J_{BA}(\omega)\, e^{\beta\hbar\omega}. \tag{16.16a}$$

For the systems studied in statistical mechanics the spectrum $E\mu$ is practically continuous because of the large dimensions of the system; therefore the summation over the states in (16.16) is essentially an integration, which can "remove" the δ-function. Thus, the spectral intensity is in general not a δ-type function; only in particular cases of "ideal" systems, in which the elementary excitations are undamped, can they have the form of a δ-function.

To derive the relations (16.15) it would not be necessary to use the eigenfunctions of the operator $\mathcal{H}$. For this it is sufficient to note that $\langle B(t')A(t)\rangle$ depends only on the difference $t-t'$. Thus, the first of relations (16.15) is simply the definition of the Fourier component of the time correlation function; here it is assumed that such an expansion is possible[2]. The second relation (16.15) can be obtained from the first by the replacement $t-t' \to t-t'+(i\hbar/\theta)$, because

---

[1] The spectral representations for the time correlation functions and Green functions of statistical mechanics were first used in the article of Callen and Welton [22] on the theory of fluctuations and noise and were later widely used by many authors [1,3,4,60-64,68].

[2] A. Ya. Khinchin [16] has shown that for a continuous, stationary random process the correlation functions can be represented in the form of a Fourier-Stieltjes integral:

$$\langle (A - \langle A\rangle)(A(t) - \langle A\rangle)\rangle = \int_{-\infty}^{\infty} \cos \omega t \, dF(\omega)$$

(A represents dynamical variables of classical mechanics, $A^* = A$), where $F(\omega)$ is a nondecreasing function with bounded variation, called the spectrum of the process. Instead of a Fourier-Stieltjes integral one can use simply a Fourier integral, if one allows $\frac{dF(\omega)}{d\omega} = J_{AA}(\omega)$ to be a generalized function.

$$\left\langle B(0)\,A\left(t+\frac{i\hbar}{\theta}\right)\right\rangle = \langle A(t)\,B(0)\rangle, \tag{16.17}$$

which is easily verified by inspection, by carrying out a cyclic permutation of the operators under the spur sign. In fact, after the permutation which shifts the operator B to the first place, we obtain

$$\begin{aligned}\langle A(t)\,B(0)\rangle = Q^{-1}\,\mathrm{Sp}\,\{e^{-\beta\mathcal{H}}e^{i\mathcal{H}t/\hbar}Ae^{-i\mathcal{H}t/\hbar}B\} = \\ = Q^{-1}\,\mathrm{Sp}\left\{Be^{-\left(\beta-\frac{it}{\hbar}\right)\mathcal{H}}Ae^{\left(\beta-\frac{it}{\hbar}\right)\mathcal{H}}e^{-\beta\mathcal{H}}\right\},\end{aligned}$$

i.e., the relation (16.17).

For all real systems the correlations decrease with the increase of time, i.e.,

$$\lim_{|t-t'|\to\infty}\langle A(t)\,B(t')\rangle = \langle A\rangle\langle B\rangle$$

(A and B are not integrals of motion); thus if $\langle A\rangle=0$ or $\langle B\rangle=0$, then

$$\lim_{|t-t'|\to\infty}\langle A(t)\,B(t')\rangle = 0.$$

If new operators $A(t)-\langle A\rangle, B(t)-\langle B\rangle$, are introduced, then they will lose their correlations in time. Then the expansion (16.15) can be written in the form

$$\begin{aligned}\langle (B(t')-\langle B\rangle)(A(t)-\langle A\rangle)\rangle = \langle B(t')\,A(t)\rangle - \langle B\rangle\langle A\rangle = \\ = \frac{1}{2\pi}\int_{-\infty}^{\infty} J_{BA}(\omega)\,e^{i\omega(t'-t)}d\omega.\end{aligned} \tag{16.15a}$$

In what follows we shall always assume that if $\langle B(t')A(t)\rangle$ approaches a finite limit as $|t-t'|\to\infty$, then its expansion in a Fourier integral has the meaning of (16.15a).

If $J_{BA}(\omega)$ is a continuous function, then in accordance with the Riemann Lebesgue Lemma

$$\lim_{|t-t'|\to\infty} \langle (B(t') - \langle B\rangle)(A(t) - \langle A\rangle)\rangle = 0.$$

If $J_{BA}(\omega)$ has δ-function singularities at some frequencies, the correlation functions (16.15a) will not approach zero as $|t-t'|\to\infty$, but will oscillate. If these frequencies are incommensurable, the correlation functions are almost periodic.

The time average of the correlation functions is equal to zero:

$$\lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T}\frac{1}{2\pi}\int_{-\infty}^{\infty} J_{BA}(\omega)\, e^{-i\omega t}\, dt\, d\omega =$$
$$= \lim_{T\to\infty}\frac{1}{2T}\int_{-\infty}^{\infty} J_{BA}(\omega)\,\delta(\omega)\, d\omega = \lim_{T\to\infty}\frac{J_{BA}(0)}{2T} = 0,$$

if the spectral intensity is finite at $\omega=0$, which is a characteristic of the spectrum of a random, ergodic process[1]. In what follows we shall assume that $J_{BA}(\omega)$ does not have a δ-form at $\omega=0$. This is essential for the unique definition of the Green function from equations (16.9) [70].

The time correlation functions for any finite system, i.e., before taking the limit $V\to\infty$, are almost periodic functions of $t-t'$, as was shown by Bocchiery and Loinger [71] and Percival [71a]. This is a quantum mechanical theorem analogous to the Poincare recurrence theorem of classical mechanics[2]. The decay of the correlation functions for real systems can be obtained only after passing to the limit $V\to\infty$ ($V/N=\text{const}$), which is as if to eliminate the long Poincare cycles.

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[1] The connection between the spectrum of a stationary random process and the ergodicity property is established by the Wiener-Khinchin theorem [16,69].

[2] According to the Poincare recurrence theorem any isolated mechanical system in a finite volume will repeatedly approach arbitrarily closely to its initial state. A very elegant and simple proof of this theorem and its precise formulation can be found in the book of Katz [72].

If A or B is an integral of motion, then the time correlation function in general is independent of time. Indeed, let A be an integral of motion. Then

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar} = A(0)$$

and, consequently,

$$\langle A(t) B(t')\rangle = \langle A(t-t') B(0)\rangle = \langle A(0) B(0)\rangle.$$

Let us demonstrate one important property of the spectral intensity, which we shall need in what follows. We shall show that the spectral intensity $J_{A^+A}(\omega)$ of the time correlation function, constructed from the conjugate operators A^+ and A, is non-negative, i.e., in the spectral expansion

$$\langle A^+(t') A(t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} J_{A^+A}(\omega)\, e^{i\omega(t'-t)}\, d\omega \tag{16.18}$$

it is alway true that

$$J_{A^+A}(\omega) \geqslant 0. \tag{16.18a}$$

From the expression (16.16) for the spectral intensity it follows that

$$J_{A^+A}(\omega) = 2\pi Q^{-1}\sum_{\nu,\mu}(C_\mu^* A^+(0)\, C_\nu)(C_\nu^* A(0)\, C_\mu)\, e^{-E_\mu/\theta}\,\delta\left(\frac{E_\mu - E_\nu}{\hbar} - \omega\right) \geqslant 0,$$

because all of the terms under the summation sign are non-negative. Thus, the spectral intensity $J_{A^+A}(\omega)$ cannot by negative. From the proof above it follows directly that $J_{AA^+}(\omega)$ is also non-negative.

16.3. Spectral Representation and Dispersion Relation for Green Functions.

Let us now consider the spectral representations for Green functions, first for the retarded and advanced functions. They are easily obtained by using the spectral representations (16.15) for the time correlation functions. Indeed, let $G_r(\omega)$ be the Fourier component of the Green function $G_r(t-t')$:

$$G_r(t-t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} G_r(\omega)\, e^{-i\omega(t-t')}\, d\omega,$$
$$G_r(\omega) = \int_{-\infty}^{\infty} G_r(t)\, e^{i\omega t}\, dt. \tag{16.19}$$

For the Fourier components of the Green functions we use the same notation as for the Green functions themselves, distinguishing them only by their arguments. Sometimes we shall also make use of the notation $\langle\langle A|B\rangle\rangle_\omega$:

$$\langle\langle A(t)\, B(t')\rangle\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle\langle A|B\rangle\rangle_\omega\, e^{-i\omega(t-t')}\, d\omega. \tag{16.19a}$$

Substituting in the second of equations (16.19) the expression (16.1) for $G_r(t)$, we obtain

$$G_r(\omega) = \frac{1}{i\hbar}\int_{-\infty}^{\infty} \theta(t-t')\{\langle A(t)\, B(t')\rangle - \eta\,\langle B(t')\, A(t)\rangle\}\, e^{i\omega(t-t')}\, dt.$$

Here in the integrand, besides the discontinuous function, are the time correlation functions. Using the representation (16.15) for them, we have

$$G_r(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega'\, J_{BA}(\omega')\,(e^{\hbar\omega'/\theta} - \eta)\,\frac{1}{i\hbar}\int_{-\infty}^{\infty} dt\, e^{i(\omega-\omega')t}\,\theta(t). \tag{16.20}$$

We represent the discontinuous function $\theta(t)$ in the form

$$\theta(t) = \int_{-\infty}^{t} e^{\varepsilon t}\,\delta(t)\, dt \qquad (\varepsilon \to 0,\ \varepsilon > 0), \tag{16.21}$$

or, since

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ixt}\, dx, \tag{16.22}$$

in another very convenient form:

$$\theta(t)=\frac{i}{2\pi}\int_{-\infty}^{\infty}\frac{e^{-ixt}}{x+i\varepsilon}\,dx. \tag{16.23}$$

It is easy to verify that a function so defined indeed has the properties of the discontinuous θ-function. We shall consider x as a complex variable and consider that the integral is carried out along the contour depicted in Figure 1. The integrand has a pole in the lower half plane.

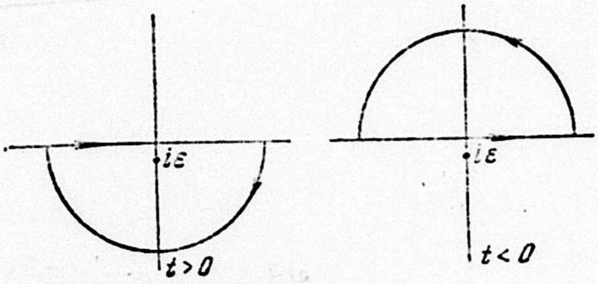

Fig. 1

For t>0 the contour must be closed in the lower half plane and the integral (16.23) is equal to one. For t<0 the contour must be closed in the upper half plane and the integral (16.23) is equal to zero.

The discontinuous θ-function can be represented also by means of the contour integral

$$\theta(t)=\frac{i}{2\pi}\int_{C_r} e^{-itx}\frac{dx}{x}=\begin{cases}0 & \text{for } t<0,\\ 1 & \text{for } t>0,\end{cases}$$

where the integration is carried out along the contour C_r, which is depicted in Figure 2.

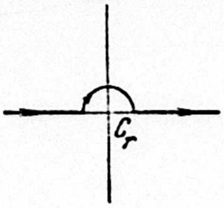

Fig. 2

Using (16.23) and (16.22), we obtain

$$\frac{1}{2\pi i}\int_{-\infty}^{\infty} e^{i(\omega-\omega')t}\,\theta(t)\,dt=\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{\delta(\omega-\omega'-x)}{x+i\varepsilon}\,dx=\frac{1}{2\pi}\,\frac{i}{\omega-\omega'+i\varepsilon}.$$

Thus, $G_r(\omega)$ - the Fourier component of the retarded Green function $G_r(t)$ - is equal to

$$G_r(\omega)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left(e^{\hbar\omega'/\theta}-\eta\right)J_{BA}(\omega')\,\frac{d\omega'}{\omega-\omega'+i\varepsilon}. \qquad (16.24)$$

Repeating the same calculations for $G_\alpha(\omega)$ - the Fourier component of the advanced Green function $G_\alpha(t)$ - we obtain

$$G_a(\omega)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left(e^{\hbar\omega'/\theta}-\eta\right)J_{BA}(\omega')\,\frac{d\omega'}{\omega-\omega'-i\varepsilon}. \qquad (16.24a)$$

We write formulas (16.24) and (16.24a) as a single formula

$$G_{r,a}(\omega)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left(e^{\hbar\omega'/\theta}-\eta\right)J_{BA}(\omega')\,\frac{d\omega'}{\omega-\omega'\pm i\varepsilon}, \qquad (16.24b)$$

where the plus corresponds to the subscript r, and the minus corresponds to the subscript α.

As yet we have considered ω to be a real quantity. The function (16.24b) can be analytically continued into the complex ω plane. Indeed, considering ω to be complex, we obtain

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left(e^{\hbar\omega'/\theta}-\eta\right)J_{BA}(\omega')\,\frac{d\omega'}{\omega-\omega'}=$$

$$=\begin{cases}G_r(\omega) & \text{for } \operatorname{Im}\omega>0,\\ G_a(\omega) & \text{for } \operatorname{Im}\omega<0.\end{cases} \quad (16.25) \qquad (16.25)$$

Therefore the function $G_{r,\alpha}(\omega)$ can be considered, following [15], to be a single analytic function in the complex plane, having a singularity on the real axis. In what follows we shall omit the subscripts r,α and write simply $G(\omega)$, considering ω to be complex. We then write the relation (16.25) in the form

$$G(\omega) = \langle\langle A \mid B\rangle\rangle_{\omega} = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left(e^{\hbar\omega'/\theta} - \eta\right) J_{BA}(\omega')\,\frac{d\omega'}{\omega-\omega'}. \qquad (16.26)$$

The analyticity of $G(\omega)$ follows from a theorem proved by N. N. Bogolyubov and O. S. Parasyuk in the theory of dispersion relations [73]. According to this theorem it is necessary and sufficient for the analyticity of $G(\omega)$ that $G_r(t)$ (or $G_\alpha(t)$) be generalized functions in the sense of Sobolev-Schwartz, which is not too stringent a demand.

Let us consider first the analytic properties of $G_r(\omega)$. According to (16.19) we have

$$G_r(\omega) = \int_{-\infty}^{\infty} G_r(t)\, e^{i\omega t}\, dt, \qquad (16.27)$$

for which $G_r(t)=0$ for $t<0$.

We shall show that the function $G_r(\omega)$ can be analytically continued into the region of complex ω in the upper half plane. Let ω have a positive, non-zero imaginary part γ:

14 $$\omega = \mathrm{Re}\,\omega + i\,\mathrm{Im}\,\omega = \alpha + i\gamma, \qquad \gamma > 0.$$

Then we have

$$G_r(\alpha + i\gamma) = \int_{0}^{\infty} G_r(t)\, e^{i\alpha t - \gamma t}\, dt. \qquad (16.28)$$

The term $e^{-\gamma t}$ plays the role of a cut-off factor which guarantees the convergence of the integral (16.28) and its derivatives with respect to ω under sufficiently general assumptions about the function $G_r(t)$ [73]. Thus, the function $G_r(\omega)$ can be analytically continued into the upper half plane.

It can be shown analogously that the function $G_\alpha(\omega)$ can be analytically continued into the lower half plane:

$$\omega = \alpha + i\gamma, \qquad \gamma < 0.$$

If a branch cut is made along the real axis, then the function

$$G(\omega) = \begin{cases} G_r(\omega) \text{ for } & \operatorname{Im}\omega > 0, \\ G_a(\omega) \text{ for } & \operatorname{Im}\omega < 0 \end{cases} \tag{16.29}$$

can be considered as a single analytic function, made up of two branches, one of which is defined in the upper and the other in the lower half plane of the complex ω plane.

If $G(\omega)$ is known, then the spectral intensity $J_{BA}(\omega)$ can be found by the relationship

$$G(\omega + i\varepsilon) - G(\omega - i\varepsilon) = \frac{1}{i\hbar}\left(e^{\hbar\omega/\theta} - \eta\right) J_{BA}(\omega), \tag{16.30}$$

where ω is real, and $\varepsilon \to 0$. Indeed, forming the difference of expressions (16.26) for real ω

$$G(\omega + i\varepsilon) - G(\omega - i\varepsilon) =$$
$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left(e^{\hbar\omega'/\theta} - \eta\right) J_{BA}(\omega')\left\{\frac{1}{\omega' - \omega + i\varepsilon} - \frac{1}{\omega' - \omega - i\varepsilon}\right\} d\omega'$$

and making use of the representation of the δ-function

$$\delta(x) = \frac{1}{2\pi i}\left\{\frac{1}{x - i\varepsilon} - \frac{1}{x + i\varepsilon}\right\}, \tag{16.31}$$

we obtain the relationship (16.30), which plays an important role in applications of Green functions.

Thus, if we can in some way uncouple the chain of equations for the Green functions (16.9) and find the Green function $G(\omega)$, then using (16.30) we can construct the spectral intensity $J_{BA}(\omega)$ and find expressions for the time correlation functions (16.15).

We shall obtain simple but important relations between the Green functions and the spectral intensities of the correlation functions.

Using the symbolic identity

$$\frac{1}{\omega-\omega'\pm i\varepsilon}=\mathcal{P}\,\frac{1}{\omega-\omega'}\mp i\pi\delta(\omega-\omega'), \tag{16.32}$$

in the integrands of the formulas (16.24) and (16.24a), where $\varepsilon \to 0, \varepsilon > 0$, and $\mathcal{P}$ denotes the principal value of the integral. Here $\omega-\omega'$ is considered as a real variable. Then we obtain[1]

$$\begin{aligned} G_r(\omega) &= \frac{1}{2\pi\hbar}\,\mathcal{P}\int\limits_{-\infty}^{\infty}(e^{\hbar\omega'\beta}-\eta)\,J_{BA}(\omega')\,\frac{d\omega'}{\omega-\omega'}-\frac{i}{2\hbar}(e^{\hbar\omega\beta}-\eta)\,J_{BA}(\omega),\\ G_a(\omega) &= \frac{1}{2\pi\hbar}\,\mathcal{P}\int\limits_{-\infty}^{\infty}(e^{\hbar\omega'\beta}-\eta)\,J_{BA}(\omega')\,\frac{d\omega'}{\omega-\omega'}+\\ &\qquad\qquad +\frac{i}{2\hbar}(e^{\hbar\omega\beta}-\eta)\,J_{BA}(\omega), \end{aligned} \tag{16.33}$$

from which follows the connection between the real and imaginary parts of the Green functions ($J_{BA}(\omega)$ is assumed real):

$$\begin{aligned} \operatorname{Re} G_r(\omega) &= \frac{1}{\pi}\,\mathcal{P}\int\limits_{-\infty}^{\infty}\frac{\operatorname{Im} G_r(\omega')}{\omega'-\omega}\,d\omega',\\ \operatorname{Re} G_a(\omega) &= -\frac{1}{\pi}\,\mathcal{P}\int\limits_{-\infty}^{\infty}\frac{\operatorname{Im} G_a(\omega')}{\omega'-\omega}\,d\omega'. \end{aligned} \tag{16.34}$$

---

[1] The relations (16.33) express the well-known properties of the limiting values of a Cauchy integral upon shifting the point ω onto the contour of integration. These properties were first established by Yu. V. Sokhotskiy in 1873, and then by K. Plemel' in 1908 (see the textbook on the theory of functions of a complex variable by M. A. Lavrent'yev and B. V. Shabat [74]).

The relations (16.34) are called dispersion relations. If the spectral intensity is real, these relations follow directly from (16.33), because in that case

$$\operatorname{Im} G_r(\omega) = -\frac{1}{2\hbar}\left(e^{\hbar\omega/\theta} - \eta\right) J_{BA}(\omega),$$
$$\operatorname{Im} G_a(\omega) = \frac{1}{2\hbar}\left(e^{\hbar\omega/\theta} - \eta\right) J_{BA}(\omega), \tag{16.34a}$$

but the relations (16.34) are valid not only in that case. The dispersion relations (16.34) follow from the analyticity of $G_r(\omega)$ in the upper, and $G_a(\omega)$ in the lower half planes in the complex ω plane (see (16.28)). Indeed, if $G_r(\omega)$ is analytic in the upper half plane, and $G_a(\omega)$ in the lower, then they can be represented in the form of Cauchy integrals:

$$G_r(\omega) = \frac{1}{2\pi i}\int_{i\delta-\infty}^{i\delta+\infty} \frac{G_r(\omega')}{\omega'-\omega}\,d\omega' \qquad (\operatorname{Im}\omega > \delta > 0),$$
$$G_a(\omega) = -\frac{1}{2\pi i}\int_{-i\delta-\infty}^{-i\delta+\infty} \frac{G_a(\omega')}{\omega'-\omega}\,d\omega' \quad (\operatorname{Im}\omega < -\delta < 0). \tag{16.35}$$

It is assumed that for any positive δ

$$|G_{r,a}(\omega)| \leqslant \frac{A(\delta)}{|\omega|} \text{ for } \operatorname{Im}\omega > \delta \text{ (or } \operatorname{Im}\omega < -\delta),$$

and therefore, the integral along the path of radius R which closes the contour in the upper (or lower) half plane approaches zero as $R\to\infty$.

Let us take the path of integration down to the real axis, having let $\delta\to 0$. Then

$$G_{r,a}(\omega) = \pm\frac{1}{2\pi i}\int_{-\infty}^{\infty} \frac{G_{r,a}(\omega')}{\omega'-\omega}\,d\omega'. \tag{16.36}$$

We now let the point ω approach the real axis, putting $\omega\to\omega\pm i\varepsilon(\varepsilon\to 0)$, and we rewrite (16.36) in the form

$$G_{r,a}(\omega) = \pm \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{G_{r,a}(\omega')}{\omega' - \omega \mp i\varepsilon} d\omega'. \tag{16.36a}$$

The dispersion relations (16.34) follow from (16.36a) by using the symbolic identity (16.32).

Consequently, a detailed knowledge of $G_r(t-t')$ (or $G_a(t-t')$) is not required to derive the dispersion relations; it is sufficient to know that the Green function is retarded (or advanced), i.e., that it is equal to zero for $t<t'$ (or for $t>t'$), and that its Fourier components fall off sufficiently rapidly as $\omega\to\infty$.

The spectral representations (16.26) and the dispersion relations (16.34) for the Green functions lead directly to the spectral representations and dispersion relations for the kinetic coefficients, because the latter are expressed through the retarded Green functions (see (15.66a)). We discuss these questions in a subsequent paragraph, which is devoted to the fluctuation-dissipation theorems.

The spectral representations derived above are for the retarded and advanced Green functions, which are applied in the theory of irreversible processes. However, in statistical physics the causal Green functions, for which diagrammatic techniques have been worked out [60-64,75], are applied rather often. Spectral representations for causal Green functions can be found in [76,60,61].

16.4. Sum Rules.

From the existence of the spectral expansions for the Green functions there follow for these functions some simple identities - sum rules, which find application in the theory of nonequilibrium processes, for example, in the theory of electrical conductivity and magnetism [1,3,4].

For the retarded Green functions we have by definition

$$\langle\langle A \mid B\rangle\rangle_\omega^r = \int_{-\infty}^{\infty} \langle\langle AB(t)\rangle\rangle^r e^{-i\omega t} dt. \tag{16.37}$$

Integrating this relationship over all ω, we obtain

$$\int_{-\infty}^{\infty} \langle\langle A \mid B\rangle\rangle^{r}_{\omega}\, d\omega = \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{0} \frac{1}{i\hbar} \langle [A,\ B(t)] \rangle e^{-i\omega t}\, dt =$$

$$= \int_{-\infty}^{0} \frac{2\pi}{i\hbar} \langle [A,\ B(t)] \rangle \delta(t)\, dt.$$

Thus, for the retarded Green functions there exists the identity

$$\int_{-\infty}^{\infty} \langle\langle A \mid B\rangle\rangle^{r}_{\omega}\, d\omega = \frac{\pi}{i\hbar} \langle [A(0),\ B(0)] \rangle, \tag{16.38}$$

called a sum rule. This name stems from the fact that such relations were first obtained in a matrix form, containing sums over quantum states.

An analogous relationship is valid for advanced Green functions, but with the opposite sign on the right hand side:

$$\int_{-\infty}^{\infty} \langle\langle A \mid B\rangle\rangle^{a}_{\omega}\, d\omega = -\frac{\pi}{i\hbar} \langle [A(0),\ B(0)] \rangle, \tag{16.38a}$$

To obtain sum rules of a different type we integrate (16.37) by parts, setting $<[A,B(t)]>|_{t=-\infty}=0$. We obtain

$$\langle\langle A \mid B\rangle\rangle^{r}_{\omega} = \frac{1}{\hbar\omega} \langle [A(0),\ B(0)] \rangle - \frac{1}{\hbar\omega} \int_{-\infty}^{0} \left\langle \left[A,\ \frac{dB(t)}{dt}\right] \right\rangle e^{-i\omega t}\, dt,$$

and thus,

$$\int_{-\infty}^{\infty} \{\hbar\omega \langle\langle A \mid B\rangle\rangle^{r}_{\omega} - \langle [A(0),\ B(0)] \rangle\}\, d\omega =$$

$$= -2\pi \int_{-\infty}^{0} \left\langle \left[A,\ \frac{dB(t)}{dt}\right] \right\rangle \delta(t)\, dt = -\pi \left\langle \left[A,\ \frac{dB(t)}{dt}\right] \right\rangle_{t=0}, \tag{16.39}$$

and analogously for the advanced Green functions

$$\int_{-\infty}^{\infty} \{\hbar\omega \langle\langle A \mid B\rangle\rangle^{a}_{\omega} - \langle [A(0),\ B(0)] \rangle\}\, d\omega = \pi \left\langle \left[A,\ \frac{dB(t)}{dt}\right] \right\rangle_{t=0}. \tag{16.39a}$$

Relations (16.39) and (16.39a) are sum rules of the second type.

From the convergence of the integrals on the left hand side of (16.39) and (16.39a) it follows that the retarded and advanced Green functions behave as $1/\omega$ as $\omega\to\infty$:

$$\langle\langle A \mid B\rangle\rangle_\omega^{r,a} \approx \langle[A(0),\ B(0)]\rangle \frac{1}{\hbar\omega}, \tag{16.40}$$

provided that the average commutator (or anticommutator) on the right hand side of relation (16.40) is non-zero; otherwise they fall off even faster as ω increases.

Continuing to integrate by parts in (16.37) up to terms of n^{th} order, we obtain

$$\langle\langle A \mid B\rangle\rangle_\omega^r = \frac{1}{\hbar\omega}\left\{\langle[A(0),\ B(0)]\rangle + \sum_{k=1}^{n}\left\langle\left[A,\ \frac{d^k B(t)}{dt^k}\right]\right\rangle_{t=0}\frac{1}{(i\omega)^k}\right\} -$$
$$- \frac{i}{(i\omega)^{n+1}}\int_{-\infty}^{0}\left\langle\left[A,\ \frac{d^{n+1}B(t)}{dt^{n+1}}\right]\right\rangle e^{-i\omega t}\,dt, \tag{16.41}$$

from which follows a generalized sum rule of the second type:

$$\int_{-\infty}^{\infty}\left\{\langle\langle A|B\rangle\rangle_\omega^r - \frac{1}{\hbar\omega}\left\{\langle[A,\ B]\rangle - \sum_{k=1}^{n}\left\langle\left[A,\ \frac{d^k B(t)}{dt^k}\right]\right\rangle_{t=0}\frac{1}{(i\omega)^k}\right\}\right\}\omega^{n+1}\,d\omega =$$
$$= -\frac{\pi}{i^n}\left\langle\left[A,\ \frac{d^{n+1}B(t)}{dt^{n+1}}\right]\right\rangle_{t=0}. \tag{16.41a}$$

Similar relations for the advanced Green functions differ from (16.41a) only by the sign on the right hand side of the equation.

From (16.41a) we obtain as $n\to\infty$ an asymptotic expansion in powers of $1/\omega$; it is identical for the retarded and advanced Green functions. We obtain the same expansion if in the equation for the Green functions (16.9) in the Fourier representation

$$\langle\langle A \mid B\rangle\rangle_\omega = \frac{1}{\hbar\omega}\langle[A,\ B]\rangle - \frac{i}{\omega}\left\langle\left\langle A \,\middle|\, \frac{dB}{dt}\right\rangle\right\rangle_\omega$$

we carry out a successive iteration and eliminate terms with time derivatives by using similar equations, in which $B \to \frac{dB}{dt}$, $\frac{dB}{dt} \to \frac{d^2B}{dt^2}$ etc.

The sum rules which were considered earlier are applied in the theory of irreversible processes, for example, for the electrical conductivity tensor, magnetic susceptibility (see § 18), which are expressed through the retarded Green functions.

16.5. Symmetry of Green Functions.

Let us now consider the symmetry properties of the correlation functions and the Green functions (see [1,77]).

From the definitions of the retarded and advanced Green functions (16.1) it follows that

$$\langle\langle A(t)B(t')\rangle\rangle_r = \eta\langle\langle B(t')A(t)\rangle\rangle_a, \qquad (16.42)$$

i.e., that the retarded Green functions with the commutator (η=1) are equal to the advanced functions of the same type with permuted operators, and the retarded functions with the anticommutator (η=-1) goes over into the advanced functions, with the opposite sign, upon a permutation of the operators.

Taking the Fourier components in (16.1) of the Green functions

$$\langle\langle A(t)B(t')\rangle\rangle_r = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle A|B\rangle\rangle_\omega^r e^{-i\omega(t-t')}\,d\omega,$$

$$\langle\langle B(t')A(t)\rangle\rangle_a = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\langle B|A\rangle\rangle_\omega^a e^{-i\omega(t-t')}\,d\omega,$$

we obtain the symmetry conditions for them:

$$\langle\langle A|B\rangle\rangle_\omega^r = \eta\langle\langle B|A\rangle\rangle_{-\omega}^a. \qquad (16.43)$$

Here ω is everywhere real.

We make use of the analytic continuation of the Green functions into the complex plane (16.29) to write the symmetry condition (16.43) in the form

$$\langle\langle A|B\rangle\rangle_\omega = \eta\langle\langle B|A\rangle\rangle_{-\omega}. \tag{16.43a}$$

We obtain another useful symmetry property by taking the complex conjugate of the expressions (16.1) for the retarded and advanced Green functions:

$$\langle\langle A(t)\,B(t')\rangle\rangle^* = \eta\,\langle\langle A^+(t)\,B^+(t')\rangle\rangle. \tag{16.44}$$

Using the commutator for the Green functions we obtain in the particular case of Hermitian operators

$$\langle\langle A(t)\,B(t')\rangle\rangle^* = \langle\langle A(t)\,B(t')\rangle\rangle \tag{16.44a}$$

for $A=A^+$, $B=B^+$, $\eta=1$. Thus, the commutator Green functions of Hermitian operators are real.

In the case in which the equations of motion for the operators are invariant with respect to a reversal of time, i.e., with respect to the replacement

$$t\to-t, \quad t'\to-t', \quad i\to-i,$$

the Green functions have still other symmetry properties. The equations of motion of particles in the absence of a magnetic field, for example, are symmetric with respect to time reversal.

Let the equations of motion for A and B be invariant with respect to time reversal, for which $A\to\varepsilon_A A$, $B\to\varepsilon_B B$, where $\varepsilon_A,\varepsilon_B=\pm1$, depending on the parity of the operators under an inversion of velocities. Let us consider the spectral expansion

$$\langle A(t)\,B(t')\rangle = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} J_{AB}(\omega)\,e^{i\omega(t-t')}\,d\omega. \tag{16.45}$$

Upon making the replacement $t\to-t$, $t'\to-t'$, $i\to-i$ the left hand side of this equation is multiplied by $\varepsilon_A\varepsilon_B$, and on the right hand side $J_{AB}(\omega)$ goes over into

$J^{*}_{AB}(\omega)$ (a consequence of the replacement of i by -i). Thus, in the case considered

$$J_{AB}(\omega) = J^{*}_{AB}(\omega)\,\varepsilon_A\varepsilon_B,$$
$$J_{AB}(\omega) = J^{*}_{AB}(\omega) \quad \textbf{for} \quad \varepsilon_A\varepsilon_B = 1, \tag{16.46}$$

i.e., the spectral intensity is real for operators with the same parity.

Comparing (16.45) and its complex conjugate

$$\langle B^{+}(t')\,A^{+}(t)\rangle = \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} J_{AB}(\omega)\,e^{-i\omega(t-t')}\,d\omega, \tag{16.46a}$$

where we have made use of the reality of the spectral intensity, we verify that

$$\langle A(t)\,B(t')\rangle = \langle B^{+}(t)\,A^{+}(t')\rangle, \tag{16.47}$$

and, thus,

$$\langle\langle A \mid B\rangle\rangle_{\omega} = \langle\langle B^{+} \mid A^{+}\rangle\rangle_{\omega}. \tag{16.48}$$

In the case in which the magnetic field is not zero, the spectral intensity of the time correlation functions is no longer real, but because the equations of motion are invariant with respect to time reversal and a simultaneous reversal of the direction of the magnetic field (H→-H), the spectral intensity has the symmetry property

$$J_{AB,\,H}(\omega) = J^{*}_{AB,\,-H}(\omega)\,\varepsilon_A\varepsilon_B \tag{16.49}$$

instead of (16.46), which holds in the absence of a field. Thus, the Green functions have the symmetry property

$$\langle\langle B^{+}(t)\,A^{+}(t')\rangle\rangle_{H} = \langle\langle A(t)\,B(t')\rangle\rangle_{-H}\,\varepsilon_A\varepsilon_B,$$
$$\langle\langle B^{+} \mid A^{+}\rangle\rangle_{\omega,\,H} = \langle\langle A \mid B\rangle\rangle_{\omega,\,-H}\,\varepsilon_A\varepsilon_B \tag{16.50}$$

instead of (16.47) and (16.48).

The symmetry relations considered in this section will be necessary later in § 17 to establish the properties of the complex conductivity and susceptibility.

§ 17. Fluctuation-Dissipation Theorems and Dispersion Relations

The relationships between the kinetic coefficients or susceptibilities, which define the reaction of the system to an external perturbation, and the equilibrium fluctuations are called fluctuation-dissipation theorems. The Kubo formulas for the electrical conductivity (15.76) and (15.77) are a particular case of these theorems. The fluctuation-dissipation theorems for the general case were first formulated by Callen and Welton [22] as generalized Nyquist theorems [78], which are known from the theory of electrical noise in linear circuits. The fluctuation-dissipation theorems are further generalized and applied to the thermodynamics of irreversible processes in the articles [79-81,1,11].

In § 15 expressions for the kinetic coefficients (or for the generalized susceptibility and conductivity) were obtained through the retarded Green functions, and in § 16 the general properties of the Green functions were discussed. The Callen-Welton fluctuation-dissipation theorem, the dispersion relations, the sum rules, and the symmetry relations for the kinetic coefficients and the generalized susceptibility follow directly from these properties.

17.1. Dispersion Relations, Sum Rules and the Onsager Reciprocity Relations for Generalized Susceptibility.

Let an external, time dependent, mechanical perturbation act on the system. The perturbation is switched on adiabatically and is described by adding to the Hamiltonian a term

$$H_t^1 = -\sum_{j=1}^{n} F_j(t)\, \alpha_j, \tag{17.1}$$

$F_j(t) \sim e^{\varepsilon t}$ as $t \to -\infty, \varepsilon > 0$, where the α_j are dynamical variables, and $F_j(t)$ is the "force" with which the external field acts on the variable α_j, i.e., the force conjugate to it; $F_j(t)$ is considered to be a known function of time.

The perturbation (17.1) is conveniently represented in the form of a scalar product of n-dimensional vectors:

$$H'_t = -(F(t)\cdot\alpha), \tag{17.1a}$$

where

10 $$\alpha = (\alpha_1, \ldots, \alpha_n), \quad F(t) = (F_1(t), \ldots, F_n(t)).$$

Taking the perturbation in the form (17.1), we assume that in statistical equilibrium $F_j^0=0$ (or $\langle\alpha_j\rangle_0=0$). If this is not the case and in statistical equilibrium $F_j^0\neq 0$, then for the perturbation one must take the deviation of the interaction energy from its equilibrium value and not (17.1):

$$H^1_t = -\sum_{j=1}^{n} (F_j(t) - F_j^0)\alpha_j. \tag{17.1b}$$

In what follows for brevity we shall write the perturbation in the form (17.1), assuming that for the case in which $F_j^0\neq 0$, that the equilibrium value of $F_j(t)$ has been subtracted out.

In accordance with (15.47) the reaction of the system to the perturbation (17.1) is equal to

$$\langle\alpha\rangle = \langle\alpha\rangle_0 + \int_{-\infty}^{t} \varkappa(t-t')\cdot F(t')\,dt', \tag{17.2}$$

where

$$\varkappa(t-t') = -\langle\langle\alpha(t)\,\alpha(t')\rangle\rangle \tag{17.2a}$$

is the generalized reaction matrix with components

$$\varkappa_{ik}(t-t') = -\langle\langle\alpha_i(t)\,\alpha_k(t')\rangle\rangle. \tag{17.2b}$$

The double brackets denote the retarded Green function (15.48) in the quantum case and (15.19) in the classical case.

Since the retarded Green function is non-zero only for positive arguments, then it is always true that

$$\varkappa(t-t') = 0 \quad \text{for} \quad t<t', \tag{17.3}$$

which is an expression of the causality principle; the reaction of a system cannot precede in time the perturbation which produces the reaction. In a phenomenological theory in which the explicit expressions (17.2a) do not exist for the reaction matrix, the causality principle (17.3) is taken as a fundamental physical postulate of the theory [82].

Let us expand the functions F(t),<α> in Fourier integrals:

$$\langle \alpha \rangle = \langle \alpha \rangle_0 + \frac{1}{2\pi} \int_{-\infty}^{\infty} \alpha(\omega) e^{-i\omega t} \, d\omega,$$
$$F(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{-i\omega t} \, d\omega, \tag{17.4}$$

where α(ω) and F(ω) are the Fourier components:

$$\alpha(\omega) = \int_{-\infty}^{\infty} (\langle \alpha \rangle - \langle \alpha \rangle_0) e^{i\omega t} \, dt, \tag{17.4a}$$
$$F(\omega) = \int_{-\infty}^{\infty} F(t) e^{i\omega t} \, dt.$$

Substituting the expansions (17.4) into (17.2) we obtain an algebraic equation instead of the integral relations for the linear reaction

(17.5)

where
$$\alpha(\omega) = \varkappa(\omega) \cdot F(\omega),$$

$$\varkappa_{ik}(\omega) = \int_{-\infty}^{\infty} \varkappa_{ik}(t) e^{i\omega t} \, dt = -\langle\langle \alpha_i \mid \alpha_k \rangle\rangle_\omega =$$
$$= \int_0^{\infty} \int_0^{\beta} \langle \dot{\alpha}_k \alpha_i (t + i\hbar\lambda) \rangle e^{i\omega t - \varepsilon t} \, dt \, d\lambda \tag{17.5a}$$

is the generalized susceptibility matrix[1]. Formula (17.5a) expresses the fluctuation-dissipation theorem of Kubo.

As the generalized susceptibility is expressed through the retarded Green functions, all of the properties of the Green functions considered in § 16 are extended to the susceptibility.

Separating $\varkappa(\omega)$ into real and imaginary parts,

$$\varkappa(\omega) = \varkappa'(\omega) + i\varkappa''(\omega), \tag{17.6}$$

we obtain from (16.34) the dispersion relations for the generalized susceptibility or Kramers-Kronig relations:

$$\varkappa'(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\varkappa''(u)}{u-\omega}\,du, \qquad \varkappa''(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\varkappa'(u)}{u-\omega}\,du. \tag{17.7}$$

Similar relations between the real and imaginary parts of the index of refraction were first obtained in classical electrodynamics by Kramers [83] and Kronig [84] already by 1926-1927.

From the reality of α and $F(t)$ it follows that

$$\alpha(\omega) = \alpha^{*}(-\omega), \quad F(\omega) = F^{*}(-\omega), \tag{17.8}$$

and therefore

$$\varkappa(\omega) = \varkappa^{*}(-\omega), \tag{17.9}$$

---

[1] Sometimes, for example in [82], in addition to the generalized susceptibility matrix $\varkappa(\omega)$ the generalized admittance matrix is introduced

$$Y(\omega) = -i\omega\varkappa(\omega)$$

as is the inverse to this matrix, generalized impedance,

$$Z(\omega) = i\omega^{-1}\varkappa^{-1}(\omega).$$

Then the equation for the linear reaction (17.5) takes on the form

$$\alpha(\omega) = \frac{1}{-i\omega}Y(\omega)\cdot F(\omega), \text{ for } Y(\omega) = i\omega\,\langle\langle u \mid \alpha\rangle\rangle_{\omega}.$$

from which it follows that the real part of the generalized susceptibility $x(\omega)$ is even, and the imaginary part is odd with respect to ω:

$$\varkappa'(\omega)=\varkappa'(-\omega),\quad \varkappa''(\omega)=-\varkappa''(-\omega). \tag{17.9a}$$

By means of (17.9a) the Kramers-Kronig relations can be written in the form

$$\begin{gathered}\varkappa'(\omega)=\frac{1}{\pi}\mathcal{P}\int\limits_0^\infty \varkappa''(u)\frac{2u}{u^2-\omega^2}\,du,\\ \varkappa''(\omega)=-\frac{1}{\pi}\mathcal{P}\int\limits_0^\infty \varkappa'(u)\frac{2\omega}{u^2-\omega^2}\,du.\end{gathered} \tag{17.10}$$

From the sum rules for the retarded Green functions (16.38) and (16.39) there follows a sum rule for the generalized susceptibility:

$$\begin{gathered}\frac{1}{\pi}\int\limits_{-\infty}^{\infty}\varkappa_{ik}(\omega)\,d\omega=\frac{i}{\hbar}\langle[a_i,\,a_k]\rangle,\\ \frac{1}{\pi}\int\limits_{-\infty}^{\infty}\{\hbar\omega\varkappa_{ik}(\omega)+\langle[a_i,\,a_k]\rangle\}\,d\omega=\left\langle\left[a_i,\,\frac{da_k}{dt}\right]_{t=0}\right\rangle.\end{gathered} \tag{17.11}$$

From the symmetry property (16.50) for the Green functions it follows that for the generalized susceptibility

$$\varkappa_{ik}(\omega,\,H)=\varkappa_{ki}(\omega,\,-H)\,\varepsilon_i\varepsilon_k,\qquad \varepsilon_i,\,\varepsilon_k=\pm 1, \tag{17.12}$$

and in the absence of a magnetic field

$$\varkappa_{ik}(\omega)=\varkappa_{ki}(\omega)\,\varepsilon_i\varepsilon_k. \tag{17.12a}$$

Dividing the susceptibility into symmetric and antisymmetric parts

$$\varkappa^s_{ik} = \frac{1}{2}(\varkappa_{ik} + \varkappa_{ki}), \quad \varkappa^a_{ik} = \frac{1}{2}(\varkappa_{ik} - \varkappa_{ki}), \tag{17.13}$$

we verify that x^s is even, and x^α is odd with respect to an inversion of the magnetic field **H**:

$$\varkappa^s_{ik}(\omega, H) = \varkappa^s_{ki}(\omega, -H), \; \varkappa^a_{ik}(\omega, H) = -\varkappa^a_{ki}(\omega, -H) \text{ for } \varepsilon_i\varepsilon_k = 1. \tag{17.14}$$

These symmetry properties (17.12) and (17.14) are called the Onsager reciprocity relations for the generalized susceptibility. They thus result from the theory of the linear reaction of a system to mechanical perturbations and the invariance of the equations of motion with respect to time reversal with the replacement **H**→-**H**. They are valid also for the kinetic coefficients, independently of the type of perturbation - mechanical or thermal - which is producing the irreversible process.

The reciprocity relations for the kinetic coefficients were established in 1931 by Onsager [85], who proceeded from a hypothesis about the character of the damping of the fluctuations in time. In particular, he assumed that they obey the same equations as do the average values, and he made use of the invariance of the equations of motion of the particles with respect to time reversal and the inversion of the magnetic field.

The Onsager relations reflect on a macroscopic level the invariance of the microscopic equations of motion. They have a very great significance for the theory of irreversible processes. In fact they are the basis for all of nonequilibrium thermodynamics a good exposition of which can be found in the monograph by deGroot and Mazur [82], and also in the books [86-90]. We shall again return to a discussion of the Onsager reciprocity relations in section 17.3 and in Chapter IV for the case of thermal perturbations.

17.2. Callen-Welton Fluctuation-Dissipation Theorem for Generalized Susceptibility.

Fluctuation-dissipation theorems relate the characteristics of a dissipative process (for example, the complex susceptibility $x_{ik}(\omega)$ or conductivity $\sigma_{\alpha\beta}(\omega)$) with equilibrium fluctuations in the system. Thus, they express nonequilibrium properties through equilibrium properties.

In section 17.1 we considered the Kubo fluctuation theorem (17.5a). The Callen-Welton fluctuation-dissipation theorem is another representation of the Kubo formula. It follows from the theory of the linear reaction and from the spectral representation for the retarded Green function (16.24). For the complex susceptibility $\chi_{ik}(\omega)$ we obtain

$$\varkappa_{ik}(\omega) = -\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}(e^{\hbar u/\theta}-1)\,J_{\alpha_k\alpha_i}(u)\frac{du}{\omega-u+i\varepsilon} = \frac{i}{2\hbar}(e^{\hbar\omega/\theta}-1)\,J_{\alpha_k\alpha_i}(\omega) - \frac{1}{2\pi\hbar}\mathcal{P}\int_{-\infty}^{\infty}(e^{\hbar u/\theta}-1)\,J_{\alpha_k\alpha_i}(u)\frac{du}{\omega-u}, \qquad (17.15)$$

where

$$J_{\alpha_k\alpha_i}(\omega) = \int_{-\infty}^{\infty}\langle(\alpha_k(t)-\langle\alpha_k\rangle_0)(\alpha_i(t')-\langle\alpha_i\rangle_0)\rangle\, e^{-i\omega(t-t')}\,dt \qquad (17.15a)$$

is the Fourier component of the time correlation function, relating α_k and α_i. In the time correlation function in (17.15a) the averaging is carried out over an equilibrium ensemble, but we shall not use a subscript 0 on the brackets to indicate this. We denote by this subscript only $\langle\alpha_k\rangle_0$.

Formula (17.15) represents the complex susceptibility through the spectral intensity of the equilibrium fluctuations (17.15a) and expresses the Callen-Welton fluctuation-dissipation theorem. In the classical case, taking the limit $\hbar\to 0$ in (17.15), we obtain

$$\varkappa_{ik}(\omega) = -\frac{1}{2\pi\theta}\int_{-\infty}^{\infty}J_{\alpha_k\alpha_i}(u)\frac{u\,du}{\omega-u+i\varepsilon}. \qquad (17.15b)$$

We express the spectral intensity $J_{\alpha_k\alpha_i}(\omega)$ in terms of $J_{\alpha_i\alpha_k}(-\omega)$ by using (16.16a):

$$J_{\alpha_k\alpha_i}(\omega) = J_{\alpha_i\alpha_k}(-\omega)\,e^{-\hbar\omega/\theta}. \qquad (17.16)$$

Let us introduce the symmetrized time correlation functions

$$\{\alpha_k(t),\,\alpha_i(t')\} = \frac{1}{2}(\langle\alpha_k(t)\,\alpha_i(t')\rangle + \langle\alpha_i(t')\,\alpha_k(t)\rangle), \qquad (17.17)$$

which are symmetric with respect to i,k with replacement t↔t′, and which have Fourier components

$$J_{\{\alpha_k\alpha_i\}}(\omega) = \frac{1}{2}\{J_{\alpha_k\alpha_i}(\omega) + J_{\alpha_i\alpha_k}(-\omega)\} = J_{\alpha_k\alpha_i}(\omega)\frac{1}{2}(1+e^{\hbar\omega/\theta}), \qquad (17.17a)$$

which follows from (17.16). By using (17.17a) we can write the fluctuation-dissipation theorem (17.15) in the form

$$\varkappa_{ik}(\omega) = -\frac{1}{\pi\hbar}\int_{-\infty}^{\infty} \mathrm{th}\frac{\hbar u}{2\theta} J_{\{\alpha_k\alpha_i\}}(u)\frac{du}{\omega - u + i\varepsilon}. \qquad (17.18)$$

The factor th($\hbar u/2\theta$) (hyperbolic tangent) in the integrand of formula (17.18) is proportional to the average energy of an oscillator with frequency u, because

$$2\bar{n} + 1 = \mathrm{th}\frac{\hbar u}{2\theta}, \qquad \bar{n} = \frac{1}{e^{\hbar u/\theta} - 1}.$$

Up to this time we have expressed the generalized susceptibility through the time correlation functions. One can obtain also the inverse relations, expressing fluctuations in terms of the generalized susceptibility. The fluctuation-dissipation theorem was first obtained by Callen and Welton in just such a form.

From formula (17.18) it follows that

$$\varkappa^*_{ik}(\omega) - \varkappa_{ki}(\omega) = $$
$$= -\frac{1}{\pi\hbar}\int_{-\infty}^{\infty} \mathrm{th}\frac{\hbar u}{2\theta}\left\{J^*_{\{\alpha_k\alpha_i\}}(u)\frac{1}{\omega - u - i\varepsilon} - J_{\{\alpha_i\alpha_k\}}(u)\frac{1}{\omega - u + i\varepsilon}\right\}du.$$

Taking into account that as a consequence of the assumed hermiticity of α_i and α_k

$$J^*_{\alpha_k\alpha_i}(u) = J_{\alpha_i\alpha_k}(u),$$

we obtain

$$\varkappa^{*}_{ik}(\omega) - \varkappa_{ki}(\omega) = \frac{2}{i\hbar}\,\mathrm{th}\,\frac{\hbar\omega}{20}\,J_{\{a_i a_k\}}(\omega), \qquad (17.19)$$

i.e.,

$$\mathrm{Im}\,\varkappa'_{ik}(\omega) = \frac{1}{\hbar}\mathrm{th}\,\frac{\hbar\omega}{20}\,\mathrm{Re}\,J_{\{a_i a_k\}}(\omega), \quad \mathrm{Re}\,\varkappa^{a}_{ik}(\omega) = \frac{1}{\hbar}\,\mathrm{th}\,\frac{\hbar\omega}{20}\,\mathrm{Im}\,J_{\{a_i a_k\}}(\omega), \qquad (17.19a)$$

and the inverse relation

$$\{(a_i(t) - \langle a_i\rangle_0),\ (a_k(t') - \langle a_k\rangle_0)\} = \qquad (17.19b)$$
$$= \frac{i\hbar}{4\pi}\int\limits_{-\infty}^{\infty}(\varkappa^{*}_{ik}(\omega) - \varkappa_{ki}(\omega))\,{}^{a}\mathrm{cth}\,\frac{\hbar\omega}{20}\,e^{i\omega(t-t')}\,d\omega,$$

from which it follows that for t=t′

Key:
a. hyperbolic cotangent

$$\{(a_i - \langle a_i\rangle_0),\ (a_k - \langle a_k\rangle_0)\} =$$
$$= \frac{i\hbar}{4\pi}\int\limits_{-\infty}^{\infty}(\varkappa^{*}_{ik}(\omega) - \varkappa_{ki}(\omega))\,\mathrm{cth}\,\frac{\hbar\omega}{20}\,d\omega. \qquad (17.19c)$$

For the particular case of a single variable we obtain

$$\langle(a - \langle a\rangle_0)^2\rangle = \frac{\hbar}{2\pi}\int\limits_{-\infty}^{\infty}\varkappa''(\omega)\,\mathrm{cth}\,\frac{\hbar\omega}{20}\,d\omega. \qquad (17.19d)$$

Relations (17.19) and (17.19c) were obtained by Callen, Barash, and Jackson [81], and formula (17.19d) by Callen and Welton [22]. Relations (17.19c) and (17.19d) have the form of sum rules (see section 16.4).

17.3. Linear Relation Between Current and Forces; Kinetic Coefficients and Their Characteristics.

The rate of change of a dynamical variable α_j with respect to time $\dot{\alpha}_j$ is called the current operator (or dynamical variable), and its average value $\langle\dot{\alpha}_j\rangle$ is called the current. In states of statistical equilibrium there are no currents, because

$$\langle\dot{\alpha}_j\rangle_0 = \frac{d}{dt}\langle\alpha_j\rangle_0 = 0,$$

therefore, they characterize a nonequilibrium state.

It is convenient to introduce an n-dimensional vector of current operators

$$\dot{\alpha} = (\dot{\alpha}_1, \ldots, \dot{\alpha}_n).$$

Using the theory of the linear reaction we find the connection between currents and forces $F(t)$ when the forces are sufficiently small.

Under the influence of the perturbation (17.1) there arises in the system, in accordance with (15.47), the currents

$$\langle\dot{\alpha}_l\rangle = \sum_k \int_{-\infty}^{t} L_{ik}(t-t')\, F_k(t')\, dt' \tag{17.20}$$

or

$$\langle\dot{\alpha}\rangle = \int_{-\infty}^{t} L(t-t')\cdot \boldsymbol{F}(t')\, dt', \tag{17.20a}$$

where

$$L(t-t') = -\langle\langle\dot{\alpha}(t)\,\alpha(t')\rangle\rangle \tag{17.20b}$$

is a tensor with components

$$L_{ik}(t-t') = -\langle\langle\dot{\alpha}_i(t)\,\alpha_k(t')\rangle\rangle = \int_0^{\beta} \langle\dot{\alpha}_k(t'-i\hbar\lambda)\,\dot{\alpha}_i(t)\rangle\, d\lambda. \tag{17.20c}$$

Relations (17.20) and (17.20a) are called the linear relations between forces and currents.

The linear relations (17.20) are integral relations of the retarded type. Expanding the forces $F_j(t)$ and the currents $\langle\dot{\alpha}_i\rangle$ in Fourier integrals, we obtain algebraic relations between the Fourier components of the forces and the currents:

$$\alpha(\omega) = L(\omega) \cdot \boldsymbol{F}(\omega), \tag{17.21}$$

where

$$L_{ik}(\omega) = \int_{-\infty}^{\infty} L_{ik}(t) e^{i\omega t} \, dt = -\langle\langle \dot{\alpha}_i \mid \alpha_k \rangle\rangle_\omega =$$

$$= \int_0^\infty \int_0^\beta \langle \dot{\alpha}_k \dot{\alpha}_i (t + i\hbar\lambda) \rangle \, e^{i\omega t - \varepsilon t} \, dt \, d\lambda \tag{17.21a}$$

is the tensor of kinetic coefficients for periodic processes with frequency ω, and

$$\dot{\alpha}(\omega) = \int_{-\infty}^{\infty} \langle \dot{\alpha} \rangle e^{i\omega t} \, dt \tag{17.21b}$$

are the Fourier components of the currents.

The function $L_{ik}(t-t')$ is significantly different from zero only in the region $|t-t'| \sim \tau$, where τ is the correlation time, and the function tends to zero as $|t-t'| \to \infty$. If the forces $F_k(t')$ vary sufficiently slowly with time, so that their change in a time τ can be neglected, then on the right hand side of (17.20) the slowly varying function $F_k(t')$ can be taken outside the integral sign at the point $t'=t$. Then the retarded linear relations (17.20) go over into the usual linear relations relating the instantaneous values of the forces and the currents:

$$\langle \dot{\alpha}_i \rangle = \sum_k L_{ik} F_k(t), \tag{17.22}$$

where

$$L_{ik} = \int_0^\infty e^{-\varepsilon t} L_{ik}(t) \, dt = -\int_0^\infty e^{-\varepsilon t} \frac{1}{i\hbar} \langle [\dot{\alpha}_i(t), \alpha_k] \rangle \, dt =$$

$$= \int_0^\infty \int_0^\beta e^{-\varepsilon t} \langle \dot{\alpha}_k \dot{\alpha}_i (t + i\hbar\lambda) \rangle \, dt \, d\lambda = \int_{-\infty}^0 \int_0^\beta e^{\varepsilon t} \langle \dot{\alpha}_i \dot{\alpha}_k (t + i\hbar\lambda) \rangle \, dt \, d\lambda \quad (\varepsilon > 0) \tag{17.22a}$$

is the tensor of kinetic coefficients for stationary processes.

The generalized susceptibility $\chi_{ik}(\omega)$ (17.5a), introduced in the preceding section, is connected with the kinetic coefficients $L_{ik}(\omega)$ (17.21a) by the relation

$$L_{ik}(\omega) = \frac{1}{i\hbar}\langle[\alpha_i, \alpha_k]\rangle - i\omega\chi_{ik}(\omega), \tag{17.23}$$

which is obtained by integrating (17.21a) by parts. From (17.23) it follows that the imaginary part of the susceptibility is related to the real part of the kinetic coefficient and vice versa.

Dispersion relations for kinetic coefficients $L_{ik}(\omega)$ follow from (16.34):

$$\begin{gathered} L'_{ik}(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{L''_{ik}(u)}{u-\omega}\,du, \\ L''_{ik}(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{L'_{ik}(u)}{u-\omega}\,du, \\ L_{ik}(\omega) = L'_{ik}(\omega) + iL''_{ik}(\omega); \end{gathered} \tag{17.24}$$

they have the same form as $\chi_{ik}(\omega)$.

The kinetic coefficients have the property

$$L_{ik}(\omega) = L^*_{ik}(-\omega), \tag{17.25}$$

which follows from the reality of $\langle\dot{\alpha}\rangle$ and $F(t)$. Using this relation (17.24) becomes

$$\begin{gathered} L'_{ik}(\omega) = \frac{1}{\pi}\mathcal{P}\int_{0}^{\infty} L''_{ik}(u)\,\frac{2u}{u^2-\omega^2}\,du, \\ L''_{ik}(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{0}^{\infty} L'_{ik}(u)\,\frac{2\omega}{u^2-\omega^2}\,du. \end{gathered} \tag{17.24a}$$

The sum rules (16.38) and (16.39) give the relations

$$\frac{1}{\pi}\int_{-\infty}^{\infty} L_{ik}(\omega)\,d\omega = \frac{i}{\hbar}\langle[\dot{\alpha}_i,\ \alpha_k]\rangle,$$
$$\frac{1}{\pi}\int_{-\infty}^{\infty}\{\hbar\omega L_{ik}(\omega)+\langle[\dot{\alpha}_i,\ \alpha_k]\rangle\}\,d\omega = \left\langle\left[\frac{d\alpha_i}{dt},\ \frac{d\alpha_k}{dt}\right]\right\rangle_{t=0}. \tag{17.26}$$

for the kinetic coefficients.

From the symmetry properties of the Green functions (16.50), which come about from the invariance of the equations of motion with respect to time reversal and inversion of the direction of the magnetic field, follow the symmetry properties for the frequency dependent kinetic coefficients

$$L_{ik}(\omega,\ \boldsymbol{H}) = L_{ki}(\omega,\ -\boldsymbol{H})\,\varepsilon_i\varepsilon_k \tag{17.27}$$

and for the stationary kinetic coefficients (ω=0)

$$L_{ik}(\boldsymbol{H}) = L_{ki}(-\boldsymbol{H})\,\varepsilon_i\varepsilon_k \quad (L_{ik}(\boldsymbol{H}) = L_{ik}(0,\ \boldsymbol{H})), \tag{17.27a}$$

from which follow for the symmetric and antisymmetric parts

$$L^s_{ik} = \frac{1}{2}(L_{ik}+L_{ki}), \qquad L^a_{ik} = \frac{1}{2}(L_{ik}-L_{ki})$$

the symmetry conditions

$$L^s_{ik}(\omega,\ \boldsymbol{H}) = L^s_{ki}(\omega,\ -\boldsymbol{H})\,\varepsilon_i\varepsilon_k,$$
$$L^a_{ik}(\omega,\ \boldsymbol{H}) = -L^a_{ki}(\omega,\ -\boldsymbol{H})\,\varepsilon_i\varepsilon_k. \tag{17.27b}$$

The symmetry properties of the kinetic coefficients (17.27) are the Onsager reciprocity relations (or the Onsager theorem). Onsager derived them for the stationary case [85].

In this section we shall derive the Onsager theorem for the case of mechanical perturbations. We shall consider it for the case of thermal perturbations in Chapter IV.

The Welton-Callen fluctuation-dissipation theorem for the kinetic coefficients (17.21a) follows from (16.24):

$$L_{ik}(\omega) = -\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\left(e^{\hbar u/\theta}-1\right)J_{\alpha_k\dot{\alpha}_i}(u)\frac{du}{\omega-u+i\varepsilon}, \tag{17.28}$$

where

$$J_{\alpha_k\dot{\alpha}_i}(\omega) = \int_{-\infty}^{\infty}\langle\alpha_k(t)\,\dot{\alpha}_i(t')\rangle e^{-i\omega(t-t')}\,dt, \tag{17.28a}$$

or in another form

$$L_{ik}(\omega) = -\frac{1}{\pi\hbar}\int_{-\infty}^{\infty}\overset{\text{a.}}{\mathrm{th}}\frac{\hbar u}{2\theta}J_{\{\alpha_k\dot{\alpha}_i\}}(u)\frac{du}{\omega-u+i\varepsilon}, \tag{17.29}$$

Key: a. Hyperbolic tangent

where

$$J_{\{\alpha_k\dot{\alpha}_i\}}(\omega) = \frac{1}{2}\left\{J_{\alpha_k\dot{\alpha}_i}(\omega)+J_{\dot{\alpha}_i\alpha_k}(-\omega)\right\} = J_{\alpha_k\dot{\alpha}_i}(\omega)\frac{1}{2}\left(1+e^{\hbar\omega/\theta}\right) \tag{17.29a}$$

are the Fourier components of the symmetrized time correlation functions

$$\{\alpha_k(t),\ \dot{\alpha}_i(t')\} = \frac{1}{2}\left(\langle\alpha_k(t)\,\dot{\alpha}_i(t')\rangle+\langle\dot{\alpha}_i(t')\,\alpha_k(t)\rangle\right). \tag{17.29b}$$

From (17.29) there follow also other formulations of the fluctuation-dissipation theorem for the kinetic coefficients

$$L^{*}_{ik}(\omega) - L_{ki}(\omega) = \frac{2}{i\hbar}\,\mathrm{th}\frac{\hbar\omega}{2\theta}J_{\{\alpha_i\dot{\alpha}_k\}}(\omega) \tag{17.30}$$

and

$$\{\dot{\alpha}_i(t),\ \alpha_k(t')-\langle\alpha_k\rangle_0\} =$$

$$= \frac{i\hbar}{4\pi}\int_{-\infty}^{\infty}\left(L^{*}_{ik}(\omega)-L_{ki}(\omega)\right)\mathrm{cth}\frac{\hbar\omega}{2\theta}\,e^{i\omega(t-t')}\,d\omega, \tag{17.30a}$$

analogous to the relations (17.19) and (17.19b) for the generalized susceptibility.

Up to now we have considered the general case of the reaction of the system to the perturbation (17.1). We shall now derive the Welton-Callen fluctuation-dissipation theorem, the Onsager relations, and sum rules for the particular case of electrical conductivity, when the perturbation has the form (15.63). In this case

$$\sigma_{\alpha\beta}(\omega) = \frac{\operatorname{th}(\beta\hbar\omega/2)}{\hbar\omega} J_{\{\alpha,\beta\}}(\omega) - \frac{i}{\pi\hbar}\mathcal{P}\int_{-\infty}^{\infty} \frac{1}{u} J_{\{\alpha,\beta\}}(u) \operatorname{th}\frac{\beta\hbar u}{2}\frac{du}{u-\omega}, \tag{17.31}$$

where

$$J_{\{\alpha,\beta\}}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} (\langle j_\alpha(0)\, j_\beta(t)\rangle + \langle j_\beta(t)\, j_\alpha(0)\rangle)\, e^{i\omega t}\, dt = \\ = \int_{-\infty}^{\infty} \{j_\alpha(0),\ j_\beta(t)\}\, e^{i\omega t}\, dt. \tag{17.31a}$$

(In § 15 the quantity j_α is designated by J_α.)

Thus, the electrical conductivity tensor is related to equilibrium fluctuations of the current.

From (17.31) for the symmetric and antisymmetric parts of the conductivity tensor we obtain analogously to (17.19a):

$$\operatorname{Re}\sigma^s_{\alpha\beta}(\omega) = \frac{\operatorname{th}(\beta\hbar\omega/2)}{\hbar\omega}\int_{-\infty}^{\infty} \{j_\alpha(0),\ j_\beta(t)\} \cos\omega t\, dt, \\ \operatorname{Im}\sigma^a_{\alpha\beta}(\omega) = \frac{\operatorname{th}(\beta\hbar\omega/2)}{\hbar\omega}\int_{-\infty}^{\infty} \{j_\alpha(0),\ j_\beta(t)\} \sin\omega t\, dt, \tag{17.32}$$

from which for $\omega \to 0$ follows the Nyquist theorem:

$$\operatorname{Re}\sigma^s_{\alpha\beta}(0) = \frac{\beta}{2}\int_{-\infty}^{\infty} \{j_\alpha(0)\, j_\beta(t)\}\, dt. \tag{17.32a}$$

It was first established by Nyquist as the connection between fluctuations in potential difference and resistance in linear electrical circuits.

The symmetry properties of the electric conductivity tensor follow from the symmetry properties of the Green functions. For example, from (16.50) follow the Onsager reciprocity relations for the electrical conductivity:

$$\sigma_{\alpha\beta}(\omega, H) = \sigma_{\beta\alpha}(\omega, -H). \tag{17.33}$$

From the sum rules (16.38) it follows that

$$\int_{-\infty}^{\infty} \left\langle\left\langle j_\alpha \middle| \sum_l e_l x_{l\beta} \right\rangle\right\rangle_\omega^r d\omega = \frac{1}{2i\hbar} \left\langle \left[j_\alpha, \sum_l e_l x_{l\beta} \right] \right\rangle = \frac{e^2 N}{2m} \delta_{\alpha\beta}, \tag{17.34}$$

where N is the total number of particles. In (17.34) the commutation relations between position and momentum have been used:

$$[x_{j\beta}, p_{l\alpha}] = i\hbar \delta_{jl}^{\alpha\beta}.$$

The relation (17.34) can be written in the form of a sum rule for $\sigma_{\alpha\beta}(\omega)$:

$$\frac{2}{\pi} \int_{-\infty}^{\infty} \sigma_{\alpha\beta}(\omega)\, d\omega = \frac{e^2 N}{m} \delta_{\alpha\beta}. \tag{17.34a}$$

The dispersion relations for the electrical conductivity tensor have the form of (17.24) and (17.24a).

The theory of thermal radiation is connected to the theory of electrical fluctuations (see the works of S. M. Rytov [91-93] and F. V. Bunkin [94]).

If the state of the system is far from an equilibrium state and the analysis cannot be restricted to the case of the linear reaction, then for the nonlinear susceptibility one must consider correlations of a higher order[1].

---

[1] For a discussion of nonequilibrium fluctuations see the work of F. V. Bunkin [95] and the series of articles by Lax [96-99], which treat the theory of noise for a classical and a quantum case by application of the theory of Markov processes.

17.4. Order of Limiting Processes V→∞, ε→0 in Kinetic Coefficients.

In the expressions (17.22a) for the kinetic coefficients

$$L_{ik} = \lim_{\varepsilon \to 0} \lim_{V \to \infty} \int_0^\infty \int_0^\beta e^{-\varepsilon t} \langle \dot{\alpha}_k \dot{\alpha}_i (t + i\hbar\lambda) \rangle \, dt \, d\lambda \qquad (17.35)$$

it is necessary to carry out two limiting transitions V→∞ and ε→0. As we have already remarked the correct order of the limiting transitions is first to take V→∞ and then ε→0, because this guarantees the choice of the retarded solutions to the Liouville equation (see Appendices I and III). Proceeding from the explicit expression (17.35) for the kinetic coefficients, one can verify that only this order of limiting transitions will lead to a finite result for L_{ik}.

We shall make use of the spectral expansion (16.15) for the time correlation functions, assuming that the limiting transition V→∞ in the averages <...> is already carried out:

$$\langle \dot{\alpha}_k \dot{\alpha}_i (t) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} J_{\dot{\alpha}_k \dot{\alpha}_i} (\omega) \, e^{-i\omega t} \, d\omega. \qquad (17.36)$$

Substituting this expression into (17.35), we obtain

$$L_{ik} = \frac{1}{2\pi} \int_0^\infty \int_0^\beta \int_{-\infty}^{\infty} J_{\dot{\alpha}_k \dot{\alpha}_i} (\omega) \, e^{-i\omega (t + i\hbar\lambda) - \varepsilon t} \, dt \, d\lambda \, d\omega = \frac{1}{2\pi} \int_0^\infty \int_{-\infty}^{\infty} J_{\dot{\alpha}_k \dot{\alpha}_i} (\omega) \, e^{-i\omega t - \varepsilon t} \, \frac{e^{\beta\hbar\omega} - 1}{\hbar\omega} \, dt \, d\omega,$$

where the order of integration has been interchanged and the limit signs have been omitted. Because

$$\int_0^\infty e^{-i\omega t - \varepsilon t} \, dt = \frac{1}{i\omega + \varepsilon} = -i \left(\frac{\mathcal{P}}{\omega} + i\pi\delta(\omega) \right) = 2\pi\delta_+ (\omega),$$

we obtain for the kinetic coefficients the expression

$$L_{ik} = -\frac{i}{2\pi}\mathcal{P}\int_{-\infty}^{\infty} J_{\dot{\alpha}_k\dot{\alpha}_i}(\omega)\,\frac{e^{\beta\hbar\omega}-1}{\hbar\omega^2}\,d\omega + \frac{\beta}{2}J_{\dot{\alpha}_k\dot{\alpha}_i}(0).$$

Here the integral over ω is equal to zero, if there is no magnetic field.

Indeed, in that case the correlation functions are symmetric with respect to time reversal and their spectral intensity is real (see (16.46)). From (16.33) and (17.25) we obtain

$$\begin{aligned} \operatorname{Im}\langle\langle\dot{\alpha}_i\,|\,\dot{\alpha}_k\rangle\rangle_\omega &= -\frac{1}{2\hbar}\left(e^{\beta\hbar\omega}-1\right)J_{\dot{\alpha}_k\dot{\alpha}_i}(\omega),\\ \operatorname{Im}\langle\langle\dot{\alpha}_i\,|\,\dot{\alpha}_k\rangle\rangle_\omega &= -\operatorname{Im}\langle\langle\dot{\alpha}_i\,|\,\dot{\alpha}_k\rangle\rangle_{-\omega}. \end{aligned} \qquad (17.37)$$

Thus, the imaginary part of L_{ik} is proportional to the integral of a function which is odd with respect to ω and is equal to zero, because

$$\mathcal{P}\frac{1}{2\pi}\int_{-\infty}^{\infty}\operatorname{Im}\langle\langle\dot{\alpha}_i\,|\,\dot{\alpha}_k\rangle\rangle_\omega\,\frac{d\omega}{\omega^2} = 0.$$

In fact, for ω→0 it follows from (17.37) that the imaginary part of the Green function approaches zero as ω,

$$\operatorname{Im}\langle\langle\dot{\alpha}_i\,|\,\dot{\alpha}_k\rangle\rangle_\omega \approx -\frac{\beta\omega}{2}J_{\dot{\alpha}_k\dot{\alpha}_i}(0),$$

because it is assumed that the spectral intensity is finite. The integrand has a simple pole; consequently, the principal value integral is equal to zero.

Finally, for the kinetic coefficients we obtain the expression

$$L_{ik} = \frac{\beta}{2}J_{\dot{\alpha}_k\dot{\alpha}_i}(0) = \frac{\beta}{2}\int_{-\infty}^{\infty}\langle\dot{\alpha}_k\dot{\alpha}_i(t)\rangle\,dt = \frac{\beta}{2}\int_{-\infty}^{\infty}\langle\dot{\alpha}_k(t)\,\dot{\alpha}_i\rangle\,dt, \qquad (17.38)$$

which is valid in the absence of a magnetic field.

And so, the kinetic coefficients are finite for systems in which the spectral intensity of the time correlation function of currents (17.35) is finite at $\omega=0$[1].

If it is assumed that the spectral intensity $J_{\dot{\alpha}_k\dot{\alpha}_i}(\omega)$ has a δ-function singularity at $\omega=0$, i.e., if

$$J_{\dot{\alpha}_k\dot{\alpha}_i}(\omega) = C_{ki}\,\delta(\omega) + J'_{ki}(\omega),$$

where $J'_{ki}(\omega)$ is finite as $\omega\to 0$ and $C_{ki}\neq 0$, then the expression for the kinetic coefficients (17.35) diverges as $1/\varepsilon$. In fact,

$$\int_0^\infty \int_{-\infty}^\infty C_{ki}\,\delta(\omega)\, e^{-i\omega t-\varepsilon t}\,\frac{e^{\beta\hbar\omega}-1}{\beta\hbar\omega}\,dt\,d\omega = \frac{C_{ki}}{\varepsilon} \to \infty.$$

We shall now show that the order of limiting transitions, in which first $V\to\infty$ and then $\varepsilon\to 0$, is indeed necessary.

Let us suppose that the transition $V\to\infty$ has not yet been carried out and that the spectrum is discrete. In accordance with (16.16) the spectral intensity is equal to

$$J_{\dot{\alpha}_k\dot{\alpha}_i}(\omega) = 2\pi Q^{-1}\sum_{\mu,\nu} \dot{\alpha}_k^{\mu\nu}\dot{\alpha}_i^{\nu\mu}\, e^{-\beta E_\mu}\,\delta\left(\frac{E_\mu - E_\nu}{\hbar} - \omega\right), \tag{17.39}$$

where $\dot{\alpha}$ is the matrix element of the current operator. If the spectrum is discrete, then the expression loses its meaning at $\omega=0$, because the δ-function is defined only for continuous arguments. But if the limiting transition $V\to\infty$ has already been carried out, then the expression

$$L_{ik} = \beta\pi Q^{-1}\sum_{\mu,\nu} \dot{\alpha}_i^{\mu\nu}\dot{\alpha}_k^{\nu\mu}\, e^{-\beta E_\mu}\,\delta\left(\frac{E_\mu - E_\nu}{\hbar}\right) \tag{17.39a}$$

---

[1] This is the case for dissipative systems in which current fluctuations represent an ergodic process, in the terminology of the theory of random processes (see [16,17] and the lecture by Mazur [69]).

is meaningful, because the δ-function depends now on a continuous variable.

17.5. Energy Increase Due to External Mechanical Perturbation.

Under the influence of external driving forces $F_1(t),\dots,F_n(t)$ the energy and the entropy of a system can increase. Let us consider first how the energy of a system with a Hamiltonian H changes under the influence of the external perturbation (17.1).

The statistical operator satisfies the quantum Liouville equation (8.6):

$$i\hbar \frac{\partial \rho}{\partial t} = [H + H_t^1, \rho]. \qquad (17.40)$$

The change of the energy of the system under the influence of the perturbation H_t^1 is described by the dynamical variable

$$\frac{dH}{dt} = \frac{1}{i\hbar}[H, H + H_t^1] = \frac{1}{i\hbar}[H, H_t^1], \qquad (17.41)$$

because H is not an explicit function of time. The external field which is causing the perturbation H_t^1, and the perturbation itself are not included in the system. We obtain the average change in the energy by averaging (17.41) with a statistical operator ρ, which satisfies equation (17.40). Consequently,

$$\left\langle \frac{dH}{dt} \right\rangle = \mathrm{Sp}\left(\rho \frac{dH}{dt}\right) = \frac{d}{dt}\langle H \rangle = \frac{1}{i\hbar}\langle [H, H_t^1] \rangle, \qquad (17.41a)$$

where (8.18) has been used. Introducing the notation

$$\dot{H}_t^1 = \frac{1}{i\hbar}[H_t^1, H], \qquad (17.41b)$$

we rewrite (17.41a) in the form

$$\frac{d}{dt}\langle H \rangle = -\langle \dot{H}_t^1 \rangle. \qquad (17.42)$$

The operator $\dot{H}^1_t$ has the meaning of a derivative of an operator only with respect to the time variable which enters in the Heisenberg representation. We expand the right hand side of equation (17.42) by means of the relationship (15.47) from the theory of the linear reaction. We obtain

$$\frac{d}{dt}\langle H\rangle = -\int_{-\infty}^{\infty}\langle\langle \dot{H}^1_t(t)\, H^1_{t'}(t')\rangle\rangle\, dt', \tag{17.43}$$

because in a state of statistical equilibrium the currents are equal to zero:

$$\langle \dot{H}^1_t\rangle_0 = -\sum_j F_j(t)\,\langle \dot{a}_j\rangle_0 = 0.$$

Thus, the rate of change of the energy in the system under the influence of the perturbation H^1_t is defined by the retarded Green function, which relates the derivative of the perturbation $\dot{H}^1_t$ with the perturbation itself.

Using the formula (15.51) for the linear reaction we write (17.42) in the form

$$\frac{d}{dt}\langle H\rangle = \int_0^{\beta}\int_{-\infty}^{t}\langle \dot{H}^1_{t'}(t'-i\hbar\lambda)\,\dot{H}^1_t(t)\rangle\, d\lambda\, dt' =$$

$$= \beta\int_{-\infty}^{t}(\dot{H}^1_{t'}(t'),\ \dot{H}^1_t(t))\, dt', \tag{17.44}$$

where the notation which was used earlier has been introduced

$$(A(t),\ B(t')) = \beta^{-1}\int_0^{\beta}\langle A(t)\, B(t'+i\hbar\lambda)\rangle\, d\lambda \tag{17.44a}$$

for the quantum correlation functions.

Thus, the rate of change of the energy of the system (17.44) is defined by the quantum time correlation functions, which relate the operators $\dot{H}^1_t$ at different moments of time.

After substituting (17.1) into (17.44) we have

$$\frac{d}{dt}\langle H\rangle = \sum_{i,k} \int_{-\infty}^{t} L_{ik}(t-t')\,F_k(t')\,F_i(t)\,dt', \tag{17.45}$$

where

$$L_{ik}(t-t') = \beta(\dot{\alpha}_k(t'),\ \dot{\alpha}_i(t)). \tag{17.45a}$$

Using the linear relationship between forces and currents (17.20), we rewrite (17.45) in the form

$$\frac{d}{dt}\langle H\rangle = \sum_i \langle\dot{\alpha}_i\rangle F_i(t) = \langle\dot{\alpha}\rangle\cdot F(t). \tag{17.46}$$

Thus, the rate of change of the energy of a system under the influence of mechanical perturbations, which are caused by driving forces F_i, is determined by the sum of the products of the forces F_i and their conjugate currents $\langle\dot{\alpha}_i\rangle$.

We shall discuss the physical meaning of the formula (17.43) and show that it can be written in the form

$$\frac{d\langle H\rangle}{dt} = \sum_{\alpha,\beta} \hbar\omega_{\alpha\beta}\, w_{\alpha\beta}(t)\, e^{(\Omega-E_\beta)/\theta} \qquad \left(\omega_{\alpha\beta} = \frac{E_\alpha - E_\beta}{\hbar}\right), \tag{17.47}$$

where $w_{\alpha\beta}(t)$ is the probability per unit time of the transition $\beta \to \alpha$.

The meaning of formula (17.47) is evident:

$$\sum_\alpha \hbar\omega_{\alpha\beta}\, w_{\alpha\beta}(t)$$

is the probability per unit time of the change of energy for quantum transitions from the state β to all possible states α. The sum of these expressions over β with the Gibbs statistical factor $e^{(\Omega-E_\beta)/\theta}$ gives the average statistical rate of change of the energy under the influence of a perturbation as a result of all possible transitions.

According to the quantum theory of transitions (see, for example, [100]), the probability of the transition $\beta \to \alpha$ by the time t under the influence of the perturbation H_t^1 is equal to

$$W_{\alpha\beta}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} \langle\alpha\,|\,H^1_{t_1}\,|\beta\rangle e^{i\omega_{\alpha\beta}t_1}\,dt_1\right|^2 ,$$

or, if the perturbation operator is written in the Heisenberg representation,

$$W_{\alpha\beta}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} \langle\alpha\,|\,H^1_{t_1}(t_1)\,|\beta\rangle\,dt_1\right|^2. \tag{17.48}$$

For the probability per unit time of the transition β→α

$$w_{\alpha\beta}(t) = \frac{dW_{\alpha\beta}(t)}{dt} \tag{17.49}$$

we obtain the expression

$$w_{\alpha\beta}(t) = \frac{1}{\hbar^2}\int_{t_0}^{t}\{\langle\alpha|\,H^1_t(t)\,|\beta\rangle\langle\beta|\,H^1_{t_1}(t_1)\,|\alpha\rangle + \\ + \langle\beta|\,H^1_t(t)\,|\alpha\rangle\langle\alpha|\,H^1_{t_1}(t_1)\,|\beta\rangle\}\,dt_1, \tag{17.49a}$$

which is finite as $t_0 \to -\infty$, and which we shall assume in what follows.

Substituting (17.49a) into (17.47) and carrying out the summation over α and β and using the completeness of the system of eigenfunctions, we obtain formula (17.43), which was to be shown.

Using formula (17.1) we write formula (17.44) in the form

$$\frac{d\langle H\rangle}{dt} = \int_0^{\beta}\int_{-\infty}^{t}\langle\dot{\alpha}(t')\,\dot{\alpha}(t+i\hbar\lambda)\rangle : \boldsymbol{F}(t)\,\boldsymbol{F}(t')\,d\lambda\,dt', \tag{17.50}$$

where the symbol : denotes the complete contraction of tensors. Expanding the time correlation function in a Fourier integral

$$\langle\dot{\alpha}(t')\,\dot{\alpha}(t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} J_{\dot{\alpha}\dot{\alpha}}(\omega)\,e^{-i\omega(t-t')}\,d\omega \tag{17.51}$$

and carrying out the integration over λ, we rewrite (17.50) in the form

$$\frac{d\langle H\rangle}{dt} = \frac{1}{2\pi}\int_{-\infty}^{t}\int_{-\infty}^{\infty}\frac{e^{\beta\hbar\omega}-1}{\hbar\omega}J_{\dot{u}\dot{u}}(\omega):F(t)F(t')e^{-i\omega(t-t')}dt'\,d\omega. \tag{17.50a}$$

Let us consider the particular case in which forces which are constant in time are switched on adiabatically[1],

$$F(t) = Fe^{\varepsilon t}, \tag{17.52}$$

and let us show that in this case the energy increases.

Carrying out the integration over t′ in (17.50a), we obtain

$$\frac{d\langle H\rangle}{dt} = \frac{1}{2\pi}\int_{-\infty}^{\infty}J_{\dot{u}\dot{u}}(\omega):FF\,e^{2\varepsilon t}\,\frac{e^{\beta\hbar\omega}-1}{\hbar\omega}\,\frac{1}{\varepsilon+i\omega}\,d\omega$$

or using (16.32)

$$\frac{d\langle H\rangle}{dt} = \frac{\beta}{e}J_{\dot{H}^1\dot{H}^1}(0) + \frac{1}{2\pi i}\mathcal{P}\int_{-\infty}^{\infty}J_{\dot{H}^1\dot{H}^1}(\omega)\,\frac{e^{\beta\hbar\omega}-1}{\hbar\omega^2}\,d\omega, \tag{17.50b}$$

becau*e

$$J_{\dot{u}\dot{u}}(\omega):FF = J_{\dot{H}^1\dot{H}^1}(\omega).$$

The spectral intensity $J_{\dot{H}^1\dot{H}^1}(\omega)$ is positive in accordance with (16.18a), because it corresponds to the time correlation function of mutually conjugate operators.

The integral on the right hand side of (17.50b) is equal to zero, because d<H>/dt is real; below we shall verify this directly.

As the spectral intensity $J_{\dot{H}^1\dot{H}^1}(\omega)$ is real, from (16.34a) and (17.25)

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[1] The operation of adiabatic switching on of a perturbation which is constant in time is somewhat arbitrary. This is an artificial method for selecting the retarded solutions of the Liouville equation, which is evident from the analogy with the formal theory of scattering (see Appendix I and [47]).

we have

$$\operatorname{Im}\langle\langle \dot{H}^1 | \dot{H}^1 \rangle\rangle_\omega = -\frac{1}{2\hbar}\left(e^{\beta\hbar\omega} - 1\right) J_{\dot{H}^1\dot{H}^1}(\omega),$$

$$\operatorname{Im}\langle\langle \dot{H}^1 | \dot{H}^1 \rangle\rangle_\omega = -\operatorname{Im}\langle\langle \dot{H}^1 | \dot{H}^1 \rangle\rangle_{-\omega} \tag{17.53}$$

and, consequently,

$$\frac{1}{i\pi}\mathcal{P}\int_{-\infty}^{\infty} \operatorname{Im}\langle\langle \dot{H}^1 | \dot{H}^1 \rangle\rangle_\omega \frac{d\omega}{\omega^2} = 0, \tag{17.53a}$$

because the integrand is an odd function of ω. Equation (17.53a) implies that the imaginary part of (17.50b) is equal to zero. Consequently,

$$\frac{d\langle H\rangle}{dt} = \frac{\beta}{2} J_{\dot{H}^1\dot{H}^1}(0) \geqslant 0. \tag{17.54}$$

Thus, the energy of a system under the influence of a constant perturbation increases at a finite rate. For this it is necessary that the spectral intensity $J_{\dot{H}^1\dot{H}^1}(\omega)$ have no singularity of the type $\delta(\omega)$ at $\omega=0$ and that it be non-zero at this point.

We shall show that the average energy increases even in the case in which the forces are arbitrary, but are sufficiently slowly varying functions of time. Let the parameters $F_i(t')$ change very little during the time in which the correlations are lost. Then in formula (17.50) they may be taken outside the integral sign at the point $t'=t$:

$$\frac{d\langle H\rangle}{dt} = F(t)F(t) : \int_0^\beta \int_{-\infty}^{t} e^{\varepsilon t_1} \langle \dot{\alpha}(t_1)\, \dot{\alpha}(t + i\hbar\lambda)\rangle \, d\lambda \, dt_1, \tag{17.55}$$

which implies a neglect of retardation effects. Expanding the time correlation functions in (17.55) in a Fourier integral (17.51) and carrying out successive integrations over λ, t_1, and frequency, analogously to the case of constant forces, we obtain

$$\frac{d\langle H\rangle}{dt} = \frac{1}{2\theta} J_{\dot{H}^1_t\dot{H}^1_t}(0) \geqslant 0, \tag{17.56}$$

i.e., the average energy increases, if the spectral intensity at $\omega=0$ is not zero.

Let us consider the change of the energy of a system under the influence of a periodic perturbation

$$H_t^1 = \mathrm{Re}\{H^1 e^{\varepsilon t - i\omega t}\}, \tag{17.57}$$

where H^1 can be complex. We calculate the rate of change of the energy by means of (17.43). Substituting (17.57) into (17.43), we obtain

$$\frac{d\langle H\rangle}{dt} = -\frac{1}{2}\mathrm{Re}\{\langle\langle \dot{H}^{1*} \mid H^1\rangle\rangle_\omega + \langle\langle \dot{H}^1 \mid H^1\rangle\rangle_\omega e^{-2i\omega t}\}. \tag{17.58}$$

Thus, the rate of change of the energy is composed of two terms - one constant in time and one oscillatory. The constant term is positive, because

$$-\mathrm{Re}\langle\langle \dot{H}^{1*} \mid H^1\rangle\rangle_\omega > 0.$$

In fact,

$$-\mathrm{Re}\langle\langle \dot{H}^{1*} \mid H^1\rangle\rangle_\omega = \mathrm{Re}\, i\omega\langle\langle H^{1*} \mid H^1\rangle\rangle_\omega =$$
$$= -\omega\,\mathrm{Im}\langle\langle H^{1*} \mid H^1\rangle\rangle_\omega = \frac{\omega}{2\hbar}(e^{\beta\hbar\omega} - 1)\, J_{H^1 H^{1*}}(\omega) > 0,$$

where the relations (16.18), (16.19), and (16.33), and the positivity of the function $\omega(e^{\beta\hbar\omega}-1)$ have been used.

Using (17.1a) and (17.21a) we write formula (17.58) in the form

$$\frac{d\langle H\rangle}{dt} = \frac{1}{2}\mathrm{Re}\{\boldsymbol{F}^* \cdot L(\omega) \cdot \boldsymbol{F} + \boldsymbol{F} \cdot L(\omega) \cdot \boldsymbol{F} e^{-2i\omega t}\}. \tag{17.58a}$$

The average rate of change of the energy is always positive and is equal to

$$\frac{dE}{dt} = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} \frac{d\langle H\rangle}{dt}\, dt = \frac{1}{2}\mathrm{Re}\,\boldsymbol{F}^* \cdot L(\omega) \cdot \boldsymbol{F} > 0. \tag{17.59}$$

Systems whose energy increases under the influence of a periodic perturbation are called dissipative. It is necessary that they have densely distributed levels, in order that $L(\omega)$ make sense after the limiting transitions $V\to\infty, \varepsilon\to 0$.

The average rate of absorption of energy (17.59) can be represented as

$$\frac{dE}{dt} = \frac{1}{2}\{L'(\omega)^s : \mathrm{Re}\, FF^* - L''(\omega)^a : \mathrm{Im}\, FF^*\}, \tag{17.59a}$$

where $L'(\omega)^s$ is the real, symmetric part, and $L''(\omega)^\alpha$ is the imaginary, antisymmetric part of the tensor of the kinetic coefficients. The remaining terms give no contribution, because the tensor $\mathrm{Re}FF^*$ is symmetric, and $\mathrm{Im}FF^*$ is antisymmetric.

We shall now express the average absorption of energy over a single period by means of the generalized susceptibility. Using (17.58) and (17.59), we obtain

$$\frac{dE}{dt} = -\frac{\omega}{2}\,\mathrm{Im}\,\langle\langle \dot{H}^1 \mid H^1 \rangle\rangle_\omega = \frac{\omega}{2}\,\mathrm{Im}\,(F^* \cdot \varkappa(\omega) \cdot F) \tag{17.59b}$$

or

$$\frac{dE}{dt} = \frac{\omega}{2}\{\varkappa''(\omega)^s : \mathrm{Re}\, FF^* + \varkappa'(\omega)^a : \mathrm{Im}\, FF^*\}, \tag{17.59c}$$

where $x''(\omega)^s$ is the imaginary part of the symmetric susceptibility tensor, and $x'(\omega)^\alpha$ is the real part of the antisymmetric susceptibility tensor.

The asymptotic expressions for the probability per unit time of a transition under the influence of the perturbation (17.57) is used in deriving the fluctuation-dissipation theorems [22,101]:

$$\begin{aligned} w_{\alpha\beta} = \frac{\pi}{2\hbar}\{ |\langle\alpha | H^1 | \beta\rangle|^2 \delta(E_\alpha - E_\beta - \hbar\omega) + \\ + |\langle\beta | H^1 | \alpha\rangle|^2 \delta(E_\alpha - E_\beta + \hbar\omega)\}; \end{aligned} \tag{17.60}$$

this expression is applicable for a large time interval t, when the probability (17.48) becomes proportional to time, and the probability of transition $w_{\alpha\beta}$ is already independent of t.

Let us calculate the average rate of absorption of energy by means of (17.60):

$$\frac{d\langle H\rangle}{dt}=\sum_{\alpha,\beta}e^{(\Omega-E_\beta)/\Theta}\,\omega_{\alpha\beta}\frac{\pi}{2}\{|\langle\alpha|H^1|\beta\rangle|^2\delta(E_\alpha-E_\beta-\hbar\omega)+$$
$$+|\langle\beta|H^1|\alpha\rangle|^2\delta(E_\alpha-E_\beta+\hbar\omega)\}=$$
$$=\frac{\pi}{2\omega}\sum_{\alpha\beta}e^{(\Omega-E_\beta)/\Theta}\{|\langle\alpha|\dot{H}^1|\beta\rangle|^2\delta(E_\alpha-E_\beta-\hbar\omega)-$$
$$-|\langle\beta|\dot{H}^1|\alpha\rangle|^2\delta(E_\alpha-E_\beta+\hbar\omega)\}, \tag{17.61}$$

where $\omega_{\alpha\beta}=(E_\alpha-E_\beta)/\hbar$. Substituting here the integral representation of the δ-function

$$\delta(E)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}e^{iEt/\hbar}\,dt$$

and carrying out the summation over α and β, we obtain

$$\frac{d\langle H\rangle}{dt}=\frac{1}{4\hbar\omega}\int_{-\infty}^{\infty}\{\langle\dot{H}^{1*}\dot{H}^1(t)\rangle e^{-i\omega t}-\langle\dot{H}^1\dot{H}^{1*}(t)\rangle e^{i\omega t}\}\,dt=$$
$$=\frac{1}{4\hbar\omega}\{J_{\dot{H}^{1*}\dot{H}^1}(-\omega)-J_{\dot{H}^1\dot{H}^{1*}}(\omega)\}. \tag{17.62}$$

Making use of the properties (16.16a) of the spectral intensities

$$J_{\dot{H}^{1*}\dot{H}^1}(-\omega)=e^{\beta\hbar\omega}J_{\dot{H}^1\dot{H}^{1*}}(\omega),$$

we transform (17.62) to the form

$$\frac{d\langle H\rangle}{dt}=\frac{e^{\beta\hbar\omega}-1}{4\hbar\omega}J_{\dot{H}^1\dot{H}^{1*}}(\omega)\geqslant 0, \tag{17.62a}$$

i.e., the energy increases.

For $\omega=0$ formula (17.62a) takes on the form

$$\frac{d\langle H\rangle}{dt}=\frac{\beta}{4}J_{\dot{H}^1\dot{H}^{1*}}(0), \tag{17.62b}$$

which differs by a factor of 1/2 from (17.54). The source of this difference is that (17.62b) denotes the average over a period.

Thus, if one uses the asymptotic formula (17.60) for the probability per unit time of a transition, then for a periodic perturbation the energy increases monotonically. This implies that formula (17.61) gives the correct result for the average absorption over one period and averages the oscillations.

17.6. Production of Entropy.

In the preceding section we considered the effect of mechanical perturbations on the change of energy of a system. We shall now study their effect on the change of entropy.

It is first of all necessary to define the entropy for a nonequilibrium state.

The average of the negative of the logarithm of the statistical operator

$$\langle\eta\rangle = -\langle\ln\rho\rangle = -\mathrm{Sp}(\rho\ln\rho), \tag{17.63}$$

which is the entropy in an equilibrium case, cannot describe the entropy in a nonequilibrium state. In this regard,

$$\eta = -\ln\rho \tag{17.64}$$

satisfies, as does ρ, the Liouville equation

$$i\hbar\frac{\partial\eta}{\partial t} = [H + H_t', \eta] \tag{17.65}$$

(see § 8 Chapter II). Consequently, η is an integral of motion

$$\frac{d\eta}{dt} = \frac{\partial\eta}{\partial t} + \frac{1}{i\hbar}[\eta, H + H_t'] = 0, \tag{17.66}$$

from which it follows that $\langle\eta\rangle$ is constant in time

$$\frac{d}{dt}\langle\eta\rangle=\left\langle\frac{d\eta}{dt}\right\rangle=0 \qquad (17.66a)$$

and cannot possess the properties of entropy for a nonequilibrium state.

We shall not at the present time give a general definition of the entropy of a nonequilibrium state (we shall discuss this question in § 20), and we shall restrict ourselves to defining it for the case of the linear reaction.

We shall assume that the state of the system remains spatially homogeneous and stationary in time, i.e., the energy which is released is drawn off. Then it is natural to define the entropy in analogy with an equilibrium state by the thermodynamic relationship (11.24)

$$S = \frac{\langle H\rangle-\mu\langle N\rangle-\Omega}{\theta}, \qquad (17.67)$$

but assuming that the averaging is carried out over a nonequilibrium state.

The entropy (17.67) is equal to the average of the negative of the logarithm of the equilibrium distribution (9.42):

$$S = -\langle\ln\rho_0\rangle = -\mathrm{Sp}(\rho\ln\rho_0). \qquad (17.67a)$$

The time rate of change of the entropy (17.67) is equal to

$$\frac{\partial S}{\partial t}=\frac{1}{\theta}\cdot\frac{d\langle H\rangle}{dt}, \qquad (17.68)$$

because the parameters θ, μ, and Ω characterize a statistical equilibrium state and are independent of time, and the external perturbation does not change the number of particles. Using (17.45) we write the expression (17.68) in the form

$$\frac{\partial S}{\partial t}=\frac{1}{\theta}\sum_{i,k}\int_{-\infty}^{t}F_i(t)\,L_{ik}(t-t')\,F_k(t')\,dt'=$$

$$=\frac{1}{\theta}\int_{-\infty}^{t}\boldsymbol{F}(t)\cdot\boldsymbol{L}(t-t')\cdot\boldsymbol{F}(t')\,dt', \qquad (17.69)$$

or, if one can neglect the retardation, i.e., if one can assume that F(t′) changes little during the time in which the correlations die out, and one takes it outside the integral sign at the point t′=t, then

$$\frac{\partial S}{\partial t} = \frac{1}{\theta} \sum_{i,k} F_i(t) L_{ik} F_k(t). \tag{17.69a}$$

For the case of external forces which are constant in time it follows from (17.68) and (17.54) that the entropy increases:

$$\frac{\partial S}{\partial t} = \frac{1}{\theta} \sum_{i,k} F_i L_{ik} F_k > 0, \tag{17.69b}$$

For external forces which are periodic in time (see (17.57)) it follows from (17.68) and (17.69) that the average rate of change of the entropy over a single period is positive

$$\frac{\omega}{2\pi} \int_0^{2\pi/\omega} \frac{\partial S}{\partial t}\, dt = \frac{1}{\theta} \frac{1}{2} \operatorname{Re} \boldsymbol{F}^* \cdot L(\omega) \cdot \boldsymbol{F} > 0. \tag{17.70}$$

Thus, entropy appears in the system, and (17.69b) and (17.70) might be called the production of entropy.

§ 18. System of Charged Particles in a Variable Electromagnetic Field

We shall consider in this paragraph, as an example of the general theory of the linear reaction, a system of charged particles in a variable electromagnetic field. We shall study the relation between the retarded Green functions and the dielectric permittivity, the magnetic susceptibility, and electrical conductivity, both static and wave number dependent, their symmetry properties, and dispersion relations.

18.1. Dielectric Permeability and Conductivity.

In sections 15.4 and 17.3 a system of charged particles in an electric field which was variable in time, but constant in space, was considered.

We shall now consider the behavior of such a system in an electromagnetic field, which changes both in time and in space [40,41,52,56,64,102-104].

The Hamiltonian of a system in an external electromagnetic field with vector potential A(x,t) and scalar potential φ(x,t) has the form

$$H' = \frac{1}{2m} \int \psi^+(x) \left(\frac{h}{i} \nabla - \frac{e}{c} A(x, t) \right)^2 \psi(x)\, dx + \\ + \int \psi^+(x) \psi(x) e\varphi(x, t)\, dx + H_{\text{int}}, \tag{18.1}$$

where e is the charge of a particle, and H_{int} is the operator for the interaction between particles. At the present time we do not take into account the interaction of the spin of the particle with the field (see section 18.3). For simplicity we shall assume that the particles have a single kind of charge, for example, if they are electrons, then the ions can be considered as a shielding background.

In (18.1) $\psi(x)$, $\psi^+(x)$ are second quantized wave functions, i.e., operators which act on wave functions in occupation number space, and which satisfy the commutation (or anti-commutation) relations

$$\begin{gathered} \psi(x) \psi^+(x') \pm \psi^+(x') \psi(x) = \delta(x - x'), \\ \psi(x) \psi(x') \pm \psi(x') \psi(x) = 0, \\ \psi^+(x) \psi^+(x') \pm \psi^+(x') \psi^+(x) = 0, \end{gathered} \tag{18.2}$$

where the plus sign is taken for Fermi statistics, and the minus sign for Bose statistics (see [105,25] and courses of quantum mechanics [100,106,107]).

The operators $\psi(x)$, $\psi^+(x)$ are related to $\alpha_{k\sigma}$, $\alpha^+_{k\sigma}$ - the creation and annihilation operators for the state k,σ - by the relations

$$\psi(x) = \frac{1}{\sqrt{V}} \sum_{k,\sigma} e^{i(kx)} \delta_{\sigma s_z} a_{k\sigma}, \quad \psi^+(x) = \frac{1}{\sqrt{V}} \sum_{k,\sigma} e^{-i(kx)} \delta_{\sigma s_z} a^+_{k\sigma}, \tag{18.3}$$

where $\alpha_{k\sigma}$,$\alpha^+_{k\sigma}$ satisfy the commutation (or anti-commutation) relations

$$\begin{aligned} a_{k\sigma} a^+_{k_1\sigma_1} \pm a^+_{k_1\sigma_1} a_{k\sigma} &= \delta_{k\sigma,\, k_1\sigma_1}, \\ a_{k\sigma} a_{k_1\sigma_1} \pm a_{k_1\sigma_1} a_{k\sigma} &= 0, \\ a^+_{k\sigma} a^+_{k_1\sigma_1} \pm a^+_{k_1\sigma_1} a^+_{k\sigma} &= 0; \end{aligned} \tag{18.4}$$

δ_{k,k_1} is the Kronecker delta, and the argument s_z on $\psi(x)$ is not written out explicitly. It is easily verified that (18.4) follows from (18.2) and conversely.

The potentials $A(x,t)$ and $\varphi(x,t)$ define the electromagnetic field which operates on the particles. As was already noted in section 15.4, it is necessary to distinguish two cases - when the Coulomb interaction is explicitly taken into account in the Hamiltonian and when it is taken into account through a shielding field. In the first case it is necessary to account for the screening effects, but in the second case it is not, because they are already taken into account through the shielded interaction. In what follows we shall consider only the first case.

In introducing the dielectric permittivity and the magnetic permeability it must be taken into account that induced charges shield only the longitudinal part of the electric field, because they define the divergence of the field[1], and the induced currents shield only the transverse part of the magnetic field, because they define the curl of the field. Therefore the potentials $A(x,t)$ and $\varphi(x,t)$ define the electric displacement vector

$$D = -\nabla\varphi - \frac{1}{c}\frac{\partial A}{\partial t} \tag{18.5}$$

only for the longitudinal part of D, and they define

$$\mathbf{B} = \operatorname{rot} \mathbf{A} \tag{18.5a}$$

only for the transverse part of B; however, the field B is always transverse, because $\operatorname{div}\mathbf{B}=0$.

The current density operator is equal to the variational derivative of the Hamiltonian (18.1) with respect to the vector potential

$$j'(x) = -c\frac{\delta H'}{\delta A(x)}, \tag{18.6}$$

and thus,

$$j'(x) = \frac{e\hbar}{2mi}\{\psi^+(x)\nabla\psi(x) - \nabla\psi^+(x)\psi(x)\} - \frac{e^2}{mc}A(x,t)\psi^+(x)\psi(x). \tag{18.7}$$

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[1] This is sometimes not taken into account in textbooks [108], although the question was completely clear long ago, already in the works of Ewald [109] (see also [110-113]).

The current (18.7) satisfies the continuity equation (conservation of charge)

$$\frac{\partial\rho(x)}{\partial t} = -\operatorname{div} j'(x), \quad \rho(x) = e\psi^{+}(x)\psi(x) = en(x); \tag{18.7a}$$

ρ(x) is the charge density.

Separating out the linear and quadratic terms the total Hamiltonian of the system can be written in the form

$$H' = H + H_1 + H_2, \tag{18.8}$$

where

$$H_1 = -\frac{1}{c}\int j(x)\cdot A(x,\ t)\,dx + \int \rho(x)\,\varphi(x,\ t)\,dx, \tag{18.8a}$$

$$H_2 = \frac{e^2}{mc^2}\int \rho(x)\,A^2(x,\ t)\,dx,$$

and H is the Hamiltonian of the system in the absence of an electromagnetic field, and j(x) is the current operator in the absence of a field,

$$j(x) = \frac{e\hbar}{2mi}\{\psi^{+}(x)\nabla\psi(x) - \nabla\psi^{+}(x)\psi(x)\}. \tag{18.9}$$

Let us consider the reaction of a system to the adiabatic switching on of an electromagnetic field.

Let the current be zero in the absence of the field. After switching on the field the current and charge, to within the accuracy of terms linear in A(x,t) and φ(x,t), are according to (15.47) equal to

$$\begin{aligned} J(x,\ t) = \langle j'\rangle = &-\frac{e^2 n}{mc}A(x,\ t) - \\ &-\frac{1}{c}\int\int_{-\infty}^{\infty}\langle\langle j(x,\ t)\,j(x',\ t')\rangle\rangle\cdot A(x',\ t')\,dx'\,dt' + \\ &+\int\int_{-\infty}^{\infty}\langle\langle j(x,\ t)\,\rho(x',\ t')\rangle\rangle\,\varphi(x',\ t')\,dx'\,dt', \end{aligned} \tag{18.10a}$$

$$\begin{aligned} \langle\rho(x)\rangle = en &-\frac{1}{c}\int\int_{-\infty}^{\infty}\langle\langle\rho(x,\ t)\,j(x',\ t')\rangle\rangle\cdot A(x',\ t')\,dx'\,dt' + \\ &+\int\int_{-\infty}^{\infty}\langle\langle\rho(x,\ t)\,\rho(x',\ t')\rangle\rangle\,\varphi(x',\ t')\,dx'\,dt', \end{aligned} \tag{18.10b}$$

where in the integrands are retarded Green functions of tensor, vector, and scalar types, and $n=\langle\psi^+(x)\psi(x)\rangle$ is the number of particles per unit volume, which is independent of x as a consequence of the spatial homogeneity of the system.

The relations (18.10a) and (18.10b) take on an especially simple form if the functions $A(x,t)$, $\varphi(x,t)$, $J(x,t)$ and $\langle\rho(x)\rangle$ are expanded in series of plane waves

$$\begin{aligned} A(x, t) &= \frac{1}{V}\sum_k \int_{-\infty}^{\infty} A(k, \omega)\, e^{i(kx)-i\omega t}\, d\omega, \\ \varphi(x, t) &= \frac{1}{V}\sum_k \int_{-\infty}^{\infty} \varphi(k, \omega)\, e^{i(kx)-i\omega t}\, d\omega, \\ J(x, t) &= \frac{1}{V}\sum_k \int_{-\infty}^{\infty} J(k, \omega)\, e^{i(kx)-i\omega t}\, d\omega, \end{aligned} \tag{18.11}$$

the operators are written in momentum representation

$$j(x) = \frac{1}{\sqrt{V}}\sum_k j_k e^{i(kx)}, \quad \rho(x) = \frac{1}{\sqrt{V}}\sum_k \rho_k e^{i(kx)}, \tag{18.11a}$$

where

$$\begin{aligned} j_k &= \frac{e\hbar}{m\sqrt{V}}\sum_{q,\sigma}\left(q-\frac{k}{2}\right) a^+_{q-k,\sigma}\, a_{q\sigma}, \\ \rho_k &= \frac{e}{\sqrt{V}}\sum_{q,\sigma} a^+_{q-k,\sigma}\, a_{q\sigma}, \end{aligned} \tag{18.11b}$$

and the Green functions are expanded in Fourier integrals. Then the relations (18.10a) and (18.10b) become linear, algebraic relations between the Fourier transforms of current and charge and the Fourier transforms of the vector and scalar potential:

$$\begin{aligned} J(k, \omega) &= -\frac{e^2 n}{mc} A(k, \omega) - \langle\langle j_k \mid j_{-k}\rangle\rangle_\omega \cdot \frac{1}{c} A(k, \omega) + \\ &\quad + \langle\langle j_k \mid \rho_{-k}\rangle\rangle_\omega\, \varphi(k, \omega), \\ \rho(k, \omega) &= -\langle\langle \rho_k \mid j_{-k}\rangle\rangle_\omega \cdot \frac{1}{c} A(k, \omega) + \langle\langle \rho_k \mid \rho_{-k}\rangle\rangle_\omega\, \varphi(k, \omega), \end{aligned} \tag{18.12}$$

where we have made use of the fact that as a consequence of the assumed translational invariance of the problem the averages $<j_k \cdot j_{k'}>$, $<j_k \rho_{k'}>$, and $<\rho_k \rho_{k'}>$ are non-zero only for $k+k'=0$. In crystals because of the spatial inhomogeneity this property does not exist.

The relation (18.12) can be written in a form in which it does not contain the vector and scalar potential, but only the electric displacement and the magnetic field. We write the tensor and vector Green functions in such a way that their tensor or vector character is explicitly expressed. As they depend only on the vector k, and the system is assumed isotropic, the tensor function must depend linearly on the tensor $k_\alpha k_\beta$ and the unit tensor $\delta_{\alpha\beta}$, and the vector function on k_α with coefficients which depend only on $|k|$, i.e.,

$$\begin{gathered}
\chi_{\alpha\beta}(k, \omega) - \frac{e^2 n}{m} \delta_{\alpha\beta} = \langle\langle j_k^\alpha \mid j_{-k}^\beta \rangle\rangle_\omega = \\
= \frac{k_\alpha k_\beta}{k^2} \chi^l (k, \omega) + \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right) \chi^{tr} (k, \omega), \\
\langle\langle j_k^\alpha \mid \rho_{-k} \rangle\rangle_\omega = \langle\langle (k j_k) \mid \rho_{-k} \rangle\rangle_\omega \frac{k_\alpha}{k^2}, \\
\langle\langle \rho_k \mid j_{-k}^\alpha \rangle\rangle_\omega = \langle\langle \rho_k \mid (k j_{-k}) \rangle\rangle_\omega \frac{k_\alpha}{k^2},
\end{gathered} \tag{18.13}$$

where

$$\begin{gathered}
\chi^l (k, \omega) = \frac{1}{k^2} \langle\langle (k j_k) \mid (k j_{-k}) \rangle\rangle_\omega, \\
\chi^{tr} (k, \omega) = \frac{1}{2k^2} \langle\langle [k \times j_k] \cdot \mid [k \times j_{-k}] \rangle\rangle_\omega
\end{gathered} \tag{18.13a}$$

are the longitudinal and transverse parts of the susceptibility tensor

$$\chi_{\alpha\beta}(k, \omega) - \frac{e^2 n}{m} \delta_{\alpha\beta}.$$

The susceptibility $\chi_{\alpha\beta}(k,\omega)$ expresses the linear reaction of the current to the vector potential.

We obtain the second expression in (18.13a) by calculating complete contraction of the tensor $\chi_{\alpha\beta}(k,\omega)$ with $\delta_{\alpha\beta}-(k_\alpha k_\beta/k^2)$, noting that

$$\sum_{\alpha\beta} \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right)\left(\delta_{\beta\alpha} - \frac{k_\beta k_\alpha}{k^2}\right) = 2,$$

and using the vector identity

$$[k \times j_k] \cdot [k \times j_{-k}] = k^2 (j_k j_{-k}) - (k j_k)(k j_{-k}).$$

We note that the operator (kj_k) can be expressed in terms of the time derivative of ρ_k (18.11b). To do this we calculate the commutator of ρ_k with the kinetic energy operator T:

$$T = \sum_{k,\sigma} \frac{\hbar^2 k^2}{2m} a^+_{k\sigma} a_{k\sigma},$$

$$[\rho_k, T] = \frac{e\hbar^2}{\sqrt{V}} \sum_{q,\sigma} \frac{k}{m}\left(q - \frac{k}{2}\right) a^+_{q-k,\sigma} a_{q\sigma} = \hbar(kj_k).$$

Consequently, as ρ_k commutes with the interaction operator

$$H_{\text{int}} = \frac{1}{2V} \sum_{\substack{k,k_1,k_2\\ \sigma,\sigma_1}} v(k)\, a^+_{k_2\sigma} a^+_{k_1\sigma_1} a_{k_1+k,\sigma_1} a_{k_2-k,\sigma}, \tag{18.14}$$

the equation of motion for ρ_k has the form

$$\dot{\rho}_k = \frac{1}{i\hbar}[\rho_k, H] = -i(kj_k). \tag{18.15}$$

Calculating the commutator of $\dot{\rho}_k$ (18.15) and ρ_{-k}, we obtain the important commutation relation

$$\frac{1}{i\hbar}[\rho_k, \dot{\rho}_{-k}] = \frac{Ne^2}{Vm} k^2, \qquad N = \sum_{q,\sigma} a^+_{q\sigma} a_{q\sigma}, \tag{18.16}$$

which is called the longitudinal sum rule.

For the induced charge (18.12) we obtain using (18.13) and (18.15)

$$\rho(k, \omega) = \frac{1}{k^2} \langle\langle \rho_k | \dot{\rho}_{-k} \rangle\rangle_\omega \frac{i}{c} (kA(k, \omega)) + \langle\langle \rho_k | \rho_{-k} \rangle\rangle_\omega \varphi(k, \omega). \tag{18.17}$$

We express the function $\langle\langle\rho_k|\dot{\rho}_{-k}\rangle\rangle_\omega$ in terms of $\langle\langle\rho_k|\rho_{-k}\rangle\rangle_\omega$ by means of an integration by parts:

$$\langle\langle\rho_k\,|\,\dot{\rho}_{-k}\rangle\rangle_\omega = \int\limits_{-\infty}^{\infty}\langle\langle\rho_k(t)\,\dot{\rho}_{-k}\rangle\rangle e^{i\omega t}\,dt =$$

$$= \frac{1}{i\hbar}\langle[\rho_k,\ \rho_{-k}]\rangle_\omega + i\omega\langle\langle\rho_k\,|\,\rho_{-k}\rangle\rangle_\omega = i\omega\langle\langle\rho_k\,|\,\rho_{-k}\rangle\rangle_\omega, \qquad (18.18)$$

because the operators ρ_k and ρ_{-k} commute. The term with the commutator in (18.18) appears when the discontinuous function $\theta(t)$ is differentiated. Making use of (18.18) we rewrite the expression (18.17) for the induced charge in the form

$$\rho(k,\ \omega) = \frac{1}{k^2}\langle\langle\rho_k\,|\,\rho_{-k}\rangle\rangle_\omega\, i\boldsymbol{k}\cdot\boldsymbol{D}(k,\ \omega), \qquad (18.19)$$

where

$$i\boldsymbol{k}\cdot\boldsymbol{D}(k,\ \omega) = \frac{1}{c}\,i\omega\,(i\boldsymbol{k}\cdot\boldsymbol{A}(k,\ \omega) + k^2\varphi(\boldsymbol{k},\ \omega)) \qquad (18.19a)$$

which, in accordance with (18.5), has the meaning of the Fourier transform of the divergence of the electric displacement vector. Thus, we have expressed the induced charge through the longitudinal part of the electric displacement vector.

The induced charge is usually expressed through the divergence of the polarization vector P(x,t) according to the relationship

$$\underset{\text{a.}}{\rho_{\text{инд}}}(\boldsymbol{x},\ t) = -\operatorname{div}\boldsymbol{P}(\boldsymbol{x},\ t) = -\frac{1}{4\pi}\operatorname{div}(\boldsymbol{D}(\boldsymbol{x},\ t) - \boldsymbol{E}(\boldsymbol{x},\ t)), \qquad (18.20)$$

Key: a. ind(uced)

or in Fourier components

$$\rho(k,\ \omega) = \frac{1}{4\pi}\,i\boldsymbol{k}\cdot(\boldsymbol{E}(\boldsymbol{k},\ \omega) - \boldsymbol{D}(k,\ \omega)) = \frac{1}{4\pi}\left(\frac{1}{\varepsilon(k,\ \omega)} - 1\right)i\boldsymbol{k}\cdot\boldsymbol{D}(k,\ \omega), \qquad (18.20a)$$

where

$$\boldsymbol{k}\cdot\boldsymbol{D}(k,\ \omega) = \varepsilon(k,\ \omega)\,\boldsymbol{k}\cdot\boldsymbol{E}(k,\ \omega), \qquad (18.20b)$$

and $\varepsilon(\mathbf{k},\omega)$ is the dielectric permittivity, which defines the relation between the longitudinal components of the electric field and the displacement.

We note that it does not follow from (18.20b) that $D(\mathbf{k},\omega)=\varepsilon(\mathbf{k},\omega)E(\mathbf{k},\omega)$, because the induced charges shield only the longitudinal part of the electric field.

Comparing (18.19) with (18.20a), we obtain an expression for the <u>dielectric permittivity</u>, which depends on $\mathbf{k}$ and ω through the Green function:

$$\varepsilon^{-1}(k,\omega)=1+\frac{4\pi}{k^2}\langle\langle\rho_k|\rho_{-k}\rangle\rangle_\omega. \tag{18.21}$$

Let us now consider the expression for the induced current, i.e., the first of the equations (18.12), and write it using (18.13) and (18.13a) in the form

$$\begin{aligned}\boldsymbol{J}(k,\omega)={}&-\frac{e^2n}{mc}\boldsymbol{A}(k,\omega)-\langle\langle\dot{\rho}_k|\dot{\rho}_{-k}\rangle\rangle_\omega\frac{\boldsymbol{k}}{ck^4}\boldsymbol{k}\cdot\boldsymbol{A}(\boldsymbol{k},\omega)+\\&+\langle\langle\dot{\rho}_k|\rho_{-k}\rangle\rangle_\omega\frac{i\boldsymbol{k}}{k^2}\varphi(k,\omega)-\\&\qquad-\chi^{\mathrm{tr}}(k,\omega)\frac{1}{ck^2}\{k^2\cdot\boldsymbol{A}(k,\omega)-\boldsymbol{k}(\boldsymbol{k}\cdot\boldsymbol{A}(\boldsymbol{k},\omega))\},\end{aligned} \tag{18.22}$$

because in accordance with (18.13a) and (18.15) the longitudinal part of the susceptibility tensor (18.13) is equal to

$$\chi^{l}(k,\omega)=\frac{1}{k^2}\langle\langle\dot{\rho}_k|\dot{\rho}_{-k}\rangle\rangle_\omega. \tag{18.23}$$

We express the Green functions $\langle\langle\dot{\rho}_k|\dot{\rho}_{-k}\rangle\rangle_\omega$ and $\langle\langle\dot{\rho}_k|\rho_{-k}\rangle\rangle_\omega$ in terms of $\langle\langle\rho_k|\rho_{-k}\rangle\rangle_\omega$, by integrating them by parts. We obtain

$$\begin{aligned}\langle\langle\dot{\rho}_k|\rho_{-k}\rangle\rangle_\omega&=-i\omega\langle\langle\rho_k|\rho_{-k}\rangle\rangle_\omega,\\\langle\langle\dot{\rho}_k|\dot{\rho}_{-k}\rangle\rangle_\omega&=-\frac{1}{i\hbar}[\rho_k,\dot{\rho}_{-k}]+\omega^2\langle\langle\rho_k|\rho_{-k}\rangle\rangle_\omega=\\&=-\frac{ne^2}{m}k^2+\omega^2\langle\langle\rho_k|\rho_{-k}\rangle\rangle_\omega.\end{aligned} \tag{18.23a}$$

where use has been made of the longitudinal sum rule (18.16). The expression (18.22) for the induced current can be written, using (18.23) and (18.19a), in the form

$$J(k,\omega)=\langle\langle\rho_k|\rho_{-k}\rangle\rangle_\omega \frac{i\omega}{k^2}\frac{k}{k^2}\,k\cdot D(k,\omega)-$$
$$-\left(\chi^{tr}(k,\omega)+\frac{e^2n}{m}\right)\frac{1}{ck^2}\left(k^2A(k,\omega)-kk\cdot A(k,\omega)\right), \tag{18.24}$$

where the longitudinal and transverse parts of the current have been separated. The transverse part of the current can be identified with the curl of the induced magnetic moment vector M(x,t), i.e.,

$$-\frac{1}{k^2c}\left(\chi^{tr}(k,\omega)+\frac{e^2n}{m}\right)[ik\times B(k,\omega)]=c\,[ik\times M(k,\omega)]=$$
$$=\frac{c}{4\pi}[ik\times(B(k,\omega)-H(k,\omega))]=\frac{c}{4\pi}(1-\mu^{-1}(k,\omega))[ik\times B(k,$$

where $$B(k,\omega)=[ik\times A(k,\omega)] \tag{18.25}$$

is the Fourier transform of the magnetic field (18.5a), and

$$\mu^{-1}(k,\omega)=1+\frac{4\pi}{c^2k^2}\left(\chi^{tr}(k,\omega)+\frac{e^2n}{m}\right) \tag{18.26}$$

is the <u>magnetic permeability</u>, which depends on k and ω.

Using (18.21) and (18.26) the expression (18.24) for the current can be written in the form

$$J(k,\omega)=-\frac{1}{4\pi}(1-\varepsilon^{-1}(k,\omega))\,i\omega\frac{k}{k^2}(k\cdot D(k,\omega))+$$
$$+\frac{c}{4\pi}(1-\mu^{-1}(k,\omega))[ik\times B(k,\omega)]. \tag{18.27}$$

The current (18.27) can also be expressed through the electric field vector E(k,ω), by making use of the Maxwell equation

$$\operatorname{rot} \boldsymbol{E}(\boldsymbol{x}, t) = -\frac{1}{c}\frac{\partial \boldsymbol{B}(\boldsymbol{x}, t)}{\partial t}$$

in Fourier components

$$[i\boldsymbol{k} \times \boldsymbol{E}(\boldsymbol{k}, \omega)] = \frac{i\omega}{c} \boldsymbol{B}(\boldsymbol{k}, \omega) \qquad (18.28)$$

and eliminating B(k,ω) from (18.27). Then we obtain

$$\begin{aligned} \boldsymbol{J}(\boldsymbol{k}, \omega) &= \\ &= \sigma^{l}(k, \omega)\frac{\boldsymbol{k}}{k^2}(\boldsymbol{k} \cdot \boldsymbol{E}(k, \omega)) - \sigma^{tr}(k, \omega)\frac{1}{k^2}[\boldsymbol{k} \times [k \times \boldsymbol{E}(k, \omega)]], \end{aligned} \qquad (18.29)$$

where

$$\begin{aligned} \sigma^{l}(k, \omega) &= \frac{i\omega}{4\pi}(1 - \varepsilon(k, \omega)), \\ \sigma^{tr}(k, \omega) &= \frac{c^2k^2}{4\pi i\omega}(1 - \mu^{-1}(k, \omega)) \end{aligned} \qquad (18.29\text{a})$$

are the <u>longitudinal</u> <u>and</u> <u>transverse</u> <u>electrical</u> <u>conductivities</u>.

Earlier we considered the equation (18.12) for the induced current and charge. We shall show that it is sufficient to consider the first of them, and the second follows from it by using the commutation relations between charge and current.

We take the scalar product of the first of equations (18.12) with k. Making use of (18.15), we obtain

$$\begin{aligned} \boldsymbol{k} \cdot \boldsymbol{J}(k, \omega) &= \\ &= -\frac{e^2n}{mc}\boldsymbol{k} \cdot A(k, \omega) - \langle\langle \dot{\rho}_k | j_{-k} \rangle\rangle_\omega \cdot \frac{i}{c} A(k, \omega) + \langle\langle \dot{\rho}_k | \rho_{-\boldsymbol{k}} \rangle\rangle_\omega i\varphi(\boldsymbol{k}, \omega). \end{aligned} \qquad (18.30)$$

By means of an integration by parts we find

$$\langle\langle \dot{\rho}_k | j_{-k} \rangle\rangle_\omega = -\frac{1}{i\hbar}\langle[\rho_k, j_{-k}]\rangle - i\omega\langle\langle \rho_k | j_{-k} \rangle\rangle_\omega. \qquad (18.31)$$

By making use of (18.23) and (18.31) we write (18.30) in the form of a conservation law

$$k \cdot J(k, \omega) = \omega \rho(k, \omega), \tag{18.30a}$$

where use has been made of the commutation relation between Fourier components of charge and current,

$$\frac{1}{\hbar}[\rho_k, j_{-k}] = \frac{e^2}{m}\frac{N}{V}k, \quad N = \sum_{q\sigma} a^+_{q\sigma}a_{q\sigma}. \tag{18.32}$$

$$\frac{1}{\hbar}[\rho_k, j_{-k}] = \frac{e^2}{m}\frac{1}{V}\sum_{q,\sigma}\left(q - \frac{k}{2}\right)(n_{q\sigma} - n_{q+k,\sigma}),$$

which with a change of summation variables in the term with $n_{q+k,\sigma}$ leads to (18.32).

Thus, we have verified that the average values of current and charge exactly satisfy the conservation law (18.30a); therefore, in calculating the average current, we simultaneously find also the induced charge.

The converse is not true. The equation for the current does not follow from the equation for the charge, because the current can have a transverse rotational part, but the law of conservation of charge defines only its longitudinal part.

We shall obtain an equation for the curl of the current in the Fourier representation. Taking the vector product of the first of equations (18.12) with **k**, we obtain

$$\begin{aligned}[\boldsymbol{k} \times \boldsymbol{J}(\boldsymbol{k}, \omega)] &= -\frac{1}{c}\left(\frac{e^2 n}{m} + \chi^{\text{tr}}(k, \omega)\right)[\boldsymbol{k} \times \boldsymbol{A}(\boldsymbol{k}, \omega)] = \\ &= \frac{i}{c}\left(\frac{e^2 n}{m} + \chi^{\text{tr}}(k, \omega)\right)B(\boldsymbol{k}, \omega).\end{aligned} \tag{18.33}$$

In accordance with (18.26) the coefficient on the right hand side of this equation is expressed through the magnetic permeability.

In ordinary systems the term $\chi^{tr}(k,\omega)$ almost compensates for the term e^2n/m as $\omega\to 0, k\to 0$, and their sum gives only a very small diamagnetic effect (Landau diamagnetism [42,114]). This compensation is violated only in superconducting systems, because of the existence of a gap in the spectrum of elementary excitations [115,116].

Let us consider what the formulas for the dielectric permittivity (18.21) and the longitudinal susceptibility (18.23) yield in the limiting case of a spatially homogeneous medium, i.e., for $\mathbf{k}\to 0$. In this case it is necessary to make explicit the uncertainty in the formulas. To within an accuracy of terms linear in $\mathbf{k}$ we have

$$\rho_k = \frac{1}{\sqrt{V}} \int \rho(x)\, e^{-i(kx)}\, dx \simeq \frac{1}{\sqrt{V}} \int \rho(x)\, dx - \frac{ik}{\sqrt{V}} \int x\rho(x)\, dx,$$

i.e.,

$$\rho_k \cong \frac{eN}{\sqrt{V}} - \frac{ik}{\sqrt{V}} P_d \tag{18.34}$$

where

$$P_d = \int x\rho(x)\, dx \tag{18.34a}$$

is the total dipole moment operator. Consequently, as $\mathbf{k}\to 0$ the formula (18.21) takes on the form

$$\varepsilon^{-1}(0,\omega) = 1 + \frac{4\pi}{3V} \langle\langle P_d \cdot | P_d \rangle\rangle_\omega, \tag{18.35}$$

where use has been made of the assumed isotropy of the medium. The dot denotes the scalar product.

From formula (18.23) we obtain as $\mathbf{k}\to 0$

$$\chi^{l}(0,\omega) = \frac{1}{3} \langle\langle \dot{P}_d \cdot | P_d \rangle\rangle_\omega . \tag{18.36}$$

18.2. Symmetry Properties, Dispersion Relations.

The susceptibility tensor (18.13), and also the dielectric permittivity (18.21) and the magnetic permeability (18.26), have the symmetry property (17.9), (17.25):

$$\chi_{\alpha\beta}(k, \omega) = \chi^*_{\alpha\beta}(-k, -\omega),$$
$$\varepsilon(k, \omega) = \varepsilon^*(-k, -\omega),$$
$$\mu(k, \omega) = \mu^*(-k, -\omega), \tag{18.37}$$

as do all generalized susceptibilities and kinetic coefficients. This follows from the reality of $\chi_{\alpha\beta}(x-x', t-t')$.

Taking into account, in addition, the symmetry of the Green functions with respect to an inversion of the spatial coordinates $x \leftrightarrow -x$, which is equivalent to the replacement $k \leftrightarrow -k$, we have

$$\langle\langle j^\alpha_k | j^\beta_{-k} \rangle\rangle_\omega = \langle\langle j^\alpha_{-k} | j^\beta_k \rangle\rangle_\omega, \quad \langle\langle \rho_k | \rho_{-k} \rangle\rangle_\omega = \langle\langle \rho_{-k} | \rho_k \rangle\rangle_\omega. \tag{18.38}$$

Consequently, the susceptibility tensor (18.13), and also the dielectric permittivity (18.21) and the magnetic permeability (18.26), possess the symmetry properties:

$$\chi_{\alpha\beta}(k, \omega) = \chi^*_{\alpha\beta}(k, -\omega) = \chi_{\alpha\beta}(-k, \omega),$$
$$\varepsilon(k, \omega) = \varepsilon^*(k, -\omega) = \varepsilon(-k, \omega),$$
$$\mu(k, \omega) = \mu^*(k, -\omega) = \mu(-k, \omega). \tag{18.37a}$$

Thus, the real parts of $\chi_{\alpha\beta}(k,\omega)$, $\varepsilon(k,\omega)$, and $\mu(k,\omega)$ are symmetric with respect to the replacement $\omega \leftrightarrow -\omega$, and the imaginary parts are antisymmetric:

$$\mathrm{Re}\,\chi_{\alpha\beta}(k, \omega) = \mathrm{Re}\,\chi_{\alpha\beta}(k, -\omega),$$
$$\mathrm{Re}\,\varepsilon(k, \omega) = \mathrm{Re}\,\varepsilon(k, -\omega),$$
$$\mathrm{Re}\,\mu(k, \omega) = \mathrm{Re}\,\mu(k, -\omega),$$
$$\mathrm{Im}\,\chi_{\alpha\beta}(k, \omega) = -\mathrm{Im}\,\chi_{\alpha\beta}(k, -\omega),$$
$$\mathrm{Im}\,\varepsilon(k, \omega) = -\mathrm{Im}\,\varepsilon(k, -\omega),$$
$$\mathrm{Im}\,\mu(k, \omega) = -\mathrm{Im}\,\mu(k, -\omega). \tag{18.39}$$

Using (18.39) we obtain from (16.34) the Kramers-Kronig dispersion relations[1] for the susceptibility $\chi_{\alpha\beta}(\mathbf{k},\omega)$:

$$\operatorname{Re}\chi_{\alpha\beta}(\boldsymbol{k},\omega)-\frac{e^2 n}{m}\delta_{\alpha\beta}=\frac{2}{\pi}\mathcal{P}\int_0^\infty\frac{u}{u^2-\omega^2}\operatorname{Im}\chi_{\alpha\beta}(\boldsymbol{k},u)\,du, \tag{18.40}$$

$$\operatorname{Im}\chi_{\alpha\beta}(\boldsymbol{k},\omega)=-\frac{2\omega}{\pi}\mathcal{P}\int_0^\infty\frac{\operatorname{Re}\chi_{\alpha\beta}(\boldsymbol{k},u)-\frac{e^2 n}{m}\delta_{\alpha\beta}}{u^2-\omega^2}\,du.$$

18.3. <u>System of Particles with Spin in an Electromagnetic Field.</u>

We shall consider the action of an electromagnetic field on a system of particles with spin and calculate the average current and magnetic moment, which is associated with the spin of the particles.

The interaction of the spins of the particles with the magnetic field H(x,t) is defined by the operator

$$H'=-\int \boldsymbol{M}(x)\cdot\boldsymbol{H}(\boldsymbol{x},t)\,dx, \tag{18.41}$$

where

$$\boldsymbol{M}(x)=\sum_s\psi^+(x,s)\frac{e\hbar}{2mc}\sigma\psi(\boldsymbol{x},s) \tag{18.41a}$$

is the magnetic moment density operator, and σ_x, σ_y, σ_z are the Pauli matrices. We shall assume that the spin of the particles is equal to 1/2.

The perturbation operator (18.41) can be written in the form

$$H'=\int \boldsymbol{M}(\boldsymbol{x})\cdot\operatorname{rot}\boldsymbol{A}(\boldsymbol{x},t)\,dx=-\frac{1}{c}\int j_m(\boldsymbol{x})\cdot\boldsymbol{A}(x,t)\,dx, \tag{18.42}$$

where

$$j_m(\boldsymbol{x})=c\operatorname{rot}\boldsymbol{M}(x) \tag{18.42a}$$

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[1] A generalization of the Kramers-Kronig formulas to the relativistic case was achieved by M. A. Leontovich [117,112].

is the current operator associated with the magnetic moment of the particles. Indeed, in agreement with the usual definition of current (18.6)

$$j_m(x) = -c\frac{\delta H'}{\delta A(x)}. \tag{18.43}$$

In accordance with (15.47) the perturbation (18.41) changes the magnetic moment

$$\langle M(x)\rangle = \langle M(x)\rangle_0 + \int\int_{-\infty}^{t} \chi_m(xt, x't')\cdot H(x', t')\,dx'\,dt', \tag{18.44}$$

where

$$\chi_m(xt, x't') = -\langle\langle M(x, t)\,M(x', t')\rangle\rangle \tag{18.44a}$$

is the magnetic susceptibility tensor associated with the spin.

The relationship (18.44) has an especially simple form in the Fourier representation. Putting

$$\begin{aligned} \langle M(x)\rangle &= \langle M(x)\rangle_0 + \frac{1}{V}\sum_k \int_{-\infty}^{\infty} M(k, \omega)\,e^{i(kx)-i\omega t}\,d\omega, \\ M(x, t) &= \frac{1}{\sqrt{V}}\sum_k M_k(t)\,e^{i(kx)} \end{aligned} \tag{18.45}$$

and making use of the spatial homogeneity of the system, we obtain

$$M(k, \omega) = \chi_m(k, \omega)\cdot H(k, \omega), \tag{18.46}$$

where

$$\chi_m(k, \omega) = -\langle\langle M_k \mid M_{-k}\rangle\rangle_\omega \tag{18.46a}$$

is the magnetic susceptibility tensor of the spin system in the Fourier representation.

For the case of a spatially constant magnetic field formulas (18.46) and

(18.46a) go over into (15.82) and (15.83), which were considered earlier. The tensor $\chi_m(k,\omega)$ satisfies the symmetry conditions and dispersion relations, analogous to (18.39) and (18.40).

18.4. System of Particles with a Dipole Moment.

Another case, which is of interest for the theory of dielectrics, is a system of interacting particles with dipole moments.

We shall calculate the polarization of such a system, induced by an electric field. The interaction of the dipole moments of the particles with the electric field is described by the operator

$$H' = -\int P(x)\cdot E(x, t)\,dx, \tag{18.47}$$

where P(x) is the operator (or dynamical variable) of the dipole moment density. The perturbation (18.47) induces a dipole moment with density

$$\langle P(x)\rangle = \langle P(x)\rangle_0 + \int\int_{-\infty}^{t} \alpha(x - x', t - t')\,E(x', t')\,dx'\,dt', \tag{18.48}$$

where

$$\alpha(x - x', t - t') = -\langle\langle P(x, t), P(x', t')\rangle\rangle \tag{18.48a}$$

is the dielectric polarizability tensor of a system of electric dipoles, and $\langle P(x)\rangle_0$ is the dipole moment density in the equilibrium state as $E\to 0$, which may be non-zero for ferrodielectrics. Going over in (18.48) to a Fourier representation of the type (18.45) and making use of the spatial homogeneity of the system, we obtain

$$P(k, \omega) = \alpha(k, \omega)\cdot E(k, \omega), \tag{18.49}$$

where

$$\alpha(k, \omega) = -\langle\langle P_k \,|\, P_{-k}\rangle\rangle_\omega$$

is the dielectric polarizability tensor of the system as a function of k,ω.

For a system in a uniform electric field or for sufficiently long wave lengths, when the change in the field in a correlation length can be neglected,

the connection between the induced moment and the field is local,

$$P(\omega) = \alpha(\omega) \cdot E(\omega), \tag{18.50}$$

$$\alpha(\omega) = -\langle\langle P \mid P \rangle\rangle_{\omega}, \tag{18.50a}$$

where

$$P = \int P(x)\, dx$$

is the total electric dipole moment. Expanding formula (18.50a) in terms of the matrix elements of the polarization operator P_i, we obtain

$$\operatorname{Re} \alpha_{xx}(\omega) = Q^{-1} \sum_{k,\, n} e^{-\beta E_k} \frac{2\omega_{nk}}{\omega_{nk}^2 - \omega^2} \left| P_x^{kn} \right|^2, \tag{18.51}$$

$$\operatorname{Im} \alpha_{xx}(\omega) = Q^{-1} \sum_{k,\, n} e^{-\beta E_k} \frac{1}{2} \left| P_x^{kn} \right| \left(\delta(\omega_{nk} - \omega) - \delta(\omega_{nk} + \omega)\right),$$

where

$$P_x^{kn} = (C_k^* P_x C_n), \qquad \omega_{nk} = (E_n - E_k)/\hbar,$$

and C_k and E_k are the wave function and energy of the state k, respectively.

Thus, we have obtained the Kramers-Heisenberg formula [100,106,107] by means of statistical averaging.

CHAPTER IV

NONEQUILIBRIUM STATISTICAL OPERATOR

In Chapter III nonequilibrium processes, which could be represented as the reaction of the system to external mechanical perturbations, were studied. There exist, however, irreversible processes, which arise from thermal perturbations, i.e., which are caused by internal inhomogeneities in the system, as for example, diffusion, thermal conductivity, and viscosity. Sometimes one attempts to express them in terms of mechanical perturbations. Such an approach has the disadvantage that it assumes prior knowledge of the equations of nonequilibrium thermodynamics and makes use of the analogy with mechanical perturbations. In addition, the separation of perturbations into mechanical and thermal is in general justified only in the linear approximation. In higher approximations mechanical perturbations create inhomogeneities in the distributions of mass, energy, and momentum, and therefore, lead to the appearance of thermal perturbations.

In order to develop the statistical thermodynamics of nonequilibrium processes, which would also include thermal perturbations, it is, strictly speaking, necessary to construct statistical ensembles which represent the macroscopic conditions in which the systems are found. This turns out to be possible if one is interested in the behavior of the system for time scales which are not too small, when the details of the initial state of the system have already become inessential and the number of parameters necessary to describe the state has been reduced. The idea of abbreviating the description of the system belongs to N. N. Bogolyubov and was used by him to construct kinetic equations on the basis of the Liouville equation [1].

In this chapter we shall formulate the statistical theory of irreversible processes by the method of statistical ensembles for nonequilibrium systems [2-5,184-190], generalizing the usual method of Gibbs ensembles, which was presented in Chapters I and II. This possibility of transferring the ideas of Gibbs to nonequilibrium statistical mechanics was first mentioned by Callen and Welton [6] in connection with the fluctuation-dissipation theorem.

In studying irreversible processes caused by mechanical perturbations all authors use the same method - the dynamical treatment of the perturbations with the condition of statistical equilibrium at some initial time (usually at $t=-\infty$). Many different methods have been proposed to study thermal perturbations. Following Zwanzig [7], these methods can be divided into the following groups.

1. Indirect methods of the theory of the linear reaction, based on representing the effect of thermal perturbations in terms of mechanical perturbations, because the same transfer processes might be caused both by external fields and by inhomogeneities in the system (Montroll [8], Luttinger [9], Kadanoff and

Martin [10], Jackson and Mazur [11], Felderhof and Oppenheim [12]). The usual procedure is first to calculate the susceptibility from a fictitious external perturbation, which could cause the given nonequilibrium state. The susceptibility is used to calculate kinetic coefficients using the fluctuation-dissipation theorem and a limiting transition to zero wave number and zero frequency of the perturbation. In these methods the validity of macroscopic equations, for example, the Navier-Stokes equation, is assumed beforehand.

2. Methods which use the theory of stochastic processes and the Fokker-Planck equation. These methods, which were used first in the theory of Brownian motion, were developed mainly by Kirkwood [13] and M. Green [14] with the assumption that the processes were Markov processes. The first significant results in the general theory of irreversible processes, namely the connection between the kinetic coefficients and the time correlation functions, were obtained by Kirkwood and M. Green with just this approach. The method of stochastic processes has been further developed by various authors [15-21]. It has recently been improved by Mori and Kubo by taking into account retardation in the Langevin equation [22-24].

This group also includes the work of Helfand [25], where the Einstein relation for the mean square deviation of a Brownian particle in a time t, $<R^2>=6Dt$ (D is the diffusion coefficient), is generalized and applied to expressing the kinetic coefficients in terms of the correlation functions.

3. Methods based on a hypothesis about the character of the damping out or regression of fluctuations. This approach was first used in the classic articles of Onsager [26], who expressed the hypothesis that the damping out of fluctuations is governed by the same law as is the change of the corresponding macroscopic variables[1]. Taking into account in addition the reversibility of the microscopic equations of motion, he established his reciprocity relations for the kinetic coefficients (see section 17.3). Kubo, Yokota, and Nakajima [28] made use of this method to construct a theory of thermal perturbations in irreversible processes. It was later used also by Felderhof and Oppenheim [12], who took into account the spatial and temporal dispersion of the kinetic coefficients.

4. Methods based on the use of local equilibrium distributions as the initial condition for the Liouville equation. In this method it is assumed that in weakly nonequilibrium states a distribution which is similar in form to the Gibbs distribution is established in small volumes, but the parameters of the distribution depend on the point in space (local equilibrium distribution), and corrections to this distribution are sought. This approach was developed mainly by Mori [29-31]. H. Green [32] obtained expressions for the kinetic coefficients by making use of a local Maxwell distribution as the initial condition for the Liouville equation, using the method of Chapman and

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[1] For a discussion of the Onsager hypothesis on the damping out of fluctuations and on the limits of its applicability see the monograph by deGroot and Mazur [27], Chapter IV, and the literature cited therein.

Enskog for its solution. The connection between the correlation formulas for the kinetic coefficients and the Chapman-Enskog method has been analyzed by Ernst [33]. M. I. Klinger [34] applied the method of Mori to the theory of transport phenomena in semiconductors, and B. N. Provotorov [35] applied it to spin systems. S. V. Peletminskiy and A. A. Yatsenko [36] developed it further and extended its region of applicability to smaller time scales, so that it has become applicable also for constructing kinetic equations for strongly non-equilibrium states.

5. The methods of Gibbs statistical ensembles for nonequilibrium systems, which have been developed in two different variants: the method of the nonequilibrium statistical operator, proposed by the author [2-5], and based on the construction of local integrals of motion, and the method of McLennan [37-40], which is based on taking into account the influence of the thermostat through forces which are not derivable from a potential. Both methods [2-5] and [37-40] were developed independently and lead essentially to identical results, but the method [2-5] is evidently simpler for applications. The method of the nonequilibrium statistical operator will be discussed in the present chapter on the basis of [2-5,184-190], and the connection between this method and the method of McLennan is discussed in Appendices II and III.

The method [2-5] has been applied by many authors [41-57] to the various problems of the theory of irreversible processes. This method is especially simple for constructing hydrodynamic equations, for example, taking into account internal degrees of freedom (the author [4], L. A. Pokrovskiy [41]), relativistic hydrodynamics [5], and equations of the Grad type (T. M. Khazanovich and V. A. Savchenko [42]). L. L. Buishvili and the author [43], L. L. Buishvili [44], and G. R. Khutsishvili [45] have applied this method to the theory of nuclear spin diffusion; L. L. Buishvili, N. S. Bendiashvili, N. P. Giorgadze, M. D. Zviadadze, and G. R. Khutsishvili [46-50] have applied it to the theory of nuclear magnetic resonance and dynamic polarization of nuclei in solids. T. N. Khazanovich has applied it to the relaxation of nuclear magnetism in liquids [183]; L. L. Buishvili, M. D. Zviadadze [51], and V. G. Grachev [52] have applied it to the theory of spin-lattice relaxation of impurity centers. V. P. Kalashnikov has applied this method to the theory of spin-lattice relaxation of conduction electrons [53] and to the theory of hot electrons in semiconductors [54], where it turns out to be applicable not only for linear dissipative processes, but also in the case of strong nonlinearity in the electric field. The method gives the correct result for the rate of exchange of energy between subsystems with a small interaction between them for a state which is highly nonlinear in terms of the thermodynamic forces, as was demonstrated by L. A. Pokrovskiy [55]. He also showed [56] that the method can be applied to obtain generalized kinetic equations, which are the same as those in the article by Peletminskiy and Yatsenko [36], for a corresponding choice of parameters to describe the state of the system. Using the same method one can construct not only the usual kinetic equations, but also equations of the Fokker-Planck type, as was shown by A. G. Bashkirov and the author [57,190]. (Applications of the method can be seen also in [191-215].)

The classification presented of the methods of study of thermal perturbations is not completely rigorous, because in many works the indirect method of the theory of linear reactions is combined with the Onsager hypothesis [12] or with the use of the local equilibrium distribution as an initial condition [10].

For the different methods used to investigate thermal perturbations see the reviews of Chester [58], Zwanzig [7], Ernst and others [216], and the monograph by Rice and Gray [59], where an extensive bibliography is presented. All these methods lead to identical results for the kinetic coefficients, but each has its own region of applicability. Some authors have expressed, however, doubt in the validity of the expressions for the kinetic coefficients in terms of the correlation functions [60,61], but these doubts have turned out to be unjustified [62], and the doubts were removed by the same authors [63,64].

Nonequilibrium corrections to the equilibrium distribution function are calculated in the majority of the enumerated works, except [2-5,37,38]. The basic question which will interest us in what follows is how to construct the total statistical operator (or, in the classical case, the distribution function) for nonequilibrium processes, proceeding from general principles, i.e., how to generalize the ideas of Gibbs statistical ensembles for the nonequilibrium case. In the article [2] a nonequilibrium statistical operator was constructed for stationary processes by means of a generalization of the class of integrals of motion on which the operator can depend; their meaning will be explained in § 21. McLennan [37,38] obtained a nonequilibrium statistical operator for nonstationary processes by another method, considering the effect of the thermostat by means of forces which are not derivable from a potential. The method of local integrals of motion [5] leads to exactly the same distribution as the method of McLennan [37,38].

In order to construct local integrals of motion it is necessary to formulate conservation laws for mechanical quantities in operator form (or in the form of relations for the dynamical variables) and to find expressions for the corresponding densities and currents of mechanical quantities. This problem is considered in § 19 for various systems.

§ 19. Conservation Laws

Conservation laws play a fundamental role in all of theoretical physics. The phenomenological thermodynamics of irreversible processes is based on conservation laws for the average values of physical quantities, for example particle number, energy, and momentum [27]. The statistical thermodynamics of nonequilibrium processes, which will be presented below, also proceeds from conservation laws, but not for the average values of dynamical quantities, but for the dynamical quantities themselves. Thus, conservation laws will be considered not from a macroscopic point of view, but from a microscopic point of view.

In this paragraph we discuss conservation laws for a system of identical particles with a direct interaction, and for a mixture of particles with internal degrees of freedom. The latter case is essentially quantum mechanical in nature. These examples allow us to obtain local conservation laws for energy, momentum, and particle number in a form sufficiently general to serve in what follows as the basis for constructing the statistical thermodynamics of nonequilibrium processes.

19.1. Local Conservation Laws in Classical Mechanics.

Let us consider the conservation laws for energy, momentum, and particle number in local form for the case of classical mechanics. The quantum case will be considered later.

Let a system of identical interacting particles be described by the Hamiltonian (1.2)

$$H = \sum_i \left(\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi(|x_i - x_j|) \right), \tag{19.1}$$

where $\phi(|x_i - x_j|)$ is the potential energy of interaction between particles, and m is the mass of a particle. Hamilton's equations (1.1), describing the motion of the particles, have the form

$$\dot{x}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{m}, \qquad \dot{p}_i = -\frac{\partial H}{\partial x_i} = \sum_{j \neq i} F_{ij}, \tag{19.2}$$

where

$$F_{ij} = -F_{ji} = -\frac{\partial \phi(|x_i - x_j|)}{\partial x_i} \tag{19.2a}$$

is the interaction force between particles i and j.

The role of a dynamical variable - the number density of the particles - is played by the function

$$n(x) = \sum_i \delta(x_i - x), \tag{19.3}$$

where the summation is carried out over all particles, because the integral of (19.3) over the volume is equal to the total number of particles, and the average of the integral over a small volume is equal to the average number of particles in this volume. The coordinates of the particles $\mathbf{x}_i$ in (19.3) change in time in accordance with the equations of motion (19.2); consequently, the time derivative of n(**x**) is equal to

$$\frac{\partial n(x)}{\partial t} = \sum_i \dot{\delta}(x_i(t) - x) = \sum_i \dot{x}_i \cdot \nabla_i \delta(x_i - x),$$

i.e.,

$$\frac{\partial n(x)}{\partial t} = -\operatorname{div} j(x), \tag{19.4}$$

where

$$j(x) = \sum_i \frac{p_i}{m} \delta(x_i - x) \tag{19.5}$$

is the particle number current density. Equation (19.4) is the law of conservation of particle number in local form.

As in any field theory, the densities of mechanical quantities and the densities of their currents are not uniquely defined: the densities are defined to within an accuracy of the divergence of an arbitrary vector, and the currents are defined to within an accuracy of the curl of an arbitrary vector. Indeed, in an integration over the volume the divergence parts contribute only surface integrals, and the divergence of the curl part is equal to zero. This non-uniqueness is related to the fact that quantities like the density are not observable. Only their integrals over a volume which is macroscopically small, but which contains a large number of particles, are observable; in this case the surface contribution can be neglected.

We shall now obtain the law of conservation of momentum in local form. It is natural to introduce the quantity

$$p(x) = mj(x) = \sum_i p_i \delta(x_i - x). \tag{19.6}$$

as a momentum density. The integral of (19.6) over the entire volume is equal to the total momentum **P**,

$$\int p(x)\,dx = \sum_i p_i = P, \tag{19.6a}$$

and the average value of (19.6) gives the momentum current density.

Differentiating (19.6) with respect to time, we obtain

$$\frac{\partial \boldsymbol{p}(\boldsymbol{x})}{\partial t} = -\nabla \cdot \sum_i \frac{1}{m} p_i p_i \delta(x_i - \boldsymbol{x}) + \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \boldsymbol{F}_{ij} (\delta(\boldsymbol{x}_i - \boldsymbol{x}) - \delta(\boldsymbol{x}_j - \boldsymbol{x})), \tag{19.7}$$

where $p_i p_i$ is a tensor; the expression in the second summation sign in (19.7) is symmetrized by using (19.2a).

Equation (19.7) still does not have the form of a local conservation law, because the second term on the right hand side is not in the form of a divergence. In order to transform it to such a form, we note that in what follows we shall be interested not in the dynamical variables themselves, but in integrals of the dynamical variables multiplied by functions which change little in a length of the order of the radius of the interaction force.

Let us consider the second term on the right hand side of (19.7)

$$B(x) = \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} F_{ij} (\delta(x_i - x) - \delta(x_j - x)) \tag{19.8}$$

and show how it can be represented in the form of the divergence of a tensor.

Let us multiply B(x) by an arbitrary vector function of position A(x), which changes little in a length of the order of the radius of the influence of the forces, and consider the integral of (19.8) over all space

$$\int A(x) \cdot \boldsymbol{B}(x)\, dx = \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} F_{ij} \cdot (A(x_i) - A(x_j)). \tag{19.9}$$

The force F_{ij} is significantly different from zero only for distances of the order of the radius of the influence of the forces, and the function A(x), by assumption, changes little in such distances; therefore the difference $A(x_i)-A(x_j)$ can be expanded in a Taylor series in $x_i-x_j=x_{ij}$ in which only the first term is kept:

$$\boldsymbol{A}(\boldsymbol{x}_i) - \boldsymbol{A}(\boldsymbol{x}_j) \cong \sum_{\beta} \frac{\partial \boldsymbol{A}}{\partial x_\beta} x_{ij}^{\beta}.$$

Consequently,

$$\int B(x)\cdot A(x)\,dx = \frac{1}{2}\sum_{i,j,\beta} F_{ij}\cdot\frac{\partial A(x_i)}{\partial x_i^\beta}x_{ij}^\beta = \frac{1}{2}\sum_{i,j,\beta}\int F_{ij}\cdot\frac{\partial A(x)}{\partial x^\beta}x_{ij}^\beta\,\delta(x_i-x)\,dx,$$

or, after an integration by parts,

$$\int B(x)\cdot A(x)\,dx = -\frac{1}{2}\sum_{i,j}\int A(x)\cdot\sum_\beta\frac{\partial}{\partial x_\beta}F_{ij}x_{ij}^\beta\,\delta(x_i-x)\,dx,$$

from which we obtain, on the basis of the arbitrariness of A(x),

$$B_\alpha(x) = -\sum_\beta\frac{\partial}{\partial x_\beta}\frac{1}{2}\sum_{i,j}F_{ij}^\alpha x_{ij}^\beta\,\delta(x_i-x). \tag{19.10}$$

Thus, the quantity (19.8) can be approximately represented in the form of the divergence of a tensor, and (19.7) can be written in the form of a local conservation law:

$$\frac{\partial\rho_\alpha(x)}{\partial t} = -\sum_\beta\frac{\partial T_{\beta\alpha}(x)}{\partial x_\beta}, \tag{19.11}$$

where

$$T_{\beta\alpha}(x) = \sum_i\left(\frac{1}{m}p_i^\alpha p_i^\beta + \frac{1}{2}\sum_{j\neq i}F_{ij}^\alpha x_{ij}^\beta\right)\delta(x_i-x) \tag{19.12}$$

is the symmetric stress tensor. Indeed, as the forces are centrally symmetric, then

$$F_{ij}^\alpha x_{ij}^\beta = -\frac{\partial\phi(|x_{ij}|)}{\partial|x_{ij}|}\cdot\frac{1}{|x_{ij}|}\cdot x_{ij}^\alpha x_{ij}^\beta$$

is a symmetric tensor.

We note that we would obtain the same result for $T_{\alpha\beta}(x)$, if in (19.8) the δ-functions were formally expanded in a Taylor series, keeping two terms of the expansion:

$$\delta(x_j - x) = \delta(x_i - x) + (x_j - x_i) \cdot \nabla_i \delta(x_i - x).$$

The arguments presented with the arbitrary, slowly varying function make precise the meaning of such an expansion of δ-functions. The process of representing equation (19.7) in the form of a divergence of a tensor can be continued further, and corrections of a higher order of smallness can be found for $T_{\beta\alpha}(x)$. The method described here is applicable also to the quantum case (see the following section of this paragraph)[1].

Let us now consider the law of conservation of energy in local form. It is natural to define the quantity

$$H(x) = \sum_i \left(\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi(|x_i - x_j|) \right) \delta(x_i - x) \tag{19.13}$$

as the dynamical variable of energy density. It is evident that

$$H = \int H(x)\, dx \tag{19.14}$$

is the Hamiltonian of the system. Differentiating (19.13) and taking into account the equations of motion (19.2), we obtain

$$\begin{aligned} \frac{\partial H(x)}{\partial t} = &- \nabla \cdot \sum_i \left(\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi(|x_i - x_j|) \right) \frac{p_i}{m} \delta(x_i - x) + \\ &+ \frac{1}{4} \sum_{\substack{i,\, j \\ (i \neq j)}} \frac{1}{m} (p_i + p_j) \cdot F_{ij} (\delta(x_i - x) - \delta(x_j - x)). \end{aligned} \tag{19.15}$$

Carrying out the same procedure of smoothing of operators as was used earlier in the derivation of equation (19.11), we obtain

$$\frac{\partial H(x)}{\partial t} = - \operatorname{div} j_H(x), \tag{19.16}$$

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[1] An exact representation in the form of a divergence is possible in (19.11) and (19.12), but with an auxiliary integration over the parameter in (19.12) [217,218,225].

where

$$\begin{aligned} j_H(x) = \sum_i \left(\frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi(|x_i - x_j|) \right) \frac{p_i}{m} \delta(x_i - x) + \\ + \frac{1}{4} \sum_{i,j} \frac{1}{m} (p_i + p_j) \cdot F_{ij} x_{ij} \delta(x_i - x) \qquad (x_{ij} = x_i - x_j) \end{aligned} \tag{19.17}$$

is the energy current density vector. It can be written in the same approximation in a different form:

$$j_H(x) = \sum_i \left(\frac{p_i p_i}{2m} + \frac{1}{2} \sum_{j \neq i} \phi(|x_i - x_j|) U + \frac{1}{2} \sum_{j \neq i} x_{ij} F_{ij} \right) \cdot \frac{p_i}{m} \delta(x_i - x), \tag{19.17a}$$

where the expression in the round brackets is a tensor, and U is the unit tensor.

And thus, the equations of the conservation of energy, particle number, and momentum in local form are

$$\begin{aligned} \frac{\partial H(x)}{\partial t} &= -\operatorname{div} j_H(x), \\ \frac{\partial n(x)}{\partial t} &= -\operatorname{div} j(x), \\ \frac{\partial p(x)}{\partial t} &= -\operatorname{Div} T(x), \end{aligned} \tag{19.18}$$

where the densities of the mechanical quantities are defined by the expressions: H(x)-(19.13), n(x)-(19.3), p(x) and j(x)-(19.6), j_H(x)-(19.17) and (19.17a), T(x)-(19.12).

We note that the Fourier components of the functions n(x), H(x), and p(x)

$$\begin{aligned} n_k &= \int n(x) e^{-i(kx)} dx, \\ H_k &= \int H(x) e^{-i(kx)} dx, \\ p_k &= \int p(x) e^{-i(kx)} dx \end{aligned} \tag{19.19}$$

represent collective variables. Indeed,

$$n_k = \sum_j e^{-i(kx_j)},$$

$$H_k = \sum_j \frac{p_j^2}{2m} e^{-i(kx_j)} + \frac{1}{2V} \sum_q \nu(q)(n_q n_{k-q} - n_k), \qquad (19.19a)$$

$$p_k = \sum_j p_j e^{-i(kx_j)} \qquad \left(\nu(q) = \int \phi(|x|) e^{-i(qx)} dx\right)$$

depend on the coordinates and momenta of all particles symmetrically.

Collective variables are convenient for the study of collective properties of many particle systems, especially systems with long ranged (for example Coulomb) interaction forces. These variables are used in the articles [65-68].

19.2. Local Conservation Laws in Quantum Mechanics.

Let us consider now the laws of conservation of energy, momentum, and particle number in local form for a quantum mechanical system of identical particles with a direct interaction between them.

In order to obtain a simple, local form for the conservation laws we carry out a smoothing of operators over inhomogeneities smaller than the radius of action of the forces between the particles, just as in the preceding section for classical dynamical variables. Conservation laws for other systems can also be obtained by a similar method.

A quantum mechanical system of identical particles of mass m with a direct interaction by means of the potential $\phi(x)$ is described by a Hamiltonian in the representation of second quantization

$$H = \int \psi^+(x) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + \frac{1}{2} \int \phi(x - x') \psi^+(x') \psi(x') dx' \right\} \psi(x) dx, \qquad (19.20)$$

where the operators $\psi(x)$ and $\psi^+(x')$, acting on a wave function in the occupation number representation, satisfy Fermi or Bose commutation relations:

$$\begin{aligned} \psi(x)\psi^+(x') \mp \psi^+(x')\psi(x) &= \delta(x - x'), \\ \psi(x)\psi(x') \mp \psi(x')\psi(x) &= 0, \\ \psi^+(x)\psi^+(x') \mp \psi^+(x')\psi^+(x) &= 0, \end{aligned} \qquad (19.20a)$$

where the plus sign corresponds to Fermi statistics, and the minus sign corresponds to Bose statistics. If the particles have spin, then in addition to the coordinates x one must take into account the spin variable, and then in (19.20) it is necessary to carry out a summation over the spin variables in addition to the integration over x.

It is convenient to write the Hamiltonian (19.20), using an integration by parts, in the form

$$H = \int H(x)\, dx, \tag{19.21}$$

where

$$H(x) = \frac{\hbar^2}{2m} \nabla\psi^+(x) \cdot \nabla\psi(x) + \\ + \frac{1}{2} \int \phi(x - x')\, \psi^+(x)\, \psi^+(x')\, \psi(x')\, \psi(x)\, dx' \tag{19.21a}$$

is the energy density operator, chosen to be hermitian.

The energy density operator (19.21a) is not completely defined by the condition (19.21), because the divergence of any vector can be added to H(x); for example, one can define

$$H(x) = -\frac{\hbar^2}{4m} \{\nabla^2\psi^+(x)\, \psi(x) + \psi^+(x)\, \nabla^2\psi(x)\} + H_{\text{int}}(x) = \\ = \frac{\hbar^2}{2m} \left\{\nabla\psi^+(x) \cdot \nabla\psi(x) - \frac{1}{2} \nabla^2 n(x)\right\} + H_{\text{int}}(x) \tag{19.21b}$$

or

$$H(x) = -\frac{\hbar^2}{8m} \{\nabla^2\psi^+(x)\, \psi(x) - 2\nabla\psi^+(x) \cdot \nabla\psi(x) + \psi^+(x)\, \nabla^2\psi(x)\} + \\ + H_{\text{int}}(x) = \frac{\hbar^2}{2m} \left\{\nabla\psi^+(x) \cdot \nabla\psi(x) - \frac{1}{4} \nabla^2 n(x)\right\} + H_{\text{int}}(x), \tag{19.21c}$$

where

$$n(x) = \psi^+(x)\, \psi(x) \tag{19.22}$$

is the number density operator, and

$$H_{\text{int}}(x) = \frac{1}{2} \int \phi(x - x')\, \psi^+(x)\, \psi^+(x')\, \psi(x')\, \psi(x)\, dx'$$

is the interaction energy density operator.

This ambiguity in defining densities of quantities exists in any field theory.

The definition (19.21a) is usually used in quantum field theory.

The operator $\psi(x)$ satisfies the equations of motion, which follow from (19.20) and (19.20a):

$$i\hbar \frac{\partial\psi(x)}{\partial t} = [\psi(x), H] = -\frac{\hbar^2}{2m}\nabla^2\psi(x) + \int \phi(x)\, n(x')\, \psi(x)\, dx', \tag{19.23}$$

where n(x) is the number density operator (19.22).

The operator n(x) satisfies a conservation law, which follows from the equations of motion for $\psi(x)$ and $\psi^+(x)$:

$$\frac{\partial n(x)}{\partial t} + \operatorname{div} j(x) = 0, \tag{19.24}$$

where

$$j(x) = \frac{\hbar}{2mi}\{\psi^+(x)\nabla\psi(x) - \nabla\psi^+(x)\psi(x)\} \tag{19.24a}$$

is the particle number current operator. Expression (19.24a) is the quantum analog of the classical particle current density (19.5).

We shall derive the equation for conservation of momentum in local form, which is necessary for deriving the hydrodynamic equations. The momentum density operator p(x) for a single component system differs from the particle current operator (19.24a) only by a factor of the mass of a particle

$$p(x) = mj(x). \tag{19.25}$$

The equations of motion for p(x) have the form

$$\begin{aligned}\dot{p}_\alpha(x) + \sum_\beta \frac{\partial}{\partial x_\beta}\frac{\hbar^2}{2m}\left\{\frac{\partial\psi^+(x)}{\partial x_\beta}\frac{\partial\psi(x)}{\partial x_\alpha} + \frac{\partial\psi^+(x)}{\partial x_\alpha}\frac{\partial\psi(x)}{\partial x_\beta} - \frac{1}{2}\frac{\partial^2 n(x)}{\partial x_\beta\,\partial x_\alpha}\right\} =\\ = -\int \frac{\partial\phi(x-x')}{\partial x_\alpha}\psi^+(x)\psi^+(x')\psi(x')\psi(x)\,dx' = -B_\alpha(x)\\ (\alpha = 1,\ 2,\ 3).\end{aligned} \tag{19.26}$$

Equation (19.26) still does not have the usual form of a conservation law, because the operator $B_\alpha(x)$ is not represented in the form of a divergence of a tensor, but, as we shall verify below, this can be done with excellent accuracy for real systems with a short effective radius of interaction between molecules. Indeed, we are interested not in the operator $B_\alpha(x)$ itself, but in integrals of the operator of the type $\int A(x)\cdot B(x)dx$, where $A(x)$ is some arbitrary vector function of position, which changes little in a distance of the order of the radius of the interaction forces between particles; we shall consider such integrals in § 20 and further.

We have

$$\int A_\alpha(x)\,B_\alpha(x)\,dx = \int A_\alpha(x)\,\frac{\partial\phi(x-x')}{\partial x_\alpha}\,F(x,x')\,dx\,dx' = \\ = \frac{1}{2}\int (A_\alpha(x) - A_\alpha(x'))\,\frac{\partial\phi(x-x')}{\partial x_\alpha}\,F(x,x')\,dx\,dx',$$

where

$$F(x,x') = \psi^+(x)\,\psi^+(x')\,\psi(x')\,\psi(x)$$

is an operator which is symmetric in x,x'; we shall assume that the function $\phi(x-x')$ is radially symmetric.

Using the fact that $A_\alpha(x')$ is a slowly varying function, we expand it in a series in $x-x'=x_1$, keeping terms of first order; after carrying out an integration by parts, we have

$$\int A_\alpha(x)\,B_\alpha(x)\,dx \cong \frac{1}{2}\sum_\beta \int dx\,\frac{\partial A_\alpha(x)}{\partial x_\beta}\int dx_1\,x_{1\beta}\,\frac{\partial\phi(x_1)}{\partial x_{1\alpha}}\,F(x,x-x_1) = \\ = -\frac{1}{2}\int dx\,A_\alpha(x)\sum_\beta \frac{\partial}{\partial x_\beta}\int dx'\,(x_\beta - x'_\beta)\,\frac{\partial\phi(x-x')}{\partial x_\alpha}\,F(x,x').$$

As $A_\alpha(x)$ is arbitrary, we obtain

$$B_\alpha(x) = -\sum_\beta \frac{\partial}{\partial x_\beta}\,\frac{1}{2}\int (x_\beta - x'_\beta)(x_\alpha - x'_\alpha)\,\frac{1}{r}\,\frac{d\phi(r)}{dr}\times \\ \times\,\psi^+(x)\,\psi^+(x')\,\psi(x')\,\psi(x)\,dx', \qquad r = |x - x'|;$$

consequently, $B_\alpha(x)$ is the divergence of a tensor. Using this expression the equation of motion for the momentum density (19.26) takes on the form of a local conservation law:

$$\frac{\partial p_\alpha(x)}{\partial t} + \sum_\beta \frac{\partial}{\partial x_\beta} T_{\beta\alpha}(x) = 0, \tag{19.27}$$

where

$$T_{\beta\alpha}(x) = \frac{\hbar^2}{2m}\left\{\frac{\partial\psi^+(x)}{\partial x_\beta}\frac{\partial\psi(x)}{\partial x_\alpha} + \frac{\partial\psi^+(x)}{\partial x_\alpha}\frac{\partial\psi(x)}{\partial x_\beta} - \frac{1}{2}\frac{\partial^2 n(x)}{\partial x_\beta\,\partial x_\alpha}\right\} - \\ - \frac{1}{2}\int (x_\beta - x'_\beta)(x_\alpha - x'_\alpha)\frac{1}{r}\frac{d\phi(r)}{dr}\psi^+(x)\psi^+(x')\psi(x')\psi(x)\,dx' \tag{19.27a}$$

is the stress tensor operator, analogous to the classical expression (19.12).

The symmetry of the stress tensor follows from (19.27a)

$$T_{\alpha\beta}(x) = T_{\beta\alpha}(x),$$

which is related to the radial symmetry of the interaction forces.

One can take into account also higher terms in the expansion in x-x′ by the same method; this brings terms with higher derivatives of $\psi(x)$ into the expression for $T_{\beta\alpha}(x)$, but these terms are very small for short ranged forces (see the footnote on page 263).

We shall now obtain the conservation equation for energy density, which we shall need later in order to study transfer of energy. Using the commutation relations or the equations of motion (19.23), we obtain for the energy density operator (19.21a)

$$\frac{\partial H(x)}{\partial t} + \operatorname{div} j'_H(x) = B(x), \tag{19.28}$$

where

$$j'_H(x) = \frac{\hbar^3}{4m^2 i}\{\nabla\psi^+(x)\nabla^2\psi(x) - \nabla^2\psi^+(x)\nabla\psi(x)\} + \\ + \frac{1}{2}\int \phi(x - x')\psi^+(x')j(x)\psi(x')\,dx', \tag{19.28a}$$

$$B(x) = -\frac{1}{2}\int \nabla\phi(x - x')\cdot\{\psi^+(x')j(x)\psi(x') + \\ + \psi^+(x)j(x')\psi(x)\}\,dx'.$$

Following the method of smoothing small inhomogeneities, which was used earlier in deriving the equations of momentum conservation in local form, we represent B(x) approximately as the divergence of a vector. To do this we construct the expression

$$\begin{aligned}\int A(\boldsymbol{x})\,B(\boldsymbol{x})\,d\boldsymbol{x} &= \\ &= -\frac{1}{4}\int A(\boldsymbol{x})\left(\nabla\phi(\boldsymbol{x}-\boldsymbol{x}')-\nabla'\phi(\boldsymbol{x}-\boldsymbol{x}')\right)\cdot\boldsymbol{F}(\boldsymbol{x},\boldsymbol{x}')\,d\boldsymbol{x}\,d\boldsymbol{x}' = \\ &= -\frac{1}{4}\int\left(A(\boldsymbol{x})-A(\boldsymbol{x}')\right)\nabla\phi(\boldsymbol{x}-\boldsymbol{x}')\cdot\boldsymbol{F}(\boldsymbol{x},\boldsymbol{x}')\,d\boldsymbol{x}\,d\boldsymbol{x}',\end{aligned}$$

where $\boldsymbol{F}(\boldsymbol{x},\boldsymbol{x}') = \psi^{+}(\boldsymbol{x}')\,\boldsymbol{j}(\boldsymbol{x})\,\psi(\boldsymbol{x}') + \psi^{+}(\boldsymbol{x})\,\boldsymbol{j}(\boldsymbol{x}')\,\psi(\boldsymbol{x})$

is an operator which is symmetric with respect to x,x′, and A(x) is an arbitrary function which changes little in a distance of the order of the radius of interaction between particles.

Using the fact that A(x′) is a slowly varying function, we expand it in a series in $x_1 = x - x'$, keeping terms of first order. After an integration by parts we have

$$\begin{aligned}\int A(\boldsymbol{x})\,B(\boldsymbol{x})\,d\boldsymbol{x} &\cong \\ &\cong -\frac{1}{4}\int\sum_{\alpha}\frac{\partial A(\boldsymbol{x})}{\partial x_\alpha}\,x_{1\alpha}\nabla\phi(\boldsymbol{x}_1)\cdot\boldsymbol{F}(\boldsymbol{x},\boldsymbol{x}-\boldsymbol{x}_1)\,d\boldsymbol{x}\,d\boldsymbol{x}_1 = \\ &= \int d\boldsymbol{x}\,A(\boldsymbol{x})\sum_{\alpha}\frac{\partial}{\partial x_\alpha}\frac{1}{4}\int d\boldsymbol{x}_1\,x_{1\alpha}\nabla\phi(\boldsymbol{x}_1)\cdot\boldsymbol{F}(\boldsymbol{x},\boldsymbol{x}-\boldsymbol{x}_1).\end{aligned}$$

Because A(x) is arbitrary, we obtain

$$\begin{aligned}B(\boldsymbol{x}) &= \sum_{\alpha}\frac{\partial}{\partial x_\alpha}\frac{1}{4}\int x_{1\alpha}\nabla\phi(\boldsymbol{x}_1)\cdot\boldsymbol{F}(\boldsymbol{x},\boldsymbol{x}-\boldsymbol{x}_1)\,d\boldsymbol{x}_1 = \\ &= \operatorname{div}\frac{1}{4}\int(\boldsymbol{x}-\boldsymbol{x}')\nabla\phi(\boldsymbol{x}-\boldsymbol{x}')\cdot\left(\psi^{+}(\boldsymbol{x}')\,\boldsymbol{j}(\boldsymbol{x})\,\psi(\boldsymbol{x}')+\right. \\ &\qquad\qquad\left.+\,\psi^{+}(\boldsymbol{x})\,\boldsymbol{j}(\boldsymbol{x}')\,\psi(\boldsymbol{x})\right)d\boldsymbol{x}'.\end{aligned}$$

Thus, we have approximately represented B(x) as the divergence of a vector. Equation (19.28) has the form of the local conservation of energy law:

$$\frac{\partial H(x)}{\partial t} + \operatorname{div} j_H(x) = 0, \tag{19.29}$$

where

$$j_H(x) = -\frac{\hbar^3}{4m^2 i}\{\nabla^2\psi^+(x)\nabla\psi(x) - \nabla\psi^+(x)\nabla^2\psi(x)\} + \\ + \frac{1}{2}\int \phi(x-x')\psi^+(x')j(x)\psi(x')\,dx' - \\ - \frac{1}{4}\int (x-x')\nabla\phi(x-x')\cdot(\psi^+(x')j(x)\psi(x') + \psi^+(x)j(x')\psi(x))\,dx' \tag{19.29a}$$

is the energy current operator, corresponding to the classical expression (19.17a).

Proceeding from the definition (19.21c) for H(x), we obtain

$$\frac{\partial H(x)}{\partial t} + \operatorname{div}\left\{j_H(x) - \frac{\hbar^2}{8m}\nabla \operatorname{div} j(x)\right\} = 0,$$

i.e., expression (19.29), but with a different definition of the energy current operator $j_H(x)$.

Thus, we have obtained a complete system of conservation laws for energy, particle number, and momentum in local form for the case of a quantum mechanical system of identical particles:

$$\begin{aligned} \frac{\partial H(x)}{\partial t} &= -\operatorname{div} j_H(x), \\ \frac{\partial n(x)}{\partial t} &= -\operatorname{div} j(x), \\ \frac{\partial p(x)}{\partial t} &= -\operatorname{Div} T(x). \end{aligned} \tag{19.30}$$

This system is analogous to the classical equations (19.18), but the densities of mechanical quantities in this system are quantum mechanical operators. For example, H(x) is defined by equation (19.21a), n(x) by equation (19.22), p(x) by equation (19.25), $j_H(x)$ by equation (19.29a), j(x) by equation (19.24a), T(x) by equation (19.27a).

It is convenient to write the conservation laws (19.30) in the form of a single equation:

$$\frac{\partial P_m(x)}{\partial t} + \nabla \cdot j_m(x) = 0 \qquad (m = 0, 1, 2), \tag{19.31}$$

where

$$P_0(x) = H(x), \qquad P_1(x) = p(x), \qquad P_2(x) = n(x) \tag{19.31a}$$

are the densities of mechanical quantities, and

$$j_0(x) = j_H(x), \qquad j_1(x) = T(x), \qquad j_2(x) = j(x) \tag{19.31b}$$

are the current densities.

In the more general case, when the inhomogeneities of the system at distances of the order of the effective radius of the interaction between particles cannot be neglected, one cannot introduce $j_m(x)$ explicitly, and the equations of balance of mechanical quantities are written in the form

$$\frac{\partial P_m(x, t)}{\partial t} = \frac{1}{i\hbar}\,[P_m(x, t), H]. \tag{19.31c}$$

In the conservation equations for mechanical quantities (19.30) we have not written a law of conservation of angular momentum. This is not accidental, because for our case of centrally symmetric forces the law of conservation of angular momentum follows from the law of conservation of momentum. Indeed, let us introduce the tensor density of angular momentum $m_{\alpha\beta}(x)$ by the definition:

$$m_{\alpha\beta}(x) = x_\alpha p_\beta(x) - x_\beta p_\alpha(x), \tag{19.32}$$

where $p(x)$ is the momentum density operator. We shall assume that the particles do not have an intrinsic angular momentum; otherwise it must be taken into account in (19.32). The tensor $m_{\alpha\beta}(x)$ satisfies the equation of motion

$$\frac{\partial m_{\alpha\beta}(x)}{\partial t} = x_\alpha \frac{\partial p_\beta(x)}{\partial t} - x_\beta \frac{\partial p_\alpha(x)}{\partial t} = -\sum_\gamma \left\{ x_\alpha \frac{\partial T_{\gamma\beta}(x)}{\partial x_\gamma} - x_\beta \frac{\partial T_{\gamma\alpha}(x)}{\partial x_\gamma} \right\} =$$
$$= -\sum_\gamma \frac{\partial}{\partial x_\gamma}\{x_\alpha T_{\gamma\beta}(x) - x_\beta T_{\gamma\alpha}(x)\} + T_{\alpha\beta}(x) - T_{\beta\alpha}(x).$$

In the case of central forces which we are considering, the tensor $T_{\alpha\beta}(x)$ is symmetric, and the equation for $m_{\alpha\beta}(x)$ already has the form of a conservation law:

$$\frac{\partial m_{\alpha\beta}(x)}{\partial t} + \sum_{\gamma} \frac{\partial}{\partial x_{\gamma}} \{x_{\alpha} T_{\gamma\beta}(x) - x_{\beta} T_{\gamma\alpha}(x)\} = 0. \tag{19.33}$$

Thus, in the case of central forces the law of conservation of angular momentum follows from the law of conservation of momentum. For noncentral forces the tensor $T_{\alpha\beta}(x)$ is not symmetric, and the angular momentum $\int m_{\alpha\beta}(x)dx$ is not conserved, but this means only that it is necessary to take into account the contribution to the total angular momentum of the internal degrees of freedom, for example to take into account the angular momentum of rotation of the molecules, or of the spin of the particles (see [41]). To take into account noncentral forces without introducing internal degrees of freedom would be inconsistent[1].

19.3. Virial Theorem for the Nonhomogeneous Case.

The virial theorem, classical and quantum, for the case of statistical equilibrium was discussed in Chapters I and II in sections 5.3 and 11.3. We shall now discuss how to generalize it to a spatially inhomogeneous case.

In the quantum case we shall begin with expression (19.27a) for the stress tensor (in the classical case it is necessary to use expression (19.12)). In what follows we shall consider the quantum mechanical case.

If in a gas (or a liquid) there are no hydrodynamic currents, then the stress tensor $\langle T_{\alpha\beta}(x)\rangle$ coincides with the pressure tensor $\langle P_{\alpha\beta}(x)\rangle$. If there exist currents with average velocity

$$\langle (x)\, u\rangle / \langle (x)\, f\rangle = (x)\, v \tag{19.34}$$

then to define the pressure tensor one must go to a moving system of coordinates, in which the hydrodynamic velocity is equal to zero, and define the pressure tensor in this system.

The transition to a system moving with velocity v(x) can be carried out by means of a canonical transformation of the operators

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[1] In this case the tensor $T_{\alpha\beta}(x)$ can be symmetrized by making use of the ambiguity in its definition [69].

$$\psi(x) = \psi'(x)\, e^{i\varphi(x)}, \qquad v(x) = \frac{\hbar}{m} \nabla\varphi(x). \tag{19.35}$$

Then $T_{\alpha\beta}(x)$ is transformed to $T'_{\alpha\beta}(x)$, which we shall call the pressure tensor operator $P_{\alpha\beta}(x)$:

$$P_{\alpha\beta}(x) = T_{\alpha\beta}(x) - m\left(v_\alpha j_\beta(x) + v_\beta j_\alpha(x)\right) + mn(x)\, v_\alpha v_\beta. \tag{19.36}$$

In analogy with ordinary hydrodynamics one can define the pressure operator as one-third of the trace of the tensor $P_{\alpha\beta}(x)$:

$$p(x) = \frac{1}{3} \sum_\alpha P_{\alpha\alpha}(x). \tag{19.37}$$

Thus, $p(x)$ is a scalar operator, equal to

$$\begin{aligned} p(x) = \frac{\hbar^2}{3m} \left\{ \nabla\psi^+(x) \cdot \nabla\psi(x) - \frac{1}{4} \nabla^2 n(x) \right\} - \\ - \frac{1}{6} \int (x - x') \cdot \nabla\phi(x - x')\, \psi^+(x)\, \psi^+(x')\, \psi(x')\, \psi(x)\, dx' - \\ - \frac{2}{3} mv(x) \cdot j(x) + \frac{1}{3} mn(x)\, v^2(x). \end{aligned} \tag{19.37a}$$

Averaging (19.37a), we obtain the virial theorem for the inhomogeneous case:

$$\begin{aligned} \langle p(x) \rangle = \frac{\hbar^2}{3m} \left\{ \langle \nabla\psi^+(x) \cdot \nabla\psi(x) \rangle - \frac{1}{4} \nabla^2 \langle n(x) \rangle \right\} - \frac{2}{3} m \frac{v^2(x)}{2} - \\ - \frac{1}{6} \int (x - x') \cdot \nabla\phi(x - x')\, \langle \psi^+(x)\, \psi^+(x')\, \psi(x')\, \psi(x) \rangle\, dx', \end{aligned} \tag{19.37b}$$

where <...> denotes an averaging, for which <j(x)>=<n(x)>v(x).

It is easily verified that the average pressure for the homogeneous case in which v(x)=0 satisfies the virial theorem in the usual form (11.15). Indeed, in this case

$$\langle n(\boldsymbol{x})\rangle_0 = \text{const} \quad \text{и} \quad \nabla^2 \langle n(\boldsymbol{x})\rangle_0 = 0,$$

where $<\ldots>_0$ is an averaging over an equilibrium state; therefore the average equilibrium pressure is equal to

$$p = \langle p(\boldsymbol{x})\rangle_0 = \frac{2}{3}\frac{\hbar^2}{2m}\langle \nabla\psi^+(\boldsymbol{x})\cdot\nabla\psi(\boldsymbol{x})\rangle - \\ - \frac{1}{6}\int (\boldsymbol{x}-\boldsymbol{x}')\cdot\nabla\phi(\boldsymbol{x}-\boldsymbol{x}')\,F_2(\boldsymbol{x}-\boldsymbol{x}')\,d\boldsymbol{x}', \tag{19.38}$$

where $$F_2(\boldsymbol{x}-\boldsymbol{x}') = \langle \psi^+(\boldsymbol{x})\,\psi^+(\boldsymbol{x}')\,\psi(\boldsymbol{x}')\,\psi(\boldsymbol{x})\rangle_0 \tag{19.38a}$$

is the equilibrium pair correlation function.

In formula (19.38) the first term is equal to 2/3 of the average kinetic energy density, and the second term is 1/3 of the virial of the interaction forces, i.e., (19.38) coincides with (11.15).

In sections 5.3 and 11.3 the virial theorem was proved by the method of infinitesimal dilatation (5.9b) and (11.10b) of the scales of the coordinates and momenta; thus, it is an exact theorem. It might seem strange that we obtained it from an approximate expression for $T_{\alpha\beta}(\boldsymbol{x})$. We shall verify that there is no contradiction here, and for the homogeneous state the higher terms in the expansion do not contribute to $<T_{\alpha\beta}(\boldsymbol{x})>_0$. Using the same method as in section 19.2 and taking into account all terms of the expansion, we obtain

$$T_{\alpha\beta}(\boldsymbol{x}) = \frac{\hbar^2}{2m}\left\{\frac{\partial\psi^+(\boldsymbol{x})}{\partial x_\alpha}\frac{\partial\psi(\boldsymbol{x})}{\partial x_\beta} + \frac{\partial\psi^+(\boldsymbol{x})}{\partial x_\beta}\frac{\partial\psi(\boldsymbol{x})}{\partial x_\alpha} - \frac{1}{2}\frac{\partial^2 n(\boldsymbol{x})}{\partial x_\alpha\,\partial x_\beta}\right\} - \\ - \sum_{n\geqslant 1}\frac{1}{n!}\frac{\partial^{n-1}}{\partial x_\beta^{n-1}}\int\frac{\partial\phi(\boldsymbol{x}-\boldsymbol{x}')}{\partial x_\alpha}(x_\beta - x'_\beta)^n\,\psi^+(\boldsymbol{x})\,\psi^+(\boldsymbol{x}')\,\psi(\boldsymbol{x}')\,\psi(\boldsymbol{x})\,d\boldsymbol{x}'.$$

For the homogeneous state the pair correlation function (19.38a) depends only on the difference $\boldsymbol{x}-\boldsymbol{x}'$, and therefore the average values of the integrals on the right hand side of this expression do not depend on $\boldsymbol{x}$. Consequently, in $<T_{\alpha\beta}(\boldsymbol{x})>_0$ in the sum over n there remains only one term n=1, which gives the virial of the forces.

19.4. Conservation Laws for a Mixture of Gases or Liquids.

In the preceding section we studied the conservation laws of particle number, energy, and momentum by means of the example of a system of identical particles with pairwise interactions. Let us now consider the conservation laws for a mixture of various gases or liquids, restricting ourselves to the case in which there are no chemical reactions among the components and there is no excitation of the internal degrees of freedom of the molecules. This example is of interest, because it enables one to study the mutual transfer of energy and momentum between components, as these quantities are already not integrals of motion for a single component.

The Hamiltonian of a system of l types of interacting molecules has the form

$$H=\sum_{i}^{l}\int\psi_i^+(x)\left\{-\frac{\hbar^2}{2m_i}\nabla^2+\sum_{k}\frac{1}{2}\int\phi_{ik}(x-x')\psi_k^+(x')\psi_k(x')\,dx'\right\}\times \\ \times\psi_i(x)\,dx, \tag{19.39}$$

where $\phi_{ik}(x-x')$ is the potential energy of interaction of the particles of types i and k - assumed to be radially symmetric, and the second quantization operators $\psi_i(x)$ and $\psi_k(x)$ for each component satisfy the commutation relations for Fermi or Bose statistics

$$\psi_i(x)\psi_i^+(x')\pm\psi_i^+(x')\psi_i(x)=\delta(x-x'),$$
$$\psi_i(x)\psi_i(x')\pm\psi_i(x')\psi_i(x)=0,$$

depending on the parity of the spin of the molecule, and they commute for $i\neq k$, i.e., for different components.

We write the Hamiltonian (19.39) in the form

$$H=\sum_i\int H_i(x)\,dx, \tag{19.39a}$$

where

$$H_i(x)=\frac{\hbar^2}{2m_i}\nabla\psi_i^+(x)\cdot\nabla\psi_i(x)+ \\ +\sum_k\frac{1}{2}\int\phi_{ik}(x-x')\psi_i^+(x)\psi_k^+(x')\psi_k(x')\psi_i(x)\,dx' \tag{19.39b}$$

is the energy density of the i^{th} component with the interaction with other components taken into account.

The particle number of the i^th component is represented by the operator

$$N_i = \int n_i(x)\,dx, \quad n_i(x) = \psi_i^+(x)\,\psi_i(x) \tag{19.40}$$

and is conserved, because

$$\frac{\partial n_i(x)}{\partial t} + \operatorname{div} j_i(x) = 0, \tag{19.41}$$

where

$$j_i(x) = \frac{\hbar}{2m_i i}\{\psi_i^+(x)\,\nabla\psi_i(x) - \nabla\psi_i^+(x)\,\psi_i(x)\} \tag{19.41a}$$

is the particle current density operator of the i^th component. This is a consequence of the fact that chemical reactions do not take place between the components.

The equation for the conservation of energy of the i^th component in local form is

$$\frac{\partial H_i(x)}{\partial t} + \operatorname{div} j_{H_i}(x) = J_{H_i}(x), \tag{19.42}$$

where

$$\begin{aligned} j_{H_i}(x) = {} & \frac{\hbar^3}{4m_i^2 i}\{\nabla\psi_i^+(x)\,\nabla^2\psi_i(x) - \nabla^2\psi_i^+(x)\,\nabla\psi_i(x)\} + \\ & + \sum_k \frac{1}{2}\int \phi_{ki}(x-x')\,\psi_k^+(x')\,j_i(x)\,\psi_k(x')\,dx' - \\ & - \sum_k \frac{1}{8m_k}\int (x-x')\,\nabla\phi_{ki}(x-x')\cdot\{\psi_k^+(x')\,j_i(x)\,\psi_k(x') + \\ & + \psi_i^+(x')\,j_k(x)\,\psi_i(x') + \psi_k^+(x)\,j_i(x')\,\psi_k(x) + \psi_i^+(x)\,j_k(x')\,\psi_i(x)\}\,dx' \end{aligned} \tag{19.42a}$$

is the energy current density of the i^th component, and

$$\begin{aligned} J_{H_i}(x) = -\sum_m \frac{1}{4}\int \nabla\phi_{mi}(x-x')\cdot\{n_m(x')\,j_i(x) + n_i(x)\,j_m(x') - \\ - n_i(x')\,j_m(x) - n_m(x)\,j_i(x')\}\,dx' \end{aligned} \tag{19.42b}$$

is an operator representing the rate of change of energy of the i^th component as a consequence of its interaction with other components. In obtaining the equations (19.42)-(19.42b) we have made use of the method of smoothing of operators over small inhomogeneities, which was discussed in section 19.2.

The operator $J_{H_i}(\mathbf{x})$ in equation (19.42) satisfies the relation

$$\sum_i J_{H_i}(x) = 0, \tag{19.42c}$$

which is a consequence of the conservation of the total energy. It is impossible to represent this operator as the divergence of a vector, because $H_i = \int H_i(\mathbf{x})\,d\mathbf{x}$ is not an integral of motion.

The total energy density

$$H(x) = \sum_i H_i(x) \tag{19.43}$$

satisfies a conservation law of the usual form

$$\frac{\partial H(\mathbf{x})}{\partial t} + \operatorname{div} \mathbf{j}_H(\mathbf{x}) = 0, \tag{19.44}$$

where

$$\mathbf{j}_H(\mathbf{x}) = \sum_i \mathbf{j}_{H_i}(\mathbf{x}) \tag{19.44a}$$

is the total energy current density. The rate of change of the energy of the i^{th} component is equal to the integral of (19.42) over volume:

$$\frac{\partial H_i}{\partial t} = J_{H_i}, \tag{19.45}$$

where

$$J_{H_i} = -\sum_m \frac{1}{2} \int \nabla\phi_{mi}(\mathbf{x} - \mathbf{x}') \cdot (n_m(\mathbf{x}')\,\mathbf{j}_i(\mathbf{x}) + n_i(\mathbf{x})\,\mathbf{j}_m(\mathbf{x}'))\,dx\,dx' \tag{19.45a}$$

is the total energy current operator for the i^{th} component, for which

$$\sum_i J_{H_i} = 0. \tag{19.45b}$$

Equations (19.45) and (19.45b) describe the transfer of energy between components of the mixture. Using these equations one can study the relaxation of this process, if the energy transfer is carried out slowly (for example, when there is a large mass difference between the components).

The conservation equations for the momentum of the i^{th} component and the total momentum in local form are

$$\frac{\partial p_i(x)}{\partial t} + \mathrm{Div}\, T_i(x) = f_i(x),$$
$$\frac{\partial p(x)}{\partial t} + \mathrm{Div}\, T(x) = 0, \qquad (19.46)$$

where

$$p_i(x) = m_i j_i(x), \qquad p(x) = \sum_i m_i j_i(x) \qquad (19.46a)$$

are the momentum densities of the i^{th} component and total momentum, and

$$T_i^{\alpha\beta}(x) = \frac{\hbar^2}{2m_i}\left\{\frac{\partial\psi_i^{+}(x)}{\partial x_\alpha}\frac{\partial\psi_i(x)}{\partial x_\beta} + \frac{\partial\psi_i^{+}(x)}{\partial x_\beta}\frac{\partial\psi_i(x)}{\partial x_\alpha} - \frac{1}{2}\frac{\partial^2 n_i(x)}{\partial x_\alpha\,\partial x_\beta}\right\} -$$
$$-\sum_j \frac{1}{4}\int (x_\beta - x'_\beta)(x_\alpha - x'_\alpha)\frac{1}{r}\frac{d\phi_{ji}(r)}{dr} \times$$
$$\times \{\psi_j^{+}(x)\psi_i^{+}(x')\psi_i(x')\psi_j(x) + \psi_j^{+}(x')\psi_i^{+}(x)\psi_i(x)\psi_j(x')\}\, dx',$$
$$T^{\alpha\beta}(x) = \sum_i T_i^{\alpha\beta}(x) \qquad (19.46b)$$

are the stress tensor of the i^{th} component and the total stress tensor, and

$$f_i(x) = -\sum_{j\neq i}\frac{1}{2}\int \nabla\phi_{ji}(x-x')(n_j(x')n_i(x) - n_j(x)n_i(x'))\,dx' \qquad (19.46c)$$

is the operator for the density of viscous force between the i^{th} component and the remaining components. The sum of all viscous forces $f_i(x)$ is equal to zero,

$$\sum_i f_i(x) = 0. \qquad (19.46d)$$

The total momentum of the i^{th} component

$$P_i = \int p_i(x)\,dx \tag{19.47}$$

is not conserved, because

$$\frac{\partial P_i}{\partial t} = F_i, \tag{19.47a}$$

where

$$F_i = \int f_i(x)\,dx = \\ = -\sum_{j \neq i} \frac{1}{2} \int \nabla\phi_{ji}(x-x')\{n_j(x)\,n_i(x') - n_j(x')\,n_i(x)\}\,dx\,dx' \tag{19.47b}$$

is the viscous force between the i^{th} component and the remaining components. The total momentum is, of course, conserved, because

$$\sum_i F_i = 0. \tag{19.47c}$$

It is convenient to write equations (19.42), (19.41), and (19.46) in the form of a single matrix equation:

$$\frac{\partial P_{mi}(x)}{\partial t} + \nabla \cdot j_{mi}(x) = J_{mi}(x), \tag{19.48}$$

where

$$\begin{aligned} P_{0i}(x) &= H_i(x), & P_{1i}(x) &= p_i(x), & P_{2i}(x) &= n_i(x), \\ j_{0i}(x) &= j_{H_i}(x), & j_{1i}(x) &= T_i(x), & j_{2i}(x) &= j_i(x), \\ J_{0i}(x) &= J_{H_i}(x), & J_{1i}(x) &= f_i(x), & J_{2i}(x) &= 0, \end{aligned} \tag{19.48a}$$

i.e.,

$P_{mi}(x)$ is the matrix of densities of mechanical quantities - energy, momentum, and particle number;

$j_{mi}(x)$ is the matrix of currents;

$J_{mi}(x)$ is the matrix of the sources.

19.5. Conservation Laws for a System of Particles with Intrinsic Degrees of Freedom.

If a gas or a liquid is made up of complex molecules, then it is possible to excite the internal degrees of freedom, for example vibrations, rotations, or others. The exchange of energy between the internal and translational degrees of freedom may be inhibited, and then relaxation phenomena are possible; these processes correspond to the slow establishment of equilibrium between the external and internal degrees of freedom. In order to study these phenomena, it is necessary to formulate the laws of conservation of particle number, energy, and momentum for a subsystem with given internal molecular states, which we shall do in this section, following the article [4].

Let us denote by y the set of variables $y_1, y_2, \dots$, describing the internal degrees of freedom of the molecule, and by **x** the coordinates of its center of mass. The Hamiltonian of the system has the form

$$H = \int \psi^+(x, y) \left\{ -\frac{\hbar^2\nabla^2}{2m} + H_{\text{int}}(y) + \frac{1}{2}\int \psi^+(x', y')\,\Phi(xy, x'y')\,\psi(x', y')\,dx'\,dy' \right\} \psi(x, y)\,dx\,dy, \tag{19.49}$$

where $\Phi(xy, x'y') = \Phi(x'y', xy)$ is the operator for the energy of interaction between molecules, and $H_{\text{int}}(y)$ is the Hamiltonian of the internal degrees of freedom, for which

$$H_{\text{int}}(y)\,\varphi_i(y) = E_i\varphi_i(y), \quad \psi(x, y) = \frac{1}{\sqrt{V}}\sum_{ki} a_{ki}\,e^{i(kx)}\,\varphi_i(y), \tag{19.49a}$$

where $\varphi_i(y)$ and E_i are the eigenfunction and energy of the internal state i, and α_{ki} are the second quantization operators in occupation number space k and i.

We introduce the second quantized operators $\psi_i(x)$, which describe a subsystem with a given quantum number i:

$$\psi_i(x) = \frac{1}{\sqrt{V}}\sum_k a_{ki}\,e^{i(kx)}, \quad \psi(x, y) = \sum_i \varphi_i(y)\,\psi_i(x). \tag{19.49b}$$

The operators $\psi_i(x)$ satisfy the commutation relations

$$\begin{gathered} \psi_i(x)\,\psi_j^+(x') \pm \psi_j^+(x')\,\psi_i(x) = \delta_{ij}\,\delta(x - x'), \\ \psi_i(x)\,\psi_j(x') \pm \psi_j(x')\,\psi_i(x) = 0, \end{gathered} \tag{19.49c}$$

in which the plus sign is taken if the spin of the molecule is odd, and the minus sign if it is even. The relations (19.49c) follow from the commutation relations for α_{ki}.

Using (19.49a) and (19.49b) we write the Hamiltonian (19.49) in the form

$$H = \sum_i \int \psi_i^+(x)\left(-\frac{\hbar^2}{2m}\nabla^2 + E_i\right)\psi_i(x)\,dx + \\ + \frac{1}{2}\sum_{ijkl}\int \psi_i^+(x)\,\psi_j^+(x')\,\phi_{ij}^{kl}(x, x')\,\psi_k(x')\,\psi_l(x)\,dx\,dx', \qquad (19.50)$$

where the function $\phi_{ij}^{kl}(x,x')$ has the form

$$\phi_{ij}^{kl}(x, x') = \int \varphi_i^*(y)\,\varphi_j^*(y')\,\phi(xy,\ x'y')\,\varphi_k(y')\,\varphi_l(y)\,dy\,dy' \qquad (19.50a)$$

and has the symmetry properties

$$\phi_{ij}^{kl}(x, x') = \phi_{ji}^{lk}(x', x), \quad \phi_{ij}^{kl}(x, x')^* = \phi_{lk}^{ji}(x, x'), \qquad (19.50b)$$

which follow from the symmetry of the function $\phi(xy,x'y')$ with respect to the replacement $x \leftrightarrow x'$, $y \leftrightarrow y'$ and the hermiticity of the interaction operator.

The function $\phi_{ij}^{kl}(x,x')$ plays the role of an interaction potential between the molecules in the states k and l, and the result of the interaction is to convert these molecules to the states i and j. One can imagine that a chemical reaction is taking place between the molecules according to the scheme

$$(k) + (l) \rightleftarrows (i) + (j).$$

The function $\phi_{ij}^{kl}(x,x')$ can be estimated from the effective cross section for an inelastic collision with the transition $k,l \to i,j$. The Hamiltonian (19.50) is similar to the Hamiltonian for a mixture of gases (19.39), with the difference that in this case the internal energy of the molecules E_i and the possibility of transitions $k,l \rightleftarrows i,j$ upon collisions are taken into account.

The Hamiltonian in the form (19.50) was used in [4]. It can be regarded as the original model for a system of particles with internal degrees of freedom. It could have been written down immediately; the preceding arguments were given only to suggest the approach. A more detailed account of internal degrees of freedom is given in the articles by L. A. Pokrovskiy [41,209].

The operator $\psi_i(x)$ satisfies the equation of motion

$$i\hbar \frac{\partial \psi_i(x)}{\partial t} = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + E_i \right\} \psi_i(x) + \\ + \frac{1}{2} \sum_{jkl} \int \psi_j^+(x') \left(\phi_{ij}^{kl}(x, x') + \phi_{ji}^{kl}(x', x) \right) \psi_k(x') \psi_l(x) \, dx'. \tag{19.51}$$

The number of particles in the state i

$$n_i(x) = \psi_i^+(x) \psi_i(x) \tag{19.52}$$

is not conserved, because transitions from one internal state to another are possible upon collisions. The operator $n_i(x)$ satisfies the balance equation

$$\frac{\partial n_i(x)}{\partial t} + \operatorname{div} j_i(x) = J_i(x), \tag{19.53}$$

where

$$J_i(x) = \frac{1}{2i\hbar} \sum_{jkl} \int \left\{ \psi_i^+(x) \psi_j^+(x') \left(\phi_{ij}^{kl}(x, x') + \phi_{ji}^{kl}(x', x) \right) \psi_k^+(x') \psi_l(x) - \\ - \psi_i^+(x) \psi_k^+(x') \left(\phi_{ij}^{kl}(x, x')^* + \phi_{ji}^{kl}(x', x)^* \right) \psi_j(x') \psi_i(x) \right\} dx' \tag{19.53a}$$

is the operator for the rate of "reaction" of formation of particles in the state i. The particle current operator $j_i(x)$ has the usual form (19.41a).

The total density of particles in all internal states

$$n(x) = \sum_i n_i(x)$$

is conserved, because using (19.50a) we have

$$\sum_i J_i(x) = 0. \tag{19.53b}$$

On the other hand, the number of particles in the state i

$$N_i = \int n_i(x)\,dx \tag{19.54}$$

is not conserved, because

$$\frac{\partial N_i}{\partial t} = \int J_i(x)\,dx = J_i, \tag{19.54a}$$

where J_i is the operator of the rate of formation of particles in the state i, which is non-zero.

The density of internal energy in the state i

$$H_i(x) = E_i n_i(x) \tag{19.55}$$

satisfies the balance equation

$$\frac{\partial H_i(x)}{\partial t} + \operatorname{div} E_i j_i(x) = E_i J_i(x), \tag{19.55a}$$

and the total energy in the state i

$$H_i = \int H_i(x)\,dx \tag{19.56}$$

satisfies the equation

$$\frac{\partial H_i}{\partial t} = E_i J_i. \tag{19.57}$$

The conservation equations (19.53), (19.55a), (19.54a), and (19.57) allow one to investigate the relaxation of internal degrees of freedom, which we shall discuss in § 23.

The total system of conservation laws for the case of a system with internal degrees of freedom can be written in matrix form (19.48), where the subscript i denotes the internal degree of freedom, and

$$J_{2i}(x) = J_i(x), \tag{19.58}$$

and not zero as before, i.e., there are sources not only of energy and momentum, but also of particle number. This is the most general form of the conservation laws.

§ 20. Local Equilibrium Distributions.

To define thermodynamic functions of nonequilibrium states it is necessary to construct the corresponding statistical ensemble which represents systems in a nonequilibrium state.

Sometimes this is done by means of a switching on of an auxiliary field, which would make the thermodynamic state an equilibrium state, while leaving it inhomogeneous, as is done in the textbook of statistical physics by M. A. Leontovich [70]. However it is impossible to include a temperature inhomogeneity by means of any auxiliary field, unless one uses the somewhat artificial procedure of switching on a gravitational field, which obeys the general theory of relativity [9]. Therefore we shall make use of a different method, which is based on the introduction of Gibbs local equilibrium distributions.

20.1. Statistical Operator and Distribution Functions for a Local Equilibrium System.

The concept of a Gibbs statistical ensemble can be carried over to nonequilibrium stationary systems in the following manner.

In this case a Gibbs statistical ensemble will denote a collection of systems found in identical stationary external conditions, i.e., having identical types of contact with thermostats and semipermeable membranes and having all possible values of the microscopic parameters compatible with the given values of the microscopic parameters. The microscopic parameters are not assigned exactly, but to within definite small limits of the order of the possible fluctuations.

In a system found in stationary external conditions some stationary distribution is established, which we shall call stationary local equilibrium. If the external conditions depend on time, then the local equilibrium distribution will not be stationary. In order to define precisely the local equilibrium ensemble it is necessary to define the distribution function corresponding to it or the statistical operator.

Let a nonequilibrium state be specified by an inhomogeneous distribution of energy and particle number; the densities of these quantities correspond to the operators $H(x)$ and $n(x)$ (see (19.21a), (19.22)) or to the corresponding Fourier components

$$H_k = \int e^{-i(kx)} H(x)\,dx,$$
$$n_k = \int e^{-i(kx)} n(x)\,dx, \qquad (20.1)$$

which for a single component system have the form

$$H_k = \sum_q \frac{\hbar^2}{2m} (q, q+k)\, a_q^+ a_{q+k} + \\ + \frac{1}{2V} \sum_{k_1'+k_2'=k_1+k_2+k} \nu(k_2'-k_2)\, a_{k_1}^+ a_{k_2}^+ a_{k_2'} a_{k_1'}$$ (20.1a)

$$n_k = \sum_q a_q^+ a_{q+k} \qquad \left(H_k^+ = H_{-k},\ n_k^+ = n_{-k}\right).$$

We shall assume that these variables are sufficient to describe the macroscopic state of the system.

In the classical case H_k and n_k are the collective variables (19.19a).

We note that the zero^th Fourier components of the energy density and particle density are integrals of motion:

$$H_k|_{k=0} = H_0 = H, \qquad n_k|_{k=0} = n_0 = N.$$ (20.1b)

Thus, for sufficiently small k they are close to integrals of motion.

The simplest method of constructing the local equilibrium statistical operator (or distribution function) is based on information theory; the connection between information theory and statistical mechanics was discussed in §§4 and 10 (see [71,72]).

The statistical operator or distribution function is defined from the maximum of the information entropy, which in the quantum case is equal to (10.1)

$$S_u = -\langle \ln \rho \rangle = -\operatorname{Sp}(\rho \ln \rho) \quad (\operatorname{Sp}\rho = 1),$$ (20.2)

or in the classical case is equal to (4.5)

(20.2a)

$$S_u = -\langle \ln f \rangle = -\int f \ln f \, d\Gamma$$

with the auxiliary conditions that the average Fourier components of energy and particle density be constant upon variation of ρ or f

$$\langle H_k \rangle = \text{const}, \qquad \langle n_k \rangle = \text{const} \tag{20.2b}$$

and with the constant normalization

$$\langle 1 \rangle = \text{const}. \tag{20.2c}$$

Here the brackets denote either quantum or classical averaging.

As usual, we look for the absolute extremum of the function

$$S' = -\operatorname{Sp}(\rho \ln \rho) - \sum_k \beta_{-k} \operatorname{Sp}(\rho H_k) + \sum_k \nu_{-k} \operatorname{Sp}(\rho n_k) - \lambda \operatorname{Sp} \rho,$$

where $\beta_{-k}, \nu_{-k}, \lambda$ are Lagrange multipliers, defined by equations (20.2b,c). The extremum condition for S′, i.e., the equality to zero of its variation with respect to ρ, gives the statistical operator of the local equilibrium distribution:

$$\rho_l = Q_l^{-1} \exp\left\{-\sum_k (\beta_{-k} H_k - \nu_{-k} n_k)\right\}, \tag{20.3}$$

where

$$Q_l = \operatorname{Sp} \exp\left\{-\sum_k (\beta_{-k} H_k - \nu_{-k} n_k)\right\} \tag{20.3a}$$

is the corresponding statistical sum.

For the classical case we obtain by exactly the same method the local equilibrium distribution function:

$$f_l = Q_l^{-1} \exp\left\{-\sum_k (\beta_{-k} H_k - \nu_{-k} n_k)\right\}, \tag{20.4}$$

where

$$Q_l = \int \exp\left\{-\sum_k (\beta_{-k} H_k - \nu_{-k} n_k)\right\} d\Gamma. \tag{20.4a}$$

In external form (20.3) and (20.4) are identical; the difference is in the fact that in (20.3) H_k and n_k are operators, but in (20.4) they are functions of the coordinates and momenta of the particles.

Going over from the Fourier components H_k, n_k to the operators for the density of energy and particle number $H(x)$ and $n(x)$, we write (20.3) and (20.3a) in the form

$$\rho_l = Q_l^{-1} \exp\left\{-\int \beta(\boldsymbol{x})\,[H(\boldsymbol{x}) - \mu(\boldsymbol{x})\,n(\boldsymbol{x})]\,d\boldsymbol{x}\right\},$$

$$Q_l = \mathrm{Sp}\exp\left\{-\int \beta(\boldsymbol{x})\,[H(\boldsymbol{x}) - \mu(\boldsymbol{x})\,n(\boldsymbol{x})]\,d\boldsymbol{x}\right\}, \qquad (20.5)$$

where

$$\beta(\boldsymbol{x}) = \sum_k \beta_k e^{i(kx)}, \qquad \beta(\boldsymbol{x})\,\mu(\boldsymbol{x}) = \sum_k \nu_k e^{i(kx)}, \qquad (20.6)$$

and $\beta(x)$ plays the role of the local inverse temperature, and $\mu(x)$ of the local chemical potential.

For the classical case (20.4) and (20.4a) can be written in the same form as (20.5):

$$f_l = Q_l^{-1} \exp\left\{-\int \beta(\boldsymbol{x})\,[H(\boldsymbol{x}) - \mu(\boldsymbol{x})\,n(\boldsymbol{x})]\,d\boldsymbol{x}\right\}, \qquad (20.7)$$

$$Q_l = \int \exp\left\{-\int \beta(\boldsymbol{x})\,[H(\boldsymbol{x}) - \mu(\boldsymbol{x})\,n(\boldsymbol{x})]\,d\boldsymbol{x}\right\} d\Gamma.$$

In the particular case in which the temperature and chemical potential are spatially homogeneous, (20.7) and (20.5) go over into the Gibbs grand canonical distribution (3.30) and (9.42).

We have shown that (20.3) corresponds to the extremum of the information entropy. We shall now show that this extremum corresponds to a maximum, by making use of the inequality (10.2)

$$\mathrm{Sp}(\rho\ln\rho) \geqslant \mathrm{Sp}(\rho\ln\rho_l), \qquad (20.8)$$

which holds for any two statistical operators. The equality is attained only for $\rho = \rho_l$.

Substituting (20.3) into (20.8), we obtain

$$S_u = -\,\mathrm{Sp}(\rho\ln\rho) \leqslant \ln Q_l + \sum_k (\beta_{-k}\langle H_k\rangle - \nu_{-k}\langle n_k\rangle), \qquad (20.9)$$

where

$$\langle H_k\rangle = \mathrm{Sp}(\rho H_k) = \mathrm{Sp}(\rho_l H_k) = \langle H_k\rangle_l, \quad \langle n_k\rangle = \langle n_k\rangle_l. \qquad (20.9a)$$

Using (20.9a) the inequality (20.9) can be written in the form

$$S_u = -\operatorname{Sp}(\rho \ln \rho) \leqslant -\operatorname{Sp}(\rho_l \ln \rho_l), \tag{20.8a}$$

where the equality holds only for $\rho=\rho_l$.

Consequently, the local equilibrium distribution (20.3) (and also (20.4)) corresponds to a maximum of the information entropy with the auxiliary conditions that the average Fourier components of energy and particle number be constant and that the normalization be preserved.

In the general case for systems with conservation laws in the matrix form (19.48) the local equilibrium distribution has the form

$$\rho_l = Q_l^{-1} \exp\left\{ -\sum_{i,m} \int F_{im}(x,t) P_{mi}(x)\,dx \right\}. \tag{20.10}$$

The possibility of introducing a local equilibrium distribution is related to the fact that there exist two scales for the relaxation time, which are of different orders of magnitude [1,30]: the relaxation time τ for establishing statistical equilibrium in the entire system, which depends on the volume of the system, and another significantly smaller relaxation time $\tau_r \ll \tau$, which defines the time for establishing equilibrium in a volume which is macroscopically small, but which contains a large number of particles; this time does not depend on the volume of the entire system. A local equilibrium state is at first established in a time τ_r in such small volumes, and after this the system tends slowly to the Gibbs distribution with a characteristic time τ, if there are no external influences which prevent this.

The kinetic theory of gases is also founded on the existence of relaxation times of different orders of magnitude - the collision time, the time on the mean free path, and the time for establishing equilibrium in the entire volume. This idea was first enunciated and systematically developed as the basis for approximations in the work of N. N. Bogolyubov on dynamic problems in statistical physics [1].

Two scales for the relaxation time do not always exist. For highly dilute gases τ_r can be of the order of τ, and the local equilibrium distribution loses its meaning.

The local equilibrium distribution is sometimes introduced by means of nonrigorous intuitive considerations [30]. We shall give a brief account of these considerations. Let us assume that in a time τ_r in a macroscopically small volume ΔV around the point x a "quasi-Gibbs" distribution is established with local temperature $T(x)=\beta^{-1}(x)$ and chemical potential $\mu(x)$. It is proportional to the Gibbs factor

$$\exp\left\{-\beta(x)\left(\int\limits_{\Delta V} H(x)\,dx-\mu(x)\int\limits_{\Delta V} n(x)\,dx\right)\right\}.$$

Considering that such distributions in different volumes ΔV are statistically independent, we multiply these operators, and we come to the local equilibrium distribution (20.5). The weak point in this argument is that the operators $H(x)$ at different points do not commute, and the product of the exponentials is not equal to the exponential of the sum.

We shall now investigate the physical meaning of the parameters β_k and ν_k. They can be expressed in terms of $\langle H_k\rangle_l$ and $\langle n_k\rangle_l$ through the equations

$$\langle H_k\rangle_l=\mathrm{Sp}\,(\rho_l H_k),\qquad \langle n_k\rangle_l=\mathrm{Sp}\,(\rho_l n_k). \tag{20.11}$$

Differentiating $\ln Q_l$ with respect to β_{-k} and ν_{-k}, we obtain the relations

$$\langle H_k\rangle_l=-\left(\frac{\partial \ln Q_l}{\partial\beta_{-k}}\right)_\nu,\qquad \langle n_k\rangle_l=\left(\frac{\partial \ln Q_l}{\partial\nu_{-k}}\right)_\beta, \tag{20.12}$$

analogous to the thermodynamic equalities (3.33a).

We introduce the entropy of the local equilibrium distribution by the relationship

$$\begin{aligned} S=-\,\mathrm{Sp}\,(\rho_l\ln\rho_l)=\ln Q_l+\sum_k(\beta_{-k}\langle H_k\rangle_l-\nu_{-k}\langle n_k\rangle_l)= \\ =\ln Q_l+\int\beta(x)(\langle H(x)\rangle_l-\mu(x)\langle n(x)\rangle_l)\,dx. \end{aligned} \tag{20.13}$$

It can be regarded as a function of $\langle H_k\rangle_l$ and $\langle n_k\rangle_l$, if one considers β_k and ν_k to be expressed through $\langle H_k\rangle_l$ and $\langle n_k\rangle_l$ from the solution of the system of equations (20.12). Then we have

$$\beta_{-k}=\frac{\partial S}{\partial\langle H_k\rangle_l},\qquad \nu_{-k}=-\frac{\partial S}{\partial\langle n_k\rangle_l}, \tag{20.14}$$

because upon varying (20.13) the remaining terms cancel on the basis of (20.12).

Equalities (20.12) and (20.13) can be written also in the form of functional derivative relations:

$$\langle H(\boldsymbol{x})\rangle_l - \mu(\boldsymbol{x})\langle n(\boldsymbol{x})\rangle_l = -\left(\frac{\delta Q_l}{\delta\beta(\boldsymbol{x})}\right)_{\mu(\boldsymbol{x})}, \qquad \langle n(\boldsymbol{x})\rangle_l = \beta^{-1}(\boldsymbol{x})\left(\frac{\delta Q_l}{\delta\mu(\boldsymbol{x})}\right)_{\beta(\boldsymbol{x})} \tag{20.14a}$$

and

$$\beta(\boldsymbol{x}) = \frac{\delta S}{\delta\langle H(\boldsymbol{x})\rangle_l}, \qquad \mu(\boldsymbol{x})\beta(\boldsymbol{x}) = -\frac{\delta S}{\delta\langle n(\boldsymbol{x})\rangle_l}. \tag{20.14b}$$

The thermodynamic relations (20.12)-(20.14b) can be considered as a generalization to the nonequilibrium case of the usual thermodynamic relations (11.7), (11.24), and (11.25). This implies that $\beta(\mathbf{x})=T(\mathbf{x})^{-1}$ can be interpreted as the inverse temperature at the point $\mathbf{x}$, and $\mu(\mathbf{x})$ can be interpreted as the chemical potential at the same point.

The functional $Q_l[\beta(\mathbf{x}),\mu(\mathbf{x})]$ (20.5), (20.7) plays the role of the statistical sum (or statistical integral), and the functional $S(\langle H(\mathbf{x})\rangle_l, \langle n(\mathbf{x})\rangle_l)$ plays the role of the entropy; thus, for a local equilibrium state thermodynamic functionals play the role of thermodynamic functions.

The local equilibrium distribution is easily generalized to an l-component system with an inhomogeneous distribution of momentum density and particle number. In this case, in addition to the Fourier coefficients of the operators for energy density H_k and the number of particles of the α-component n_k^α, it is necessary to use the Fourier coefficient of the operator for momentum density $\mathbf{p}_k$:

$$p_k = \int e^{-i(kx)}\, p(x)\, dx, \qquad p(x) = \sum_\alpha m_\alpha j_\alpha(x). \tag{20.15}$$

In the representation of second quantization

$$p_k = \sum_{\alpha,\, q_\alpha} \hbar\left(q_\alpha + \frac{k}{2}\right) a^+_{q_\alpha} a_{q_\alpha + k}. \tag{20.15a}$$

For **k**=0 we have $H_0=H$, $n_0^\alpha=N_\alpha$, and $\mathbf{p}_0=\mathbf{P}$, where N_α is the number of particles of the type α, and $\mathbf{P}$ is the total momentum. All these quantities are integrals of motion; consequently, for small **k** they are slowly varying. This is evident if only from the fact that the conservation laws (19.30) in the momentum representation have the form

$$\frac{\partial H_k}{\partial t} = -k\cdot j_k^H, \qquad \frac{\partial p_k}{\partial t} = -k\cdot T_k, \qquad \frac{\partial n_k^\alpha}{\partial t} = -k\cdot j_k,$$

where the right-hand sides contain the small vector **k**.

Choosing the operators H_k, n_k^α, p_k to be fundamental, we define the statistical operator for the local equilibrium state by analogy with (20.3) from the extremum of the information entropy (20.2) with the auxiliary conditions:

$$\langle H_k\rangle = \text{const}, \quad \langle n_k^\alpha\rangle = \text{const}, \quad \langle p_k\rangle = \text{const}. \qquad (20.16)$$

Then

$$\rho_l = Q_l^{-1}\exp\left\{-\sum_k\left(\beta_{-k}H_k - \sum_\alpha \nu_{-k}^\alpha n_k^\alpha - \gamma_{-k}\cdot p_k\right)\right\}, \qquad (20.17$$

or

$$\rho_l = Q_l^{-1}\exp\left\{-\int\beta(x)\left[H(x) - \sum_\alpha\left(\mu_\alpha(x) - \frac{m_\alpha}{2}v^2(x)\right)n_\alpha(x) - v(x)\cdot p(x)\right]dx\right\}, \qquad (20.17a)$$

where the notation

$$\left(\mu_\alpha(x) - \frac{m_\alpha}{2}v^2(x)\right)\beta(x) = \nu_\alpha(x) = \sum_k \nu_k^\alpha e^{i(kx)},$$
$$v(x)\beta(x) = \gamma(x) = \sum_k \gamma_k e^{i(kx)} \qquad (20.17b)$$

has been introduced, and where

$$Q_l = \operatorname{Sp}\exp\left\{-\int\beta(x)\left[H(x) - \sum_\alpha\left(\mu_\alpha(x) - \frac{m_\alpha}{2}v^2(x)\right)n_\alpha(x) - v(x)\cdot p(x)\right]dx\right\} = \operatorname{Sp}\exp\left\{-\sum_k\left(\beta_{-k}H_k - \sum_\alpha \nu_{-k}^\alpha n_k^\alpha - \gamma_{-k}\cdot p_k\right)\right\} \qquad (20.17c)$$

is the statistical sum - a functional of the parameters (20.17b).

In expression (20.17a) $\beta(\mathbf{x})$ is the inverse temperature, $\mu_\alpha(\mathbf{x})$ is the chemical potential of the α-component, and $\mathbf{v}(\mathbf{x})$ is the mass velocity.

The physical meaning of such a choice of parameters is easy to understand. The average logarithm of ρ defines the entropy. In order to exclude systematic motion of the liquid, it is necessary to choose a system of coordinates moving together with the element of liquid with velocity **v**(x). In this system of coordinates we define the statistical operator

$$\rho_l = Q_l^{-1} \exp\left\{ - \int \beta(x) \left[H'(x) - \sum_{\alpha} \mu_\alpha(x)\, n'_\alpha(x) \right] dx \right\}, \tag{20.18}$$

where $H'(x)$ and $n'_\alpha(x) = n_\alpha(x)$ are the densities of energy and particle number of the type α in the moving system.

We go over by means of the canonical transformation (19.35) to the laboratory system, where the energy density H(x) and the momentum density **p**(x) are:

$$H'(x) = H(x) - v(x) \cdot p(x) + \frac{v^2(x)}{2} \rho(x), \tag{20.18a}$$

$$p'(x) = p(x) - \rho(x)\, v(x),$$

where

$$\rho(x) = \sum_{\alpha} m_\alpha n_\alpha(x) \tag{20.18b}$$

is the mass density operator.

Substituting (20.18a) into (20.18), we arrive at (20.17a).

We define the mass velocity **v**(x) by the relation

$$v(x) = \frac{\langle p(x) \rangle_l}{\langle \rho(x) \rangle_l}, \tag{20.19}$$

and therefore

$$\langle p'(x) \rangle_l = \mathrm{Sp}\,(\rho_l p(x)) = 0, \tag{20.19a}$$

i.e., the average momentum in the co-moving system is equal to zero.

It follows from (20.19) that the variational derivative of Q_l with respect to **v**(x) is equal to zero:

$$\frac{\delta \ln Q_l}{\delta v(x)} = \beta(x) \{ \langle p(x) \rangle_l - \langle \rho(x) \rangle_l\, v(x) \} = 0. \tag{20.19b}$$

If the average hydrodynamic velocities $\mathbf{v}_\alpha(\mathbf{x})$ and temperatures $T_\alpha(\mathbf{x}) = \beta_\alpha^{-1}(\mathbf{x})$ for the various components are considered distinct, then the statistical operator for the local equilibrium state with such a "separation" of temperature and velocities of the components can be defined in the form

$$\rho_l = Q_l^{-1} \exp\left\{-\sum_a \int \beta_a(x)\left[H'_a(x) - \mu_a(x)\, n'_a(x)\right] dx\right\}, \tag{20.20}$$

where for each component is chosen its own co-moving system of coordinates, moving with the velocity $v_\alpha(\mathbf{x})$. In this case, going over to the laboratory system, we write the statistical operator (20.20) in the form

$$\rho_l = Q_l^{-1} \exp\Big\{-\sum_a \int \beta_a(x)\Big[H_a(x) - \left(\mu_a(x) - \frac{m_a}{2} v_a^2(x)\right) n_a(x) - v_a(x) \cdot p_a(x)\Big] dx\Big\}, \tag{20.20a}$$

for which

$$\frac{\delta \ln Q_l}{\delta v_a(x)} = \beta_a(x)\{\langle p_a(x)\rangle_l - \langle \rho_a(x)\rangle_l\, v_a(x)\} = 0 \tag{20.20b}$$

$$(\rho_a(x) = m_a n_a(x)).$$

If the molecules are not spherical, then the transfer of angular momentum in collisions must be taken into account. In the same way as we introduced earlier in the velocity of hydrodynamic motion $\mathbf{v}(\mathbf{x})$, we can also introduce the average angular velocity of rotational motion $\omega(\mathbf{x})$. To do this it is first necessary to define the statistical operator in a system which is rotating locally with velocity $\omega(\mathbf{x})$, which is equal to the average velocity of rotational motion of the particles in the neighborhood of the given point. In this system the systematic rotation of the particles is compensated for by the motion of the system of coordinates (see [41]). The distribution function and the hydrodynamic equations for systems of molecules with internal angular momentum were considered earlier by Grad [73] and Curtiss [74]; the latter generalized the Boltzmann kinetic equation and the Chapman-Enskog theory to the case of molecules which do not have radial symmetry.

The calculation of average values by means of ρ_l is a rather complicated problem, although in the local approximation, if the parameters $\beta(\mathbf{x})$ and $\mu_\alpha(\mathbf{x})$ change little over distances of the order of the correlation length of the quantities $H(\mathbf{x})$ and $n(\mathbf{x})$, the leading term in the calculation of the averages is very simple. It is equal to

$$\langle A\rangle_l = (\langle A\rangle_0)_{\beta=\beta(x),\ \ldots,\ \mu_a=\mu_a(x)},$$

i.e., in equilibrium averages it is necessary to replace the equilibrium parameters by their position-dependent values. This relationship can be shown by summing the corresponding terms of the perturbation series.

20.2. Thermodynamic Equalities.

We obtain thermodynamic equalities for an inhomogeneous system by varying the statistical sum (20.17c):

$$Q_l = \mathrm{Sp}\exp\left\{-\sum_m \int F_m(x)\,P_m(x)\,dx\right\}, \qquad (20.17d)$$

where

$$\begin{aligned} F_0(x) &= \beta(x), & P_0(x) &= H(x), \\ F_1(x) &= -\beta(x)\,v(x), & P_1(x) &= p(x), \\ F_{a+1}(x) &= -\beta(x)\left(\mu_a(x) - \frac{m_a}{2}v^2(x)\right), & P_{a+1}(x) &= n_a(x) \end{aligned} \qquad (20.17e)$$

$$(a = 1,\ 2,\ \ldots),$$

over the local parameters $F_m(x)$, from which we have

$$\frac{\delta \ln Q_l}{\delta F_m(x)} = -\langle P_m(x)\rangle_l, \qquad (20.21)$$

or in more explicit form

$$\begin{aligned} -\frac{\delta \ln Q_l}{\delta\beta(x)} &= \langle H'(x)\rangle_l - \sum_a \mu_a(x)\,\langle n_a(x)\rangle_l, \\ \frac{\delta \ln Q_l}{\delta\mu_a(x)} &= \beta(x)\,\langle n_a(x)\rangle_l, \\ \frac{\delta \ln Q_l}{\delta v(x)} &= 0, \end{aligned} \qquad (20.21a)$$

where $H'(x)$ is the energy density in the co-moving system.

The relations (20.21a) are natural generalizations of the thermodynamic equalities (11.25), which hold for the case of statistical equilibrium.

From the relations (20.21a) in the variational derivatives we obtain for the total variation of Q_l:

$$\delta \ln Q_l = \int \Big\{ -(\langle H'(\mathbf{x})\rangle_l - \sum_a \mu_a(\mathbf{x}) \langle n_a(\mathbf{x})\rangle_l)\, \delta\beta(\mathbf{x}) + \\ + \beta(\mathbf{x}) \sum_a \langle n_a(\mathbf{x})\rangle_l\, \delta\mu_a(\mathbf{x}) \Big\}\, d\mathbf{x}. \tag{20.21b}$$

Denoting

$$\ln Q_l = -\int \beta(\mathbf{x})\, \Omega(\mathbf{x})\, d\mathbf{x}, \tag{20.21c}$$

we obtain

$$\int \Big\{ \delta(\beta(\mathbf{x})\, \Omega(\mathbf{x})) - \Big(\langle H'(\mathbf{x})\rangle_l - \sum_a \mu_a(\mathbf{x}) \langle n_a(\mathbf{x})\rangle_l\Big) \delta\beta(\mathbf{x}) + \\ + \beta(\mathbf{x}) \sum_a \langle n_a(\mathbf{x})\rangle_l\, \delta\mu_a(\mathbf{x}) \Big\}\, d\mathbf{x} = 0,$$

from which it follows, because the volume is arbitrary, that

$$\delta(\beta(x)\, \Omega(x)) = \langle H'(x)\rangle_l\, \delta\beta(x) - \sum_a \langle n_a(x)\rangle_l\, \delta(\beta(x)\, \mu_a(x)). \tag{20.22}$$

Equation (20.22) is called the Gibbs-Duhem relation.

We introduce the density of entropy S(x) by the relation

$$\beta^{-1}(x)\, S(x) = \langle H'(\mathbf{x})\rangle_l - \sum_a \mu_a(x) \langle n_a(\mathbf{x})\rangle_l - \Omega(\mathbf{x}), \tag{20.23}$$

analogous to (11.24), and rewrite the thermodynamic equality (20.22) in the form

$$-\delta\Omega(x) = S(x)\, \delta\beta^{-1}(x) + \sum_a \langle n_a(\mathbf{x})\rangle_l\, \delta\mu_a(\mathbf{x}) \tag{20.24}$$

$$\beta^{-1}(\mathbf{x})\, \delta S(x) = \delta\langle H'(x)\rangle_l - \sum_a \mu_a(\mathbf{x})\, \delta\langle n_a(\mathbf{x})\rangle_l. \tag{20.24a}$$

We introduce quantities computed with respect to a unit mass, namely

$$s(\mathbf{x}) = \frac{S(\mathbf{x})}{\langle \rho(\mathbf{x})\rangle_l} \tag{20.23a}$$

the entropy per unit mass,

$$u(x) = \frac{\langle H'(x)\rangle_t}{\langle \rho(x)\rangle_t} \tag{20.23b}$$

the energy per unit mass in the moving system, and

$$c_\alpha(x) = \frac{m_\alpha \langle n_\alpha(x)\rangle_t}{\langle \rho(x)\rangle_t} \tag{20.23c}$$

the relative mass concentration of particles of the α-component. Then the thermodynamic equality (20.24a) takes on the more familiar form

$$T(\boldsymbol{x})\,\delta s(\boldsymbol{x}) = \delta u(\boldsymbol{x}) + p(\boldsymbol{x})\,\delta v(\boldsymbol{x}) - \sum_\alpha \frac{\mu_\alpha(\boldsymbol{x})}{m_\alpha}\,\delta c_\alpha(\boldsymbol{x}), \tag{20.24b}$$

where

$$v(\boldsymbol{x}) = \frac{1}{\langle \rho(\boldsymbol{x})\rangle_t} \tag{20.24c}$$

is the specific volume per unit mass, and

$$p(\boldsymbol{x}) = -\,\Omega(\boldsymbol{x}) = T(\boldsymbol{x})\,S(\boldsymbol{x}) - \langle H'(\boldsymbol{x})\rangle + \sum_\alpha \mu_\alpha(\boldsymbol{x})\,\langle n_\alpha(\boldsymbol{x})\rangle_t \tag{20.24d}$$

is the pressure.

The thermodynamic equality (20.24b) is analogous to the equality (5.8), and (20.24d) is analogous to the relations (3.34) and (5.27) of equilibrium thermodynamics.

We have considered the variation of quantities in the co-moving system, moving with the center of mass of the element with velocity **v(x)**; consequently, (20.24b) can be written in the form of a relation in the total derivatives:

$$T(\boldsymbol{x})\,\frac{ds(\boldsymbol{x})}{dt} = \frac{du(\boldsymbol{x})}{dt} + p(\boldsymbol{x})\,\frac{dv(\boldsymbol{x})}{dt} - \sum_\alpha \mu_\alpha(\boldsymbol{x})\,\frac{dc_\alpha(\boldsymbol{x})}{dt}, \tag{20.24e}$$

where

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v(x) \cdot \nabla.$$

The relation (20.24e) is usually postulated in nonequilibrium thermodynamics as an expression of the hypothesis about local equilibrium [27].

20.3. Fluctuations in a Local Equilibrium Ensemble.

The local equilibrium distribution (20.17a) allows one to calculate fluctuations in the densities of energy, particle number, and momentum through the variation of the average values of the densities of these physical quantities with respect to local parameters $\beta(x)$, $\mu_\alpha(x)$, and $v(x)$, just as in §§ 6 and 12 for the Gibbs grand ensemble the fluctuations of mechanical quantities were expressed through derivatives of their average values with respect to the corresponding parameters.

We shall calculate the variation of the average value of an arbitrary operator $A(x)$ with respect to $\beta(x)$, $\mu_\alpha(x)$, and $v(x)$. We have

$$\langle A(x) \rangle_l = Q_l^{-1} \operatorname{Sp} \left\{ e^{-\int \beta(x) \tilde{H}(x) dx} A(x) \right\}, \tag{20.25}$$

where

$$\tilde{H}(x) = H(x) - \sum_\alpha \left[\mu_\alpha(x) - \frac{m_\alpha}{2} v^2(x) n_\alpha(x) \right] - v(x) \cdot p(x) = $$
$$= H'(x) - \sum_\alpha \mu_\alpha(x) n_\alpha(x). \tag{20.25a}$$

Noting that for any operator the variation of an exponential is equal to (12.13), and taking into account that the variation of Q_l gives the thermodynamic relations (20.21), we obtain

$$\begin{aligned} \frac{\delta \langle A(x) \rangle_l}{\delta \beta(x')} &= -(A(x), \tilde{H}(x')), \\ \frac{\delta \langle A(x) \rangle_l}{\delta \mu_a(x')} &= \beta(x')(A(x), n_a(x')), \\ \frac{\delta \langle A(x) \rangle_l}{\delta v(x')} &= \beta(x')(A(x), p(x') - \rho(x') v(x')), \end{aligned} \tag{20.26}$$

where the following notation has been introduced for the quantum correlation functions:

$$(A(x), B(x')) = \int_0^1 \langle (A(x) - \langle A(x)\rangle_l)(B(x', i\tau) - \langle B(x')\rangle_l)\rangle_l \, d\tau, \tag{20.26a}$$

$$B(i\tau) = e^{-\tau \int \beta(x)\tilde{H}(x)\,dx} B e^{\tau \int \beta(x)\tilde{H}(x)\,dx}. \tag{20.26b}$$

The notation (20.26a) and (20.26b) is analogous to that used earlier in § 12 in equations (12.18) and (12.16). In the limiting case of classical mechanics the quantum correlation functions (20.26a) go over into the classical correlation functions:

$$(A(x), B(x')) = \langle (A(x) - \langle A(x)\rangle_l)(B(x') - \langle B(x')\rangle_l)\rangle_l. \tag{20.26c}$$

From (20.26) we find the fluctuations in the densities of energy, particle number, and momentum:

$$\begin{aligned} \frac{-\delta\langle H(x)\rangle_l}{\delta\beta(x')} &= (H(x), \tilde{H}(x')), \\ \frac{\delta\langle n_a(x)\rangle_l}{\delta\mu_\beta(x')} &= \beta(x')(n_a(x), n_\beta(x')), \\ \frac{\delta\langle p(x)\rangle_l}{\delta v(x')} &= \beta(x')(p(x), p(x') - \rho(x')v(x')). \end{aligned} \tag{20.27}$$

Other variational derivatives can also be expressed in terms of the correlation functions in a similar fashion.

Let us consider the more general case of a nonequilibirum ensemble in which the state is defined not only by H(x), n_α(x), and p(x), but also by the quantities ξ_k(x), which in general are not the densities of integrals of motion. In this case one can also construct a statistical operator, which defines the specified average values of ξ_k(x), which are equal to the averages $<\xi_k(x)>_l$ over a local equilibrium state.

The statistical operator with a fixed value of $<\xi_k(x)>$, corresponding to the maximum of the information entropy (20.2), has the form

$$\begin{aligned} \rho_l = Q_l^{-1} \exp\Big\{ -\int \beta(x) \Big[H(x) - \sum_a \Big(\mu_a(x) - \\ - \frac{m_a}{2} v^2(x) n_a(x) \Big) - v(x) \cdot p(x) + \sum_k a_k(x)\xi_k(x) \Big] dx \Big\}, \end{aligned} \tag{20.28}$$

where $\alpha_k(x)$ is an auxiliary field, which makes $\langle\xi_k(x)\rangle_l \neq 0$. The average value $\langle\xi_k(x)\rangle$ corresponds to the state (20.28), and it is equal to

$$\langle\xi_k(x)\rangle_l = -\frac{1}{\beta(x)}\frac{\delta \ln Q_l}{\delta a_k(x)}, \tag{20.29}$$

where the variation is carried out with constant $\beta(x)$ and $\mu_\alpha(x)$ and variable $\alpha_k(x)$.

It is convenient to write the statistical operator (20.28) in a more symmetric form:

$$\rho = \exp\left\{-\Phi[F_0(x), \ldots, F_n(x)] - \sum_{i=0}^{n}\int F_i(x) P_i(x)\, dx\right\}, \tag{20.30}$$

where

$$\begin{aligned} F_0(x) &= \beta(x), & P_0(x) &= H(x), \\ F_1(x) &= -\beta(x) v(x), & P_1(x) &= p(x), \\ F_{\alpha+1}(x) &= -\beta(x)\left[\mu_\alpha(x) - \frac{m_\alpha}{2} v^2(x)\right], & P_{\alpha+1}(x) &= n_\alpha(x) \\ F_i(x) &= \beta(x) a_i(x), & P_i(x) &= \xi_i(x) \end{aligned} \tag{20.30a}$$

$$(\alpha = 1, 2, \ldots, l;\ i = l+1, \ldots, n)$$

$$\Phi[F_0(x), \ldots, F_n(x)] = \ln Q \tag{20.30b}$$

is the Massieu-Planck functional.

In §§ 6 and 12 it was shown that in the theory of fluctuations it is very convenient to use the Massieu-Planck function (6.4) and (12.7). The Massieu-Planck functional (20.30b) also turns out to be very useful in the study of fluctuations in spatially inhomogeneous systems [3].

We write the statistical operator (20.30) in the form

$$\rho = \exp\left\{-S - \sum_{i=0}^{n}\int F_i(x)\left(P_i(x) - \langle P_i(x)\rangle_l\right) dx\right\}, \tag{20.31}$$

where

$$S = \Phi + \sum_{i=0}^{n}\int F_i(x)\langle P_i(x)\rangle_l\, dx \tag{20.31a}$$

is the entropy, considered as a functional of $\langle P_i(x)\rangle_l$. The relation (20.31a) is the analog for thermodynamic functionals of the Legendre transformation

(3.10b) for thermodynamic functions.

From the normalization condition of the statistical operator in the form (20.30)

$$\Phi = \ln \operatorname{Sp} \exp \left\{ -\sum_{i=0}^{n} \int F_i(x) P_i(x)\, dx \right\}, \tag{20.32}$$

we obtain, by varying it with respect to $F_i(x)$, the thermodynamic equalities

$$\frac{\delta \Phi}{\delta F_i(x)} = -\langle P_i(x) \rangle_l \qquad (i = 0,\ 1,\ \ldots,\ n). \tag{20.33}$$

Analogously, from the normalization condition for the statistical operator in the form (20.31)

$$S = \ln \operatorname{Sp} \exp \left\{ -\sum_{i=0}^{n} \int F_i(x) (P_i(x) - \langle P_i(x) \rangle_l)\, dx \right\}, \tag{20.34}$$

we obtain by varying it with respect to $\langle P_i(x) \rangle_l$ the thermodynamic equalities

$$\frac{\delta S}{\delta \langle P_i(x) \rangle_l} = F_i(x). \tag{20.35}$$

We express fluctuations in terms of the variation of the average value of $\langle P_i(x) \rangle_l$ with respect to $F_m(x)$. We have

$$\delta \langle P_i(x) \rangle_l = \operatorname{Sp} (P_i(x)\, \delta\rho).$$

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Making use of (20.30), (12.13), and (20.33) we obtain for the variation of $\delta\rho$

$$\delta\rho = -\sum_{i=0}^{n} \int_0^1 \int e^{-A\tau} (P_i(x') - \langle P_i(x') \rangle_l)\, e^{A\tau}\, e^{-A}\, \delta F_i(x')\, d\tau\, dx',$$

where

$$A = \Phi + \sum_i \int F_i(x) P_i(x)\, dx. \tag{20.36}$$

Consequently,

$$\delta\langle P_i(x)\rangle_l = -\sum_m \int (P_i(x),\ P_m(x'))\,\delta F_m(x')\,dx', \tag{20.37}$$

where

$$(P_i(x),\ P_m(x')) = \int_0^1 \langle P_i(x)\,e^{-A\tau}(P_m(x') - \langle P_m(x')\rangle_l)\,e^{A\tau}\rangle_l\,d\tau. \tag{20.37a}$$

It follows from (20.37) that the quantum correlation function (20.37a) is expressed through the variational derivative of $\langle P_i(x)\rangle_l$ with respect to $F_m(x')$:

$$\frac{\delta\langle P_i(x)\rangle_l}{\delta F_m(x')} = -(P_i(x),\ P_m(x')). \tag{20.37b}$$

We shall generalize the Einstein thermodynamic theory of fluctuations [75,76], discussed in § 6 for the equilibrium case, to the case of a local equilibrium state, following [3]. For the local equilibrium distribution (20.30) one can introduce a macroscopic functional or macroscopic distribution function, similar to the function (6.11).

We introduce a macroscopic distribution function W for the Fourier components P_k^i of the variables $P_i(x)$

$$P_k^i = \int P_i(x)\,e^{-i(kx)}\,dx, \quad F_i^k = \frac{1}{V}\int F_i(x)\,e^{-i(kx)}\,dx \qquad (i = 0,\ 1,\ \ldots,\ n), \tag{20.38}$$

which gives the probability that the parameters $\ldots P_k^0 \ldots P_k^n \ldots$ lie in the region $\ldots \Delta P_k^0 \ldots \Delta P_k^n \ldots$ around the point $\ldots P_k^0 \ldots P_k^n \ldots$:

$$\begin{aligned} W\,\Delta P_k^0 \ldots \Delta P_k^n &= \Omega\,\Delta P_k^0 \ldots \Delta P_k^n \exp\Big\{-\Phi - \sum_{k,\,i} F_{-k}^i P_k^i\Big\} = \\ &= \Omega\,\Delta P_k^0 \ldots \Delta P_k^n \exp\Big\{-\Phi - \sum_i \int F_i(x)\,P_i(x)\,dx\Big\}, \end{aligned} \tag{20.39}$$

where the quantities P_k^i are considered now not as operators, but as ordinary functions, although we make use of the same notation as for the corresponding operators.

The quantity $\Omega\Delta P^0_k\ldots\Delta P^n_k$ can be interpreted as the number of microstates in the region $\ldots\Delta P^0_k\ldots\Delta P^n_k\ldots$. It can be estimated from the entropy s of the microcanonical ensemble, in which the parameters $\ldots P^0_k\ldots P^n_k\ldots$ are specified in the region $\ldots\Delta P^0_k\ldots\Delta P^n_k\ldots$:

$$s = \ln\frac{\Omega}{\Omega_0}, \tag{20.40}$$

where Ω_0 is a constant which is at the present time not essential to us, and which we shall define later from the normalization condition for W.

Using (20.40) and (20.34), we write the macroscopic distribution function (20.39) in the form

$$\begin{aligned} W &= \Omega_0 \exp\left\{-\Phi + s - \sum_i \int F_i(x)\, P_i(x)\, dx\right\} = \\ &= \Omega_0 \exp\left\{s - S - \sum_i \int F_i(x)\left(P_i(x) - \langle P_i(x)\rangle_l\right) dx\right\}, \end{aligned} \tag{20.39a}$$

where S is the entropy in the local equilibrium grand canonical ensemble (20.31a).

As a consequence of the equivalence of statistical ensembles, which was demonstrated in § 13, the entropy in the local equilibrium grand canonical ensemble is the same function of $\langle P^0_k\rangle,\ldots,\langle P^n_k\rangle$ as the entropy in the local equilibrium microcanonical ensemble is of $P^0_k,\ldots,P^n_k$, i.e., S and s are identical functions, but of different variables. Therefore it is convenient to expand s-S in a functional series in $\Delta P_i(\mathbf{x}) = P_i(\mathbf{x}) - \langle P_i(\mathbf{x})\rangle_l$ and to retain, because of the smallness of the fluctuations, only terms through second order:

$$\begin{aligned} s - S &= \sum_i \int F_i(x)\, \Delta P_i(x)\, dx + \\ &+ \frac{1}{2}\sum_{im} \int\int \frac{\delta^2 S}{\delta\langle P_i(x_1)\rangle_l\, \delta\langle P_m(x_2)\rangle_l}\, \Delta P_i(x_1)\, \Delta P_m(x_2)\, dx_1\, dx_2. \end{aligned} \tag{20.41}$$

Substituting (20.41) into (20.39a) and using the fact that the linear terms cancel, we obtain

$$W = A\exp\left\{\frac{1}{2}\sum_{im}\int\int\frac{\delta^2 S}{\delta\langle P_i(\boldsymbol{x}_1)\rangle_l\,\delta\langle P_m(\boldsymbol{x}_2)\rangle_l}\Delta P_i(\boldsymbol{x}_1)\,\Delta P_m(\boldsymbol{x}_2)\,d\boldsymbol{x}_1\,d\boldsymbol{x}_2\right\}, \tag{20.42}$$

or

$$W = A\exp\left\{-\frac{1}{2}\sum_{im}\int\int f_{im}(\boldsymbol{x}_1, \boldsymbol{x}_2)\,\Delta P_i(\boldsymbol{x}_1)\,\Delta P_m(\boldsymbol{x}_2)\,d\boldsymbol{x}_1\,d\boldsymbol{x}_2\right\}, \tag{20.42a}$$

where

$$f_{im}(\boldsymbol{x}_1, \boldsymbol{x}_2) = -\frac{\delta^2 S}{\delta\langle P_i(\boldsymbol{x}_1)\rangle_l\,\delta\langle P_m(\boldsymbol{x}_2)\rangle_l} \tag{20.42b}$$

is a function which describes the correlation of fluctuations in space, and which we shall consider again below.

Formulas (20.41)-(20.42b) are a direct generalization of formulas (6.14)-(6.17a).

There exist especially simple relations for the fluctuations, if the parameters $F_i(\mathbf{x})$ and the quantity $P_i(\mathbf{x})$ are expressed in the Fourier representation (20.38). Then

$$\rho = \exp\left\{-\Phi - \sum_{i,\,k} F_i^{-k} P_k^i\right\}. \tag{20.43}$$

The entropy (20.31a) is now already not a functional, but a function of the Fourier components of $\langle P_k^i\rangle$.

Instead of the thermodynamic equalities (20.33) in terms of variational derivatives we obtain relations in terms of ordinary derivatives

$$\frac{\partial\Phi}{\partial F_i^{-k}} = -\langle P_k^i\rangle_l \tag{20.44}$$

and for the quantum correlation functions we obtain the expressions

$$(P_{k_1}^i, P_{k_2}^m) = -\frac{\partial\langle P_{k_1}^i\rangle_l}{\partial F_m^{-k_2}} = -\frac{\partial\langle P_{k_2}^m\rangle_l}{\partial F_i^{-k_1}}, \tag{20.44a}$$

analogous to the formulas (20.33) and (20.37b).

In the Fourier representation the macroscopic distribution function (20.42) has the form

$$W = A \exp\left\{ \frac{1}{2} \sum_{\substack{im \\ k_1 k_2}} \frac{\partial^2 S}{\partial \langle P^i_{k_1} \rangle_l \partial \langle P^m_{k_2} \rangle_l} \Delta P^i_{k_1} \Delta P^m_{k_2} \right\}, \qquad (20.45)$$

where $\Delta P^i_k = P^i_k - \langle P^i_k \rangle_l$. As before we regard the quantity P^i_k not as a dynamical variable, but as an ordinary variable. Thus, the Gaussian distribution (20.45) is approximately valid for the Fourier components of P^i_k.

The argument of the exponential (20.45) can be expressed in terms of the correlation function. In this connection,

$$\frac{\partial S}{\partial \langle P^i_k \rangle_l} = F_i^{-k}, \qquad (20.45a)$$

where S is the entropy (20.31a). Consequently,

$$- \sum_{m' k'_2} \frac{\partial^2 \Phi}{\partial F_i^{-k_1} \partial F_{m'}^{-k'_2}} \frac{\partial^2 S}{\partial \langle P^{m'}_{k'_2} \rangle_l \partial \langle P^m_{k_2} \rangle_l} =$$

$$= \sum_{m' k'_2} \frac{\partial \langle P^i_{k_1} \rangle_l}{\partial F_{m'}^{-k'_2}} \frac{\partial F_{m'}^{-k'_2}}{\partial \langle P^m_{k_2} \rangle_l} = \frac{\partial \langle P^i_{k_1} \rangle_l}{\partial \langle P^m_{k_2} \rangle_l} = \delta^{im}_{k_1 k_2}, \qquad (20.45b)$$

analogous to the formula (6.24). Thus, the matrices of the second derivatives of Φ and S are mutual inverses.

Formula (20.45) describes the correlation of the Fourier components (20.38) and, thus, expresses the connection between fluctuations at different points. If one takes into account the correlation only between the Fourier coefficients P^i_k and $P^m_{-k} = P^{m*}_k$, i.e., if one makes use of the nearness of the state to a spatially homogeneous state, then the formula (20.45) can be approximately written in the form

$$W = A \exp\left\{ -\frac{1}{2V} \sum_{i,m,k} f_k^{im} \Delta P_k^i \Delta P_{-k}^m \right\}, \tag{20.46}$$

where

$$f_k^{im} = \int f_{im}(x) e^{-i(xk)} dx = -V \frac{\partial^2 S}{\partial \langle P_k^i \rangle_l \partial \langle P_{-k}^m \rangle_l}, \quad f_k^{im} = f_{-k}^{mi}. \tag{20.46a}$$

The effect of such a spatial correlation is the basis for the theory of fluctuations near a critical point (Ornstein and Zernike [77]). This theory was developed further in the article by Klein and Tisza [78]; we shall discuss it in the following section, following [3].

20.4. Critical Fluctuations.

Using the probability distribution functions (20.45) and (20.46) one can study fluctuations near a critical point, where they can increase dramatically.

We shall first consider some exact relations for fluctuations.

It is convenient to write the distribution function (20.45) in the form of an exponential of the complete contraction of a product of matrices with elements i,m:

$$W = A \exp\left\{ -\frac{1}{2V} \sum_{k_1 k_2} f_{k_1 k_2} : \Delta P_{k_1} \Delta P_{-k_2} \right\}, \tag{20.47}$$

where $f_{k_1 k_2}$ is a matrix with elements

$$f_{k_1 k_2}^{im} = \frac{1}{V} \int f_{im}(x_1, x_2) e^{-i(k_1 x_1) + i(k_2 x_2)} dx_1 dx_2 = -V \frac{\partial^2 S}{\partial \langle P_{k_1}^i \rangle_l \partial \langle P_{-k_2}^m \rangle_l}, \tag{20.47a}$$

ΔP_k is a vector with components ΔP_k^i, and the symbol : denotes the complete contraction of a product of matrices. In the coordinate representation the function (20.47) has the form

$$W = A \exp\left\{ -\frac{1}{2} \int f(x_1, x_2) : \Delta P(x_1) \Delta P(x_2) dx_1 dx_2 \right\}. \tag{20.47b}$$

The distribution function (20.47) can be written in a still more compact form:

$$W = A\exp\left\{-\frac{1}{2V} f : \Delta P \Delta P^{+}\right\}, \qquad (20.47c)$$

where f is a matrix with elements $f^{im}_{k_1k_2}$, ΔP is a matrix with elements ΔP^{i}_{k}, and the symbol : denotes a contraction over all indices im, k_1k_2.

Fluctuations calculated by means of a Gaussian distribution function, as is well known (see formula (6.22)), are expressed through the matrix which is inverse to f, i.e.,

$$g = \frac{1}{V}\langle \Delta P \Delta P^{+}\rangle = f^{-1}, \qquad (20.48)$$

or in explicit form

$$\sum_{k_1} f_{kk_1} g_{k_1k'} = \delta_{kk'}, \qquad (20.48a)$$

where $\delta_{kk'}$ is the Kronecker symbol. On the left hand side of (20.48a) is understood also a contraction over all indices, except i and m, and on the right hand side is understood a unit matrix in the indices i and m; these indices will not be written out explicitly. Thus, (20.48a) coincides with (20.45b).

In the x-representation equation (20.48a) is an integral equation

$$\int f(x_1, x_1)\, g(x_1, x')\, dx_1 = \delta(x - x'), \qquad (20.49)$$

where

$$g(x_1, x') = \frac{1}{V}\sum_{k,k_2} e^{i(k,x_1) - i(k_2,x')} g_{k,k_2} = (P(x_1), P(x')). \qquad (20.49a)$$

Equation (20.49) can be satisfied only if f and g have δ-type singularities when their arguments are identical (similar characteristics of correlation functions are well known in the theory of fluctuations). Consequently, it is convenient to regularize this equation by separating out the δ-type singularities. We introduce instead of f and g the functions f_1 and g_1, which already have no such singularities:

$$f(x, x_1) = A(x)\left(\delta(x - x_1) - f_1(x, x_1)\right), \qquad (20.50)$$
$$g(x_1, x') = A_1(x')\left(\delta(x_1 - x') + g_1(x_1, x')\right).$$

We find the function $A_1(\mathbf{x})$ by integrating the second of relations (20.50) twice over a small volume ΔV near the point $\mathbf{x}=\mathbf{x}_1$, the dimensions of which are chosen such that the contribution from g_1 can be neglected. Then

$$\left\langle \int_{\Delta V} \Delta P(\boldsymbol{x}')\,d\boldsymbol{x}' \int_{\Delta V} \Delta P(\boldsymbol{x}')\,d\boldsymbol{x}' \right\rangle = \int_{\Delta V} A_1(\boldsymbol{x}')\,d\boldsymbol{x}',$$

from which we find, by applying the mean value theorem,

$$A_1(\boldsymbol{x}) = (\Delta V^{-1}) \left\langle \int_{\Delta V} \Delta P(\boldsymbol{x})\,d\boldsymbol{x} \int_{\Delta V} \Delta P(\boldsymbol{x})\,d\boldsymbol{x} \right\rangle.$$

For the volume ΔV one can choose the volume per particle, $\Delta V=\langle n(\mathbf{x})\rangle^{-1}$; in this case, of course, the condition that ΔV be small will be satisfied.

Substituting (20.50) into (20.49), we obtain an integral equation for g_1:

$$\begin{gathered} g_1(\boldsymbol{x}, \boldsymbol{x}') = f_1(\boldsymbol{x}, \boldsymbol{x}') + \int f_1(\boldsymbol{x}, \boldsymbol{x}_1)\, g_1(\boldsymbol{x}_1, \boldsymbol{x}')\,d\boldsymbol{x}', \\ A(\boldsymbol{x})\, A_1(\boldsymbol{x}) = 1. \end{gathered} \qquad (20.51)$$

This is the Ornstein-Zernike integral equation for the inhomogeneous case [3]. The function f_1 is usually called the direct correlation function. The function g_1 satisfies a normalization condition, which is obtained from the second of equations (20.50) by means of a double integration over $\mathbf{x}_1, \mathbf{x}'$:

$$\int\int A_1(\boldsymbol{x}')\, g_1(\boldsymbol{x}_1, \boldsymbol{x}')\,d\boldsymbol{x}_1\,d\boldsymbol{x}' = \langle \Delta P\, \Delta P \rangle - \int A_1(\boldsymbol{x})\,d\boldsymbol{x}, \qquad (20.51a)$$

where

$$\Delta P = \int \Delta P(\boldsymbol{x})\,d\boldsymbol{x}, \quad \langle \Delta P\, \Delta P \rangle = -\frac{\partial \langle P \rangle}{\partial \bar{F}}, \quad \bar{F} = \frac{1}{V} \int F(\boldsymbol{x})\,d\boldsymbol{x}.$$

For the homogeneous case f_1 and g_1 depend only on the difference of the arguments, and equation (20.51a) goes over into the usual Ornstein-Zernike equation [77-79]:

$$g_1(\mathbf{x}-\mathbf{x}') = f_1(\mathbf{x}-\mathbf{x}') + \int f_1(\mathbf{x}-\mathbf{x}_1)\, g_1(\mathbf{x}_1-\mathbf{x}')\, d\mathbf{x}_1 \tag{20.52}$$

with the normalization condition

$$\int g_1(x)\, dx = -\frac{1}{V}\frac{\partial\langle P\rangle}{\partial \bar{F}}\frac{1}{A} - 1. \tag{20.52a}$$

The spatially homogeneous case can be considered, by proceeding directly from (20.46):

$$W = A\exp\left\{-\frac{1}{2V}\sum_{k} f_k : \Delta P_k\, \Delta P_k^{*}\right\}, \tag{20.53}$$

where f_k is a matrix with elements f_k^{lm}, for which

$$f_k = \int f(x)\, e^{-i(kx)}\, dx = -V\frac{\partial^2 S}{\partial\langle P_k\rangle_l \langle \partial P_k^{*}\rangle_l} = f_{kk}. \tag{20.53a}$$

Instead of (20.48a) we shall have the quite simple expression

$$f_k g_{-k} = 1, \tag{20.54}$$

which is equivalent to the integral equation

$$\int f(\mathbf{x}-\mathbf{x}_1)\, g(\mathbf{x}_1-\mathbf{x}')\, d\mathbf{x}_1 = \delta(\mathbf{x}-\mathbf{x}'). \tag{20.54a}$$

After regularizing this equation we again come to the usual Ornstein-Zernike equation.

Let us now consider the solution of the Ornstein-Zernike equation. In solving equation (20.52) one assumes that the function $f(\mathbf{x})$ falls off sufficiently rapidly with distance that its even moments $\int \mathbf{x}^{2n} f(\mathbf{x})\, d\mathbf{x}$ are finite, and the odd moments are equal to zero because of the spatial isotropy. One expands the function $g(\mathbf{x})$ in a Taylor series and keeps terms through second order, which reduces the integral equation to a differential equation [79]. The same results can be obtained in a simpler fashion by expanding f_k in (20.53) in a series in k^2 and keeping several terms, which we shall also do later.

Let us investigate the behavior of the fluctuation correlation function

$$\langle \Delta P_i(x)\, \Delta P_m(x') \rangle$$

at large distances $|\mathbf{x}-\mathbf{x}'|$ in the case of spatial homogeneity. To do this we expand f_k^{im} of (20.53a) in a series in powers of k^2, keeping terms through k^4. The expansion in small values of **k** implies that we are considering the behavior of the correlation function for large $|\mathbf{x}-\mathbf{x}'|$. The coefficients for odd powers of **k** are equal to zero because of the spatial isotropy of $f(\mathbf{x})$. We have

$$f_k^{im} = a_{im} + b_{im} k^2 + c_{im} k^4, \qquad (20.55)$$

where

$$a_{im} = \int f_{im}(\mathbf{x})\, d\mathbf{x}, \quad b_{im} = -\frac{1}{3!} \int f_{im}(\mathbf{x})\, \mathbf{x}^2\, d\mathbf{x},$$
$$c_{im} = \frac{1}{5!} \int f_{im}(\mathbf{x})\, \mathbf{x}^4\, d\mathbf{x}. \qquad (20.55a)$$

In this we assume that the integrals (20.55a) converge, i.e., that $f_{im}(\mathbf{x})$ is a short range function.

At a critical point the zero order term of this expansion, i.e., the matrix

$$f_0 = a = \int f(\mathbf{x})\, d\mathbf{x} = -V \frac{\partial^2 S}{\partial(P_\alpha)\, \partial(P_\beta)} = -V \frac{\partial^2 S}{\partial(P_i)\, \partial(P_m)} \qquad (20.55b)$$

becomes positive semidefinite, which corresponds to the stability limit. In this case the determinant of the matrix f_0^{im} is zero

$$|f_0^{im}| = 0, \qquad (20.55c)$$

and the inverse matrix to f_0, which in accordance with (20.48) determines the fluctuations, approaches infinity. Therefore, if correlations between fluctuations at different points were not taken into account, the fluctuations would become infinite. In reality the fluctuations only increase strongly at the critical point, and this increase is suppressed by the correlations between the fluctuations.

The average value of the fluctuations is expressed by the inverse of the matrix f_k, i.e.,

$$\langle \Delta P^l_{\boldsymbol{k}}\, \Delta P^m_{-\boldsymbol{k}} \rangle = V\left(a + bk^2 + ck^4\right)^{-1}_{lm}. \tag{20.56}$$

The Ornstein-Zernike theory follows from (20.56) with c=0. The case with c≠0 also presents no difficulty.

For the correlation function

$$g_{lm}(\boldsymbol{x} - \boldsymbol{x}') = \frac{1}{V}\sum_{\boldsymbol{k}} \langle \Delta P^l_{\boldsymbol{k}}\, \Delta P^m_{-\boldsymbol{k}} \rangle\, e^{i(\boldsymbol{k},\, \boldsymbol{x}-\boldsymbol{x}')} \tag{20.57}$$

we obtain the expression

$$g_{lm}(\boldsymbol{x} - \boldsymbol{x}') = \sum_{\boldsymbol{k}} (a + bk^2 + ck^4)^{-1}_{lm}\, e^{i(\boldsymbol{k},\, \boldsymbol{x}-\boldsymbol{x}')}, \tag{20.57a}$$

which satisfies the differential equation

$$(a - b\nabla^2 + c\nabla^4)\, g(\boldsymbol{x}) = V\,\delta(\boldsymbol{x}), \tag{20.58}$$

where g(x) is a matrix with elements $g_{lm}(x)$. The differential equation (20.58) is considered in the Ornstein-Zernike theory with c=0. One can find g(x) by solving this equation, but it is simpler to calculate the integral (20.57a) directly.

In the case considered by Ornstein and Zernike (c=0) we obtain for the fluctuation correlation function in a diagonal representation

$$g_{ii}(r) = \frac{V}{2\pi^2}\,\frac{1}{r}\int_0^\infty (a_{ii} + b_{ii}k^2)^{-1}\sin(kr)\,k\,dk = \frac{V b_{ii}^{-1}}{4\pi r}\, e^{-\sqrt{a_{ii}/b_{ii}}\, r}, \quad \text{if} \quad a_{ii}/b_{ii} > 0, \tag{20.59}$$

i.e., an exponential decay with distance. Here α_{ii}, b_{ii}, and c_{ii} are the expansion coefficients of f_k in a diagonal representation.

At a critical point, i.e., for α_{ii}=0, we obtain

$$g_{ii}(r) \cong \frac{V}{4\pi b_{ii}}\,\frac{1}{r}, \tag{20.59a}$$

i.e., the fluctuations die out very slowly.

In the more general case in which $c_{ii} \neq 0$, we obtain

$$g_{ii}(r) = \frac{V}{2\pi^2}\frac{1}{r}\int_0^\infty (a_{ii} + b_{ii}k^2 + c_{ii}k^4)^{-1} \sin(kr)\, k\, dk =$$

$$= \frac{V}{4\pi}\frac{1}{r} \operatorname{Re} \{(b_{ii}^2 - 4a_{ii}c_{ii})^{-1/2}(e^{-\alpha_1 r} - e^{-\alpha_2 r})\}, \tag{20.59b}$$

where

$$\alpha_1^2 = -\frac{1}{2}c_{ii}^{-1}\left(b_{ii} - \sqrt{b_{ii}^2 - 4a_{ii}c_{ii}}\right),$$

$$\alpha_2^2 = -\frac{1}{2}c_{ii}^{-1}\left(b_{ii} + \sqrt{b_{ii}^2 - 4a_{ii}c_{ii}}\right),$$

if $\operatorname{Re}\alpha_1 > 0$, $\operatorname{Re}\alpha_2 > 0$.

Thus, the fluctuations decay exponentially and oscillate. At a critical point $\alpha_{ii} = 0$, $\alpha_1 = 0$, and $\alpha_2^2 = -b_{ii}/c_{ii}$. Consequently,

$$g(r) = \frac{V}{4\pi b_{ii}}\frac{1}{r}\left(1 - \cos\sqrt{\frac{b_{ii}}{c_{ii}}}\, r\right).$$

Experimental investigation of fluctuations in solid binary solutions near a critical point of separation of the mixture [79] indicates the existence of damped and oscillatory fluctuations in the correlation functions connecting the densities of the various components.

Critical fluctuations were considered in the article by Klein and Tisza [78] by dividing the system into small cells and making the limiting transition to a continuum, which is a somewhat artificial approach. The meaning of this method lies in the use of a definite, but, perhaps, not very felicitous representation for the functionals, which are the thermodynamic functions in the inhomogeneous case. As we shall verify below, the Fourier representation for the thermodynamic functionals is significantly simpler and more natural and reduces them to functions.

The theory of critical fluctuations is semiphenomenological, because it makes use of a macroscopic distribution function. We present it as a simple example of the application of the local equilibrium distribution function.

20.5. Absence of Dissipation Processes in a Local Equilibrium State.

We shall show that dissipative processes are absent in the local equilibrium state (20.17a), i.e., there is no thermal conductivity, diffusion, or viscosity. We shall calculate the average values of the currents of energy, particle number, and momentum, $\mathbf{j}_H(\mathbf{x})$, $\mathbf{j}_\alpha(\mathbf{x})$, $\mathbf{T}(\mathbf{x})$ over the local equilibrium distribution.

Let us first put $\mathbf{v}(\mathbf{x})=0$. Then the statistical operator (or distribution function) is equal to

$$\rho_l = Q_l^{-1} \exp\left\{-\int \beta(x)\left[H(x) - \sum_i \mu_i(x) n_i(x)\right] dx\right\}, \tag{20.60}$$

where H(**x**) is expressed by formula (19.13) in the classical case and by (19.21a) in the quantum case. Expression (20.60) contains only the densities of energy (19.13), (19.21a) and particle number (19.3), (19.22), which are invariant with respect to a reversal of momenta, i.e., they are even quantities. Therefore ρ_l is also invariant with respect to this operation, i.e., it is an even quantity. On the other hand, with this transformation the α-components of the particle number current $\mathbf{j}^\alpha(\mathbf{x})$, energy current $\mathbf{j}^\alpha_H(\mathbf{x})$, and the non-diagonal elements of the tensor $\mathbf{T}_{\alpha\beta}(\mathbf{x})$, which depend on p_α and p_β, change sign; consequently, the average of these quantities over (20.60) is equal to zero. The local equilibrium average of the integral part of the non-diagonal elements $\mathbf{T}_{\alpha\beta}(\mathbf{x})$ is zero because it contains products of $(\mathbf{x}_\beta-\mathbf{x}'_\beta)(\mathbf{x}_\alpha-\mathbf{x}'_\alpha)$ with the two particle distribution function, which depends only on $|\mathbf{x}-\mathbf{x}'|$ in the local approximation. This is evident from (19.5), (19.17a), and (19.12) in the classical case and (19.24a), (19.29a), and (19.27a) in the quantum case.

Consequently, when averaging with respect to ρ_l, the quantities j(**x**), j_H(**x**) and the nondiagonal elements $T_{\alpha\beta}$(**x**) go to zero since under the spur (or integral) sign quantities of different parity are produced:

$$\begin{aligned} \langle j(x)\rangle_l &= \mathrm{Sp}(\rho_l j(x)) = 0, \\ \langle j_H(x)\rangle_l &= \mathrm{Sp}(\rho_l j_H(x)) = 0, \\ \langle T_{\alpha\beta}(x)\rangle_l &= \mathrm{Sp}(\rho_l T_{\alpha\beta}(x)) = \delta_{\alpha\beta}\langle T_{\alpha\alpha}(x)\rangle_l = \delta_{\alpha\beta}\langle p(x)\rangle_l, \end{aligned} \tag{20.61}$$

where the following is introduced:

$$\langle p(x)\rangle_l = \frac{1}{3}\sum_\alpha \langle T_{\alpha\alpha}(x)\rangle_l,$$

which conveys pressure (19.37).

Now let v(**x**) ≠ 0. We shall discuss a coordinate system moving with velocity **v(x)** employing the transformation

$$p_i = p'_i + mv(x),$$

in the classical case and the canonical transformation (19.35) in the quantum case[1]. For v(**x**) we select the average mass velocity, i. e.

$$v(x) = \frac{\langle p(x)\rangle_l}{\langle \rho(x)\rangle_l}. \qquad (20.62)$$

The energy, pulse, and particle number densities are transformed in the following manner:

$$\begin{aligned} H(x) &= H'(x) + v(x)\cdot p'(x) + \frac{1}{2}\rho(x)v^2(x), \\ p(x) &= p'(x) + \rho(x)v(x), \quad n_i(x) = n'_i(x), \end{aligned} \qquad (20.63)$$

where

$$\rho(x) = \sum_i m_i n_i(x). \qquad (20.63a)$$

In the new variables the statistical operator takes the form

$$\rho_l = Q_l^{-1}\exp\left\{-\int \beta(x)\left[H'(x) - \sum_i \mu_i(x)n'_i(x)\right]dx\right\}, \qquad (20.64)$$

where H'(**x**), n'_i(**x**) have the same form as before, but with ψ(**x**) replaced by ψ'(**x**), while in the classical case p_i is replaced by p'_i. In the system in motion we have

$$\begin{aligned} &\langle j'_H(x)\rangle_l = 0, \quad \langle j'_i(x)\rangle_l = 0, \\ &\langle T'_{\alpha\beta}(x)\rangle_l = \langle p(x)\rangle_l\,\delta_{\alpha\beta}, \end{aligned} \qquad (20.65)$$

where p(**x**) is the hydrostatic pressure operator (19.37); it is not written with a stroke since hydrostatic pressure is determined right in the system moving with mass velocity.

In converting to a coordinate system moving with velocity v(**x**), the particle number current (19.24a), energy (19.29a), and pulse (19.27a) are transformed by the formulas

$$\begin{aligned} j_i(x) &= j'_i(x) + n_i(x)v(x), \\ j_H(x) &= j'_H(x) + \left\{H'(x) + \rho(x)\frac{v^2(x)}{2} + (v(x)\cdot p'(x))\right\}v(x) + \\ &\qquad + \frac{v^2(x)}{2}p'(x) + T'(x)\cdot v(x) + \frac{\hbar^2}{4m}(\nabla n\nabla)v(x), \\ T(x) &= T'(x) + v(x)p'(x) + p'(x)v(x) + \rho(x)v(x)v(x). \end{aligned} \qquad (20.66)$$

In the (20.66) formula for j_H(**x**) the term $\frac{\hbar^2}{4m}(\nabla n(x)\nabla)v(x)$ has a purely quantum origin and is very small when v(**x**) and n(**x**) vary little at a distance on the order of a de Broglie wave length corresponding to the average particle energy; therefore, we shall omit the term having

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[1] In the classical case the velocity field can be nonpotential, while quantum vortices require a special treatment.

a velocity gradient. Now, the density and current conversion formulas take the form

$$\begin{aligned}
H(\mathbf{x}) &= H'(\mathbf{x}) + \mathbf{v}(\mathbf{x})\,\mathbf{p}(\mathbf{x}) + \frac{1}{2}\rho(\mathbf{x})\,v^2(\mathbf{x}),\\
n_i(\mathbf{x}) &= n_i'(\mathbf{x}), \quad \mathbf{j}_i(\mathbf{x}) = \mathbf{j}_i'(\mathbf{x}) + n_i(\mathbf{x})\,\mathbf{v}(\mathbf{x}),\\
\mathbf{p}(\mathbf{x}) &= \mathbf{p}'(\mathbf{x}) + \rho(\mathbf{x})\,\mathbf{v}(\mathbf{x}),\\
\mathbf{j}_H(\mathbf{x}) &= \mathbf{j}_H'(\mathbf{x}) + \left\{ H'(\mathbf{x}) + \rho(\mathbf{x})\frac{v^2(\mathbf{x})}{2} + (\mathbf{p}'(\mathbf{x})\cdot\mathbf{v}(\mathbf{x}))\right\}\mathbf{v}(\mathbf{x}) +\\
&\qquad + \frac{v^2(\mathbf{x})}{2}\,\mathbf{p}'(\mathbf{x}) + T'(\mathbf{x})\cdot\mathbf{v}(\mathbf{x}),\\
T(\mathbf{x}) &= T'(\mathbf{x}) + \mathbf{v}(\mathbf{x})\,\mathbf{p}'(\mathbf{x}) + \mathbf{p}'(\mathbf{x})\,\mathbf{v}(\mathbf{x}) + \rho(\mathbf{x})\,\mathbf{v}(\mathbf{x})\,\mathbf{v}(\mathbf{x}), \qquad (20.67)
\end{aligned}$$

which are valid in both the quantum and classical case.

Since the relationships (20.65) are valid in the system having local velocity $\mathbf{v}(\mathbf{x})$, by averaging with respect

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to the local equilibrium distribution, we obtain

$$\begin{gathered}
\langle H(\boldsymbol{x})\rangle_l = \langle H'(\boldsymbol{x})\rangle_l + \frac{1}{2}\langle \rho(\boldsymbol{x})\rangle_l v^2(\boldsymbol{x}), \\
\langle n_i(\boldsymbol{x})\rangle_l = \langle n'_i(\boldsymbol{x})\rangle_l, \quad \langle j_i(\boldsymbol{x})\rangle_l = \langle n_i(\boldsymbol{x})\rangle_l \boldsymbol{v}(\boldsymbol{x}), \\
\langle p(\boldsymbol{x})\rangle_l = \langle \rho(\boldsymbol{x})\rangle_l \boldsymbol{v}(\boldsymbol{x}), \\
\langle j_H(\boldsymbol{x})\rangle_l = \left\{ h(\boldsymbol{x}) + \langle \rho(\boldsymbol{x})\rangle_l \frac{v^2(\boldsymbol{x})}{2} \right\} \boldsymbol{v}(\boldsymbol{x}), \\
\langle T(\boldsymbol{x})\rangle_l = \langle p(\boldsymbol{x})\rangle_l U + \langle \rho(\boldsymbol{x})\rangle_l \boldsymbol{v}(\boldsymbol{x}) \boldsymbol{v}(\boldsymbol{x}),
\end{gathered} \qquad (20.68)$$

where

$$h(\boldsymbol{x}) = \langle H'(\boldsymbol{x})\rangle_l + \langle p(\boldsymbol{x})\rangle_l \qquad (20.68a)$$

is the enthalpy density, $\langle p(\mathbf{x})\rangle_l$ is the average pressure, and U is the unit tensor.

From formula (20.68) it is evident that in the local equilibrium state there exist only currents characteristic of an ideal liquid [82]. Currents of energy and particle number are proportional to the mass velocity, and the momentum current is a bilinear function of the mass velocity. These currents do not depend on the gradients of thermodynamic parameters and have a convective character.

The local equilibrium distribution (20.17a) is defined from the condition of maximum information entropy with fixed values of $\langle H(\mathbf{x})\rangle_l$, $\langle p(\mathbf{x})\rangle_l$ and $\langle n_i(\mathbf{x})\rangle_l$. This implies that there exists an arbitrariness in the specification of these quantities or of the corresponding thermodynamic (and hydrodynamic) parameters $\beta(\mathbf{x},t)$, $\mathbf{v}(\mathbf{x},t)$ and $\mu_i(\mathbf{x},t)$. We shall specify them in such a way that they satisfy the hydrodynamic equations for an ideal liquid. The currents (20.68) correspond to exactly this case. We put

$$\begin{gathered}
\frac{\partial \langle H(\boldsymbol{x})\rangle_l}{\partial t} = -\nabla \cdot \langle j_H(\boldsymbol{x})\rangle_l, \\
\frac{\partial \langle p(\boldsymbol{x})\rangle_l}{\partial t} = -\nabla \cdot \langle T(\boldsymbol{x})\rangle_l, \\
\frac{\partial \langle n_i(\boldsymbol{x})\rangle_l}{\partial t} = -\nabla \cdot \langle j_i(\boldsymbol{x})\rangle_l
\end{gathered} \qquad (20.69)$$

or in more compact notation

$$\frac{\partial \langle P_m(\boldsymbol{x})\rangle_l}{\partial t} = -\nabla \cdot \langle j_m(\boldsymbol{x})\rangle_l. \qquad (20.69a)$$

These equations cannot be obtained simply by averaging the conservation laws (19.18) over ρ_l, because ρ_l does not satisfy the Liouville equation, and therefore for it the derivatives of averages of operators are not equal to, in general, the averages of their derivatives.

Making use of relations (20.68) and the equation of balance of total mass and kinetic energy

$$\begin{aligned}&\frac{\partial}{\partial t}\langle\rho(x)\rangle_l=-\operatorname{div}\langle\rho(x)\rangle_l\,v(x,t),\\&\frac{\partial}{\partial t}\langle\rho(x)\rangle_l\,\frac{v^2(x,t)}{2}=-\operatorname{div}\left\{\langle\rho(x)\rangle_l\,\frac{v^2(x,t)}{2}\,v(x,t)\right\}-v(x,t)\cdot\nabla p(x),\end{aligned}$$

we write the equations (20.69) for the hydrodynamics of an ideal liquid in the form

$$\begin{aligned}\frac{du}{dt}&=\frac{\partial u}{\partial t}+v\cdot\nabla u=-(u+p)\operatorname{div}v,\\\frac{dn_i}{dt}&=\frac{\partial n_i}{\partial t}+v\cdot\nabla n_i=-n_i\operatorname{div}v,\\\frac{dv}{dt}&=\frac{\partial v}{\partial t}+v\cdot\nabla v=-\rho^{-1}\nabla p,\end{aligned}\tag{20.69b}$$

where

$$\begin{aligned}&u=\langle H'(x)\rangle_l,\quad n_i=\langle n_i'(x)\rangle_l=\langle n_i(x)\rangle_l,\\&v=v(x,t),\qquad \rho=\langle\rho(x)\rangle_l,\quad p=p(x),\end{aligned}\tag{20.69c}$$

i.e., u is the energy density in the co-moving system.

We shall show that for the local equilibrium distribution it follows from (20.69) that the entropy

$$S=-\langle\ln\rho_l\rangle_l=\Phi+\sum_m\int F_m(x,t)\langle P_m(x)\rangle_l\,dx,\tag{20.70}$$

where

$$\Phi=\ln\operatorname{Sp}\exp\left\{-\sum_m\int F_m(x,t)\,P_m(x)\,dx\right\},\tag{20.70a}$$

i.e., it cannot be produced in the system, but can only flow in or flow out through its surface.

The time derivative of the entropy (20.70) is equal to

$$\frac{\partial S}{\partial t} = \sum_m \int F_m(\boldsymbol{x}, t) \frac{\partial}{\partial t} \langle P_m(\boldsymbol{x}) \rangle_l \, d\boldsymbol{x}, \tag{20.71}$$

because from (20.70a) it follows that

$$\frac{\partial \Phi}{\partial t} = - \sum_m \int \frac{\partial F_m(\boldsymbol{x}, t)}{\partial t} \langle P_m(\boldsymbol{x}) \rangle_l \, d\boldsymbol{x}. \tag{20.71a}$$

Making use of the hydrodynamic equation (20.69a), we write (20.71) in the form

$$\begin{aligned}\frac{\partial S}{\partial t} &= - \sum_m \int F_m(\boldsymbol{x}, t) \nabla \cdot \langle j_m(\boldsymbol{x}) \rangle_l \, d\boldsymbol{x} = \\ &= - \sum_m \int F_m(\boldsymbol{x}, t) \langle j_m(\boldsymbol{x}) \rangle_l \cdot d\sigma + \sum_m \int \nabla F_m(\boldsymbol{x}, t) \cdot \langle j_m(\boldsymbol{x}) \rangle_l \, d\boldsymbol{x},\end{aligned} \tag{20.71b}$$

where on the right hand side of the equation in the first sum the integral is taken over the surface of the system. The second sum in (20.71b) is equal to

$$\begin{aligned}&\sum_m \nabla F_m(\boldsymbol{x}, t) \cdot \langle j_m(\boldsymbol{x}) \rangle_l = \\ &= \left\{ \langle j_H(\boldsymbol{x}) \rangle_l - \langle T(\boldsymbol{x}) \rangle_l \cdot v(\boldsymbol{x}, t) + \langle \rho(\boldsymbol{x}) \rangle_l \frac{v^2(\boldsymbol{x}, t)}{2} v(\boldsymbol{x}, t) \right\} \cdot \nabla \beta(\boldsymbol{x}, t) - \\ &\quad - \beta(\boldsymbol{x}, t) \{ \langle T(\boldsymbol{x}) \rangle_l - \langle \rho(\boldsymbol{x}) \rangle_l v(\boldsymbol{x}, t) v(\boldsymbol{x}, t) \} : \nabla v(\boldsymbol{x}, t) - \\ &\quad - \sum_i v(\boldsymbol{x}, t) \langle n_i(\boldsymbol{x}) \rangle_l \cdot \nabla \beta(\boldsymbol{x}, t) \mu_i(\boldsymbol{x}, t).\end{aligned} \tag{20.71c}$$

The last summation in (20.71c) can be expressed in terms of the gradient of the function

$$\Phi(\boldsymbol{x}) = \beta(\boldsymbol{x}, t) p(\boldsymbol{x}, t), \tag{20.71d}$$

where p(x,t) is the pressure, and use has been made of the Gibbs-Duhem relation (20.22) and (20.24d):

$$\delta\Phi(x) = \delta(\beta(x,t)\,p(x,t)) = \\ = -\langle H'(x)\rangle_l\,\delta\beta(x,t) + \sum_i \langle n_i(x)\rangle_l\,\delta\nu_i(x,t), \qquad (20.72)$$

$$\nu_i(x\,t,) = \beta(x,t)\,\mu_i(x,t), \quad \Phi = \ln Q_l = \int \Phi(x)\,dx,$$

from which it follows that

$$\frac{\partial\Phi(x)}{\partial\beta(x,t)} = -\langle H'(x)\rangle_l, \qquad \frac{\partial\Phi(x)}{\partial\nu_i(x,t)} = \langle n_i(x)\rangle_l. \qquad (20.72a)$$

The gradient of $\Phi(x)$ as a function of $\beta(x,t)$ and $\nu_1(x,t)$ is equal to

$$\nabla\Phi(x) = \frac{\partial\Phi(x)}{\partial\beta(x,t)}\nabla\beta(x,t) + \sum_i \frac{\partial\Phi(x)}{\partial\nu_i(x,t)}\nabla\nu_i(x,t) = \\ = -\langle H'(x)\rangle_l\nabla\beta(x,t) + \sum_i \langle n_i(x)\rangle_l\nabla\nu_i(x,t). \qquad (20.72b)$$

Making use of this relationship, we write (20.71c) in the form

$$\sum_m \nabla F_m(x,t)\cdot\langle j_m(x)\rangle_l = \Big\{\langle j_H(x)\rangle_l - \\ -\Big(\langle H'(x)\rangle_l - \langle\rho(x)\rangle_l\frac{v^2(x,t)}{2}\Big)v(x,t) - \langle T(x)\rangle_l\cdot v(x,t)\Big\}\cdot\nabla\beta(x,t) - \\ -\{\langle T(x)\rangle_l - U\,p(x) - \langle\rho(x)\rangle_l\,v(x,t)\,v(x,t)\} : \beta(x,t)\nabla v(x,t) - \\ -\operatorname{div}(v(x,t)\beta(x,t)\,p(x)) = -\operatorname{div}(v(x,t)\beta(x,t)\,p(x)), \qquad (20.73)$$

because the factors in front of $\nabla\beta(x,t)$ and $\nabla v(x,t)$ are zero on the basis of (20.68).

In addition,

$$\sum_m F_m(x,t)\langle j_m(x)\rangle_l + \beta(x,t)\,v(x,t)\,p(x) = \langle j_s(x)\rangle_l = v(x.\,t)\,S(x), \qquad (20.74)$$

because from (20.23) it follows that

$$\beta^{-1}(x, t)\, S(x) = \langle H'(x)\rangle_l + p(x) - \sum_i \langle n_i(x)\rangle_l\, \mu_i(x, t). \tag{20.75}$$

Using (20.73) and (20.74) we write the entropy balance equation (20.71) in the form of a surface integral:

$$\frac{\partial S}{\partial t} = - \int v(x, t)\, S(x) \cdot d\sigma, \tag{20.76}$$

or in local form

$$\frac{\partial S(x)}{\partial t} = - \operatorname{div}\,(v(x, t)\, S(x)). \tag{20.76a}$$

Thus, the entropy in a local equilibrium state can change only by flowing in or out of the volume of the system. Consequently, dissipative processes are absent in a local equilibrium state, and although such a state describes nonequilibrium processes, they are nevertheless reversible processes.

Thus, the local equilibrium distribution allows one to determine the thermodynamic functions of nonequilibrium states and to obtain thermodynamic equalities for inhomogeneous systems, but it does not allow one to describe transfer processes. This is related to the fact that ρ_l is not a solution of the Liouville equation, because H(**x**), n(**x**), and p(**x**) are not integrals of motion. We note, however, that these quantities are defined only up to the divergence of a vector or a tensor, which can be used to construct a statistical operator satisfying the Liouville equation [2-5]. This question is discussed in the following paragraph, where the local equilibrium distribution is changed such that it can describe irreversible transfer processes.

§ 21. Statistical Operator for Nonequilibrium Systems

The existence of exact, i.e., valid for any interaction, expressions for kinetic coefficients in terms of equilibrium time correlation functions, which we discussed in Chapter III suggests that they can be obtained by generalizing the statistical operator to nonequilibrium states and expanding it in terms of the small gradients of the thermodynamic parameters. We shall show, following the works of the author [2-5,184-186], that the method of Gibbs, which was presented in Chapters I and II, can be generalized to the nonequilibrium case to construct a nonequilibrium statistical operator or distribution function, which allow one to obtain transfer equations and to calculate kinetic coefficients in terms of correlation functions, and which go over to the Gibbs distribution for the equilibrium case. The results of the theory of the linear reaction, which was discussed in Chapter III, follow from the linear approximation for these distributions.

In what follows the idea of N. N. Bogolyubov on the hierarchy of relaxation times in nonequilibrium statistical mechanics [1] will have very great significance; this idea is contained in the following[1].

If the initial distribution is arbitrary, then in the initial stages the state of the system can differ markedly from an equilibrium state, and its description requires the specification of a large number of distribution functions: not only the single particle and two particle functions, but also higher order functions, which change rapidly in time in accordance with the Liouville equation.

However, for many systems with a large number of particles (for example, for gases with small density or small interaction during a time on the order of a collision time) the "synchronization" of the distribution functions begins very rapidly, when all distribution functions are completely defined by the single particle distribution function (this is also called the kinetic stage). A kinetic equation for the single particle distribution function has been successfully constructed from the Liouville equation for this stage.

For large time scales (for gases this is significantly larger than the time between collisions) the number of parameters necessary to describe the state of the system is further reduced, and the hydrodynamic stage begins, which can be described by hydrodynamic equations (together with the thermal conductivity equation), i.e., it can be described by the first few moments of the distribution function (the average particle number, average energy, and average velocity). The distribution function begins to depend on time only through these parameters.

Later we shall show that a description of the hydrodynamic stage is possible by means of some nonequilibrium distribution function or statistical operator, which depend on time through their parameters, and we shall show that this is possible not only for dilute gases and systems with weak interactions, but also for the more general case of condensed media.

The Gibbs construction of equilibrium statistical ensembles, which was considered in Chapters I and II, is based on the Liouville theorem, according to which the time derivative of the statistical operator (or distribution

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[1] A very clear presentation of these ideas of N. N. Bogolyubov can be seen in the article by Uhlenbeck in the book [83].

function) is equal to zero, if it is a function only of integrals of motion. The Gibbs distribution (3.30) and (9.42) is obtained by assuming that the energy and particle number are additive integrals of motion. We shall later proceed, as in the equilibrium case, from the Liouville theorem, but we shall generalize the class of integrals of motion on which the statistical operator or distribution function can depend.

21.1. Nonequilibrium Statistical Operator.

We shall attempt to construct a statistical operator for a nonequilibrium system (for example, a liquid), consisting of l components, taking into account the transfer of energy, particle number, and momentum.

Let us consider the state of a system which is macroscopically defined by specifying the temperature field, the chemical potential, and the velocity (i.e., the density of energy, momentum, and particle number) as a function of position and time. The system can be considered to be in thermal, material, and mechanical contact with a collection of thermostats and reservoirs, which provide the given distribution of parameters.

We shall assume that the chosen parameters are sufficient to define macroscopically the state of the system. If this is not the case, for example, if the system cannot be described by a single temperature, or in general the concept of temperature loses its meaning, it is necessary to find another more complete set of quantities characterizing the state of the system.

The construction of the Gibbs grand ensemble is based on (see sections 3.4 and 9.4) the laws of conservation of energy and particle number. We shall also proceed from the laws of conservation of energy, particle number, and momentum, but in local form, which was discussed in detail in § 19:

$$\begin{gathered}\frac{\partial H(x,t)}{\partial t}+\operatorname{div} j_H(x,t)=0,\\ \frac{\partial n_i(x,t)}{\partial t}+\operatorname{div} j_i(x,t)=0 \qquad (i=1,2,\ldots,l),\end{gathered} \tag{21.1}$$

$$\begin{gathered}\frac{\partial p(x,t)}{\partial t}+\operatorname{Div} T(x,t)=0,\\ p(x,t)=\sum_i m_i j_i(x,t),\end{gathered} \tag{21.1a}$$

where $H(\mathbf{x})$, $n_i(\mathbf{x})$, and $\mathbf{p}(\mathbf{x})$ are the operators for the density of energy, particle number, and momentum, $\mathbf{j}_H(\mathbf{x})$ is the energy current density, $\mathbf{j}_i(\mathbf{x})$ is the particle number current density, and $T(\mathbf{x})$ is the momentum current tensor or the stress tensor. The form of these operators is assumed to be known. For example, for a multicomponent mixture of various particles with a direct interaction in the quantum case they are expressed by formulas (19.39b), (19.43), (19.40), (19.41a), (19.42a), (19.44a), (19.46b), and in the classical case for a single component system they are expressed by formulas (19.13), (19.5), (19.6), (19.17), (19.12).

All operators considered in the quantum case are in the Heisenberg representation, for example

$$H(\mathbf{x}, t) = e^{iHt/\hbar} H(\mathbf{x}) e^{-iHt/\hbar} \qquad (H(\mathbf{x}, 0) = H(\mathbf{x})), \tag{21.2}$$

where H is independent of time. In classical mechanics the Heisenberg representation (21.2) is replaced by the action of the evolution operator (see section 2.3)

$$H(\mathbf{x}, t) = e^{-iLt} H(\mathbf{x}), \tag{21.2a}$$

where L is the Liouville operator (21.6).

If the system being considered consists of subsystems with a weak interaction, which leads only to a slow exchange of energy or momentum, then one can discuss equations of balance for energy and momentum for each subsystem. Then the right hand sides of equations (21.1), written for each component separately, will contain source terms, expressing the exchange of energy and momentum among the subsystems (see equations (19.42) and (19.46)).

If excitation of internal degrees of freedom (or chemical reactions) are possible in molecular collisions, then the equation for the density of particles with a given quantum number (or molecules of a given type) will contain on the right hand side a term which represents a source of particles with the given quantum number as a consequence of the excitation of the internal degrees of freedom or flux of molecules which take part in the chemical reaction (see equation (19.53)).

It is convenient to write the conservation laws (21.1) in a more compact form, analogous to (19.48):

$$\frac{\partial P_m(\mathbf{x}, t)}{\partial t} + \nabla \cdot j_m(\mathbf{x}, t) = 0 \qquad (m = 0, 1, \ldots, l+1), \tag{21.3}$$

where

$$\begin{aligned} P_0(\mathbf{x}) &= H(\mathbf{x}), & j_0(\mathbf{x}) &= j_H(\mathbf{x}), \\ P_1(\mathbf{x}) &= \mathbf{p}(\mathbf{x}), & j_1(\mathbf{x}) &= T(\mathbf{x}), \\ P_{i+1}(\mathbf{x}) &= n_i(\mathbf{x}), & j_{i+1}(\mathbf{x}) &= j_i(\mathbf{x}) \quad (i = 1, 2, \ldots, l). \end{aligned} \tag{21.3a}$$

From the definitions (21.3a) it follows that the densities $P_m(\mathbf{x})$ can be scalar or vector, and the currents $j_m(\mathbf{x})$ can be vector or tensor. The dot after the nabla operator denotes a scalar product, i.e., the divergence of a vector or a tensor.

In what follows we shall consider only the quantum case, because the classical case is completely analogous.

For the construction of the statistical operator which describes nonequilibrium processes use is made of the fact that in irreversible processes there are various relaxation time scales, a discussion of which was given at the beginning of this paragraph, and we shall be interested in the state of the system for time scales which are not too small.

We shall assume that during a small interval of time τ a nonequilibrium distribution is established, which depends on time only through its parameters and is a slowly varying function of time, with characteristic time $\tau_1 >> \tau$. Then we shall seek the statistical operator ρ for $t >> \tau$ as an integral of the quantum Liouville equation (8.6)

$$\frac{\partial \rho}{\partial t} + \frac{1}{i\hbar}[\rho, H] = 0,$$

in which the partial derivative of ρ denotes a differentiation with respect to time of the time dependent parameters F_m which enter into ρ. As the parameters are defined by the external conditions in which the system is found, then this term is the result of an external action on the system, which renders it nonstationary.

Depending on the choice of the parameters F_m and the operators P_m, such an approach is possible both in the hydrodynamic and in the kinetic stages. The discussion which follows in this chapter refers to the hydrodynamic stage.

To construct the statistical operator ρ, which describes the nonequilibrium state of the system, we shall make use of the collection of operators $B_m(x,t)$, depending on position x and time t through the values of the parameters $F_m(x,t)$.

Let $B_m(x,t)$ satisfy the equation

$$\frac{\partial B_m(x, t)}{\partial t} + \frac{1}{i\hbar}[B_m(x, t), H] = 0. \qquad (21.4)$$

Then, if $\rho(t)$ is a functional of the $B_m(x,t)$ as functions of x, i.e.,

$$\rho(t) = \rho\{\ldots B_m(x, t) \ldots\}, \qquad (21.5)$$

then $\rho(t)$ satisfies the Liouville equation. Indeed, the functional (21.5) can be considered as a function of the Fourier components of $B_m(x,t)$ with respect to x, and these components satisfy the equation (21.4), and consequently ρ itself satisfies the equation.

To construct the quantities $B_m(x,t)$ we shall proceed from the equations of balance of energy, particle number, and momentum in differential form (21.1) or in the more compact form (21.3).

We construct operators which depend on time through $F_m(x,t)$, having taken the part of the operators $F_m(x,t+t_1)P_m(x,t_1)$ which is invariant with respect to the evolution with the Hamiltonian H, i.e.,

$$B_m(x,t) = \widetilde{F_m(x,t)\,P_m(x)} = \\ = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t_1} F_m(x,\, t+t_1)\, P_m(x,\, t_1)\, dt_1 \qquad (\varepsilon \to 0), \tag{21.6}$$

where the parameters $F_m(x,t)$ have the meaning of the thermodynamic parameters (20.17), which now depend on time:

$$\begin{aligned} F_0(x,t) &= \beta(x,\, t), \\ F_1(x,t) &= -\beta(x,\, t)\, v(x,\, t), \\ F_{i+1}(x,\, t) &= -\beta(x,\, t)\left(\mu_i(x,\, t) - \frac{m_i}{2} v^2(x,\, t)\right); \end{aligned} \tag{21.6a}$$

$\beta(x,t)$ is the inverse temperature, $\mu_i(x,t)$ is the chemical potential, and $v(x,t)$ is the mass velocity (their meaning will be explained below, see (21.15) and (21.16)). The time argument of the operator $P_m(x,t_1)$ denotes the Heisenberg representation (21.2) for H independent of time; we shall for the present be restricted to this case. The parameter ε tends to zero, but after the transition to the thermodynamic limit.

The operation of taking the invariant part, smoothing the oscillatory terms, is used in the formal theory of scattering to impose boundary conditions which exclude the advanced solutions of the Schroedinger equation [84,85] (see Appendix I); we then select by the same method the retarded solutions of the Liouville equation.

If the parameters $F_m(x)$ are independent of time, then

$$\begin{aligned} B_m(x) &= F_m(x)\, \widetilde{P_m(x)}, \\ \widetilde{P_m(x)} &= \varepsilon \int_{-\infty}^{0} e^{\varepsilon t} P_m(x,\, t)\, dt = P_m(x) + \int_{-\infty}^{0} e^{\varepsilon t}\, \nabla \cdot j_m(x,\, t)\, dt, \end{aligned} \tag{21.7}$$

where $\widetilde{P_m(x)}$ are local integrals of motion, which differ from the corresponding densities $P_m(x)$ only by divergences, and therefore also have the meaning of densities of energy, momentum, and particle number. We shall show that they are indeed local integrals of motion as $\varepsilon \to 0$.

In the Heisenberg representation equations (21.7) have the form

$$\widetilde{P_m(x, t)} = P_m(x, t) + \int_{-\infty}^{0} e^{\varepsilon t_1} \nabla \cdot j_m(x, t+t_1)\, dt_1. \tag{21.7a}$$

Differentiating (21.7a) with respect to time and taking into account the conservation laws (21.3), we obtain:

$$\begin{aligned} \frac{\partial \widetilde{P_m(x, t)}}{\partial t} &= \frac{\partial P_m(x, t)}{\partial t} + \int_{-\infty}^{0} e^{\varepsilon t_1} \nabla \cdot \frac{\partial j_m(x, t+t_1)}{\partial t}\, dt_1 = \\ &= \varepsilon \int_{-\infty}^{0} e^{\varepsilon t_1} P_m(x, t+t_1)\, dt_1, \end{aligned} \tag{21.8}$$

i.e., the derivative of (21.7) is expressed through the same integral which appears on the right hand side of (21.7), but with an additional factor of ε. Consequently, $\partial\widetilde{P_m(x,t)}/\partial t$ tends to zero as $\varepsilon \to 0$, if the integrals on the right hand side of (21.8) are finite, and thus, the $\widetilde{P_m(x,t)}$ are local integrals of motion for $\varepsilon \to 0$.

We call $\widetilde{P_m(x,t)}$ integrals of motion, although they are conserved only in the limit $\varepsilon \to 0$ (which is taken after the thermodynamic limit), and it would be more correct to call them "quasi-integrals of motion". In what follows we shall not make this stipulation, calling them local integrals of motion. We note that the operations of taking the invariant part and taking the thermodynamic limit do not commute[1].

Making use of an integration by parts we write the operators (21.6) in the form

$$\begin{aligned} B_m(x, t) &= F_m(x, t)\, P_m(x) - \\ &- \int_{-\infty}^{0} e^{\varepsilon t_1} \left\{ F_m(x, t+t_1)\, \dot{P}_m(t_1) + \frac{\partial F_m(x, t+t_1)}{\partial t} P_m(x, t_1) \right\} dt_1. \end{aligned} \tag{21.9}$$

---

[1] We might note the close analogy of this property with the VanHove condition [86] of the "diagonal singularity" of matrix elements, which also appears when the volume of the system (or number of particles) approaches infinity.

They satisfy the equation

$$\frac{\partial B_m(x,t)}{\partial t} + \frac{1}{i\hbar}\left[B_m(x,t), H\right] =$$
$$= \varepsilon \int_{-\infty}^{0} e^{\varepsilon t_1} \left\{ F_m(x, t+t_1)\, \dot{P}_m(x, t_1) + \frac{\partial F_m(x, t+t_1)}{\partial t} P_m(x, t_1) \right\} dt_1,$$

where on the right hand side are operators of the same type as in (21.9), but with the parameter ε in front of the integral. Consequently, $B_m(x,t)$ satisfies equation (21.4) as ε→0.

For the functional (21.5) we choose the same form as for the local equilibrium state (20.17a):

$$\rho(t) = Q^{-1} \exp\left\{ -\sum_m \int B_m(x, t)\, dx \right\},$$
$$Q = \operatorname{Sp} \exp\left\{ -\sum_m \int B_m(x, t)\, dx \right\} \tag{21.10}$$

or in explicit form

$$\rho(t) = Q^{-1} \exp\left\{ -\sum_m \varepsilon \int \int_{-\infty}^{0} e^{\varepsilon t_1} F_m(x, t+t_1)\, P_m(x, t_1)\, dx\, dt_1 \right\} =$$
$$= Q^{-1} \exp\left\{ -\sum_m \int \left\{ F_m(x, t)\, P_m(x) - \int_{-\infty}^{0} e^{\varepsilon t_1} \left(F_m(x, t+t_1)\, \dot{P}_m(x, t_1) + \right.\right.\right.$$
$$\left.\left.\left. + \frac{\partial F_m(x, t+t_1)}{\partial t_1} P_m(x, t_1) \right) dt_1 \right\} dx \right\}, \tag{21.10a}$$

where ε→0 after the thermodynamic limit in the calculation of the averages. For the distribution function in the classical case we choose an analogous expression

$$f(t) = Q^{-1} \exp\left\{ -\sum_m \int B_m(x, t)\, dx \right\},$$
$$Q = \int \exp\left\{ -\sum_m \int B_m(x, t)\, dx \right\} d\Gamma, \tag{21.10b}$$

which, in contradistinction to (21.10), is not an operator, but a function of the coordinates and momenta of all particles[1].

We check that (21.10) indeed satisfies the Liouville equation (21.3) as $\varepsilon \to 0$.

Let us recall that if ρ satisfies the Liouville equation, then

$$\eta = -\ln\rho \tag{21.11}$$

also satisfies the Liouville equation (see (8.24) and (2.23)).

In our case

$$\begin{aligned}\frac{\partial\eta}{\partial t} + \frac{1}{i\hbar}[\eta, H] = \varepsilon \sum_m \int \int_{-\infty}^{0} e^{\varepsilon t_1} \Big\{ F_m(x, t+t_1) P_m(x, t_1) + \\ + \frac{\partial F_m(x, t+t_1)}{\partial t_1} (P_m(x, t_1) - \langle P_m(x, t_1)\rangle) \Big\} dt_1\, dx,\end{aligned} \tag{21.12}$$

i.e., on the right hand side of (21.12) are operators of the same type as in the second term of the exponential (21.10a), and thus, $\ln\rho$ satisfies the Liouville equation in the limit $\varepsilon \to 0$.

Using the conservation laws (21.3) and carrying out an integration by parts, neglecting surface integrals, we represent the statistical operator (21.10a) in the form

$$\begin{aligned}\rho(t) = Q^{-1} \exp\Big\{ -\sum_m \int (F_m(x, t) P_m(x) - \\ - \int_{-\infty}^{0} e^{\varepsilon t_1} (\nabla F_m(x, t+t_1) \cdot j_m(x, t_1) + \frac{\partial F_m(x, t+t_1)}{\partial t_1} P_m(x, t_1)) dt_1) dx \Big\}.\end{aligned} \tag{21.10c}$$

---

[1] We point out the formal similarity of the expression for the average of $-\langle \ln\rho \rangle$ with the Lagrangian which is chosen for the formulation of the variational principle in the theory of transfer phenomena on the basis of the method of conjugate functions (see [87]). Evidently there exists a deep connection between the method of the nonequilibrium statistical operator and the variational principle. This is indicated by the extremal properties of the nonequilibrium statistical operator which are established in the article [170] (see § 27).

If j_m is a tensor, then it is assumed that it is symmetric.

The statistical operator (21.10c) is already not an exact solution of the usual Liouville equation for $\varepsilon \to 0$ because of the neglect of currents of energy, particles, and momenta through the surface of the system. These terms correspond to the "nonpotential forces", which McLennan introduces to describe the effect of the thermostat [37-40] (see Appendices II and III).

In the stationary case (21.10a) goes over into the distribution

$$\begin{aligned}\rho &= Q^{-1}\exp\left\{-\sum_m \int F_m(x)\,\widetilde{P}_m(x)\,dx\right\} = \\ &= Q^{-1}\exp\left\{-\sum_m \int \left(F_m(x)P_m(x) - \int_{-\infty}^{0} e^{\varepsilon t} F_m(x)\,\dot{P}_m(x,t)\,dt\right)dx\right\},\end{aligned} \tag{21.10d}$$

where the $\widetilde{P}_m(x)$ are also densities of integrals of motion, differing from $P_m(x)$ only by a divergence, and (21.10c) goes over into the expression

$$\rho = Q^{-1}\exp\left\{-\sum_m \int \left(F_m(x)P_m(x) - \int_{-\infty}^{0} e^{\varepsilon t} j_m(x,t)\cdot\nabla F_m(x)\,dt\right)dx\right\}, \tag{21.10c}$$

which was obtained in the article [2].

It is more convenient, however, to consider the stationary case as the limit of the nonstationary case in which $\partial F_m/\partial t \to 0$. In this way the terms representing the free evolution of the operators are more naturally compensated.

Substituting the expressions (21.6a) into (21.10c) for the parameters $F_m(x,t)$ and (21.3a) for the densities $P_m(x)$, we write the statistical operator (21.10c) in expanded form:

$$
\begin{aligned}
\rho(t) = Q^{-1}\exp\Big\{ -\int \beta(x,\ t)\Big[H(x) - \sum_i \Big(\mu_i(x,\ t) - \\
- \frac{m_i}{2} v^2(x,\ t)\, n_i(x)\Big) - v(x,\ t)\cdot p(x)\Big]\, dx + \\
+ \int \int_{-\infty}^{0} e^{\varepsilon t_1}\Big(j_H(x,\ t_1)\cdot \nabla\beta(x,\ t+t_1) + H(x,\ t_1)\frac{\partial\beta(x,\ t+t_1)}{\partial t_1} - \\
- \sum_i j_i(x,\ t_1)\cdot\nabla\beta(x,\ t+t_1)\Big(\mu_i(x,\ t+t_1) - \frac{m_i}{2} v^2(x,\ t+t_1)\Big) + \\
+ \sum_i n_i(x,\ t_1)\frac{\partial}{\partial t_1}\beta(x,\ t+t_1)\Big(\mu_i(x,\ t+t_1) - \frac{m_i}{2} v^2(x,\ t+t_1)\Big) - \\
- T(x,\ t_1) : \nabla\beta(x,\ t+t_1)\, v(x,\ t+t_1) - \\
- p(x,\ t_1)\cdot\frac{\partial}{\partial t_1}\beta(x,\ t+t_1)\, v(x,\ t+t_1)\Big)\, dt_1\, dx\Big\}.
\end{aligned}
\qquad (21.10f)
$$

Here ∇ and $\partial/\partial t_1$ act on all thermodynamic parameters β, μ_i, v standing to the right of them. The statistical operator (21.10f) was obtained by McLennan by a different method [37,38], based on the introduction of nonpotential forces, describing the influence of the thermostat (see Appendix II). Other derivations of (21.10a) can be seen in § 27, Appendix III, and in [186-189].

Let us consider particular cases of the distribution (21.10f).

If all parameters $F_m(x)$ are constant in space, then (21.10f) goes over into the Gibbs distribution for the grand ensemble of a system moving as a whole with velocity v:

$$
\begin{aligned}
\rho_0 = Q_0^{-1}\exp\Big\{-\sum_m F_m P_m\Big\} = \\
= Q_0^{-1}\exp\Big\{-\beta\Big(H - \sum_i \mu_i N_i - v\cdot P + \tfrac{1}{2} v^2 \sum_i m_i N_i\Big)\Big\}.
\end{aligned}
\qquad (21.13)
$$

If in (21.10f) the term with currents is neglected, then one obtains the statistical operator of the local equilibrium distribution

$$
\begin{aligned}
\rho_l = Q_l^{-1}\exp\Big\{-\sum_m F_m(x,\ t)\, P_m(x)\, dx\Big\} = \\
= Q_l^{-1}\exp\Big\{-\int\beta(x,\ t)\Big[H(x) - \sum_i\Big(\mu_i(x,\ t) - \frac{m_i}{2} v^2(x,\ t)\Big) n_i(x) - \\
- v(x,\ t)\cdot p(x)\Big]\, dx\Big\},
\end{aligned}
\qquad (21.14)
$$

which was used by Mori [29-31] as an initial condition for the solution of the Liouville equation. The local equilibrium statistical operator is not a solution of the Liouville equation, and it does not describe irreversible processes, although for small gradients of thermodynamic parameters it differs only slightly from (21.10f). This circumstance is the reason for the success of the Mori theory.

21.2. Physical Meaning of Parameters.

We shall discuss in more detail the meaning of the parameters $F_m(\mathbf{x},t)$ which go into the statistical operator (21.10)-(21.10c).

We choose the parameters $F_m(\mathbf{x},t)$ such that they have the significance of the thermodynamic parameters (21.6a), conjugate to $\langle P_m(\mathbf{x})\rangle$, and such that they satisfy the thermodynamic equalities (20.21). For this it is sufficient to require that the average values of $P_m(\mathbf{x})$ over the distribution (21.10a), (21.10c) be equal to the averages over the local equilibrium distribution, i.e., that

$$\langle P_m(x)\rangle = \langle P_m(x)\rangle_l, \tag{21.15}$$

which gives the conditions for defining the parameters $F_m(\mathbf{x},t)$. In fact, then

$$\frac{\delta \ln Q_l}{\delta F_m(x,t)} = -\langle P_m(x)\rangle_l = -\langle P_m(x)\rangle, \tag{21.16}$$

where

$$Q_l = \mathrm{Sp}\exp\left\{-\sum_m \int F_m(x,t)\,P_m(x)\,dx\right\}. \tag{21.16a}$$

Such a definition of the thermodynamic parameters is well known from the kinetic theory of gases. In the theory of irreversible processes such a definition is used by Green [14], Mori [30], McLennan [37-40], and many other authors.

The meaning of such a definition of the parameters $F_m(\mathbf{x},t)$ corresponds to introducing the concept of thermodynamic functions of the nonequilibrium states [70,14], by which is understood the thermodynamic functions of that local equilibrium state which is characterized by the same quantities $\langle P_m(\mathbf{x})\rangle$, as the given nonequilibrium state. The local equilibrium state can be regarded as an equilibrium state in fictitious external fields.

The introduction of the statistical operator (21.10a-f), depending on the local parameters $F_m(\mathbf{x},t)$, is based on the assumptions that the parameters are sufficient to describe the macroscopic state of the system, and that fluctuations of local mechanical quantities are not too large. The condition for the applicability of the method can be formulated in the following way.

If the macroscopic state of the system can be described by the parameters $F_m(x,t)$, then the corresponding statistical operator has the form (21.10a).

The parameters $F_m(x,t)$ can have the meaning of (21.6a); then the statistical operator is applicable to the description of the hydrodynamic stage, but this is not necessary. The method is applicable also for another, more general choice of parameters. For example, they can be chosen such that the statistical operator is applicable also for the description of the kinetic stage, and one can obtain generalized kinetic equations [56] (see § 25).

If the fluctuations are large, then the state is characterized not only by the average values of mechanical quantities, but also by their dispersions and the latter can also be considered as thermodynamic parameters characterizing the macroscopic state of the system. The completeness of the choice of parameters characterizes the representativeness of the statistical ensemble. For example, a statistical ensemble which is characterized only by the average values of velocities cannot be used to represent turbulent motion. For this it is necessary to introduce a random field of velocities and their correlations.

21.3. The Meaning of Local Integrals of Motion.

We shall make several more remarks about the meaning of local integrals of motion in the form (21.6), (21.7).

If one assumes that for the operator $P_m(x,t)$ the limit $\lim\limits_{t\to-\infty} P_m(x,t)$ exists, then the operation of taking the invariant part coincides with the operation of averaging over time, i.e.,

$$\lim_{\varepsilon\to 0} \varepsilon \int_{-\infty}^{0} e^{\varepsilon t} P_m(x,t)\,dt = \lim_{T\to\infty} \frac{1}{T} \int_{-T}^{0} P_m(x,t)\,dt = P_m(x,-\infty).$$

According to Tauber's theorem [88], if one of these limits exists and $P_m(x,t)$ is bounded from below, then the second limit also exists and is equal to the first.

In reality $\lim\limits_{t\to-\infty} P_m(x,t)$ is not completely defined; only the limit of the expression

$$\langle A\rangle = Q^{-1}\,\mathrm{Sp}\left\{A\exp\left(-\sum_m \int \widetilde{F_m(x,t)\,P_m(x)\,dx}\right)\right\}$$

exists for any operator A, representing an observable quantity, where first V→∞, and then ε→0; therefore, the Tauber theorem is not applicable, and, in general, one cannot substitute a time averaging for taking the invariant part. If one nevertheless makes this replacement, then one also obtains local integrals of motion, but with a different definition of the meaning of the improper integrals, namely

$$\overline{P_m(x)} = \frac{1}{T}\int_{-T}^{0} P_m(x,t)\,dt = P_m(x) + \int_{-T}^{0}\left(1+\frac{t}{T}\right)\nabla\cdot j_m(x,t)\,dt, \qquad (21.17)$$

i.e., integrals in the sense of Cesaro, not in the sense of Abel as in (21.7).

The quantities (21.17) are also conserved as T→∞. In this connection,

$$\lim_{T\to\infty}\overline{\dot{P}_m(x)} = \lim_{T\to\infty}\frac{1}{T}\int_{-T}^{0}\dot{P}_m(x,t)\,dt = \\ = \lim_{T\to\infty}\frac{P_m(x,0)-P_m(x,-T)}{T} = 0.$$

The application of local integrals of motion in the form (21.17) is inconvenient, as we shall verify in section 22.3, because it requires an additional definition of the meaning of the resulting integrals.

Formula (21.17) corresponds to the usual time smoothing of dynamical variables, but (21.7) corresponds to their causal time smoothing, which was discussed at the end of § 2.

The choice of local integrals of motion in the form (21.6) and (21.7) is not unique. For example, instead of choosing integrals of motion of the retarded type, as (21.6) and (21.7), one can choose the advanced type, i.e.,

$$\widetilde{P'_m(x)} = P_m(x) - \int_{0}^{\infty} e^{-\varepsilon t}\,\nabla\cdot j(x,t)\,dt, \qquad (21.18)$$

or a superposition of retarded and advanced solutions.

The quantity (21.18) is conserved as ε→0, just as is (21.7a), because

$$\frac{\partial\widetilde{P'_m(x,t)}}{\partial t} = -\varepsilon\int_{0}^{\infty} e^{-\varepsilon t'}\,\nabla j_m(x,t+t')\,dt'$$

analogous to the relation (21.8).

As we shall verify in section 22.4, local integrals of motion of the advanced type (21.18) give not an increase, but a decrease of the local production of entropy; therefore, one must reject the choice of (21.18) in constructing the statistical operator[1].

The choice of local integrals of motion of the retarded type, as was already mentioned earlier, implies the imposition of boundary conditions which exclude advanced solutions of the Liouville equation, i.e., conditions of causality, which is intimately connected with the choice of boundary conditions in the formal theory of scattering. This connection becomes especially obvious by comparing with the boundary conditions of the formal theory of scattering in the exposition of Gell-Mann and Goldberger [84,85], where retarded solutions of the Schroedinger equation are selected also by means of the limiting transition $\varepsilon\to 0$ in integrals of the type (21.6) and (21.7) after the limiting transition $V\to\infty$ (see Appendices I and III).

We shall show that the nonequilibrium statistical operator (21.10a) corresponds to the invariant part of the logarithm of the local equilibrium operator (21.14), i.e., that

$$\ln\rho = \widetilde{\ln\rho_l} = \varepsilon\int_{-\infty}^{0} e^{\varepsilon t_1}\ln\rho_l(t+t_1,\ t_1)\,dt_1, \tag{21.19}$$

where $\varepsilon\to 0$ after $V\to\infty$. The first argument in ρ_l denotes the time dependence through the parameters, and the second argument denotes the time dependence through the Heisenberg representation for the operators. We have

$$\ln\rho_l(t+t_1,\ t_1) = -\Phi_l(t+t_1) - \sum_m\int F_m(x,\ t+t_1)\,P_m(x,\ t_1)\,dx, \tag{21.20}$$

where

$$\Phi_l(t+t_1) = \ln \operatorname{Sp}\exp\left\{-\sum_m\int F_m(x,t+t_1)\,P_m(x)\,dx\right\}. \tag{21.21}$$

---

[1] The choice of the advanced solution leads to an associated equation of thermal conductivity

$$-c\frac{\partial T^+}{\partial t} = \varkappa\nabla^2 T^+$$

with a different sign in front of the time derivative than in the usual equation for thermal conductivity. The associated temperature T^+ is convenient as an auxiliary concept for the formulation of the variational principle [87]. Associated equations for other quantities are introduced analogously.

Using (21.20) we write (21.19) in the form

$$\rho = \exp\left\{ -\Phi - \sum_m \varepsilon \int_{-\infty}^{0} \int e^{\varepsilon t_1} F_m(\boldsymbol{x}, t + t_1) P_m(\boldsymbol{x}, t_1)\, dt_1\, d\boldsymbol{x} \right\}, \tag{21.22}$$

where

$$\begin{aligned} \Phi &= \varepsilon \int_{-\infty}^{0} e^{\varepsilon t_1} \Phi_t(t + t_1)\, dt_1 = \\ &= \varepsilon \int_{-\infty}^{0} dt_1\, e^{\varepsilon t_1} \ln \mathrm{Sp} \left\{ - \sum_m \int F_m(\boldsymbol{x}, t + t_1) P_m(\boldsymbol{x})\, d\boldsymbol{x} \right\}. \end{aligned} \tag{21.23}$$

On the other hand, from the requirement that the normalization be conserved after taking the invariant part we obtain

$$\Phi = \ln \mathrm{Sp} \exp\left\{ - \sum_m \varepsilon \int_{-\infty}^{0} \int e^{\varepsilon t_1} F_m(x, t + t_1) P_m(\boldsymbol{x}, t_1)\, dt_1\, d\boldsymbol{x} \right\}. \tag{21.24}$$

From (21.23) it follows that

$$\delta\Phi = -\varepsilon \int_{-\infty}^{0} \int e^{\varepsilon t_1} \langle P_m(\boldsymbol{x}) \rangle_l^{t+t_1} \delta F_m(\boldsymbol{x}, t + t_1)\, dt_1\, d\boldsymbol{x}, \tag{21.25}$$

and from (21.24) that

$$\delta\Phi = -\varepsilon \int_{-\infty}^{0} \int e^{\varepsilon t_1} \langle P_m(\boldsymbol{x}, t_1) \rangle^t \delta F_m(\boldsymbol{x}, t + t_1)\, dt_1\, d\boldsymbol{x}. \tag{21.25a}$$

Consequently, fulfillment of the condition

$$\langle P_m(\boldsymbol{x}, t_1) \rangle^t = \langle P_m(\boldsymbol{x}) \rangle_l^{t+t_1} \tag{21.26}$$

guarantees conservation of the normalization, because in this case the variations (21.25) and (21.25a) coincide. For the case of statistical equilibirum (21.23) and (21.24) also coincide.

Thus, conditions (21.15), which were assumed earlier in order to satisfy the thermodynamic equalities can be obtained from the condition of conservation of the normalization after taking the invariant part of the local equilibrium operator (see [184,185,188]).

§ 22. Tensor, Vector, and Scalar Processes. Equations of Hydrodynamics, Thermal Conductivity, and Diffusion in a Multicomponent Liquid

In this paragraph we shall obtain linear relations between currents and thermodynamic forces, the production of entropy, and transfer equations with the example of a multicomponent liquid. We shall study tensor, vector, and scalar transfer processes, in which the currents and thermodynamic forces are either tensors (shear viscosity), or vectors (thermal conductivity, diffusion, thermal diffusion, the Dufour effect), or scalars (second viscosity).

22.1. Transfer Processes in a Multicomponent Liquid; Statistical Operator.

We shall consider the processes of transfer of energy, momentum, and particle number in an isotropic, multicomponent system (a liquid or a gas), when the statistical operator has the form (21.10c):

$$\rho = Q^{-1}\exp\Big\{-\sum_m \int \Big[F_m(\boldsymbol{x},\ t)\,P_m(\boldsymbol{x}) - \int_{-\infty}^{0} e^{\varepsilon t_1}\Big(j_m(\boldsymbol{x},\ t_1)\cdot\nabla F_m(\boldsymbol{x},\ t+t_1) + P_m(\boldsymbol{x},\ t_1)\times \times\frac{\partial F_m(\boldsymbol{x},\ t+t_1)}{\partial t}\Big)\,dt_1\Big]\,d\boldsymbol{x}\Big\}, \tag{22.1}$$

where

$$F_0(\boldsymbol{x},\ t) = \beta(\boldsymbol{x},t), \qquad P_0(\boldsymbol{x}) = H(\boldsymbol{x}),$$
$$F_1(\boldsymbol{x},\ t) = -\beta(\boldsymbol{x},\ t)\,v(x,\ t), \qquad P_1(\boldsymbol{x}) = p(\boldsymbol{x}),$$

$$F_{i+1}(\boldsymbol{x},\ t) = -\beta(\boldsymbol{x},\ t)\Big(\mu_i(\boldsymbol{x},\ t) - \frac{m_i}{2}v^2(x,\ t)\Big),\ P_{i+1}(\boldsymbol{x}) = n_i(\boldsymbol{x}),$$
$$j_0(\boldsymbol{x}) = j_H(\boldsymbol{x}),\qquad j_1(x) = T(\boldsymbol{x}),\qquad j_{i+1}(x) = j_i(x)\qquad (i \geqslant 1). \tag{22.1a}$$

The exponential in (22.1) contains time derivatives of the thermodynamic forces, in addition to their gradients. The time derivatives can also be expressed in terms of the gradients by means of the equations of hydrodynamics [38].

Restricting ourselves to the local approximation, we shall consider that the pressure p(**x**) at the point **x** is a function of the values $\beta(\mathbf{x})$ and $\nu_i(\mathbf{x})$

at the same point, i.e., $p(\mathbf{x})=p(\beta(\mathbf{x}),\ldots,\nu_i(\mathbf{x})\ldots)$; consequently,

$$\nabla p=\frac{\partial p}{\partial\beta}\nabla\beta+\sum_i\frac{\partial p}{\partial\nu_i}\nabla\nu_i. \tag{22.2}$$

This assumption may be violated close to critical points (see section 20.4). Taking into account (22.2) the last of the system of equations (20.69b), i.e., the Euler equation, takes on the form

$$\frac{dv}{dt}=-\frac{1}{\langle\rho\rangle}\frac{\partial p}{\partial\beta}\nabla\beta-\frac{1}{\langle\rho\rangle}\sum_i\frac{\partial p}{\partial\nu_i}\nabla\nu_i, \tag{22.3}$$

$$\langle\rho\rangle=\langle\rho(x)\rangle,$$

where

$$\frac{d}{dt}=\frac{\partial}{\partial t}+v\cdot\nabla$$

is the total time derivative. We make use of the thermodynamic equalities (20.72a), which, taking into account (20.71b,d), and (20.69c), have the form

$$\frac{\partial\beta p}{\partial\beta}=-u,\qquad\frac{\partial\beta p}{\partial\nu_i}=n_i, \tag{22.4}$$

or

$$\frac{\partial p}{\partial\beta}=-\frac{u+p}{\beta},\qquad\frac{\partial p}{\partial\nu_i}=\frac{n_i}{\beta}, \tag{22.4a}$$

where

$$u=\langle H'(x)\rangle_l$$

is the energy density, and

$$n_i=\langle n_i(x)\rangle_l$$

is the particle number density, and we write (22.3) in the form

$$\frac{dv}{dt}=\frac{u+p}{\langle\rho\rangle\beta}\nabla\beta-\sum_i\frac{n_i}{\langle\rho\rangle\beta}\nabla\nu_i. \tag{22.5}$$

Thus, the time derivative of the velocity is expressed in terms of the gradient of the thermodynamic parameters β and ν_i, and the velocity $\mathbf{v}$.

One can express $\partial\beta/\partial t$ analogously in terms of these gradients. Restricting ourselves as before to the local approximation, i.e., assuming that $\beta(\mathbf{x})=\beta(u(\mathbf{x}),\ldots,n_i(\mathbf{x})\ldots)$, we obtain

$$\frac{d\beta}{dt}=\frac{\partial\beta}{\partial u}\frac{du}{dt}+\sum_i\frac{\partial\beta}{\partial n_i}\frac{dn_i}{dt}, \tag{22.6}$$

or making use of the first and second equations of the system (20.69b)

$$\frac{d\beta}{dt} = -(u+p)\frac{\partial\beta}{\partial u}\operatorname{div}\boldsymbol{v} - \sum_i \frac{\partial\beta}{\partial n_i} n_i \operatorname{div}\boldsymbol{v} = \\ = \left\{\frac{\partial p}{\partial\beta}\frac{\partial\beta}{\partial u} - \sum_i \frac{\partial p}{\partial\nu_i}\frac{\partial\beta}{\partial n_i}\right\}\beta\operatorname{div}\boldsymbol{v}, \qquad (22.6a)$$

where use has been made of the thermodynamic equalities (22.4a).

In accordance with (20.35)

$$\beta = \frac{\partial S}{\partial u}, \qquad -\nu_i = \frac{\partial S}{\partial n_i}, \qquad (22.7)$$

where S is the entropy as a function of u, n_i. Consequently, β and ν_i are related by the thermodynamic equality

$$\frac{\partial\beta}{\partial n_i} = -\frac{\partial\nu_i}{\partial u} = \frac{\partial^2 S}{\partial u\,\partial n_i}, \qquad (22.7a)$$

and one can therefore rewrite (22.6a) in the form

$$\frac{d\beta}{dt} = \left\{\frac{\partial p}{\partial\beta}\frac{\partial\beta}{\partial u} + \sum_i \frac{\partial p}{\partial\nu_i}\frac{\partial\nu_i}{\partial u}\right\}\beta\operatorname{div}\boldsymbol{v} = \beta\left(\frac{\partial p}{\partial u}\right)_n \operatorname{div}\boldsymbol{v}, \qquad (22.8)$$

i.e., the partial derivative of β with respect to time is expressed through $v\nabla\beta$ and div **v**.

Assuming further that $\nu_i(x)=\nu_i(u(x)\ldots n_k(x)\ldots)$, we obtain

$$\frac{d\nu_i}{dt} = \frac{\partial\nu_i}{\partial u}\frac{du}{dt} + \sum_k \frac{\partial\nu_i}{\partial n_k}\frac{dn_k}{dt} = \\ = -\frac{\partial\nu_i}{\partial u}(u+p)\operatorname{div}\boldsymbol{v} - \sum_k \frac{\partial\nu_i}{\partial n_k} n_k \operatorname{div}\boldsymbol{v}, \qquad (22.9)$$

or, taking into account (22.4a) and (22.7) and the thermodynamic equality

$$\frac{\partial\nu_i}{\partial n_k} = \frac{\partial\nu_k}{\partial n_i}, \qquad (22.9a)$$

which is derived analogously to (22.7a), we obtain

$$\frac{d\nu_i}{dt} = \left\{\frac{\partial p}{\partial \beta}\frac{\partial \nu_i}{\partial u} - \sum_k \frac{\partial p}{\partial \nu_k}\frac{\partial \nu_i}{\partial n_k}\right\}\beta \operatorname{div} \boldsymbol{v} =$$

$$= \beta\left\{\frac{\partial p}{\partial \beta}\frac{\partial \nu_i}{\partial u} - \sum_k \frac{\partial p}{\partial \nu_k}\frac{\partial \nu_k}{\partial n_i}\right\}\operatorname{div} \boldsymbol{v} =$$

$$= -\beta\left\{\frac{\partial p}{\partial \beta}\frac{\partial \beta}{\partial n_i} + \sum_k \frac{\partial p}{\partial \nu_k}\frac{\partial \nu_k}{\partial n_i}\right\}\operatorname{div} \boldsymbol{v} = -\beta\left(\frac{\partial p}{\partial n_i}\right)_u \operatorname{div} \boldsymbol{v}. \qquad (22.9b)$$

Finally, for the time derivatives of the thermodynamic parameters in the hydrodynamic approximation for an ideal liquid we have

$$\frac{d\beta}{dt} = \beta\left(\frac{\partial p}{\partial u}\right)_n \operatorname{div} \boldsymbol{v},$$

$$\frac{d\nu_i}{dt} = -\beta\left(\frac{\partial p}{\partial n_i}\right)_u \operatorname{div} \boldsymbol{v}, \qquad (22.10)$$

$$\frac{d\boldsymbol{v}}{dt} = \frac{u+p}{\langle\rho\rangle\beta}\nabla\beta - \sum_i \frac{n_i}{\langle\rho\rangle\beta}\nabla\nu_i.$$

We now express the sum

$$\sum_m j_m(\boldsymbol{x}) \cdot \nabla F_m(\boldsymbol{x},\ t),$$

which is in the exponential in formula (22.1), in terms of $\nabla\beta$, $\nabla\nu_i = \nabla\beta\mu_i$, and $\nabla \mathbf{v}$. We obtain

$$\sum_m j_m(\boldsymbol{x}) \cdot \nabla F_m = \boldsymbol{j}_H(\boldsymbol{x}) \cdot \nabla\beta - \sum_i \boldsymbol{j}_i(\boldsymbol{x}) \cdot \nabla\beta\left(\mu_i - \frac{m_i v^2}{2}\right) - T(\boldsymbol{x}) : \nabla\beta\boldsymbol{v} =$$

$$= \left(\boldsymbol{j}_H(\boldsymbol{x}) - T(\boldsymbol{x}) \cdot \boldsymbol{v} + \boldsymbol{p}(\boldsymbol{x})\frac{v^2}{2}\right) \cdot \nabla\beta - \sum_i \boldsymbol{j}_i(\boldsymbol{x}) \cdot \nabla\nu_i -$$

$$- \beta(T(\boldsymbol{x}) - \boldsymbol{v}\boldsymbol{p}(\boldsymbol{x})) : \nabla\boldsymbol{v}, \qquad (22.11)$$

or

$$\sum_m j_m(\boldsymbol{x}) \cdot \nabla F_m =$$

$$= -\frac{\boldsymbol{p}(\boldsymbol{x})}{\langle\rho\rangle} \cdot \beta\nabla p + \left(\boldsymbol{j}_H(\boldsymbol{x}) - T(\boldsymbol{x}) \cdot \boldsymbol{v} + \boldsymbol{p}(\boldsymbol{x})\frac{v^2}{2} - \frac{u+p}{\langle\rho\rangle}\boldsymbol{p}(\boldsymbol{x})\right) \cdot \nabla\beta -$$

$$- \sum_i \left(\boldsymbol{j}_i(\boldsymbol{x}) - \frac{\langle n_i\rangle}{\langle\rho\rangle}\boldsymbol{p}(\boldsymbol{x})\right) \cdot \nabla\nu_i - \beta(T(\boldsymbol{x}) - \boldsymbol{v}\boldsymbol{p}(\boldsymbol{x})) : \nabla\boldsymbol{v}, \qquad (22.11a)$$

because taking into account (22.2) and (22.4a) for the pressure gradient we have

$$\nabla p = -\frac{u+p}{\beta}\nabla\beta + \sum_i \frac{\langle n_i\rangle}{\beta}\nabla\nu_i. \tag{22.11b}$$

Such a description is convenient, because in averaging over a local equilibrium state the coefficient of $\nabla\nu_i$ averages to zero,

$$\langle j_i(x)\rangle_l - \frac{\langle n_i\rangle}{\langle\rho\rangle}\langle p(x)\rangle_l = \langle j_i(x)\rangle_l - \langle n_i\rangle v(x) = 0.$$

We express
$$\sum_m P_m(x)\frac{\partial F_m(x,t)}{\partial t},$$

i.e., the second term in the exponential in formula (22.1), in terms of $\nabla\beta$, $\nabla\nu_i$, and ∇v. We obtain

$$\begin{aligned}\sum_m P_m(x)\frac{\partial F_m}{\partial t} &= H(x)\frac{\partial\beta}{\partial t} - p(x)\cdot\frac{\partial\beta v}{\partial t} - \sum_i n_i(x)\frac{\partial}{\partial t}\beta\left(\mu_i - \frac{m_i v^2}{2}\right) = \\ &= H'(x)\frac{\partial\beta}{\partial t} - \sum_i n_i(x)\frac{\partial\nu_i}{\partial t} - \beta p'(x)\frac{\partial v}{\partial t},\end{aligned} \tag{22.12}$$

where
$$H'(x) = H(x) - p(x)\cdot v + \rho(x)\frac{v^2}{2}, \qquad p'(x) = p(x) - \rho(x)v \tag{22.12a}$$

are the densities of energy and momentum in a system moving with mass velocity v (see (20.66), (20.67)). We substitute the expressions for $\partial\beta/\partial t$, $\partial\nu_i/\partial t$, and $\partial v/\partial t$ from (22.10) into (22.12). Taking (22.11b) into account, we obtain

$$\begin{aligned}\sum_m P_m(x)\frac{\partial F_m}{\partial t} = {} & \frac{p(x)}{\langle\rho\rangle}\cdot\beta\nabla p - \left(H'(x) - \frac{\rho(x)}{\langle\rho\rangle}(u+p)\right)v\cdot\nabla\beta + \\ & + \sum_i\left(n_i(x) - \langle n_i\rangle\frac{\rho(x)}{\langle\rho\rangle}\right)v\cdot\nabla\nu_i + \\ & + \beta\left(H'(x)\left(\frac{\partial p}{\partial u}\right)_n U + \sum_i n_i(x)\left(\frac{\partial p}{\partial n_i}\right)_u U + p'(x)v\right) : \nabla v,\end{aligned} \tag{22.12b}$$

where U is the unit tensor. Combining (22.11a) with (22.12b), we note that the terms with the pressure gradient cancel each other,

$$\sum_m \left(j_m(x) \cdot \nabla F_m + P_m(x) \frac{\partial F_m}{\partial t} \right) =$$

$$= j_Q(x) \cdot \nabla\beta - \beta j^1(x) : \nabla v - \sum_i j_d^i(x) \cdot \nabla \nu_i = \sum_m j^m(x) \cdot X_m(x), \tag{22.13}$$

where

$$\begin{aligned} j^0(x) &= j_Q(x) = j'_H(x) - \frac{u+p}{\langle\rho\rangle} p'(x), \\ j^1(x) &= T'(x) - \left(\frac{\partial p}{\partial u}\right)_n H'(x)\, U - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(x)\, U, \\ j^{i+1}(x) &= j_d^i(x) = j'_i(x) - \frac{\langle n_i \rangle}{\langle\rho\rangle} p'(x) \quad (i \geqslant 1) \end{aligned} \tag{22.13a}$$

are the operators for thermal, viscous, and diffusion currents, and

$$\begin{aligned} X_0(x, t) &= \nabla\beta(x, t), \\ X_1(x, t) &= -\beta(x, t) \nabla v(x, t), \\ X_{i+1}(x, t) &= -\nabla \nu_i(x, t) = -\nabla\beta(x, t)\, \mu_i(x, t) \quad (i \geqslant 1) \end{aligned} \tag{22.13b}$$

are the corresponding thermodynamic forces.

Taking into account (22.13)-(22.13b), we write the statistical operator (22.1) in the form

$$\rho = Q^{-1} \exp\left\{ -\sum_m \int \left(F_m(x, t)\, P_m(x) - \right.\right.$$

$$\left.\left. - \int_{-\infty}^{0} e^{\varepsilon t_1} j^m(x, t_1) \cdot X_m(x, t + t_1)\, dt_1 \right) dx \right\}. \tag{22.14}$$

Unlike (22.1), this expression is approximate to within the accuracy of gradients of thermodynamic parameters in the exponential, because their time derivatives were eliminated using the hydrodynamic equations for an ideal liquid (22.10). In higher approximations, if one eliminates time derivatives using hydrodynamic equations with viscosity, thermal conductivity, and diffusion, the exponential of (22.14) will contain terms with higher spatial derivatives of F_m. Another approximation which was made in the derivation of (22.14) was the application of thermodynamic relations in local form.

22.2. Linear Relationship Between Current and Thermodynamic Forces.

If the thermodynamic forces are small, using (22.14) we obtain for the averages of the currents linear relations, which relate them to the thermodynamic forces; the relations are non-local and have time retardation.

We write the statistical operator (22.14) in the form

$$\rho = Q^{-1} e^{-A-B},$$

where

$$A = \sum_m \int F_m(x, t) P_m(\boldsymbol{x})\, d\boldsymbol{x}, \qquad (22.15)$$

$$B = -\sum_m \int \int_{-\infty}^{0} e^{\varepsilon t_1} j^m(\boldsymbol{x}, t_1) \cdot X_m(\boldsymbol{x}, t + t_1)\, d\boldsymbol{x}\, dt_1,$$

and we expand e^{-A-B} in a series in powers of B, following the same method as in § 12. For this it is convenient to introduce the operator $K(\tau)$ by means of the relation

$$e^{-(A+B)\tau} = K(\tau) e^{-A\tau}, \qquad (22.16)$$

which is equivalent to the operator equation

$$K(\tau) = 1 - \int_0^{\tau} K(\tau_1) e^{-A\tau_1} B e^{A\tau_1} d\tau_1 \qquad (22.17)$$

with the initial condition

$$K(0) = 1.$$

Iterating this equation, we obtain in the approximation linear in B

$$e^{-A-B} = e^{-A} - \int_0^1 e^{-A\tau} B e^{A\tau} e^{-A} d\tau,$$

$$\rho = \frac{e^{-A} - \int_0^1 e^{-A\tau} B e^{A\tau} e^{-A} d\tau}{\mathrm{Sp}\, e^{-A} - \int_0^1 \mathrm{Sp}\,(e^{-A\tau} B e^{A\tau} e^{-A})\, d\tau} \cong$$

$$\cong \left\{ 1 - \int_0^1 \left(e^{-A\tau} B e^{A\tau} - \langle e^{-A\tau} B e^{A\tau} \rangle_l \right) d\tau \right\} \rho_l, \tag{22.18}$$

$$\rho_l = e^{-A} / \mathrm{Sp}\, e^{-A} \tag{22.18a}$$

$$\langle \ldots \rangle_l = \mathrm{Sp}\,(\rho_l \ldots) \tag{22.18b}$$

denotes an averaging with the local equilibrium distribution (21.14), (22.18a).

Using (22.18) for the average values of the currents, we obtain

$$\begin{aligned} &\langle j^m(\boldsymbol{x}) \rangle = \\ &= \langle j^m(\boldsymbol{x}) \rangle_l + \sum_n \int \int_{-\infty}^{t} e^{\varepsilon(t'-t)} (j^m(\boldsymbol{x}),\ j^n(\boldsymbol{x}',\ t'-t)) \cdot X_n(\boldsymbol{x}',\ t')\, dt'\, d\boldsymbol{x}', \end{aligned} \tag{22.19}$$

where

$$\begin{aligned} &(j^m(\boldsymbol{x}),\ j^n(\boldsymbol{x}',\ t)) = \\ &= \beta^{-1} \int_0^{\beta} \langle j^m(\boldsymbol{x}) (j^n(\boldsymbol{x}',\ t,\ i\tau) - \langle j^n(\boldsymbol{x}',\ t) \rangle_l) \rangle_l\, d\tau \end{aligned} \tag{22.19a}$$

are the quantum time correlation functions,

$$j^n(\boldsymbol{x}',\ t,\ i\tau) = e^{-\beta^{-1} A\tau} j^n(\boldsymbol{x}',\ t)\, e^{\beta^{-1} A\tau}. \tag{22.19b}$$

The linear relations (22.19) between currents and thermodynamic forces are retarded and non-local.

Let the thermodynamic forces depend periodically on time with frequency ω,

$$X_n(\boldsymbol{x}',\ t') = X_n(\boldsymbol{x}') \cos \omega t'.$$

Then

$$\begin{aligned} \langle j^n(\boldsymbol{x}) \rangle = \langle j^m(\boldsymbol{x}) \rangle_l + \sum_n \mathrm{Re}\, e^{i\omega t} \int \int_{-\infty}^{t} e^{\varepsilon(t'-t)} \times \\ \times (j^m(\boldsymbol{x}),\ j^n(\boldsymbol{x}',\ t'-t)) \cdot X_n(\boldsymbol{x}')\, e^{i\omega(t'-t)}\, dt'\, d\boldsymbol{x}'. \end{aligned} \tag{22.19c}$$

The kinetic coefficients in (22.19c) are the Fourier components of the quantum correlation functions, i.e., taking into account the retardation leads to dispersion of the kinetic coefficients [89,90].

If retardation is neglected, i.e., if one considers that $X_n(x',t')$ changes slowly during the time of the dying out of the correlations between currents, then one can take the thermodynamic forces outside the integral over time at the point $t'=t$. Then we obtain linear relations between the thermodynamic forces and currents without retardations, but with a non-local character.

$$\langle j^m(\boldsymbol{x})\rangle = \langle j^m(\boldsymbol{x})\rangle_l + \sum_n \int L_{mn}(\boldsymbol{x}, \boldsymbol{x}') \cdot X_n(\boldsymbol{x}', t)\, d\boldsymbol{x}', \tag{22.20}$$

where

$$L_{mn}(\boldsymbol{x}, \boldsymbol{x}') = \int_{-\infty}^{0} e^{\varepsilon t} (j^m(\boldsymbol{x}),\ j^n(\boldsymbol{x}', t))\, dt \tag{22.20a}$$

are the kinetic coefficients.

In the expression (22.20a) for the kinetic coefficients in the linear approximation one can replace the averaging over the local equilibrium distribution by an averaging over the statistical equilibrium operator ρ_0 (21.13), in which the variables $F_m(x)$, which are functions of position, are replaced by the spatial averages of these parameters. For the kinetic coefficients we then obtain the expression

$$L_{mn}(\boldsymbol{x}, \boldsymbol{x}') = \beta^{-1} \int_0^{\beta} \int_{-\infty}^{0} e^{\varepsilon t} \langle j^m(\boldsymbol{x}) (j^n(\boldsymbol{x}', t + i\hbar\tau) - \langle j^n(\boldsymbol{x}')\rangle_0)\rangle_0\, d\tau\, dt, \tag{22.20b}$$

where

$$\langle \ldots \rangle_0 = \mathrm{Sp}(\rho_0 \ldots).$$

We shall assume that the currents commute with the total number of particles of the nth type N_n:

$$[j^m, N_n] = 0,$$

which is usually the case.

The expression (22.20b) for the kinetic coefficients differs from the expression obtained by Mori [29-31] because we have used ordinary, and not causal averaging;

$$L_{mn}(x, x') = \beta^{-1} \int\limits_0^\beta \int\limits_0^T \left(1 - \frac{t}{T}\right) \langle j^n(x) (j^m(x', t + i\hbar\tau) - \langle j^m(x')\rangle_0)\rangle_0 \, d\tau \, dt$$

is defined only by improper Abel integrals, and not by Cesaro integrals, as used by Mori. This is easily verified by making the replacement $t \to -t, \tau \to \beta - \tau$, and taking into account (16.17).

If the non-locality is neglected, i.e., if one considers that the thermodynamic forces change little in a correlation length, over which $L_{mn}(x,x')$ is significantly different from zero, then in (22.20) $X_n(x',t)$ can be taken outside the integral over space at the point $x'=x$. Then

$$\langle j^m(x)\rangle = \langle j^m(x)\rangle_l + \sum_n L_{mn}(x) \cdot X_n(x), \tag{22.20c}$$

where

$$L_{mn}(x) = \int L_{mn}(x, x')\, dx'. \tag{22.20d}$$

From (22.20) we obtain for the average thermal, viscous, and diffusion currents

$$\begin{aligned} \langle j_Q(x)\rangle &= \langle j'_H(x)\rangle = \sum_n \int L_{0n}(x, x') \cdot X_n(x', t)\, dx', \\ \langle T'(x)\rangle &= \langle T'(x)\rangle_l + \sum_n \int L_{1n}(x, x') \cdot X_n(x', t)\, dx', \\ \langle j_d^i(x)\rangle &= \langle j'_i(x)\rangle = \sum_n \int L_{in}(x, x') \cdot X_n(x', t)\, dx' \qquad (i \geqslant 1), \end{aligned} \tag{22.20e}$$

because in accordance with (20.65)

$$\langle j'_H(x)\rangle_l = \langle j'_i(x)\rangle_l = 0.$$

In the local approximation the linear relations are not integral relations, but rather algebraic:

$$\begin{aligned}
&\langle j_Q(x)\rangle = \langle j'_H(x)\rangle = \sum_n L_{0n}(x)\cdot X_n(x,\ t),\\
&\langle T'(x)\rangle = \langle T'(x)\rangle_l + \sum_n L_{1n}(x)\cdot X_n(x,\ t),\\
&\langle j^l_d(x)\rangle = \langle j'_l(x)\rangle = \sum_n L_{ln}(x)\cdot X_n(x,\ t) \qquad (l \geqslant 1).
\end{aligned} \tag{22.20f}$$

Noting that in (22.20a) the averaging is carried out over a local equilibrium state,

$$\rho_l = Q_l^{-1}\exp\left\{-\int \beta(x,\ t)\left(H'(x) - \sum_i \mu_i(x,\ t)\,n'_i(x)\right)dx\right\}, \tag{22.21}$$

one can omit the primes in formulas (22.13a) and (22.21), assuming that

$$\begin{aligned}
&j^0(x) = j_Q(x) = j_H(x) - \frac{u+p}{\langle\rho\rangle}\,p(x),\\
&j^1(x) = T(x) - \left(\frac{\partial p}{\partial u}\right)_n H(x)\,U - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(x)\,U,\\
&j^{l+1}(x) = j^l_d(x) = j_l(x) - \frac{\langle n_l\rangle}{\langle\rho\rangle}\,p(x),
\end{aligned} \tag{22.22}$$

and one can replace in (22.20a) the averaging with (22.21) by an averaging with

$$\rho_l = Q_l^{-1}\exp\left\{-\int \beta(x,\ t)\left(H(x) - \sum_i \mu_i(x,\ t)\,n_i(x)\right)dx\right\}. \tag{22.21a}$$

In the case in which the thermodynamic forces are constant in space, the linear relations (22.20) can be written in the form of relations between the total currents and the thermodynamic forces:

$$\langle J^m\rangle = \langle J^m\rangle_l + \sum_n V L_{mn}\cdot X_n, \tag{22.23}$$

where

$$J^m = \int j^m(x)\,dx \tag{22.23a}$$

are the total currents, and

$$L_{mn} = \frac{1}{V} \int\limits_{-\infty}^{0} e^{\varepsilon t} (J^{m}, J^{n}(t))\, dt \qquad (22.23b)$$

are the kinetic coefficients.

22.3. Onsager Reciprocity Relations.

The kinetic coefficients (22.20b) can be expressed in terms of the double-time retarded Green functions (15.48). In this connection, introducing yet another integration over t´, we write (22.20b) in the form

$$L_{mn}(x, x') = \beta^{-1} \int\limits_{-\infty}^{0} \int\limits_{-\infty}^{t} \int\limits_{0}^{\beta} e^{\varepsilon t} \left\langle j^{m}(x) \frac{d}{dt'} j^{n}(x', t' + i\hbar\tau) \right\rangle_{0} dt\, dt'\, d\tau,$$

because we assume that as t→-∞ the correlation between currents vanishes, i.e.,

$$\lim_{t \to -\infty} \langle j^{m}(x) j^{n}(x', t) \rangle_{0} = \langle j^{m}(x) \rangle_{0} \langle j^{n}(x') \rangle_{0}.$$

Carrying out the integration over τ, we obtain

$$L_{mn}(x, x') =$$
$$= \beta^{-1} \int\limits_{-\infty}^{0} \int\limits_{-\infty}^{t} e^{\varepsilon t} \frac{1}{i\hbar} \{\langle j^{m}(x) j^{n}(x', t' + i\hbar\beta)\rangle - \langle j^{m}(x) j^{n}(x', t')\rangle\}\, dt\, dt',$$

where we have omitted the 0 on the brackets <...>.

In the first term under the integral sign one can change the order of the operators with a time shift of iħβ using the identity (16.17), which in our case gives

$$\langle j^{m}(x) j^{n}(x', t + i\hbar\beta)\rangle = \langle j^{n}(x', t) j^{m}(x)\rangle.$$

from which we obtain

$$L_{mn}(x, x') = -\beta^{-1}\int_{-\infty}^{0}\int_{-\infty}^{t} e^{\varepsilon t}\frac{1}{i\hbar}\langle[j^m(x), j^n(x', t')]\rangle\, dt\, dt' =$$
$$= -\beta^{-1}\int_{-\infty}^{0}\int_{-\infty}^{t} e^{\varepsilon t}\langle\langle j^m(x)\, j^n(x', t')\rangle\rangle^r\, dt\, dt', \qquad (22.24)$$

where the bracket term in the integrand is a retarded doubletime Green function of the type (16.1). The relation (22.23b) can be written in an analogous form:

$$L_{mn} = -\frac{1}{\beta V}\int_{-\infty}^{0}\int_{-\infty}^{t} e^{\varepsilon t}\langle\langle J^m J^n(t')\rangle\rangle^r\, dt\, dt'. \qquad (22.24a)$$

The Onsager relations for the kinetic coefficients follow directly from expressions (22.24) and (22.24a) and the invariance of the Hamiltonian with respect to time reversal t→-t with the simultaneous reversal of the direction of the magnetic field **H**, **H**→-**H**. From the symmetry property (16.50) of the Green function it follows that

$$\langle\langle j^n(x)\, j^m(x', t')\rangle\rangle_H = \langle\langle j^m(x')\, j^n(x, t')\rangle\rangle_{-H},$$

because the current operators are hermitian; therefore, the Onsager reciprocity relations are valid for the kinetic coefficients

$$L_{mn}(x, x', H) = L_{nm}(x', x, -H),$$
$$L_{mn}(H) = L_{nm}(-H). \qquad (22.25)$$

If a system is rotating with constant angular velocity ω, then the rotation causes centrifugal and Coriolis forces. As the Coriolis forces change sign when the direction of the velocity is reversed, then with the reversal of time it is necessary to reverse the direction of the angular velocity. Consequently, the Onsager reciprocity relations in this case have the form

$$L_{mn}(x, x', \omega) = L_{nm}(x', x, -\omega),$$
$$L_{mn}(\omega) = L_{nm}(-\omega). \qquad (22.25a)$$

Let us consider the condition that the kinetic coefficients (22.20b) have a finite value. Since this expression and (17.35) have an identical form up to a factor of β^{-1}, which is obvious after the replacement $t\to -t, \tau\to\beta-\tau$, formula (22.20b) can be transformed in the same way as (17.35) in section 17.4. Assuming that there is no magnetic field, we obtain

$$L_{mn} = \frac{1}{2V}\int_{-\infty}^{\infty}\langle J^m(t)(J^n - \langle J^n\rangle)\rangle\,dt = \frac{1}{2V}J_{mn}(0), \tag{22.26}$$

i.e., the kinetic coefficients are proportional to the spectral intensity of the correlation function of currents for $\omega=0$ and finite when these quantities are finite, i.e., for dissipative processes (see the footnote on page 225).

We pointed out earlier (see (21.17)) the formal possibility of another definition of the improper integrals over time in the sense of the limiting transition $T\to\infty$,

$$\int_{-T}^{0}\left(1+\frac{t}{T}\right)\nabla\cdot j_m(x,t)\,dt.$$

We shall show that such a definition of the integrals is significantly less convenient than (22.20b). For the kinetic coefficients we would obtain the Mori expressions [30]

$$L_{mn} = (\beta V)^{-1}\int_{0}^{\beta}\int_{-T}^{0}\left(1+\frac{t}{T}\right)\langle J^m(J^n(t+i\hbar\tau) - \langle J^n\rangle)\rangle\,d\tau\,dt. \tag{22.27}$$

Assuming that the limiting transition $V\to\infty$ has already been effected, we calculate the limit (22.27) as $T\to\infty$. For this it is sufficient to consider the integral in the sense of (22.27) of one harmonic of the quantum correlation function, i.e.,

$$\int_{-T}^{0}\left(1+\frac{t}{T}\right)e^{-i\omega t}\,dt = -\frac{1}{i\omega} + \frac{1}{T\omega^2}(1-e^{i\omega T}). \tag{22.27a}$$

Making use of this equation and the spectral representation (16.15), we obtain for the kinetic coefficient (22.23b)

$$L_{mn} = \frac{1}{2\pi V}\int_{-\infty}^{\infty} J_{mn}(\omega)\,\frac{e^{\beta\hbar\omega}-1}{\hbar\beta\omega}\,\frac{d\omega}{-i\omega}, \tag{22.28}$$

because the contribution of the second term of (21.27a) approaches zero as $T\to\infty$. The integrand in (22.28) has a pole at $\omega=0$, because

$$J_{mn}(\omega)\frac{e^{\hbar\beta\omega}-1}{\hbar\beta\omega}$$

is finite as $\omega\to 0$ ($J_{mn}(0)$ is assumed finite). Therefore the integral in (22.28), strictly speaking, is not defined until the contour of integration is chosen. In order to give a definite meaning to this integral, we displace the contour of integration over ω from the real axis into the upper half plane by $i\varepsilon$, making the replacement $\omega\to\omega+i\varepsilon$ ($\varepsilon>0$, ω is real). Then

$$L_{mn}=\frac{1}{2\pi V}\int_{-\infty}^{\infty} J_{mn}(\omega)\,\frac{e^{\hbar\beta\omega}-1}{\hbar\beta\omega}\,\frac{d\omega}{-i(\omega+i\varepsilon)}=\frac{1}{2V}J_{mn}(0), \tag{22.29}$$

i.e., we obtain the same result as in defining the integral in the sense of (22.20b).

We note that the displacement of the contour of the ω integration by $i\varepsilon$ into the upper half plane is equivalent to introducing a damping factor $e^{\varepsilon t}$ in the integrals over time. In this way we again return to the definition of the integrals in the sense of (22.20b), and the introduction of the factor $(1+(t/T))$ turns out to be unnecessary.

The definition of the integrals in the sense of (22.27) is equivalent to the procedure of smoothing in time (21.17), which is often used in statistical mechanics of nonequilibrium processes, for example in the works of Kirkwood [13]. The arguments presented above point out the insufficiency of this procedure and the advantage of time causal smoothing (21.6).

22.4. Entropy Production in Nonequilibrium Processes.

The meaning of the thermodynamic functions for nonequilibrium states was already discussed in section 21.2 for the choice of the parameters $F_m(x,t)$. The quantity $-\langle\ln\rho\rangle$, where ρ is given by formula (21.10), cannot be chosen as the entropy, because $\ln\rho$ satisfies the Liouville equation, and the entropy would be constant, rather than increasing. We define the entropy of the nonequilibrium state (21.10), (21.10c) as the entropy of the corresponding local equilibrium state

$$\rho_l=Q_l^{-1}\exp\left\{-\sum_m\int F_m(x,t)\,P_m(x)\,dx\right\}, \tag{22.30}$$

which is characterized by the same values of the average densities (see (21.15)), i.e., we assume

$$S = -\langle \ln \rho_l \rangle_l = -\langle \ln \rho_l \rangle \tag{22.31}$$

or

$$S = \Phi + \sum_m \int F_m(\boldsymbol{x}, t) \langle P_m(\boldsymbol{x}) \rangle_l \, d\boldsymbol{x} = \\ = \Phi + \sum_m \int F_m(\boldsymbol{x}, t) \langle P_m(\boldsymbol{x}) \rangle \, d\boldsymbol{x}, \tag{22.32}$$

where

$$\Phi = \ln Q_l \tag{22.33}$$

is the Massieu-Planck function for the local equilibrium state.

We choose the local equilibrium state from the condition of maximum information entropy for arbitrary, given $\langle P_m(\mathbf{x}) \rangle_l$ (see (20.16)); this arbitrariness is removed by the conditions (21.15).

In accordance with (22.31) the entropy of a nonequilibrium state is the entropy of the equilibrium state in the auxiliary fields $F_m(\mathbf{x},t)$, which has the same distribution for the densities of mechanical quantities $\langle P_m(\mathbf{x}) \rangle$, i.e., $\langle n(\mathbf{x}) \rangle$, $\langle H(\mathbf{x}) \rangle$, $\langle p(\mathbf{x}) \rangle$, as in the original nonequilibrium state. This interpretation of the thermodynamic functions of nonequilibrium states was already given long ago by Leontovich [70] for a state with an inhomogeneous density $\langle n(\mathbf{x}) \rangle$ in the theory of fluctuations. An inhomogeneous distribution of energy $\langle H(\mathbf{x}) \rangle$ can be regarded, following Luttinger [9], as the result of the action of a gravitational field (taking into account the general theory of relativity), and an inhomogeneity of $\langle p(\mathbf{x}) \rangle$ can be regarded as a consequence of the action of a magnetic field through the vector potential.

The definition of the entropy (22.32) guarantees satisfaction of the thermodynamic equalities. In fact, we have

$$\frac{\delta \Phi}{\delta F_m(\boldsymbol{x}, t)} = -\langle P_m(\boldsymbol{x}) \rangle_l = -\langle P_m(\boldsymbol{x}) \rangle, \tag{22.34}$$

and consequently,

$$\frac{\delta S}{\delta \langle P_m(\boldsymbol{x}) \rangle} = F_m(\boldsymbol{x}, t), \tag{22.35}$$

where $S=S(\ldots\langle P_m(\mathbf{x}) \rangle\ldots)$, which confirms the correctness of the definition (22.31).

Let us calculate the change with time of the entropy (22.32):

$$\frac{\partial S}{\partial t} = \frac{\partial \Phi}{\partial t} + \sum_m \int \frac{\partial F_m(x, t)}{\partial t} \langle P_m(x) \rangle \, dx + \sum_m \int F_m(x, t) \langle \dot{P}_m(x) \rangle \, dx.$$

Differentiating (22.33), we find

$$\frac{\partial \Phi}{\partial t} = - \sum_m \int \frac{\partial F_m(x, t)}{\partial t} \langle P_m(x) \rangle \, dx,$$

and consequently

$$\frac{\partial S}{\partial t} = \sum_m \int F_m(x, t) \langle \dot{P}_m(x) \rangle \, dx. \tag{22.36}$$

Making use of the conservation laws and integrating (22.36) by parts, we obtain

$$\frac{\partial S}{\partial t} = - \sum_m \int F_m(x, t) \langle j_m(x) \rangle \cdot d\sigma + \sum_m \int \langle j_m(x) \rangle \cdot \nabla F_m(x, t) \, dx, \tag{22.36a}$$

where dσ is a surface element. Thus, the entropy can change, even if the surface integral in (22.36a) is equal to zero, i.e., unlike the energy, momentum, and particle number, the entropy in the system is not conserved.

We introduce the entropy density S(x), taking into account (20.21c) and (20.24d):

$$S = \int S(x) \, dx, \quad \Phi = \int \beta(x, t) p(x, t) \, dx, \tag{22.37}$$

$$S(x) = \sum_m F_m(x, t) \langle P_m(x) \rangle + \beta(x, t) p(x, t). \tag{22.37a}$$

Then, making use of (20.73), the equation of balance of the entropy follows from (22.36a)

$$\frac{\partial S(x)}{\partial t} = -\operatorname{div} j_S(x) + \sigma(x), \tag{22.38}$$

where

$$j_S(x) = \sum_m F_m(x, t)\langle j_m(x)\rangle + \beta(x, t)\, v(x, t)\, p(x) \tag{22.38a}$$

is the entropy current density, and

$$\sigma(x) = \sum_m (\langle j_m(x)\rangle - \langle j_m(x)\rangle_l)\cdot\nabla F_m(x, t) \tag{22.38b}$$

is the local production of entropy, i.e., the density of its sources. The quantities S(**x**), j_S(**x**), and σ(**x**) depend also on t, but for brevity we omit this argument. The production of entropy in accordance with (22.38b) is equal to the sum of the products of the thermodynamic forces with their conjugate currents.

We write the local production of entropy (22.38b) in terms of the thermodynamic forces X_m (22.13b):

$$\begin{aligned}\sigma(x) &= \sum_m (\langle j_m(x)\rangle - \langle j_m(x)\rangle_l)\cdot\nabla F_m = \\ &= \langle j'_H(x)\rangle\cdot\nabla\beta - \beta(\langle T'(x)\rangle - \langle T'(x)\rangle_l) : \nabla v - \sum_{i=1}^{l}\langle j'_i(x)\rangle\cdot\nabla\nu_i = \\ &= \sum_m (\langle j^m(x)\rangle - \langle j^m(x)\rangle_l)\cdot X_m(x),\end{aligned} \tag{22.39}$$

where use has been made of the relation (22.11) and the equality of the averages of n(**x**), H(**x**), and **p**(**x**) in the state (22.1) and a local equilibrium state.

According to (22.38a), and with use of (20.74), the average entropy current is equal to

$$\begin{aligned}j_S(x, t) &= \sum_m F_m(x, t)\langle j_m(x)\rangle + \beta(x, t)\, v(x, t)\, p(x) = \\ &= S(x)\, v(x, t) + \beta(x, t)\langle j_Q(x)\rangle - \\ &\quad - \sum_i \langle j'_i(x)\rangle\,\beta(x, t)\left(\mu_i(x, t) - \frac{\mu_i v^2(x, t)}{2}\right) - \\ &\quad - (\langle T(x)\rangle - \langle T(x)\rangle_l)\cdot\beta(x, t)\, v(x, t),\end{aligned} \tag{22.40}$$

where S(**x**) is the density of entropy (22.37a), and the average thermal, diffusion, and viscous currents are given by formulas (22.20d) or (22.20f). The first term in (22.40) represents a convection current, and the remaining terms represent irreversible transfer processes.

Substituting the linear relations (22.20) into (22.39), we obtain for the local production of entropy the expression

$$\sigma(x)=\sum_{m,n}\int L_{mn}(x,\ x'):X_n(x',\ t)\,X_m(x,\ t)\,dx'. \qquad (22.41)$$

We shall show that the total production of entropy is positive, i.e., that

$$\int \sigma(x)\,dx \geqslant 0. \qquad (22.42)$$

Indeed, (22.42) can be written in the form

$$\int \sigma(x)\,dx=\int_{-\infty}^{0} e^{\varepsilon t}(C,\ C(t))\,dt \geqslant 0 \qquad (C^{+}=C), \qquad (22.42a)$$

where the notation

$$C=\sum_{m}\int j^{m}(x)\cdot X_{m}(x,\ t)\,dx. \qquad (22.42b)$$

was introduced. The positivity of (22.42a) follows from the fact that the spectral intensity of self-adjoint operators is positive (see (16.18a)). Transforming (22.42) analogously to (17.38), we obtain

$$\int \sigma(x)\,dx=\frac{1}{2}\int_{-\infty}^{\infty}\langle C\,(C(t)-\langle C\rangle_0)\rangle_0\,dt>0, \qquad (22.43)$$

because $C=C^{+}$.

In the local approximation, when the thermodynamic forces change little over a distance of the order of the correlation length, which is usually assumed in thermodynamics, not only the total, but also the local production of entropy is positive. In this case we have

$$\sigma = \sum_{m,\,n} L_{mn} : X_n X_m. \tag{22.44}$$

The production of entropy is thus a positive definite form made up of thermodynamic forces.

Consequently, the choice of the retarded local integrals of motion (21.6) and (21.7a) leads to the law of increase of entropy. However, as was noted above, this choice is not unique. If instead of integrals of motion of the retarded type (21.7a) one chooses integrals of motion of the advanced type (21.18), then in place of formula (22.20) one obtains

$$\langle j_m(x)\rangle = \langle j_m(x)\rangle_l - \sum_n \int L_{mn}(x,\, x') \cdot X_n(x',\, t)\, dx'. \tag{22.45}$$

In this case we shall have for the production of entropy instead of (22.41)

$$\sigma(x) = -\sum_{mn} \int L_{mn}(x,\, x') : X_n(x',\, t)\, X_m(x,\, t)\, dx'$$

or in the local case

$$\sigma = -\sum_{mn} L_{mn} : X_n X_m,$$

i.e., the same expressions as before, but with a different sign; consequently, the entropy decreases rather than increasing. Therefore, under ordinary conditions the choice of local integrals of motion of the retarded type makes sense, but the choice of the advanced type does not. Cases of nonequilibrium systems, however, are possible in which there exist currents which are reflected from the boundaries. To describe such systems on a microscopic level, in general, a superposition of integrals of motion of the type (21.7a) and (21.18) turns out to be useful. An analogous situation exists in radiation problems, where one obtains standing waves by means of a superposition of retarded and advanced potentials.

Nonequilibrium thermodynamics can give a new approach to the very old question of the heat death of the universe.

The entropy of a closed, isolated system increases, as follows from (22.42). If one considers the universe as a closed, isolated system and assumes that the results of thermodynamics are applicable to it, then the universe must tend to a state of statistical equilibrium - a heat death, which in reality does not take place. This paradox has occupied scientists since the time of Boltzmann. Considering the universe to be a closed, isolated thermodynamic system is, of course, not valid. The results of thermodynamics refer to a large, but finite system, found in specified external conditions; therefore it is better to consider the observable part of the universe as a large, but finite, unisolated system. Even here there remains a paradox, because from irreversible thermodynamics it follows that the local production of entropy (22.44) is positive, and thermodynamics indicates only one possible process - the increase of entropy. The inverse process - the local decrease of entropy, not connected to the transfer of entropy, - is not allowed by thermodynamics, and it seems incomprehensible that the universe does not approach statistical equilibrium.

This paradox is still not explained at the present time, and various hypotheses have been put forth to explain it. For example, the Boltzmann fluctuation hypothesis [91,92], according to which the universe is a gigantic fluctuation from a state of statistical equilibrium. The weakness of this hypothesis is that the probability of fluctuations from a state of statistical equilibrium is extremely small and dies off exponentially, because the probability is described by a Gaussian distribution (6.16). Therefore, the appearance as a consequence of fluctuations of states which differ widely from equilibrium states is very unlikely.

Much more convincing hypotheses are based on the general theory of relativity [92,93], according to which the universe must be considered not as a closed system, but as a system in a variable gravitational field with a time dependent metric tensor. Indeed, taking gravity into account a uniform mass distribution is unstable and does not correspond to the maximum entropy. Therefore, the formation of stars and galaxies from a uniform distribution of matter can take place with a growth of entropy [94], and thus the growth of entropy does not contradict the evolution of the universe.

The conclusion about the increase of the entropy of a system, presented in this section, is based on the linear relations between thermodynamic forces and currents, which are valid only for small deviations from equilibrium. For some of the simplest cases one can demonstrate the increase of entropy also for strongly nonequilibrium states (see § 23). However, as was noted in section 15.3, there may be cases when there is no unique connection at all between the perturbation and the response, i.e., in our case between thermodynamic forces and currents, and in particular, when in nonlinear nonequilibrium thermodynamics there exists a feedback mechanism of the type (15.61). We have already cited examples of such a feedback in section 15.3.

If the state of statistical equilibrium of the universe is unstable, similar to the unstable center of the theory of nonlinear oscillations, and there exists a feedback mechanism, then fluctuations in the universe will increase, and it will go over into a highly nonlinear, but stable, self-oscillating state similar to a limit cycle in the theory of nonlinear oscillations. In such a model of the universe with feedback there would already be no paradox of heat death. In relativistic astrophysics an oscillating model of the universe is well known, in which oscillations are possible with and without the increase of entropy (see [94], Chapter 20). The case without the increase of entropy corresponds to the self-oscillating regime. These questions are still in a stage of development and are far from being resolved.

22.5. Tensor, Vector and Scalar Processes; Thermal Conductivity, Diffusion, Thermal Diffusion, the Dufour Effect, Shear and Second Viscosity.

It is convenient to write the production of entropy (22.39) in a somewhat different form, decomposing the shear stress tensor $\langle\pi\rangle=\langle T(\mathbf{x})\rangle-\langle T(\mathbf{x})\rangle_1$ and the tensor $\nabla\mathbf{v}$ into parts with a zero spur and a divergence multiplied by the unit tensor $\mathbf{U}$:

$$\langle\pi\rangle=\langle\Pi\rangle U+\langle\overset{\circ}{\pi}\rangle, \tag{22.46}$$

$$\nabla v=\frac{1}{3}U\,\mathrm{div}\,v+\overset{\circ}{\nabla}v, \tag{22.46a}$$

where

$$\langle\Pi\rangle=\frac{1}{3}\langle\pi\rangle U=\frac{1}{3}\sum_{\alpha}\langle\pi_{\alpha\alpha}\rangle. \tag{22.46b}$$

The tensors $\langle\overset{\circ}{\pi}\rangle$ and $\overset{\circ}{\nabla}\mathbf{v}$ have zero spur. The complete contraction of the tensors (22.46) and (22.46a) is equal to

$$\langle\pi\rangle:\nabla v=\langle\pi\rangle:\nabla v+\langle\Pi\rangle\,\mathrm{div}\,v. \tag{22.46c}$$

Noting that $\langle\pi\rangle$ is a symmetric tensor, we obtain

$$\langle\pi\rangle:\nabla v=\langle\overset{\circ}{\pi}\rangle:(\overset{\circ}{\nabla}v)^s+\langle\Pi\rangle\,\mathrm{div}\,v \tag{22.46d}$$

(the superscript s denotes the symmetric part of a tensor), because the complete contraction of a symmetric and an antisymmetric tensor is equal to zero.

From (22.22) it follows that the average diffusion currents are connected by the relation

$$\sum_{l} m_i\langle j_i^l(x)\rangle=\sum_{i}\left(m_i\langle j_i(x)\rangle-\frac{m_i\langle n_i\rangle}{\langle\rho\rangle}\langle p(x)\rangle\right)=0, \tag{22.47}$$

because $\langle p(x)\rangle$ is the total momentum. Taking into account (22.46d) and eliminating the l^{th} diffusion current by means of (22.47), we obtain for the production of entropy the expression

$$\sigma = \langle \boldsymbol{j}_Q(\boldsymbol{x})\rangle \cdot \nabla\beta - \sum_{i=1}^{l-1} \langle \boldsymbol{j}_d^i(\boldsymbol{x})\rangle \cdot m_i \nabla\left(\frac{\nu_i}{m_i} - \frac{\nu_l}{m_l}\right) - \\ - \beta\langle\overset{\circ}{\pi}\rangle : (\overset{\circ}{\nabla} v)^s - \beta\langle\Pi\rangle \operatorname{div} v. \tag{22.48}$$

Irreversible processes can be divided into two groups on the basis of the character of the currents and thermodynamic forces: vector processes corresponding to the first two terms in (22.48), and connected to the transfer of energy and matter; tensor processes corresponding to the third term in (22.48), representing shear viscosity, and scalar processes corresponding to the fourth term in (22.48), describing second viscosity.

For an isotropic medium the linear relations between forces and currents can be simplified, if one takes into account that in accordance with the Curie theorem currents and thermodynamic forces of different tensor rank cannot be connected with each other (a proof of this theorem can be found in [27]).

Consequently, the linear relations can be written separately for vector

$$\begin{aligned} \langle j_Q\rangle &= -L_{00} \cdot \frac{\operatorname{grad} T}{T^2} - \sum_{i=1}^{l} L_{0l} \cdot \operatorname{grad}\left(\frac{\mu_l}{T}\right), \\ \langle j_d^i\rangle &= -L_{i0} \cdot \frac{\operatorname{grad} T}{T^2} - \sum_{j=1}^{l} L_{il} \cdot \operatorname{grad}\left(\frac{\mu_l}{T}\right), \end{aligned} \tag{22.49}$$

tensor

$$\langle\overset{\circ}{\pi}\rangle = -\frac{L_{11}^{(1)}}{T} \cdot (\overset{\circ}{\nabla} v)^s \tag{22.49a}$$

and scalar processes

$$\langle\Pi\rangle = \frac{1}{3}\sum_{\alpha=1}^{3} \langle\pi_{\alpha\alpha}\rangle = -\frac{L_{11}^{(2)}}{T} \operatorname{div} v, \tag{22.49b}$$

where the kinetic coefficients are equal to

$$L_{00} = \int \int_{-\infty}^{0} e^{\varepsilon t} (j_Q(x),\ j_Q(x',\ t))\, dx'\, dt,$$

$$L_{0l} = \int \int_{-\infty}^{0} e^{\varepsilon t} (j_Q(x),\ j_d^l(x',\ t))\, dx'\, dt, \qquad (22.50)$$

$$L_{i0} = \int \int_{-\infty}^{0} e^{\varepsilon t} (j_d^i(x),\ j_Q(x',\ t))\, dx'\, dt,$$

$$L_{il} = \int \int_{-\infty}^{0} e^{\varepsilon t} (j_d^i(x),\ j_d^l(x',\ t))\, dx'\, dt,$$

$$L_{11}^{(1)} = \int \int_{-\infty}^{0} e^{\varepsilon t} (\hat{T}(x),\ \hat{T}(x',\ t))\, dx'\, dt, \qquad (22.50a)$$

$$L_{11}^{(2)} = \int \int_{-\infty}^{0} e^{\varepsilon t} \Big(p(x),\ p(x',\ t) - \left(\frac{\partial p}{\partial u}\right)_n H(x',\ t) - \\ - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(x',\ t)\Big)\, dx'\, dt.$$

Here $\mathbf{j}_Q(\mathbf{x})$ is the heat current density, defined by formula (22.22); $\mathbf{j}_H(\mathbf{x})$ is the energy current density (19.42a), and (19.44a); $\mathbf{j}_d^i(\mathbf{x})$ is the diffusion current density (22.22), where $\mathbf{j}_i(\mathbf{x})$ is the particle number current density (19.41a); $\mathbf{p}(\mathbf{x})$ is the momentum density (21.1a), and $\mathring{\mathbf{T}}(\mathbf{x})$ is the divergenceless part of the stress tensor (19.46b),

$$T(x) = \hat{T}(x) + Up(x), \qquad (22.51)$$

where $\mathbf{p}(\mathbf{x})$ is the pressure operator

$$p(x) = \frac{1}{3} \sum_{\alpha} T_{\alpha\alpha}(x), \qquad (22.51a)$$

and U is the unit tensor.

In formulas (22.50) the averaging is carried out with a local equilibrium distribution (22.21). The brackets denote the quantum correlation functions (22.19a). In the case of classical mechanics the current density operators must be replaced by the corresponding dynamical variables (see section 19.1), and the quantum correlation functions must be replaced by the classical correlation functions.

As a consequence of the Onsager reciprocity relations (22.25) we have in the absence of a magnetic field for the kinetic coefficients (22.23b) the symmetry relations

$$L_{0l} = L_{l0}, \qquad L_{il} = L_{li}, \tag{22.52}$$

or, if there is a magnetic field H,

$$L_{0l}(H) = L_{l0}(-H), \qquad L_{il}(H) = L_{li}(-H). \tag{22.52a}$$

For the case under consideration of an isotropic medium the relations (22.49)-(22.49b) and the expressions (22.50) can be still further simplified. The correlation functions, which are constructed from vectors or tensors, in this case have the form of scalars multiplied by unit tensors:

$$\begin{gathered} L_{00}^{\mu\nu} = L_0\delta_{\mu\nu}, \qquad L_{0i}^{\mu\nu} = L_{i0}^{\mu\nu} = L_i\delta_{\mu\nu}, \\ L_{11}^{(1)\,\mu\nu\mu_1\nu_1} = L_1^{(1)}\frac{1}{2}\left\{\delta_{\mu\mu_1}\delta_{\nu\nu_1} + \delta_{\mu\nu_1}\delta_{\nu\mu_1} - \frac{2}{3}\delta_{\mu\nu}\delta_{\mu_1\nu_1}\right\}. \end{gathered} \tag{22.52b}$$

The last term on the right hand side of the last expression is added in order to satisfy the properties

$$\sum_{\mu} L^{\mu\mu\mu_1\nu_1} = \sum_{\mu_1} L^{\mu\nu\mu_1\mu_1} = 0,$$

because the correlator is constructed from tensors with zero spur.

The scalar functions L_0, L_i, and L_1 are found by calculating the spur (i.e., the contraction) of the tensors on the left and right hand sides of the relations (22.52b):

$$\begin{gathered} L_0 = \frac{1}{3}\,\mathrm{Sp}\,L_{00} = L_{00}^{xx}, \\ L_i = \frac{1}{3}\,\mathrm{Sp}\,L_{0i} = \frac{1}{3}\,\mathrm{Sp}\,L_{i0} = L_{i0}^{xx}, \\ L_1^{(1)} = \frac{1}{5}\,\mathrm{Sp}\,L_{11}^{(1)} = 2L_{11}^{xyxy} \qquad (x \neq y). \end{gathered} \tag{22.52c}$$

Substituting (22.52b) into (22.49)-(22.49b), we obtain

$$\begin{aligned}
\langle j_Q\rangle &= -L_0\frac{\operatorname{grad}T}{T^2}-\sum_{i=1}^{l}L_i\operatorname{grad}\left(\frac{\mu_i}{T}\right),\\
\langle j_d^i\rangle &= -L_i\frac{\operatorname{grad}T}{T^2}-\sum_{j=1}^{l}L_{ij}\operatorname{grad}\left(\frac{\mu_j}{T}\right),\\
\langle\mathring{\pi}_{\alpha\beta}\rangle &= -\frac{L_1^{(1)}}{2T}\left\{\frac{\partial v_\alpha}{\partial x_\beta}+\frac{\partial v_\beta}{\partial x_\alpha}-\frac{2}{3}\delta_{\alpha\beta}\operatorname{div}v\right\},\\
\langle\Pi\rangle &= -\frac{L_{11}^{(2)}}{T}\operatorname{div}\boldsymbol{v},
\end{aligned}\tag{22.53}$$

where the kinetic coefficients have a scalar character and are equal to

$$\begin{aligned}
L_0 &= \frac{1}{3}\int\int_{-\infty}^{0}e^{\varepsilon t}\left(j_Q(\boldsymbol{x})\cdot j_Q(\boldsymbol{x}',t)\right)d\boldsymbol{x}'\,dt,\\
L_{0i} &= \frac{1}{3}\int\int_{-\infty}^{0}e^{\varepsilon t}\left(j_Q(\boldsymbol{x})\cdot j_d^i(\boldsymbol{x}',t)\right)d\boldsymbol{x}'\,dt,\\
L_{ij} &= \frac{1}{3}\int\int_{-\infty}^{0}e^{\varepsilon t}\left(j_d^i(\boldsymbol{x})\cdot j_d^j(\boldsymbol{x}',t)\right)d\boldsymbol{x}'\,dt,\\
L_1^{(1)} &= \frac{1}{5}\int\int_{-\infty}^{0}e^{\varepsilon t}\left(\mathring{T}(\boldsymbol{x}):\mathring{T}(\boldsymbol{x}',t)\right)d\boldsymbol{x}'\,dt;
\end{aligned}\tag{22.53a}$$

the dot in the brackets denotes the scalar product of vectors, and two dots denote the complete contraction of tensors.

Rewriting (22.53) in other, more familiar notation, we obtain

$$\begin{aligned}
\langle j_Q\rangle &= -\lambda\nabla T-\sum_{i}L_i\operatorname{grad}\left(\frac{\mu_i}{T}\right),\\
\langle j_d^i\rangle &= -L_i\frac{\operatorname{grad}T}{T^2}-\sum_{j=1}^{l}L_{ij}\operatorname{grad}\left(\frac{\mu_j}{T}\right),\\
\langle\mathring{\pi}_{\alpha\beta}\rangle &= -\eta\left\{\frac{\partial v_\alpha}{\partial x_\beta}+\frac{\partial v_\beta}{\partial x_\alpha}-\frac{2}{3}\operatorname{div}\boldsymbol{v}\,\delta_{\alpha\beta}\right\},\\
\langle\Pi\rangle &= \langle p\rangle-\langle p\rangle_l=-\zeta\operatorname{div}\boldsymbol{v},
\end{aligned}\tag{22.54}$$

where

$$\begin{aligned}
\lambda &= \frac{L_0}{T^2}=\frac{1}{3T^2}\int\int_{-\infty}^{0}e^{\varepsilon t}\left(j_Q(\boldsymbol{x})\cdot j_Q(\boldsymbol{x}',t)\right)d\boldsymbol{x}'\,dt=\\
&= \frac{1}{T^2}\int\int_{-\infty}^{0}e^{\varepsilon t}\left(j_Q^x(x),\ j_Q^x(\boldsymbol{x}',t)\right)d\boldsymbol{x}'\,dt
\end{aligned}\tag{22.54a}$$

is the coefficient of thermal conductivity,

$$\eta = \frac{L_{11}^{(1)}}{2T} = \frac{1}{10T} \int \int\limits_{-\infty}^{0} e^{\varepsilon t} (\mathring{T}(\boldsymbol{x}) : \mathring{T}(\boldsymbol{x}', t))\, d\boldsymbol{x}'\, dt =$$
$$= \frac{1}{T} \int \int\limits_{-\infty}^{0} e^{\varepsilon t} (T_{xy}(\boldsymbol{x}), T_{xy}(\boldsymbol{x}', t))\, d\boldsymbol{x}'\, dt \qquad (22.54b)$$

is the coefficient of shear viscosity, and

$$\zeta = \frac{L_{11}^{(2)}}{T} = \frac{1}{T} \int \int\limits_{-\infty}^{0} e^{\varepsilon t} \Big(p(\boldsymbol{x}), p(\boldsymbol{x}', t) - \left(\frac{\partial p}{\partial u}\right)_n H(\boldsymbol{x}', t) -$$
$$- \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(\boldsymbol{x}', t)\Big)\, d\boldsymbol{x}'\, dt \qquad (22.54c)$$

is the coefficient of second viscosity.

The kinetic coefficients λ, η, and ζ are positive.

Noting that the tensor $L_{11} = L_{11}^{(1)} + L_{11}^{(2)} U$ on the basis of (22.54), (22.54b), and (22.54c) is equal to

$$L_{11}^{\mu\nu\mu_1\nu_1} = T\eta \left\{ \delta_{\mu\mu_1}\delta_{\nu\nu_1} + \delta_{\mu\nu_1}\delta_{\nu\mu_1} - \frac{2}{3}\delta_{\mu\nu}\delta_{\mu_1\nu_1} \right\} + T\zeta\delta_{\mu\nu}\delta_{\mu_1\nu_1} \qquad (22.54d)$$

and setting $\mu=\nu=\mu_1=\nu_1$, we obtain another expression for second viscosity:

$$\zeta + \frac{4}{3}\eta = \frac{1}{T} L_{11}^{xxxx} = \frac{1}{T} \int \int\limits_{-\infty}^{0} e^{\varepsilon t} (T_{xx}(\boldsymbol{x}), T_{xx}(\boldsymbol{x}', t) -$$
$$- \left(\frac{\partial p}{\partial u}\right)_n H(\boldsymbol{x}', t) - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(\boldsymbol{x}', t))\, d\boldsymbol{x}'\, dt. \qquad (22.54e)$$

The coefficients L_i describe the transfer of matter as a consequence of a temperature gradient, i.e., thermal diffusion (or the Soret effect), and the transfer of heat as a consequence of a density gradient, i.e., the Dufour effect. Such processes are called cross processes. They will be considered in more detail in section 22.7 with the example of a binary mixture. The coefficients L_{ij} describe the transfer of matter as a consequence of a density gradient, i.e., ordinary diffusion (see section 22.7).

Expressions (22.50), (22.53a), and (22.54a-d) for the kinetic coefficients were first obtained by M. Green [14] by the method of the theory of stochastic processes for the classical case on the basis of the microcanonical ensemble. In this case in the expressions (22.54c) for second viscosity the terms with $(\partial p/\partial u)_n$ and $(\partial p/\partial n_i)_u$ may be omitted. Indeed, all kinetic coefficients can be expressed through the total currents J^m:

$$L_{mn} = \frac{1}{V}\iiint_{-\infty}^{0} e^{\varepsilon t}(j^m(x),\ j^n(x',\ t))\,dx\,dx'\,dt = \frac{1}{V}\int_{-\infty}^{0} e^{\varepsilon t}(J^m,\ J^n(t))\,dt, \tag{22.54f}$$

where

$$J^m = \int j^m(x)\,dx.$$

In (22.54f) is taken into account the fact that the average correlator depends only on $x-x'$, and one can introduce another integration over x with a factor of $1/V$. Formula (22.54c) for second viscosity then takes on the form

$$\zeta = \frac{V}{T}\int e^{\varepsilon t}\left(p,\ p(t) - \left(\frac{\partial p}{\partial u}\right)_n \frac{H}{V} - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u \frac{N_i}{V}\right)dt, \tag{22.54g}$$

where

$$p = \frac{1}{V}\int p(x)\,dx$$

is the average pressure operator, and

$$H = \int H(x)\,dx, \qquad N_i = \int n_i(x)\,dx$$

are the total Hamiltonian and total particle number of the type i. If the averaging is carried out over a microcanonical ensemble, as in the article by Green [14], then H and N_i do not experience fluctuations, and consequently, in the correlator (22.54g) the terms with $(\partial p/\partial u)_n$ and $(\partial p/\partial n_i)_u$ can be omitted. Then

$$\zeta = \frac{V}{T}\int_{-\infty}^{0} e^{\varepsilon t}(p,\ p(t))\,dt. \tag{22.54h}$$

Such an expression was also obtained by Green. However, the microcanonical ensemble is not convenient for calculations, because one must take into account the auxiliary conditions of constant H and N_i, and therefore formula (22.54g) is more effective.

Expressions (22.50), (22.53a), and (22.54a)-(22.54c) for the quantum case were obtained by Mori [29-31], who integrated the Liouville equation with an initial condition in the form of the local equilibrium grand canonical distribution (21.14). His expressions for the kinetic coefficients contain Cesaro integrals (22.7), rather than Abel integrals (22.23b) (this difference was discussed in section 22.3). In addition, in his expression (22.54g) for second viscosity terms with $(\partial p/\partial u)_n$ and $(\partial p/\partial n_i)_u$ were not taken into account. This discrepancy was later corrected by Mori himself in the article [95] by the method of collective variables. This result has been confirmed also by other authors [38, [illegible]].

Formulas for kinetic coefficients in the form of current correlation functions were obtained after Green and Mori by many other authors by means of various methods of taking into account the thermal perturbations, which were discussed at the beginning of Chapter IV, or by means of a combination of these methods.

Formula (22.54b) for the shear viscosity was obtained by Montroll [8] by the indirect method of the linear reaction, considering the viscous current created by a change in the dimensions of the container. This idea was expressed earlier by Feynman in unpublished lectures.

All formulas for the kinetic coefficients were obtained by Kadanoff and Martin [10] by means of variants of the method of the linear reaction, and they were also obtained by Luttinger [9].

Kadanoff and Martin considered a state of a liquid which was weakly nonequilibrium with respect to temperature, chemical potential, and velocity and introduced fictitious mechanical perturbations, which bring the system to the same state (the difference between the exponentials of the local equilibrium and equilibrium distributions). This perturbation is switched off instantaneously at t=0, and the system develops further according to the equations of hydrodynamics.

The average values of mechanical quantities (densities of energy, momentum, and particle number) for t≤0 can be expressed through the perturbation and the susceptibility, while the latter is expressed through the correlation functions or Green functions. By comparing these expressions with the solutions of the hydrodynamic equations one can express the susceptibility through the kinetic coefficients. Inverting these relations gives formulas for the kinetic coefficients in terms of the correlation functions.

The method of Luttinger [9] is very close to the method of Kadanoff and Martin, but Luttinger strives for a closer analogy between the auxiliary mechanical perturbations and the real fields. The perturbation in the local temperature is associated with a gravitational field, which causes the same nonuniformity in the energy density; the perturbation in the chemical potential is associated with the potential of an electric field; the perturbation in the velocity is associated with a magnetic field, which is described by a vector potential. These fields can create the same distribution of energy, mass, and momentum in an equilibrium state, as exist in the given nonequilibrium state.

We have already mentioned at the beginning of Chapter IV other articles in which formulas for the kinetic coefficients in terms of the correlation functions have been derived, and we refer the reader to the literature cited therein.

The formulas for the kinetic coefficients in terms of the correlation function in the case of sufficiently dilute gases, for which the kinetic equation of Boltzmann is applicable, lead to the same expressions for the kinetic coefficients as in the Chapman-Enskog theory [96] in the approximation which is linear in terms of the gradients of thermodynamic parameters [32,97-99]. This result is understandable, because the normal solution of the Boltzmann equation (which is studied in the Chapman-Enskog theory) is based on assumptions similar to those which are used in constructing the nonequilibrium distribution, and in particular that for a time which is sufficiently large compared to the mean time between collisions the distribution function begins to depend on time only through its thermodynamic parameters.

To obtain the Chapman-Enskog formulas from (22.53a) one can omit terms with the interaction potential in the expressions for the currents (22.22), (19.12), (19.17a), (19.27a), and (19.29a). For liquids these terms are significant. According to the Chapman-Enskog theory for monotomic ideal gases the coefficient of second viscosity is equal to zero, $\zeta=0$.

In approximations which take into account higher powers of the density the formulas (22.50) lead to the same results as the theory of N. N. Bogolyubov [1,100], which is based on solving a chain of equations for the distribution functions by means of an expansion in powers of the density. For subsequent approximations it is necessary to take into account ternary and higher order collisions, which is a very complicated problem. The connection between the calculation of kinetic coefficients and the solution of the generalized kinetic equation of Bogolyubov can be found in [33]. The theory of transfer processes can be found also in [216-226].

22.6. Transfer Processes in a Single-Component Liquid. Thermal Conductivity and Navier-Stokes Equations.

In a single-component liquid (or gas) the diffusion current density operator $\mathbf{j}_d(\mathbf{x})$ (22.13a) is identically zero, because

$$j(x) - \frac{1}{m}\,p(x) = 0; \qquad (22.55)$$

Consequently, in this liquid the processes of diffusion and thermal diffusion and the Dufour effect are absent, because

$$L_i = L_{ij} = 0. \tag{22.56}$$

In this case there remain only the processes of thermal conductivity and viscosity, which we shall discuss later. (If a single-component liquid is a mixture of isotopes, then equalization of the isotopic composition can take place in the liquid, i.e., the process of self-diffusion.)

In accordance with (20.68) in a local equilibrium state the current densities of energy, momentum, and particle number are equal to

$$\begin{gathered}\langle j_H\rangle_l = \left(u + p + \rho\frac{v^2}{2}\right)\boldsymbol{v},\\ \langle T_{\alpha\beta}\rangle_l = p\delta_{\alpha\beta} + \rho v_\alpha v_\beta,\\ \langle j\rangle_l = \rho\boldsymbol{v}, \quad \rho = \langle\rho(\boldsymbol{x})\rangle_l, \quad u = \langle H'(\boldsymbol{x})\rangle_l,\end{gathered} \tag{22.57}$$

and the corresponding entropy current in accordance with (20.74) has the form

$$j_S = S(\boldsymbol{x})\boldsymbol{v}, \tag{22.57a}$$

where S(**x**) is the entropy density (22.37a).

To study the process of thermal conductivity one can consider either the transfer equation for energy or for entropy, but the latter is more convenient, because the equation for the transfer of entropy in a local equilibrium state has a very simple form

$$\frac{\partial S(\boldsymbol{x})}{\partial t} = -\operatorname{div} j_S = -\operatorname{div}(S(\boldsymbol{x})\boldsymbol{v}) \tag{22.58}$$

(see (22.38), (22.38a)).

The linear relations between thermodynamic forces and currents (22.54) in a single-component liquid take on the form

$$\begin{aligned} \langle j_Q\rangle &= -\lambda\nabla T, \\ \langle\mathring{\pi}_{\alpha\beta}\rangle &= -\eta\left\{\frac{\partial v_\alpha}{\partial x_\beta}+\frac{\partial v_\beta}{\partial x_\alpha}-\frac{2}{3}\delta_{\alpha\beta}\operatorname{div} v\right\}, \\ \langle\Pi\rangle &= \langle p\rangle-\langle p\rangle_l=-\zeta\operatorname{div} v, \end{aligned} \tag{22.59}$$

where $\langle\mathring{\pi}\rangle$ and $\langle\Pi\rangle$ are the divergenceless and divergence parts of the viscous stress tensor,

$$\langle T_{\alpha\beta}\rangle-\langle T_{\alpha\beta}\rangle_l=\langle\mathring{\pi}_{\alpha\beta}\rangle+\langle\Pi\rangle\delta_{\alpha\beta}. \tag{22.59a}$$

The first equation of the system (22.59) is sometimes called Fick's first law.

The laws of conservation of mass, energy, and momentum and the equation of entropy balance have the forms

$$\begin{aligned} &\frac{\partial\rho}{\partial t}+\operatorname{div}\rho v=0, \\ &\frac{\partial\langle H(x)\rangle}{\partial t}+\operatorname{div}\langle j_H\rangle=0, \\ &\frac{\partial\langle p_\alpha\rangle}{\partial t}+\sum_\beta\frac{\partial\langle T_{\beta\alpha}\rangle}{\partial x_\beta}=0, \\ &\frac{\partial S(x)}{\partial t}+\operatorname{div} j_S=\sigma, \end{aligned} \tag{22.60}$$

where

$$\sigma=\langle j_Q\rangle\cdot\nabla\beta-\beta\langle\mathring{\pi}\rangle : (\mathring{\nabla} v)^s-\beta\langle\Pi\rangle\operatorname{div} v \tag{22.61}$$

is the production of entropy, and

$$j_S=S(x)v+\beta\langle j_Q\rangle+\beta\langle\mathring{\pi}\rangle\cdot v+\beta\langle\Pi\rangle v \tag{22.62}$$

is the entropy current, because the remaining terms in formulas (22.48) and (22.40) are zero.

Taking into account the linear relations (22.59), we write the production of entropy (22.61) and the entropy current (22.62) in the form

$$\sigma = \frac{\lambda}{T^2} (\nabla T)^2 + \frac{2\eta}{T} (\overset{\circ}{\nabla} \boldsymbol{v})^s : (\overset{\circ}{\nabla} \boldsymbol{v})^s + \frac{\zeta}{T} (\operatorname{div} \boldsymbol{v})^2, \tag{22.62a}$$

$$j_S = S(\boldsymbol{x})\, \boldsymbol{v} - \frac{\lambda}{T} \nabla T - \frac{2\eta}{T} (\overset{\circ}{\nabla} \boldsymbol{v})^s \cdot \boldsymbol{v} - \frac{\zeta}{T} \boldsymbol{v} \operatorname{div} \boldsymbol{v}, \tag{22.62b}$$

and the equations for the balance of energy, momentum, and entropy we write in the form

$$\begin{aligned}
&\frac{\partial}{\partial t}\left(u + \rho \frac{v^2}{2}\right) + \operatorname{div}\left(u + p + \frac{\rho v^2}{2}\right) \boldsymbol{v} = \nabla(\lambda \nabla T),\\
&\frac{\partial \rho v_\alpha}{\partial t} + \sum_\beta \frac{\partial}{\partial x_\beta} \rho v_\alpha v_\beta + \frac{\partial p}{\partial x_\alpha} =\\
&\qquad = \sum_\beta \frac{\partial}{\partial x_\beta} \eta \left(\frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \operatorname{div} \boldsymbol{v}\right) + \frac{\partial}{\partial x_\alpha} \zeta \operatorname{div} \boldsymbol{v},\\
&\frac{\partial S(x)}{\partial t} + \operatorname{div}(S(\boldsymbol{x})\, \boldsymbol{v}) =\\
&= \nabla \cdot \left(\frac{\lambda}{T} \nabla T\right) + 2\nabla \cdot \left(\frac{\eta}{T} (\overset{\circ}{\nabla} \boldsymbol{v})^s \cdot \boldsymbol{v}\right) + \nabla \cdot \left(\frac{\zeta}{T} \boldsymbol{v} \operatorname{div} \boldsymbol{v}\right) + \frac{\lambda}{T^2} (\nabla T)^2 +\\
&\qquad + \frac{2\eta}{T} (\overset{\circ}{\nabla} \boldsymbol{v})^s : (\overset{\circ}{\nabla} \boldsymbol{v})^s + \frac{\zeta}{T} (\operatorname{div} \boldsymbol{v})^2.
\end{aligned} \tag{22.63}$$

In equations (22.63) the kinetic coefficients depend on the thermodynamic parameters, for example on the pressure and temperature, and consequently, for a spatially inhomogeneous state they may depend on position. However this dependence is usually small, and these kinetic coefficients can be considered to be constant and taken outside of the gradient sign. Then

$$\begin{aligned}
&\frac{\partial}{\partial t}\left(u + \rho \frac{v^2}{2}\right) + \operatorname{div}\left(u + p + \rho \frac{v^2}{2}\right) \boldsymbol{v} = \lambda \nabla^2 T,\\
&\rho\left(\frac{\partial \boldsymbol{v}}{\partial t} + \boldsymbol{v} \cdot \nabla \boldsymbol{v}\right) + \nabla p = \eta \nabla^2 \boldsymbol{v} + \left(\zeta + \frac{1}{3}\eta\right) \nabla \operatorname{div} \boldsymbol{v},\\
&\rho\left(\frac{\partial s}{\partial t} + \boldsymbol{v} \cdot \nabla s\right) = \frac{\lambda}{T} \nabla^2 T + 2\eta \nabla \cdot \left(\frac{1}{T} (\overset{\circ}{\nabla} \boldsymbol{v})^s \cdot \boldsymbol{v}\right) +\\
&\qquad + \zeta \nabla \cdot \left(\frac{1}{T} \boldsymbol{v} \operatorname{div} \boldsymbol{v}\right) + \frac{2\eta}{T} (\overset{\circ}{\nabla} \boldsymbol{v})^s : (\overset{\circ}{\nabla} \boldsymbol{v})^s + \frac{\zeta}{T} (\operatorname{div} \boldsymbol{v})^2,
\end{aligned} \tag{22.63a}$$

where

$$s(\boldsymbol{x}) = S(\boldsymbol{x})/\rho$$

is the entropy per unit mass.

The second equation of the system (22.63a) is the Navier-Stokes equation, and the first (or the third) is the heat transfer equation. As a consequence of (22.37a) the third equation follows from the first two and the law of

conservation of mass.

If the speed of flow of the liquid is significantly smaller than the speed of sound, then the change in pressure as a consequence of the motion is very small, and one can disregard the change in density and in other thermodynamic quantities caused by the motion. Consequently, in calculating derivatives of thermodynamic quantities the pressure can be considered constant, and

$$\frac{\partial s}{\partial t} = \left(\frac{\partial s}{\partial T}\right)_p \frac{\partial T}{\partial t}, \quad \nabla s = \left(\frac{\partial s}{\partial T}\right)_p \nabla T. \tag{22.64}$$

Taking into account that

$$T\left(\frac{\partial s}{\partial T}\right)_p = C_p \tag{22.64a}$$

is the specific heat at constant pressure, we obtain

$$\frac{\partial s}{\partial t} = \frac{C_p}{T}\frac{\partial T}{\partial t}, \quad \nabla s = \frac{C_p}{T}\nabla T. \tag{22.64b}$$

Consequently, the heat transfer equation for incompressible motion of a the liquid, when div v=0, takes on the form

$$\frac{\partial T}{\partial t} + v \cdot \nabla T = \chi\nabla^2 T + \frac{2\nu T}{C_p}\nabla \cdot \left(\frac{1}{T}(\overset{\circ}{\nabla} v)^s \cdot v\right) + \frac{2\nu}{C_p}(\overset{\circ}{\nabla} v)^s : (\overset{\circ}{\nabla} v)^s, \tag{22.65}$$

where

$$\chi = \lambda/\rho C_p \tag{22.65a}$$

is the coefficient of thermal conductivity, and

$$\nu = \eta/\rho \tag{22.65b}$$

is the kinematical viscosity. In a stationary liquid, when the transfer of heat is caused exclusively by the mechanism of thermal conductivity, equation (22.65) takes on the form

$$\frac{\partial T}{\partial t} = \chi\nabla^2 T \tag{22.65c}$$

and is called the thermal conductivity equation or the Fourier equation.

22.7. Transfer Processes in a Binary Mixture. Thermal Conductivity, Diffusion and Cross Effects.

We shall consider transfer processes in a two-component liquid (or gas) in the absence of velocity gradients. In this case there exist only vector processes - thermal conductivity, diffusion, and cross effects - thermal diffusion, and the Dufour effect, and the linear relations (22.54) between thermodynamic forces and currents take on the form

$$\begin{aligned} \langle j_Q\rangle &= -\frac{L_0}{T^2}\nabla T - \sum_{i=1}^{2} L_i\nabla\left(\frac{\mu_i}{T}\right), \\ \langle j_d^i\rangle &= -L_i\frac{1}{T^2}\nabla T - \sum_{j=1}^{2} L_{ij}\nabla\left(\frac{\mu_j}{T}\right) \qquad (i = 1,\ 2). \end{aligned} \tag{22.66}$$

The diffusion currents $\langle j_d^1\rangle$ and $\langle j_d^2\rangle$ are connected by the relation

$$\sum_{i=1}^{2} m_i\langle j_d^i\rangle = 0 \tag{22.67}$$

for any ∇T, $\nabla(\mu_i/T)$, which follows from the last relationship in (22.22); consequently, the kinetic coefficients L_i and L_{ij} satisfy the relations

$$\sum_i m_i L_i = 0, \quad \sum_i m_i L_{ij} = 0. \tag{22.68}$$

In the linear relations (22.66) it is sufficient to consider only one diffusion current, for example $\langle j_d^1\rangle = \langle j_d\rangle$, because the second current can be found from equation (22.67). Taking into account (22.68) we write (22.66) in the form

$$\langle j_Q \rangle = -\frac{L_2}{T^2}\nabla T - L_1 m_1 \nabla\left(\frac{\mu}{T}\right),$$
$$\langle j_1 \rangle = -\frac{L_1}{T^2}\nabla T - L_{11} m_1 \nabla\left(\frac{\mu}{T}\right), \qquad (22.66a)$$

where the chemical potential has been introduced [82]

$$\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2}. \qquad (22.66b)$$

The chemical potential (22.66b) enters into the thermodynamic equality (20.24b). Indeed,

$$ds = \beta\, du(\mathbf{x}) + \beta p\, dv(\mathbf{x}) - \beta \sum_i \frac{\mu_i}{m_i} dC_i =$$
$$= \beta\, du(\mathbf{x}) + \beta p\, dv(\mathbf{x}) - \beta\left(\frac{\mu_1}{m_1} - \frac{\mu_2}{m_2}\right) dC, \qquad (22.69)$$

where $C_1+C_2=1$, $C=C_1=m_1n_1/\rho$ is the mass concentration, $u(\mathbf{x})=\langle H'(\mathbf{x})\rangle/\rho$ is the energy density per unit mass, and $v(\mathbf{x})=1/\rho$ is the specific volume per unit mass.

From (22.69) it follows that

$$\mu = -T\left(\frac{\partial s}{\partial C}\right)_{u,\,v}. \qquad (22.69a)$$

Let us change to the variables p,T,C in the thermodynamic functions. Then

$$\nabla\mu = \left(\frac{\partial\mu}{\partial C}\right)_{p,\,T}\nabla C + \left(\frac{\partial\mu}{\partial T}\right)_{C,\,p}\nabla T + \left(\frac{\partial\mu}{\partial p}\right)_{C,\,T}\nabla p. \qquad (22.70)$$

Substituting (22.70) into (22.66a), we obtain

$$\langle j_Q\rangle = -\lambda\nabla T + \frac{L_1}{L_{11}}\langle j_d\rangle,$$

$$\langle j_d\rangle = -\frac{1}{m_1}\rho D\left(\nabla C + \frac{K_T}{T}\nabla T + \frac{K_p}{p}\nabla p\right), \qquad (22.71)$$

where

$$\frac{L_1}{L_{11}} = m_1\left(K_T\left(\frac{\partial\mu}{\partial C}\right)_{p,T} - T^2\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right)_{C,p}\right), \qquad (22.71a)$$

and

$$\lambda = \frac{L_0}{T^2} - \frac{L_1^2}{L_{11}T^2} \qquad (22.72)$$

is the *coefficient of thermal conductivity* in the binary mixture, and

$$D = \frac{L_{11}m_1^2}{\rho T}\left(\frac{\partial\mu}{\partial C}\right)_{p,T} \qquad (22.73)$$

is the *diffusion coefficient*, and

$$\frac{\rho K_T D}{T m_1} = \frac{L_1}{T^2} + L_{11}m_1\frac{\partial}{\partial T}\left(\frac{\mu}{T}\right)_{C,p}, \qquad (22.74)$$

where $K_T D$ is the *coefficient of thermal diffusion*, and K_T is the *thermal diffusion ratio*, and

$$K_p = p\left(\frac{\partial\mu}{\partial p}\right)_{C,T}\Big/\left(\frac{\partial\mu}{\partial C}\right)_{p,T}, \qquad (22.75)$$

where $K_p D$ is the *coefficient of pressure diffusion*.

From the second equation of the system (22.71) it follows that the diffusion current is caused by gradients in concentration, temperature, and pressure (ordinary diffusion, thermal diffusion, and pressure diffusion). The last process is significant if strong pressure gradients are produced, for example in a centrifuge.

The coefficient of thermal diffusion is proportional to the product of $C_1=C$ and $C_2=1-C$, in the absence of a coefficient of diffusion, which in the first approximation is independent of the concentration. Therefore one introduces the constant of thermal diffusion

$$a = \frac{K_T}{C(1-C)}. \qquad (22.76)$$

Diffusion and thermal conductivity in our case, when v=0, are defined by the equations

$$\begin{aligned} \frac{\partial \langle n_1 \rangle}{\partial t} + \operatorname{div} \langle j_d \rangle = 0, \\ \frac{\partial S(x)}{\partial t} + \operatorname{div} j_S = \sigma, \end{aligned} \qquad (22.77)$$

where in accordance with (22.40) and (22.39)

$$j_S = \langle j_Q \rangle \beta - \sum_i \langle j_d^i \rangle \nu_i = \beta (j_Q - j_d m_i \mu), \qquad (22.77a)$$

$$\sigma = \langle j_Q \rangle \cdot \nabla \beta - \sum_i \langle j_d^i \rangle \cdot \nabla \nu_i. \qquad (22.77b)$$

Substituting (22.71) and (22.77a) into (22.77) and neglecting terms with a pressure gradient and terms of a higher order in the gradients, we obtain the system of equations

$$\begin{aligned} \frac{\partial C}{\partial t} &= D \left(\nabla^2 C + \frac{K_T}{T} \nabla^2 T \right), \\ \frac{\partial T}{\partial t} &= \chi \nabla^2 T + \frac{K_T}{C_p} \left(\frac{\partial \mu}{\partial C} \right)_{p,T} \frac{\partial C}{\partial t}, \end{aligned} \qquad (22.78)$$

which define the distribution of the concentration and the temperature in a binary mixture. In the particular case in which the temperature is a constant we obtain

$$\frac{\partial C}{\partial t} = D \nabla^2 C, \qquad (22.79)$$

i.e., the usual diffusion equation.

22.8. Another Choice of Thermodynamic Forces.

In section 22.1 we began with the nonequilibrium statistical operator in the form (22.1) and chose the thermodynamic forces in the form (22.13b) as gradients of thermodynamic parameters. There is another possible choice for the thermodynamic forces.

We shall proceed from the nonequilibrium statistical operator in the form (21.10a)

$$\rho = Q^{-1}\exp\Big\{-\sum_m \int F_m(\boldsymbol{x},\ t)P_m(\boldsymbol{x})\,d\boldsymbol{x} + \\ + \sum_m \int\int_{-\infty}^{0} e^{\varepsilon t_1}\Big(F_m(\boldsymbol{x},\ t+t_1)\dot{P}_m(\boldsymbol{x},\ t_1) + \\ + \frac{\partial F_m(\boldsymbol{x},\ t+t_1)}{\partial t}P_m(\boldsymbol{x},\ t_1)\Big)\,d\boldsymbol{x}\,dt_1\Big\} \qquad (22.80)$$

and we shall choose as the thermodynamic forces the Fourier components of the parameters $F_m(\boldsymbol{x},t)$ with respect to the spatial variables.

The statistical operator in the form (22.80) is sometimes more convenient than (22.1), because it does not require knowledge of the explicit expressions for the currents $j_m(\boldsymbol{x},t)$, the choice of which is not completely unique. This is especially important for a system with long range forces, where it is impossible to perform a smoothing of the operators over a small radius of action of the forces, as in § 19.

In an approximation which is linear in the small velocities the thermodynamic parameters $F_m(\boldsymbol{x},t)$ have the form

$$\begin{aligned} F_0(\boldsymbol{x},\ t) &= \beta(\boldsymbol{x},\ t), \\ F_i(\boldsymbol{x},\ t) &= -\beta(\boldsymbol{x},\ t)\boldsymbol{v}(\boldsymbol{x},\ t) \equiv -\boldsymbol{u}(\boldsymbol{x},\ t), \\ F_{l+1}(\boldsymbol{x},\ t) &= -\beta(\boldsymbol{x},\ t)\Big(\mu_l(\boldsymbol{x},\ t) - \frac{mv^2(\boldsymbol{x},\ t)}{2}\Big) \simeq \\ &\simeq -\beta(\boldsymbol{x},\ t)\mu_l(\boldsymbol{x},\ t) \equiv -\nu_l(\boldsymbol{x},\ t). \end{aligned} \qquad (22.81)$$

We expand the operators $P_m(\boldsymbol{x})$ and the parameters $F_m(\boldsymbol{x})$ in Fourier integrals. Then the statistical operator (22.80) takes on the form

$$\rho = Q^{-1} \exp \Big\{ - \sum_{m,\boldsymbol{k}} F_m(\boldsymbol{k}, t)\, P_m(-\boldsymbol{k}) + \sum_{m,\boldsymbol{k}} \int_{-\infty}^{0} e^{\varepsilon t} \Big(F_m(\boldsymbol{k}, t+t_1)\, \dot{P}_m(-\boldsymbol{k}, t_1) + \frac{\partial F_m(\boldsymbol{k}, t+t_1)}{\partial t} P_m(-\boldsymbol{k}, t_1) \Big) dt_1 \Big\}. \tag{22.82}$$

We eliminate the time derivatives of the parameters F_m by means of the relations (22.10), which in the approximation linear in the velocities have the form

$$\begin{aligned} \frac{\partial \beta(\boldsymbol{x}, t)}{\partial t} &= \left(\frac{\partial p}{\partial u}\right)_n \operatorname{div} \boldsymbol{u}(\boldsymbol{x}, t), \\ \frac{\partial \nu_i(\boldsymbol{x}, t)}{\partial t} &= -\left(\frac{\partial p}{\partial n_i}\right)_u \operatorname{div} \boldsymbol{u}(\boldsymbol{x}, t), \\ \frac{\partial \boldsymbol{u}(\boldsymbol{x}, t)}{\partial t} &= \frac{u+p}{\langle \rho \rangle} \nabla \beta(\boldsymbol{x}, t) - \sum_i \frac{\langle n_i \rangle}{\langle \rho \rangle} \nabla \nu_i(\boldsymbol{x}, t), \end{aligned} \tag{22.83}$$

or in Fourier components

$$\begin{aligned} \frac{\partial \beta(\boldsymbol{k}, t)}{\partial t} &= \left(\frac{\partial p}{\partial u}\right)_n i\boldsymbol{k} \cdot \boldsymbol{u}(\boldsymbol{k}, t), \\ \frac{\partial \nu_i(\boldsymbol{k}, t)}{\partial t} &= -\left(\frac{\partial p}{\partial n_i}\right)_u i\boldsymbol{k} \cdot \boldsymbol{u}(\boldsymbol{k}, t), \\ \frac{\partial \boldsymbol{u}(\boldsymbol{k}, t)}{\partial t} &= \frac{u+p}{\langle \rho \rangle} i\boldsymbol{k}\beta(\boldsymbol{k}, t) - \sum_i \frac{\langle n_i \rangle}{\langle \rho \rangle} i\boldsymbol{k}\nu_i(\boldsymbol{k}, t). \end{aligned} \tag{22.83a}$$

Substituting (22.83a) into (22.82) and making use of the relationship

$$\dot{\rho}(-\boldsymbol{k}) = i\boldsymbol{k} \cdot \boldsymbol{p}(-\boldsymbol{k}), \tag{22.84}$$

we obtain

$$\rho = Q^{-1} \exp \Big\{ - \sum_{m,\boldsymbol{k}} F_m(\boldsymbol{k}, t)\, P_m(-\boldsymbol{k}) + \sum_{m,\boldsymbol{k}} \int_{-\infty}^{0} e^{\varepsilon t_1} J_m(-\boldsymbol{k}, t_1)\, X_m(\boldsymbol{k}, t+t_1)\, dt_1 \Big\}, \tag{22.85}$$

where we have introduced the currents for energy, momentum, and particle number

$$J_0(-k) = \dot{H}(-k) - \frac{u+p}{\langle\rho\rangle}\dot{\rho}(-k),$$
$$J_1(-k) = \dot{p}(-k) - \left(\frac{\partial p}{\partial u}\right)_n ikH(-k) - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u ikn_i(-k), \qquad (22.85a)$$
$$J_{l+1}(-k) = \dot{n}_l(-k) - \frac{\langle n_l\rangle}{\langle\rho\rangle}\dot{\rho}(-k)$$

and the thermodynamic forces

$$X_0(k, t) = \beta(k, t)$$
$$X_1(k, t) = -u(k, t), \qquad (22.85b)$$
$$X_{i+1}(k, t) = -\nu_i(k, t) \qquad (i \geq 1).$$

Using the smallness of the thermodynamic forces and expanding (22.85) in a series, analogously to (22.18), we obtain

$$\rho \simeq \left\{ 1 - \int_0^1 (e^{-A\tau} B e^{A\tau} - \langle B\rangle_l)\, d\tau \right\} \rho_l, \qquad (22.86)$$

where

$$B = -\sum_{m, k} \int_{-\infty}^{0} e^{\varepsilon t_1} J_m(-k, t_1) X_m(k, t+t_1)\, dt_1. \qquad (22.86a)$$

By means of (22.86) we obtain linear relations between the thermodynamic forces and currents·

$$\langle J_m(k)\rangle = \langle J_m(k)\rangle_l + \sum_{n, k_1} \int_{-\infty}^{0} e^{\varepsilon t_1} (J_m(k), J_n(-k_1)) X_n(k_1, t+t_1)\, dt_1,$$

where in the quantum time correlation function in the integrand the averaging is carried out over a state of statistical equilibrium, and thus, because of the isotropy of space the only non-zero terms are those with $k_1=k$:

$$\langle J_m(k)\rangle = \langle J_m(k)\rangle_l + \sum_{n} \int_{-\infty}^{0} e^{\varepsilon t_1} (J_m(k), J_n(-k, t_1)) X_n(k, t+t_1)\, dt_1. \qquad (22.87)$$

If the retardation is neglected, then

$$\langle J_m(\boldsymbol{k})\rangle = \langle J_m(\boldsymbol{k})\rangle_l + \sum_n \mathscr{L}_{mn}(\boldsymbol{k})\, X_n(\boldsymbol{k}), \tag{22.87a}$$

where

$$\mathscr{L}_{mn}(\boldsymbol{k}) = \int_{-\infty}^{0} e^{\varepsilon t_1} (J_m(\boldsymbol{k}),\ J_n(-\boldsymbol{k},\ t_1))\, dt_1 \tag{22.87b}$$

are the kinetic coefficients. Taking into account that in accordance with the Curie theorem the only non-zero correlators are those connecting quantities of identical tensor rank and taking into account that in accordance with (21.15)

$$\begin{aligned} \langle \dot{\rho}(\boldsymbol{k})\rangle &= -i\boldsymbol{k}\cdot\langle \boldsymbol{p}(\boldsymbol{k})\rangle = \langle \dot{\rho}(\boldsymbol{k})\rangle_l, \\ \langle H(\boldsymbol{k})\rangle &= \langle H(\boldsymbol{k})\rangle_l, \\ \langle n_m(\boldsymbol{k})\rangle &= \langle n_m(\boldsymbol{k})\rangle_l, \end{aligned} \tag{22.88}$$

we write the linear relations (22.87a) in the form

$$\begin{aligned} \langle \dot{H}(\boldsymbol{k})\rangle &= \langle \dot{H}(\boldsymbol{k})\rangle_l + \mathscr{L}_{00}(\boldsymbol{k})\,\beta(\boldsymbol{k},\ t) - \sum_{n\geq 1} \mathscr{L}_{0n+1}(\boldsymbol{k})\,\nu_n(\boldsymbol{k},\ t), \\ \langle \dot{n}_m(\boldsymbol{k})\rangle &= \langle \dot{n}_m(\boldsymbol{k})\rangle_l + \mathscr{L}_{m0}(\boldsymbol{k})\,\beta(\boldsymbol{k},\ t) - \sum_{n\geq 1} \mathscr{L}_{mn+1}(\boldsymbol{k})\,\nu_n(\boldsymbol{k},\ t), \\ \langle \dot{\boldsymbol{p}}(\boldsymbol{k})\rangle &= \langle \dot{\boldsymbol{p}}(\boldsymbol{k})\rangle_l - \mathscr{L}_{11}(\boldsymbol{k})\cdot \boldsymbol{u}(\boldsymbol{k},\ t). \end{aligned} \tag{22.89}$$

Analogous relations without retardation have been obtained by Kubo, Yokota, and Nakajima [28] using the Onsager hypothesis on the character of the damping of fluctuations. These authors considered a single-component liquid and did not take into account the transfer of momentum, which is described by the last equation of the system (22.89). They obtained the improper integrals in (22.87b) as Cesaro integrals, rather than Abel integrals, because they did not explicitly consider the causality condition (see sections 21.3, 22.3). In addition, in the expressions for the currents they did not take into account the additional terms which compensate for the non-dissipative motion of the center of mass.

The linear relations (22.87a) have, in general, a non-local character because of the dependence of $\mathscr{L}_{mn}(k)$ on k. If we expand $\mathscr{L}_{mn}(k)$ in a series in k, keeping only the first non-vanishing terms of the expansion, we obtain

$$\mathscr{L}_{mn}(\boldsymbol{k}) \cong V L_{mn} k^2 \qquad (m,\ n = 0,\ 2,\ 3,\ \ldots),$$
$$\mathscr{L}_{11}^{\alpha\beta}(\boldsymbol{k}) = VT\eta\left(k^2\delta_{\alpha\beta} + \frac{1}{3}k_\alpha k_\beta\right) + VT\zeta k_\alpha k_\beta =$$
$$= VT\eta(k^2\delta_{\alpha\beta} - k_\alpha k_\beta) + VT\left(\zeta + \frac{4}{3}\eta\right)k_\alpha k_\beta, \tag{22.90}$$

because the odd powers of **k** are absent as a consequence of the isotropy of space. Taking into account (22.90) the linear relations (22.89) take on a local form

$$\langle \dot{H}(\boldsymbol{k})\rangle = \langle \dot{H}(\boldsymbol{k})\rangle_l + VL_{00}k^2\beta(\boldsymbol{k},\ t) - V\sum_{n\geqslant 1} L_{0n+1}k^2\nu_n(\boldsymbol{k},\ t),$$
$$\langle \dot{n}_m(\boldsymbol{k})\rangle = \langle \dot{n}_m(\boldsymbol{k})\rangle_l + VL_{m0}k^2\beta(\boldsymbol{k},\ t) - V\sum_{n\geqslant 1} L_{mn+1}k^2\nu_n(\boldsymbol{k},\ t), \tag{22.91}$$
$$\langle \dot{\boldsymbol{p}}(\boldsymbol{k})\rangle = \langle \dot{\boldsymbol{p}}(\boldsymbol{k})\rangle_l - VT\eta(k^2\boldsymbol{u}(\boldsymbol{k},\ t) +$$
$$+ \frac{1}{3}\boldsymbol{k}(\boldsymbol{k}\boldsymbol{u}(\boldsymbol{k},\ t)) - VT\zeta\boldsymbol{k}(\boldsymbol{k}\boldsymbol{u}(\boldsymbol{k},\ t)).$$

From (22.90) and (22.91) it follows that the kinetic coefficients L_{mn}, η, and ζ are equal to

$$L_{mn} = \lim_{k\to 0}\frac{\mathscr{L}_{mn}(\boldsymbol{k})}{Vk^2} \qquad (m,\ n = 0,\ 2,\ 3,\ \ldots),$$
$$\eta = \lim_{k\to 0}\frac{1}{2VTk^4}\sum_{\alpha\beta}\mathscr{L}_{11}^{\alpha\beta}(\boldsymbol{k})\left(k^2\delta_{\alpha\beta} - k_\alpha k_\beta\right), \tag{22.92}$$
$$\zeta + \frac{4}{3}\eta = \lim_{k\to 0}\frac{\boldsymbol{k}\cdot\mathscr{L}_{11}\cdot\boldsymbol{k}}{VTk^4}.$$

In the expression for η we have used the fact that

$$\sum_{\alpha\beta}(k_\alpha k_\beta - k^2\delta_{\alpha\beta})^2 = 2k^4.$$

It is easily verified that the expressions (22.92) for the kinetic coefficients are equivalent to the expressions (22.53a) obtained earlier. Indeed,

$$L_{00} = \lim_{k\to 0} \frac{1}{Vk^2} \int_{-\infty}^{0} e^{\varepsilon t} (J_0(\boldsymbol{k}),\ J_0(-\boldsymbol{k},\ t))\, dt, \tag{22.93}$$

where

$$J_0(\boldsymbol{k}) = \dot{H}(\boldsymbol{k}) - \frac{u+p}{\langle\rho\rangle} \dot{\rho}(\boldsymbol{k}), \tag{22.93a}$$

or, since

$$\dot{H}(\boldsymbol{k}) = -i\boldsymbol{k}\cdot \boldsymbol{j}_H(\boldsymbol{k}), \quad \dot{\rho}(\boldsymbol{k}) = -i\boldsymbol{k}\cdot \boldsymbol{p}(\boldsymbol{k}),$$

we have

$$J_0(\boldsymbol{k}) = -i\boldsymbol{k}\cdot\left(\boldsymbol{j}_H(\boldsymbol{k}) - \frac{u+p}{\langle\rho\rangle} \boldsymbol{p}(\boldsymbol{k})\right) = -i\boldsymbol{k}\cdot \boldsymbol{j}_Q(\boldsymbol{k}). \tag{22.93b}$$

Because of the spatial homogeneity of the system the formula (22.93) can be transformed to the form

$$\begin{aligned} L_{00} &= \lim_{k\to 0} \frac{1}{Vk^2} \int_{-\infty}^{0} e^{\varepsilon t} (\boldsymbol{j}_Q(\boldsymbol{k}),\ \boldsymbol{j}_Q(-\boldsymbol{k},\ t)) \colon \boldsymbol{kk}\, dt = \\ &= \lim_{k\to 0} \frac{1}{3V} \int_{-\infty}^{0} e^{\varepsilon t} (\boldsymbol{j}_Q(\boldsymbol{k}) \cdot \boldsymbol{j}_Q(-\boldsymbol{k},\ t))\, dt, \end{aligned} \tag{22.94}$$

where the dot denotes the scalar product of the currents. In this connection, the current tensor can be divided into transverse and longitudinal parts:

$$(j_Q^{\alpha}(\boldsymbol{k}),\ j_Q^{\beta}(-\boldsymbol{k},\ t)) = \frac{A(k,t)}{k^2}(k_\alpha k_\beta - \delta_{\alpha\beta}k^2) - B(k,\ t)\frac{k_\alpha k_\beta}{k^2}.$$

We obtain formula (22.94), if we take into account [10] that

$$\lim_{k\to 0} \int_{-\infty}^{0} e^{\varepsilon t} A(k,\ t)\, dt = \lim_{k\to 0} \int_{-\infty}^{0} e^{\varepsilon t} B(k,\ t)\, dt.$$

Formula (22.94) coincides with the first of the formulas (22.53a).

Analogously we write the last formula in (22.92):

$$\zeta + \frac{4}{3}\eta = \lim_{k\to 0} \frac{1}{Vk^4} \int_{-\infty}^{0} e^{\varepsilon t}\, \boldsymbol{k}\cdot(J_1(\boldsymbol{k}),\ J_1(-\boldsymbol{k},\ t))\cdot \boldsymbol{k}\, dt, \quad (22.94\text{a}) \tag{22.94a}$$

where

$$J_1(\boldsymbol{k}) = -i\boldsymbol{k}\cdot\left(T(\boldsymbol{k}) - \left(\frac{\partial p}{\partial u}\right)_n H(\boldsymbol{k})\,U - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(\boldsymbol{k})\,U\right) =$$

$$= -i\boldsymbol{k}\cdot\left\{\mathring{T}(\boldsymbol{k}) + U\left(p(\boldsymbol{k}) - \left(\frac{\partial p}{\partial u}\right)_n H(\boldsymbol{k}) - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(\boldsymbol{k})\right)\right\},$$

U is the unit tensor, $p(k)=-ik\cdot T(k)$, and $\mathring{T}(k)$ is the divergenceless part of the tensor

$$T(k) = \mathring{T}(k) + p(k)U. \qquad (22.95)$$

We denote

$$\Delta p(\boldsymbol{k}) = p(\boldsymbol{k}) - \left(\frac{\partial p}{\partial u}\right)_n H(\boldsymbol{k}) - \sum_i \left(\frac{\partial p}{\partial n_i}\right)_u n_i(\boldsymbol{k}).$$

Then $J_1(k)=-ik\cdot\{\mathring{T}(k)+U\Delta p(k)\}$. Consequently,

$$\zeta + \frac{4}{3}\eta = \lim_{k\to 0}\frac{1}{TVk^4}\int_{-\infty}^{0} e^{\varepsilon t}\,\boldsymbol{kk}:(\mathring{T}(\boldsymbol{k}),\ \mathring{T}(-\boldsymbol{k},\ t)):\boldsymbol{kk}\,dt +$$

$$+\lim_{k\to 0}\frac{1}{TV}\int_{-\infty}^{0} e^{\varepsilon t}\,(\Delta p(\boldsymbol{k}),\ \Delta p(-\boldsymbol{k},\ t))\,dt$$

or

$$\zeta + \frac{4}{3}\eta = \lim_{k\to 0}\frac{1}{TV}\int_{-\infty}^{0} e^{\varepsilon t}\,(\Delta p(\boldsymbol{k}),\ \Delta p(-\boldsymbol{k},\ t))\,dt +$$

$$+\lim_{k\to 0}\frac{2}{15TV}\int_{-\infty}^{0} e^{\varepsilon t}\,(\mathring{T}(\boldsymbol{k}):\ \mathring{T}(-\boldsymbol{k},\ t))\,dt. \qquad (22.96)$$

Analogously we also obtain expressions for ζ and η separately:

$$\zeta = \lim_{k\to 0}\frac{1}{TV}\int_{-\infty}^{0} e^{\varepsilon t}\,(\Delta p(\boldsymbol{k}),\ \Delta p(-\boldsymbol{k},\ t))\,dt,$$

$$\eta = \lim_{k\to 0}\frac{1}{10TV}\int_{-\infty}^{0} e^{\varepsilon t}\,(\mathring{T}(\boldsymbol{k}):\mathring{T}(-\boldsymbol{k},\ t))\,dt, \qquad (22.97)$$

which coincide with (22.54c) and (22.54b).

Thus, formulas (22.92) for the kinetic coefficients are equivalent to the formulas (22.53a) obtained earlier.

In the choice of currents and thermodynamic forces (22.85a) and (22.85b) it is convenient to put in the entropy balance equation

$$\frac{\partial S(x)}{\partial t} + \operatorname{div} j_S(x) = \sigma(x) \tag{22.98}$$

the expressions

$$j_S(x) = \sum_m F_m(x, t)\langle j_m(x, t)\rangle_l + \beta(x, t)\, v(x, t)\, p(x), \tag{22.99a}$$

$$\sigma(x) = \sum_m \left(\langle \dot{P}_m(x)\rangle - \langle \dot{P}_m(x)\rangle_l\right) F_m(x, t). \tag{22.99b}$$

Then the total production of entropy is positive,

$$\begin{aligned}\int \sigma(x)\,dx = \sum_{m,\,k} \left(\langle \dot{P}_m(k)\rangle - \langle \dot{P}_m(k)\rangle_l\right) F_m(-k) = \\ = \sum_{m,\,n,\,k} F_n(k)\,\mathscr{L}_{mn}(k)\,F_m^*(k) \geqslant 0.\end{aligned} \tag{22.100}$$

The examples considered show that to construct the hydrodynamic equations one can use for the nonequilibrium statistical operator either the expression (22.1) or the expression (22.80).

§ 23. Relaxation Processes

23.1. General Theory.

Until now it has been assumed that the macroscopic state of the system can be completely characterized by specifying the fields of temperature and mass velocity and the chemical potentials of the components. However this is not always the case. For example, in the case in which the system consists of weakly interacting subsystems, between which it is difficult to exchange energy, the approach to statistical equilibrium is effected in two stages: first, a partial equilibrium is established in the subsystems, and this partial equilibrium then slowly approaches complete statistical equilibrium, if there are no factors which prevent this. To describe the state of such a system a single temperature is not sufficient, but rather it is necessary to introduce different temperatures for its subsystems.

Such a situation can exist both for the various components because of a large difference in their masses, for example, in an electron-ion plasma [101-103], and for the various internal degrees of freedom of the molecules [100,104-107], and for the spins of the electrons and the nuclei [108,109]. The thermodynamic theory of relaxation processes in gases and liquids was developed in the articles by Kneser [110], Leontovich and Mandel'shtam [111, 112], and many other authors (see the monograph [113]). A formal scheme of taking into account the internal degrees of freedom of molecules on the basis of the Boltzmann kinetic equation was developed by Wang-chang and Uhlenbeck [106]. Their results were refined by Snyder [114], who took into account the degeneracy of states. Further development of this approach can be seen in the book [107].

Sometimes the system cannot be characterized by a single mass velocity, for example for supersonic flows, when the velocity field has gradients which are too large at the front of the shock wave, and the basic assumption of the linear dissipative theory about the smallness of the velocity gradients is violated. In this case in order not to exceed the limits of the linear dissipative processes, one makes use of a two-liquid model with two velocity fields, before and after the front of the shock wave [104,105]. The equations of two-liquid hydrodynamics are derived in the articles [115-117]. A single velocity field is also insufficient for constructing the hydrodynamics of a superfluid [118-121].

The general scheme for constructing a nonequilibrium statistical operator, which was presented in §§ 21,22, can be generalized to systems which are relaxing. For this it is necessary to formulate the conservation laws in more detail than was done earlier, separately for each weakly interacting subsystem. We have already considered conservation laws of such a type in section 19.5, where the subsystems were characterized by the quantum numbers of the internal degrees of freedom.

The conservation laws for energy, particle number, and momentum for the i^{th} subsystem have the form

$$\begin{aligned} &\frac{\partial H_i(x)}{\partial t} + \operatorname{div} j_{H_i}(x) = J_{H_i}(x), \\ &\frac{\partial n_i(x)}{\partial t} + \operatorname{div} j_i(x) = J_i(x), \\ &\frac{\partial p_i(x)}{\partial t} + \operatorname{Div} T_i(x) = f_i(x), \end{aligned} \tag{23.1}$$

where $H_i(x)$, $n_i(x)$, $p_i(x)$ are the densities of energy, particle number, and momentum of the i^{th} subsystem, $j_{H_i}(x)$, $j_i(x)$, $T_i(x)$ are the corresponding currents of energy, particle number, and momentum, $J_{H_i}(x)$ is the rate of change of energy of the i^{th} subsystem, $f_i(x)$ is the density of the force of interaction of the i^{th} subsystem with all remaining subsystems, and $J_i(x)$ is the density of particle sources.

The total energy, mass, and momentum densities

$$H(x)=\sum_i H_i(x),\quad \rho(x)=\sum_i m_i n_i(x),\quad p(x)=\sum_i p_i(x) \tag{23.2}$$

satisfy the conservation laws

$$\begin{aligned} &\frac{\partial H(x)}{\partial t}+\operatorname{div} j_H(x)=0,\\ &\frac{\partial \rho(x)}{\partial t}+\operatorname{div} p(x)=0,\\ &\frac{\partial p(x)}{\partial t}+\operatorname{Div} T(x)=0. \end{aligned} \tag{23.3}$$

The conservation laws (23.1) can be written in the form of a single equation for quantities which depend on two indices:

$$\frac{\partial P_{mi}(x)}{\partial t}+\nabla\cdot j_{mi}(x)=J_{mi}(x), \tag{23.4}$$

where we have introduced the notation

$$\begin{aligned} &P_{0i}(x)=H_i(x), && j_{0i}(x)=j_{H_i}(x), && J_{0i}(x)=J_{H_i}(x),\\ &P_{1i}(x)=p_i(x), && j_{1i}(x)=T_i(x), && J_{1i}(x)=f_i(x),\\ &P_{2i}(x)=m_i n_i(x), && j_{2i}(x)=m_i j_i(x), && J_{2i}(x)=m_i J_i(x). \end{aligned} \tag{23.5}$$

The operators $J_{mi}(x)$ satisfy the additional conditions

$$\sum_i J_{H_i}(x)=0,\quad \sum_i f_i(x)=0,\quad \sum_i m_i J_i(x)=0 \tag{23.6}$$

or

$$\sum_i J_{mi}(x)=0, \tag{23.6a}$$

denoting the conservation of total energy, momentum, and mass.

The operators (23.5) can describe subsystems with different internal degrees of freedom, but they can also have a different meaning. For example, if one considers a system in which chemical reactions are taking place, then the index i denotes the type of molecules of the reagents and products of the reaction, while the index m denotes the type of the conserved quantities (energy, mass, or momentum).

Following [4,5], we apply the general scheme of constructing a nonequilibrium statistical operator, presented in section 21.1, to a system with conservation laws (23.4).

The subsystems are characterized by the quantities $P_{mi}(x)$, and thus, the nonequilibrium statistical operator is equal to

$$\begin{aligned}\rho = Q^{-1}\exp\Big\{-\sum_{m,i}\varepsilon\int\int_{-\infty}^{0}e^{\varepsilon t_1}F_{im}(\boldsymbol{x},t+t_1)P_{mi}(\boldsymbol{x},t_1)\,dt_1\,d\boldsymbol{x}\Big\} = \\ = Q^{-1}\exp\Big\{-\sum_{m,i}\int F_{im}(\boldsymbol{x},t)P_{mi}(\boldsymbol{x})\,d\boldsymbol{x} + \\ + \sum_{m,i}\int\int_{-\infty}^{0}e^{\varepsilon t_1}\Big(\dot{P}_{mi}(\boldsymbol{x},t_1)F_{im}(\boldsymbol{x},t+t_1) + \\ + P_{mi}(\boldsymbol{x},t_1)\frac{\partial F_{im}(\boldsymbol{x},t+t_1)}{\partial t_1}\Big)dt_1\,d\boldsymbol{x}\Big\} \qquad (\varepsilon\to 0)\end{aligned} \tag{23.7}$$

or after an integration by parts

$$\begin{aligned}\rho = Q^{-1}\exp\Big\{-\sum_{m,i}\int F_{im}(\boldsymbol{x},t)P_{mi}(\boldsymbol{x})\,d\boldsymbol{x} + \\ + \sum_{m,i}\int\int_{-\infty}^{0}e^{\varepsilon t_1}\Big(j_{mi}(\boldsymbol{x},t_1)\cdot\nabla F_{im}(\boldsymbol{x},t+t_1) + P_{mi}(\boldsymbol{x},t_1)\frac{\partial F_{im}(\boldsymbol{x},t+t_1)}{\partial t_1} - \\ - J_{mi}(\boldsymbol{x},t_1)F_{im}(\boldsymbol{x},t+t_1)\Big)dt_1\,d\boldsymbol{x}\Big\},\end{aligned} \tag{23.8}$$

where

$$\begin{aligned}F_{i0}(\boldsymbol{x},t) &= \beta_i(\boldsymbol{x},t),\\ F_{i1}(\boldsymbol{x},t) &= -\beta_i(\boldsymbol{x},t)v_i(\boldsymbol{x},t),\\ F_{i2}(\boldsymbol{x},t) &= -\beta_i(\boldsymbol{x},t)\Big(\frac{\mu_i(\boldsymbol{x},t)}{m_i} - \frac{1}{2}v_i^2(\boldsymbol{x},t)\Big),\end{aligned} \tag{23.9}$$

$\beta_i(x,t)$ is the inverse temperature of the ith subsystem, $\mu_i(x,t)$ is its chemical potential, and $v_i(x,t)$ is its mass velocity, which we have introduced for a possible generalization to a two-liquid hydrodynamics.

We choose the parameters $F_{im}(x,t)$ such that they have the meaning of the thermodynamic parameters, and this is achieved if we put

$$\langle P_{mi}(\boldsymbol{x})\rangle = \langle P_{mi}(\boldsymbol{x})\rangle_l. \tag{23.10}$$

In fact, then

$$\frac{\delta \ln Q_l}{\delta F_{im}(x\ \ t)} = -\langle P_{mi}(x)\rangle_l = -\langle P_{mi}(x)\rangle, \tag{23.11}$$

where

$$\langle \ldots \rangle_l = \mathrm{Sp}\,(\rho_l \ldots),$$

$$\rho_l = Q_l^{-1} \exp\left\{ - \sum_{mi} \int F_{im}(x,\ t)\, P_{mi}(x)\, dx \right\} \tag{23.12}$$

is the local equilibrium distribution, and

$$Q_l = \mathrm{Sp} \exp\left\{ - \sum_{ml} \int F_{im}(x,\ t)\, P_{mi}(x)\, dx \right\} \tag{23.13}$$

is the statistical functional which corresponds to it.

The relations (23.11) are thermodynamic equalities for relaxing systems, which confirm the interpretation of $\beta_i(x,t)$, $\mu_i(x,t)$, and $v_i(x,t)$ as the inverse temperature, the chemical potential, and the mass velocity of the subsystems.

To explain the physical meaning of the concept of the temperature of a subsystem it is convenient to express the thermodynamic equalities in terms of the variational derivatives of the entropy:

$$S = -\langle \ln \rho_l \rangle = \ln Q_l + \sum_{ml} \int F_{lm}(x,\ t) \langle P_{mi}(x)\rangle\, dx. \tag{23.14}$$

Varying (23.14) and taking into account (23.11), we obtain

Варьируя (23.14), с учетом (23.11) получим

$$\frac{\delta S}{\delta \langle P_{mi}(x)\rangle} = F_{im}(x,\ t), \tag{23.15}$$

and thus,

$$\beta_i(x,\ t) = \frac{\delta S}{\delta \langle H_i'(x)\rangle}, \tag{23.16}$$

where $\langle H_i'(x)\rangle$ is the energy density of the ith subsystem in the co-moving system of coordinates, or for the spatially homogeneous case

$$\beta_i = \frac{\partial S}{\partial \langle H_i' \rangle}, \quad \langle H_i' \rangle = \int \langle H_i'(x) \rangle \, dx, \tag{23.16a}$$

i.e., the inverse temperature of the i^{th} subsystem is equal to the derivative of the entropy with respect to the average energy of the i^{th} subsystem.

The temperature of a subsystem does not necessarily have to be positive, but in this there is no paradox, because β_i^{-1} is not the temperature of a thermostat, as in the equilibrium case. A more detailed discussion on the meaning of negative temperature can be found in section 23.2 of this chapter.

Let us calculate the change of the entropy (23.14) with time. Taking into account the fact that

$$\frac{\partial \ln Q_l}{\partial t} = -\sum_{ml} \int \frac{\partial F_{lm}(x, t)}{\partial t} \langle P_{ml}(\mathbf{x}) \rangle \, dx, \tag{23.17}$$

we obtain

$$\begin{aligned}\frac{\partial S}{\partial t} &= \sum_{ml} \int F_{lm}(\mathbf{x}, t) \left\langle \frac{\partial P_{ml}(\mathbf{x})}{\partial t} \right\rangle d\mathbf{x} = \\ &= -\sum_{mi} \int F_{lm}(\mathbf{x}, t) \nabla \langle j_{ml}(\mathbf{x}) \rangle \cdot d\mathbf{x} + \sum_{mi} \int F_{lm}(\mathbf{x}, t) \langle J_{ml}(\mathbf{x}) \rangle \, d\mathbf{x}\end{aligned} \tag{23.18}$$

or after an integration by parts

$$\begin{aligned}\frac{\partial S}{\partial t} &= -\sum_{ml} \int F_{lm}(\mathbf{x}, t) \langle j_{ml}(\mathbf{x}) \rangle \cdot d\sigma + \\ &+ \sum_{ml} \int \langle j_{ml}(\mathbf{x}) \rangle \cdot \nabla F_{lm}(\mathbf{x}) \, d\mathbf{x} + \sum_{ml} \int F_{lm}(\mathbf{x}, t) \langle J_{ml}(\mathbf{x}) \rangle \, d\mathbf{x}.\end{aligned} \tag{23.18a}$$

In what follows we shall be restricted to the case of a single mass velocity, and we shall obtain a balance equation for entropy density.

We introduce the entropy density $S(\mathbf{x})$ and the density $\Phi(\mathbf{x})$ of the Massieu-Planck function by the relations

$$S = \int S(\mathbf{x}) \, d\mathbf{x}, \quad \Phi = \ln Q_l = \int \Phi(\mathbf{x}) \, d\mathbf{x}. \tag{23.19}$$

Then

$$S(\mathbf{x}) = \sum_{lm} F_{lm}(\mathbf{x}, t) \langle P_{ml}(\mathbf{x}) \rangle + \Phi(\mathbf{x}) \tag{23.20}$$

satisfies the balance equation

$$\frac{\partial S(x)}{\partial t} = -\operatorname{div} \boldsymbol{j}_S(x) + \sigma(x), \tag{23.21}$$

where
$$\boldsymbol{j}_S(x) = \sum_{ml} F_{lm}(x, t)\langle \boldsymbol{j}_{ml}(x)\rangle + v(x, t)\Phi(x) \tag{23.22}$$

is the entropy current density, and

$$\sigma(x) = \\ = \sum_{lm} (\langle \boldsymbol{j}_{ml}(x)\rangle - \langle \boldsymbol{j}_{ml}(x)\rangle_l)\cdot\nabla F_{lm}(x, t) + \sum_{lm} \langle J_{ml}(x)\rangle F_{lm}(x, t) \tag{23.23}$$

is the production of entropy.

In the derivation of (23.21)-(23.23) use has been made of the relationship

$$\sum_{lm} \langle \boldsymbol{j}_{ml}(x)\rangle_l \cdot \nabla F_{lm}(x, t) = -\operatorname{div}(v(x, t)\Phi(x)), \tag{23.24}$$

which can be obtained analogously to (20.73) by taking into account the thermodynamic equalities

$$\langle n_l(x)\rangle_l = \frac{\partial\Phi(x)}{\partial\nu_l(x)}, \quad \langle H'_l(x)\rangle_l = -\frac{\partial\Phi(x)}{\partial\beta_l(x)}, \quad \nu_l = \beta_l\mu_l \tag{23.25}$$

and the relations

$$\Phi(x) = \sum_l \Phi_l(x) = \sum_l \beta_l p_l, \quad p_l = \langle T'_l(x)\rangle_l; \tag{23.25a}$$

the primes, as usual, denote a system moving with velocity **v**.

The sources $J_{ml}(x)$ are not independent, because they are connected by the relationships (23.6a).

After eliminating the l^{th} source, we obtain

$$\sigma(x) = \sum_{lm} (\langle \boldsymbol{j}_{ml}(x)\rangle - \langle \boldsymbol{j}_{ml}(x)\rangle_l)\cdot\nabla F_{lm}(x, t) + \\ + \sum_{im} \langle J_{ml}(x)\rangle (F_{im}(x, t) - F_{lm}(x, t)). \tag{23.26}$$

Introducing in place of ∇F_{im} the thermodynamic forces

$$\begin{aligned} X_{i0} &= \nabla\beta_i(x, t), \\ X_{i1} &= -\beta_i(x, t)\nabla v(x, t), \\ X_{i2} &= -\frac{1}{m_i}\nabla\nu_i(x, t) = -\frac{1}{m_i}\nabla\beta_i(x, t)\mu_i(x, t), \end{aligned} \qquad (23.27)$$

we rewrite (23.26) in the explicit form

$$\begin{aligned} \sigma(x) = \sum_i \langle j'_{H_i}(x)\rangle \nabla\beta_i - \\ - \sum_i \beta_i(\langle T'_i(x)\rangle - \langle T'_i(x)\rangle_l) : \nabla v - \sum_i \langle j'_i(x)\rangle \nabla\nu_i + \\ + \sum_l \langle J'_{H_i}(x)\rangle(\beta_i - \beta_l) - \sum_i m_i \langle J_i(x)\rangle\left(\frac{\nu_l}{m_l} - \frac{\nu_l}{m_l}\right), \end{aligned} \qquad (23.26a)$$

where

$$J'_{H_i}(x) = J_{H_i}(x) - f_i(x)\cdot v.$$

Comparing (23.26a) with (22.39), we notice that in relaxing systems new sources of entropy are added - the two last terms in (23.26a), which are related to the exchange of energy and particles between subsystems.

Introducing more compact matrix notations for currents and sources

$$j^{mi}(x) = \begin{Bmatrix} j_{mi}(x) \\ J_{mi}(x) \end{Bmatrix} \qquad (23.28)$$

and for the thermodynamic forces

$$X_{im}(x, t) = \{\nabla F_{im}(x, t),\ F_{lm}(x, t) - F_{im}(x, t)\}, \qquad (23.28a)$$

we write (23.26) in the form

$$\sigma(x) = \sum_{i, m}(\langle j^{mi}(x)\rangle - \langle j^{mi}(x)\rangle_l)\cdot X_{im}(x, t), \qquad (23.29)$$

because

$$\langle J_0(x)\rangle_l = \langle J_H(x)\rangle_l = \langle J'_H(x)\rangle_l + \langle f(x)\rangle_l \cdot v(x, t) = 0,$$
$$\langle J_1(x)\rangle = \langle f(x)\rangle_l = \langle f'(x)\rangle_l = 0,$$

where the primes denote an averaging in the co-moving system, and we have taken into account formulas (19.42b) and (19.46c) and the fact that the velocity changes little over distances of the order of the radius of action of the forces.

We obtain linear relations among currents, sources, and thermodynamic forces by averaging the conservation laws (23.4) with the statistical operator (23.8) and restricting ourselves to terms which are linear in the thermodynamic forces. In the stationary case we obtain

$$\langle j^{ml}(x)\rangle = \langle j^{ml}(x)\rangle_l + \sum_{m_1 l_1} \int L^{m_1 l_1}_{ml}(x, x') \cdot X_{l_1 m_1}(x')\, dx', \qquad (23.30)$$

where

$$L^{m_1 l_1}_{ml}(x, x') = \int_{-\infty}^{0} e^{\varepsilon t} \left(j^{ml}(x),\, j^{m_1 l_1}(x', t)\right) dt$$

are the kinetic coefficients. Substituting (23.30) into (23.29), we obtain

$$\sigma(x) = \sum_{\substack{lm \\ l_1 m_1}} \int X_{l_1 m_1}(x) \cdot L^{m_1 l_1}_{ml}(x, x') \cdot X_{lm}(x')\, dx'; \qquad (23.31)$$

where as before,

$$\int \sigma(x)\, dx > 0.$$

Important special cases of the problem considered above are provided by irreversible processes in a spatially homogeneous system, consisting of weakly interacting subsystems, for example the exchange of energy between components of a mixture which are at different temperatures (see section 23.4), or a chemical reaction in a homogeneous phase (see section 23.5). The conservation laws for energy and particle number in this case have the form

$$\dot H_i = J_{H_i} = \frac{1}{i\hbar}[H_i, H], \qquad \dot N_i = J_{N_i} = \frac{1}{i\hbar}[N_i, H], \qquad (23.32)$$

where H_i and N_i are the energy and particle number of the i^{th} subsystem, for which

$$\sum_i J_{H_i} = 0, \qquad \sum_i J_{N_i} = 0. \qquad (23.32a)$$

The quasi-integrals of motion

$$\tilde H_i = H_i - \int_{-\infty}^{0} e^{\varepsilon t} \dot H_i(t)\, dt, \qquad \tilde N = N_i - \int_{-\infty}^{0} e^{\varepsilon t} \dot N_i(t)\, dt \qquad (23.32b)$$

correspond to the conservation laws, and in the stationary case the nonequilibrium statistical operator is

$$\rho = Q^{-1}\exp\Big\{-\sum_l \beta_l(\tilde{H}_l - \mu_l \tilde{N}_l)\Big\} = Q^{-1}\exp\Big\{-\sum_l \beta_l(H_l - \mu_i N_i) + \\ + \sum_l (\beta_l - \beta_1)\int_{-\infty}^{0} e^{\varepsilon t}\dot{H}_i(t)\,dt - \sum_i (\beta_l\mu_i - \beta_1\mu_1)\int_{-\infty}^{0} e^{\varepsilon t}\dot{N}_l(t)\,dt\Big\}. \qquad (23.33)$$

Averaging (23.32) with (23.33), we obtain

$$\begin{aligned} \langle \dot{H}_l\rangle &= \sum_m \{L_{\dot{H}_i\dot{H}_m}(\beta_m - \beta_1) - L_{\dot{H}_i\dot{N}_m}(\beta_m\mu_m - \beta_1\mu_1)\}, \\ \langle \dot{N}_l\rangle &= \sum_m \{L_{\dot{N}_i\dot{H}_m}(\beta_m - \beta_1) - L_{\dot{N}_i\dot{N}_m}(\beta_m\mu_m - \beta_i\mu_i)\}, \end{aligned} \qquad (23.34)$$

where

$$\begin{aligned} L_{\dot{H}_i\dot{H}_m} &= \int_{-\infty}^{0} e^{\varepsilon t}(\dot{H}_l, \dot{H}_m(t))\,dt, \\ L_{\dot{H}_i\dot{N}_m} &= \int_{-\infty}^{0} e^{\varepsilon t}(\dot{H}_l, \dot{N}_m(t))\,dt, \\ L_{\dot{N}_i\dot{N}_m} &= \int_{-\infty}^{0} e^{\varepsilon t}(\dot{N}_i, \dot{N}_m(t))\,dt \end{aligned} \qquad (23.34a)$$

are the kinetic coefficients.

Later in sections 23.2 and 23.3 we shall consider concrete examples of relaxation processes for a system of nuclear spins in a solid and for conduction electrons in a semiconductor. In the theory of rates of chemical reactions the assumption about the smallness of the difference of the chemical potentials is often not justified, and it is essential to take into account nonlinear effects, which will be considered in section 23.5.

23.2. Relaxation of Nuclear Spins in a Crystal.

As an example of an application of the method we consider, following L. L. Buishvili [46], the relaxation of nuclear spins, which are interacting with magnetic impurities and the lattice. We write the Hamiltonian of the system in the form

$$H = H_I + H_d + H_l + H_{Id} + H_{dl}. \qquad (23.35)$$

$$H_I = -\omega_n \sum_i I_i^z \qquad (23.35a)$$

is the Zeeman energy of the nuclei in a constant magnetic field, I_i^z is the z-component of the nuclear spin, and ω_n is the frequency of precession of the nuclear spin;

$$H_d = \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} u_{ij}^{\alpha\beta} I_i^\alpha I_j^\beta \tag{23.35b}$$

is the dipole-dipole interaction of the nuclear spins; H_l is the Hamiltonian of the lattice, the explicit form of which we do not require;

$$H_{Id} = \sum_{\substack{i,j \\ \alpha,\beta}} v_{ij}^{\alpha\beta} I_i^\alpha S_j^\beta \tag{23.35c}$$

is the interaction of the electron and nuclear subsystems, and S_j^β is the electron spin of the magnetic impurity. To a good approximation one can retain in (23.35c) only terms which cause flips of the nuclear spin:

$$H_{Id} = \frac{1}{2} \sum_{i,n} \left(v^{-z}(i, n) I_i^+ + v^z(i, n) I_i^- \right) S_n^z,$$
$$I_i^\pm = I_i^x \pm i I_i^y. \tag{23.35d}$$

Finally, H_{dl} is the interaction of the nuclear spins with the lattice.

We restrict ourselves to the spatially homogeneous case, when the nuclear magnetization is independent of position (distance from the impurity); otherwise it is necessary to take into account the spin diffusion of the nuclei [43,44,46].

We consider the nuclear Zeeman subsystem H_I, the dipole-dipole reservoir H_d, and the lattice, together with the remaining interactions $H_l + H_{Id} + H_{dl}$, as weakly interacting subsystems. The exchange of energy among them is described by the operator equations

$$\frac{dH_I}{dt} = \frac{1}{i\hbar}[H_I, H] = \frac{1}{i\hbar}[H_I, H_{Id}] \equiv K_I,$$
$$\frac{dH_d}{dt} = \frac{1}{i\hbar}[H_d, H] = \frac{1}{i\hbar}[H_d, H_{Id} + H_{dl}] \equiv K_d, \tag{23.36}$$

because H_I commutes with H_d. The smallness of the right hand sides in (23.36) allows one to consider the subsystems as quasi-independent.

For the stationary case the statistical operator corresponding to the chosen subsystems has the form

$$\begin{aligned}\rho &= Q^{-1}\exp\{-\beta_I\tilde{H}_I-\beta_d\tilde{H}_d-\beta(H-\tilde{H}_I-\tilde{H}_d)\}=\\ &= Q^{-1}\exp\Big\{-\beta_I H_I-\beta_d H_d-\beta(H-H_I-H_d)+\\ &+\int_{-\infty}^{0}e^{\varepsilon t}(\beta_I-\beta)K_I(t)\,dt+\int_{-\infty}^{0}e^{\varepsilon t}(\beta_d-\beta)K_d(t)\,dt\Big\},\end{aligned} \tag{23.37}$$

where β_I, β_d, and β are the inverse temperatures, respectively, of the nuclear Zeeman reservoir (NZR), the dipole-dipole reservoir (DDR), and the lattice. The concept of the temperature of the DDR was first introduced by B. N. Provotorov in articles on the theory of nuclear magnetic resonance [35].

Although the nonequilibrium statistical operator (23.37) corresponds to a stationary state, it can be applied also for a nonstationary state, considering that β_I and β_d are slowly varying functions of time.

The average value of the balance equations in operator form (23.36) calculated using (23.37), gives the relaxation equations

$$\begin{aligned}\frac{d}{dt}\langle H_I\rangle_l &= \langle K_I\rangle = \sum_i L_{Ii}(\beta_i-\beta),\\ \frac{d}{dt}\langle H_d\rangle_l &= \langle K_d\rangle = \sum_i L_{di}(\beta_i-\beta)\quad (i=I,\,d),\end{aligned} \tag{23.38}$$

where

$$L_{il}=\int_{-\infty}^{0}e^{\varepsilon t}(K_i,\,K_l(t))\,dt \tag{23.38a}$$

are the kinetic coefficients. In equations (23.38) we have taken into account that

$$\langle H_I\rangle = \langle H_I\rangle_l,\qquad \langle H_d\rangle = \langle H_d\rangle_l,$$

where the subscript l denotes an averaging with a quasi-equilibrium operator

(23.39)

and we have used the fact that

$$\rho_l = Q_l^{-1} \exp\{-\beta_I H_I - \beta_d H_d - \beta(H - H_I - H_d)\},$$
$$\langle K_I\rangle_l = \langle K_d\rangle_l = 0.$$

We express the derivatives of the average energies through the derivatives of the inverse temperatures:

$$\frac{d\langle H_I\rangle_l}{dt} \cong \frac{d\langle H_I\rangle_l}{d\beta_I}\frac{d\beta_I}{dt} = -\langle H_I^2\rangle_l \frac{d\beta_I}{dt},$$
$$\frac{d\langle H_d\rangle_l}{dt} \cong \frac{d\langle H_d\rangle_l}{d\beta_d}\frac{d\beta_d}{dt} = -\langle H_d^2\rangle_l \frac{d\beta_d}{dt}, \qquad (23.40)$$

where terms with $\langle H_d H_I\rangle$ have been neglected. Taking into account (23.40), the relaxation equations can be rewritten in the form

$$\frac{d\beta_I}{dt} = -\frac{\beta_I - \beta}{\tau_I} + \frac{\beta_d - \beta}{\tau_{Id}}, \qquad \frac{d\beta_d}{dt} = -\frac{\beta_d - \beta}{\tau_d} + \frac{\beta_I - \beta}{\tau_{dI}}, \qquad (23.41)$$

where τ_I, τ_d, τ_{Id}, and τ_{dI} are relaxation times, connected with the kinetic coefficients (23.38a) by the relations

$$\tau_I = L_{II}^{-1}\langle H_I^2\rangle_l, \qquad \tau_{Id} = -L_{Id}^{-1}\langle H_I^2\rangle_l, \qquad (23.42)$$
$$\tau_d = L_{dd}^{-1}\langle H_d^2\rangle_l, \qquad \tau_{dI} = -L_{dI}^{-1}\langle H_d^2\rangle_l.$$

For spin systems one can make use of the high temperature approximation and expand the exponential in (23.39) with respect to all quantities, except βH_1. Then the formulas for the relaxation times become

$$\tau_I^{-1}=\frac{\mathrm{Sp}(1)\beta}{\mathrm{Sp}(H_I^2)}\int_0^\beta\int_{-\infty}^0 e^{\varepsilon t}\,\frac{\mathrm{Sp}\left(e^{-\beta H_I}K_IK_I(t+i\hbar\tau)\right)}{\mathrm{Sp}\,e^{-\beta H_I}}\,d\tau\,dt,$$

$$\tau_d^{-1}=\frac{\mathrm{Sp}(1)\beta}{\mathrm{Sp}(H_d^2)}\int_0^\beta\int_{-\infty}^0 e^{\varepsilon t}\,\frac{\mathrm{Sp}\left(e^{-\beta H_I}K_dK_d(t+i\hbar\tau)\right)}{\mathrm{Sp}\,e^{-\beta H_I}}\,d\tau\,dt, \qquad (23.42a)$$

$$\tau_{Id}^{-1}=-\frac{\mathrm{Sp}(1)\beta}{\mathrm{Sp}(H_I^2)}\int_0^\beta\int_{-\infty}^0 e^{\varepsilon t}\,\frac{\mathrm{Sp}\left(e^{-\beta H_I}K_IK_d(t+i\hbar\tau)\right)}{\mathrm{Sp}\,e^{-\beta H_I}}\,d\tau\,dt,$$

$$\tau_{dI}^{-1}=-\frac{\mathrm{Sp}(1)\beta}{\mathrm{Sp}(H_d^2)}\int_0^\beta\int_{-\infty}^0 e^{\varepsilon t}\,\frac{\mathrm{Sp}\left(e^{-\beta H_I}K_dK_I(t+i\hbar\tau)\right)}{\mathrm{Sp}\,e^{-\beta H_I}}\,d\tau\,dt.$$

We note that the spurs in (23.42a) are taken over the eigenfunctions of the spin matrices.

Further calculations of the relaxation times by formulas (23.42a) can be seen in [46], and a discussion of the results is given in [122].

The nonequilibrium statistical operator allows one to introduce naturally the concept of a spin temperature, for example the spin temperature of the nuclei β_I^{-1}. It can be different from the temperature of the lattice β^{-1} and can even turn out to be negative. This does not create a paradox in nonequilibrium statistical thermodynamics, because $T_I=\beta_I^{-1}$ is not the temperature of a thermostat, but rather it is defined by the relation

$$\beta_I=\frac{\partial S}{\partial\langle H_I\rangle}, \qquad (23.43)$$

where S is the entropy.

Negative temperatures are formally introduced even for the equilibrium case [92], which is possible for systems in which the energy spectrum is bounded above, as, for example, in spin systems, because otherwise the statistical sum would diverge for negative temperatures. However, real systems which have an energy spectrum bounded from above always interact with a system whose energy spectrum is not bounded from above, and therefore the spectrum of the total system is not bounded from above; consequently, negative temperatures can be introduced in a consistent way only for the nonequilibrium case. Experimental verifications of the existence of negative temperatures can be seen in the articles [123,124].

The important case of the action of a variable magnetic field on spin systems is a nonstationary nonequilibrium process. However, this problem can be reduced formally to a stationary case, if one first eliminates the variable field with frequency ω by going over into a system of coordinates rotating with frequency ω, and then introducing in this system a nonequilibrium statistical operator. This was done in the work of L. L. Buishvili [46], and it leads naturally to the concept of temperature in a rotating system of coordinates. Unfortunately, the transition to a rotating system of coordinates cannot eliminate completely the dependence of the Hamiltonian on time, if there is an interaction of the spin system with the lattice. Therefore one first derives equations without taking the lattice into account, and then in the resulting equations introduces the corresponding terms describing the influence of the lattice. Another more consistent method of taking into account a variable field, also developed by L. L. Buishvili [46a], consists in first regarding the variable classical field as a quantum subsystem, the temperature of which then tends to infinity, and the quantum correlators of the field variables are replaced by the classical correlators. Taking into account the variable magnetic field allows one to consider by means of the nonequilibrium statistical operator the dynamical polarization of nuclei. Other applications of this method to nuclear magnetic relaxation can be seen in [193-200].

23.3. Spin-Lattice Relaxation of Conduction Electrons in Semiconductors in a Magnetic Field.

We shall consider one more application of the nonequilibrium statistical operator in the theory of relaxation processes - we shall study the spin-lattice relaxation of conduction electrons in a quantizing magnetic field, following the work of V. P. Kalashnikov [53b]. This problem is considered in the articles [125,126] by the method of the kinetic equation.

We write the Hamiltonian of the conduction electrons, interacting with optical phonons in a magnetic field, in the form

$$H = H_k + H_s + H_p + H_{ep} + H_{pl} + H_l, \tag{23.44}$$

where H_k is the kinetic energy of the electrons, and H_s is their Zeeman energy. The sum of H_k and H_s, i.e., the energy H_e of the free electrons in a magnetic field, is equal to

$$H_e = H_k + H_s = \sum_{\nu\sigma} \varepsilon_{\nu\sigma} a^+_{\nu\sigma} a_{\nu\sigma}, \tag{23.44a}$$

where

$$\varepsilon_{\nu\sigma} = \frac{p_z^2}{2m} + \hbar\omega_0\left(n + \frac{1}{2}\right) + \frac{1}{2}\sigma g \mu_0 H \qquad (\sigma = \pm 1) \tag{23.44b}$$

are the energy levels of a free electron in a magnetic field parallel to the z axis; $\rho=(n,p_x,p_z)$ are its quantum numbers, g is a factor which gives the spectroscopic splitting of conduction electrons, μ_0 is the Bohr magneton, $\omega_0=eH/mc$ is the Larmor frequency, and the last term in (23.44b) gives the Zeeman energy of the electrons H_s. Further,

$$H_p = \sum_{q\lambda} \hbar\Omega_{q\lambda} C^+_{q\lambda} C_{q\lambda}. \tag{23.44c}$$

is the energy of the optical phonons, where q and λ are respectively the momentum and polarization index of the optical phonon with energy $\hbar\Omega_{q\lambda}$;

$$H_{ep} = \sum_{\substack{\nu\sigma,\, \nu'\sigma' \\ q,\, \lambda}} \left(U^{q\lambda}_{\nu'\sigma',\, \nu\sigma} C_{q\lambda} + \dot{U}^{q\lambda}_{\nu\sigma,\, \nu'\sigma'} C^+_{q\lambda}\right) a^+_{\nu'\sigma'} a_{\nu\sigma} \tag{23.44d}$$

is the electron-phonon interaction; H_{pl} is the energy of interaction of the optical phonons with the thermostat; H_l is the energy of the thermostat. For example, if the non-electron relaxation of optical photons is connected with their decay into two acoustical phonons and the inverse process, then

$$H_{pl} = \sum_{qq'\lambda\lambda'\lambda''} \left(\Phi^{qq'q-q'}_{\lambda\lambda'\lambda''} C_{q\lambda} b^+_{q'\lambda'} b^+_{q-q',\,\lambda''} + \dot{\Phi}^{qq'q-q'}_{\lambda\lambda'\lambda''} C^+_{q\lambda} b_{q'\lambda'} b_{q-q',\,\lambda''}\right), \tag{23.44e}$$

$$H_l = \sum_{q\lambda} \hbar\omega_{q\lambda} b^+_{q\lambda} b_{q\lambda}, \tag{23.44f}$$

where $\omega_{q\lambda}$ is the frequency of the acoustical phonons.

We shall consider H_s, H_p and the remaining part of the Hamiltonian of the crystal as weakly interacting subsystems. The mutual exchange of energy between subsystems is described by the operator equations

$$\begin{aligned} \frac{dH_s}{dt} &= \frac{1}{i\hbar}[H_s, H] = \frac{1}{i\hbar}[H_s, H_{ep}] \equiv \dot{H}_{s\,(p)}, \\ \frac{dH_p}{dt} &= \frac{1}{i\hbar}[H_p, H] = \frac{1}{i\hbar}[H_p, H_{ep} + H_{pl}] \equiv \dot{H}_{p\,(e)} + \dot{H}_{p\,(l)}. \end{aligned} \tag{23.45}$$

The subsystems chosen correspond to the stationary nonequilibrium operator

$$\rho = Q^{-1}\exp\{-\beta_s\tilde{\tilde{H}}_s - \beta_p\tilde{\tilde{H}}_p - \beta(H - \tilde{\tilde{H}}_s - \tilde{\tilde{H}}_p - \mu N)\}, \qquad (23.46)$$

where

$$\tilde{\tilde{H}}_s = H_s - \int_{-\infty}^{0} e^{\varepsilon t}\dot{H}_{s\,(p)}(t)\,dt,$$
$$\tilde{\tilde{H}}_p = H_p - \int_{-\infty}^{0} e^{\varepsilon t}(\dot{H}_{p\,(e)}(t) + \dot{H}_{p\,(l)}(t))\,dt; \qquad (23.47)$$

N is the total number of electrons. Consequently,

$$\rho = Q^{-1}\exp\Big\{-\beta_s H_s - \beta_p H_p - \beta(H - H_s - H_p - \mu N) + \int_{-\infty}^{0} e^{\varepsilon t}(\beta_s - \beta)\,\dot{H}_{s\,(p)}(t)\,dt + \int_{-\infty}^{0} e^{\varepsilon t}(\beta_p - \beta)(\dot{H}_{p\,(e)}(t) + \dot{H}_{p\,(l)}(t))\,dt\Big\}, \qquad (23.48)$$

where β_s^{-1} is the spin temperature of the current carrier, and β_p^{-1} is the temperature of the "hot" phonons. The constant temperature β^{-1} is assigned to the remaining degrees of freedom of the crystal.

In the approximation which is linear in the thermodynamic forces $\beta_s-\beta$ and $\beta_p-\beta$, we write the nonequilibrium statistical operator (23.48) in the form

$$\rho = \Big\{1 - (\beta_s - \beta)\beta^{-1}\int_0^{\beta} d\tau\Big[H_s(i\hbar\tau) - \langle H_s\rangle_0 - \beta\frac{\partial\mu}{\partial\beta_s}(N(i\hbar\tau) - \langle N\rangle)\Big] - (\beta_p - \beta)\beta^{-1}\int_0^{\beta} d\tau[H_p(i\hbar\tau) - \langle H_p\rangle_0] + (\beta_s - \beta)\beta^{-1}\int_0^{\beta} d\tau\int_{-\infty}^{0} dt\, e^{\varepsilon t}\dot{H}_{s\,(p)}(t + i\hbar\tau) + (\beta_p - \beta)\beta^{-1}\int_0^{\beta} d\tau\int_{-\infty}^{0} dt\, e^{\varepsilon t}(\dot{H}_{p\,(e)}(t + i\hbar\tau) + \dot{H}_{p\,(l)}(t + i\hbar\tau))\Big\}\rho_0, \qquad (23.49)$$

where the nonequilibrium chemical potential is expanded with respect to $\beta_s-\beta$ and ρ_0 - the equilibrium statistical operator for no interaction.

We find the quantity $\partial\mu/\partial\beta_s$ from the condition $\langle N\rangle_l=\langle N\rangle_0$, i.e.,

$$(N, H_s) = \beta \frac{\partial\mu}{\partial\beta_s} (N, N). \tag{23.49a}$$

Averaging the balance equation (23.45) with the operator (23.49), we obtain the relaxation equations

$$\begin{aligned} \frac{d}{dt} \langle H_s \rangle &= (\beta_s - \beta) L_{ss} + (\beta_p - \beta) L_{sp}, \\ \frac{d}{dt} \langle H_p \rangle &= (\beta_s - \beta) L_{ps} + (\beta_p - \beta) L_{pp}, \end{aligned} \tag{23.50}$$

where

$$\begin{aligned} L_{ss} &= \int_{-\infty}^{0} dt\, e^{\varepsilon t} (\dot{H}_{s(p)}, \dot{H}_{s(p)}(t)), \\ L_{pp} &= \int_{-\infty}^{0} dt\, e^{\varepsilon t} (\dot{H}_{p(e)} + \dot{H}_{p(l)}, \dot{H}_{p(e)}(t) + \dot{H}_{p(l)}(t)), \\ L_{sp} &= \int_{-\infty}^{0} dt\, e^{\varepsilon t} (\dot{H}_{s(p)}, \dot{H}_{p(e)}(t) + \dot{H}_{p(l)}(t)), \\ L_{ps} &= \int_{-\infty}^{0} dt\, e^{\varepsilon t} (\dot{H}_{p(e)} + \dot{H}_{p(l)}, \dot{H}_{s(p)}(t)) \end{aligned} \tag{23.50a}$$

are the kinetic coefficients.

A calculation of the kinetic coefficients (23.50a) using the smallness of the electron-phonon interaction (23.44d) can be seen in the article [53c]. The scheme of calculation presented in this section has been applied by V. P. Kalashnikov to the theory of spin-lattice relaxation in semiconductors with magnetic impurities in a quantizing magnetic field [53c] and to the theory of hot electrons [54]. (See also [201-203].)

23.4. Energy Exchange Between Two Weakly Interacting Subsystems.

Up to this time we have everywhere been restricted to the case of weakly nonequilibrium systems, where in the expressions for the currents it is sufficient to take into account only terms which are linear in the thermodynamic forces, i.e., we have considered linear dissipative processes. There are often cases in the theory of transfer processes in which the linear approximation is not applicable; for example, the rate of a chemical reaction is usually nonlinear with respect to thermodynamic forces [27], and electrical conductivity in semiconductors in a strong electric field can be essentially nonlinear [54]. The method of the nonequilibrium statistical operator allows one to consider even such strongly nonequilibrium processes, i.e., the method is applicable even in the case in which it is already impossible to make use of the usual Kubo method, an account of which is given in Chapter III.

In order to take into account the nonlinear effects we shall expand the statistical operator not with respect to thermodynamic forces, which are already not small, but with respect to other small parameters, if these exist in the problem.

We shall consider the exchange of energy between two weakly interacting subsystems, when it takes place slowly, for example because of the large difference in the masses of the components or in general because of the smallness of the corresponding effective cross section, following the article by L. A. Pokrovskiy [55]. As we shall see below, such systems can be characterized by very different temperatures, and the process of exchange of energy is nonlinear with respect to thermodynamic forces.

We use the Hamiltonian of the system in the form

$$H = H_1 + H_2, \qquad (23.51)$$

where H_1 and H_2 are the Hamiltonians of the subsystems,

$$H_1 = \sum_\alpha E_\alpha a_\alpha^+ a_\alpha + u, \qquad H_2 = \sum_\mu E_\mu b_\mu^+ b_\mu, \qquad (23.52)$$
$$u = \sum_{\alpha,\alpha'\mu\mu'} \langle \alpha\mu | \Phi | \alpha'\mu' \rangle a_\alpha^+ b_\mu^+ b_{\mu'} a_{\alpha'};$$

α and μ are the quantum numbers of the particles of the first and second types, and Φ is the interaction potential between them. For simplicity we omit the interaction between identical particles. It can be considered that this is included in the renormalizations of the values of the energies of the elementary excitations E_α and E_μ, as this is done in the theory of quantum liquids [127,128].

We note that since the total Hamiltonian is an integral of motion, then in dividing the system into subsystems one can choose independently only one of them, and it makes no difference where one refers the interaction energy. If the interaction energy is essential in the balance of energy, then it can be considered as a separate reservoir of energy; for example, the dipole-dipole interaction can be taken into account in this way (see section 23.2).

The operators for the currents of energy between subsystems are equal to

$$J_1 = \dot{H}_1 = \frac{1}{i\hbar}[H_1, H] = \\ = \frac{1}{i\hbar} \sum_{\alpha\mu\alpha'\mu'} (E_{\mu'} - E_\mu)\langle\alpha\mu|\Phi|\alpha'\mu'\rangle a_\alpha^+ b_\mu^+ b_{\mu'} a_{\alpha'}, \\ J_2 = \dot{H}_2 = -J_1. \tag{23.53}$$

The relations (23.53) give equations of balance for dynamical variables and allow one to construct a nonequilibrium statistical operator. As a consequence of the smallness of the exchange of energy, the temperatures of the subsystems will change slowly with time, and one need consider only a stationary variant of the theory. Taking nonstationarity into account leads to terms of a higher order of smallness in the expression for the energy current.

Following the general method, we construct the statistical operator

$$\rho = Q^{-1}\exp\{-\beta_1(\widetilde{H}_1 - \mu_1 N_1) - \beta_2(\widetilde{H}_2 - \mu_2 N_2)\} = \\ = Q^{-1}\exp\Big\{-\beta_1(H_1 - \mu_1 N_1) - \beta_2(H_2 - \mu_2 N_2) + \\ + \int_{-\infty}^{0} e^{\varepsilon t}(\beta_1 - \beta_2)\dot{H}_1(t)\,dt\Big\}, \tag{23.54}$$

where β_1 and β_2 are the inverse temperatures, μ_1 and μ_2 are the chemical potentials, and N_1 and N_2 are the particle number operators for the subsystems.

The operator $\dot{H}_1$ contains a small parameter, because the exchange of energy is assumed to be slow. We average the current (23.53) over the distribution (23.54), retaining only terms through second order in the small parameter. We obtain

$$\langle\dot{H}_1\rangle = (\beta_1 - \beta_2)\int_{-\infty}^{0} dt\, e^{\varepsilon t}\int_0^1 d\tau\,\langle\dot{H}_1 e^{-\tau B}\dot{H}_1(t)e^{\tau B}\rangle_l, \tag{23.55}$$

where $\langle\ldots\rangle_l$ denotes an averaging over a quasi-equilibrium distribution

$$\rho_l = Q_l^{-1}e^{-B}, \tag{23.56}$$

$$B = \beta_1(H_1 - \mu_1 N_1) + \beta_2(H_2 - \mu_2 N_2), \tag{23.57}$$

where in H_1 the interaction u is omitted.

The relation (23.55) appears superficially like a linear relation between the thermodynamic force $\beta_1-\beta_2$ and the current $<\dot{H}_1>$, but it is actually nonlinear with respect to $\beta_1-\beta_2$, because the averaging is carried out over the quasi-equilibrium distribution (23.56) rather than the equilibrium distribution.

The relation (23.55) is valid also in the case in which the interaction between particles is taken into account in the operators H_1, H_2. Then the operator (23.53) will include additional terms, which depend on the interaction potentials between the identical particles.

We shall calculate the average energy current (23.55). Substituting (23.53) into (23.55) and integrating over τ, we obtain

$$\langle \dot{H}_1 \rangle = - \int_{-\infty}^{0} dt\, e^{\varepsilon t} (\beta_1 - \beta_2) \sum_{\substack{\alpha\mu\alpha'\mu' \\ \alpha_1\mu_1\alpha_1'\mu_1'}} \frac{1}{i\hbar} \left(E_{\mu_1'} - E_{\mu_1} \right) (E_{\mu'} - E_{\mu}) \times$$
$$\times \langle \alpha\mu | \Phi | \alpha'\mu' \rangle \langle \alpha_1\mu_1 | \Phi | \alpha_1'\mu_1' \rangle \frac{G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1}(-t)}{\beta_1 (E_\alpha - E_{\alpha'}) + \beta_2 (E_\mu - E_{\mu'})}, \tag{23.58}$$

where we have introduced the Green function

$$G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1}(t - t_1) =$$
$$= (i\hbar)^{-1} \theta(t - t_1) \left\langle \left[a_\alpha^+ b_\mu^+ b_{\mu'} a_{\alpha'},\, e^{\frac{-iH(t-t_1)}{\hbar}} a_{\alpha_1}^+ b_{\mu_1}^+ b_{\mu_1'} a_{\alpha_1'} e^{\frac{iH(t-t_1)}{\hbar}} \right] \right\rangle_t \tag{23.59}$$

which is a generalization of the doubletime Green functions (15.48), considered in § 16, to the case of a quasi-equilibrium ensemble.

In the case of a weak interaction the interaction can be neglected in the Green function (23.59) in the Heisenberg representation for the operators, because in (23.58) there is already a factor of second order in the interaction. Therefore the Green function (23.59) can be calculated directly by pairing the operators according to the Wick theorem:

$$G^{\alpha\mu\alpha'\mu'}_{\alpha_1'\mu_1'\alpha_1\mu_1}(t-t_1)=(i\hbar)^{-1}\theta(t-t_1)\,e^{\frac{i}{\hbar}(E_\alpha+E_\mu-E_{\alpha'}-E_{\mu'})(t-t_1)}\times$$
$$\times\{n_\alpha n_\mu(1\pm n_{\alpha'})(1\pm n_{\mu'})-n_{\alpha'}n_{\mu'}(1\pm n_\alpha)(1\pm n_\mu)\}\times$$
$$\times\,\delta_{\alpha\alpha_1'}\delta_{\mu\mu_1'}\delta_{\mu'\mu_1}\delta_{\alpha'\alpha_1}, \tag{23.60}$$

where the upper sign is taken for Bose statistics and the lower for Fermi statistics, and n_α, n_μ are the occupation numbers

$$n_\alpha=\left(e^{\beta_1(E_\alpha-\mu_1)}\mp 1\right)^{-1},\qquad n_\mu=\left(e^{\beta_2(E_\mu-\mu_2)}\mp 1\right)^{-1}. \tag{23.60a}$$

Substituting (23.60) into (23.58), we obtain

$$\langle\dot H_1\rangle=-(\beta_1-\beta_2)\sum_{\alpha\mu\alpha'\mu'}\frac{1}{\hbar^2}(E_\mu-E_{\mu'})^2\frac{|\langle\alpha\mu|\Phi|\alpha'\mu'\rangle|^2}{\beta_1(E_\alpha-E_{\alpha'})+\beta_2(E_\mu-E_{\mu'})}\times$$
$$\times\int_{-\infty}^{0}e^{-\frac{i}{\hbar}(E_\alpha+E_\mu-E_{\alpha'}-E_{\mu'})t+\varepsilon t}\,dt\,\times$$
$$\times\{n_\alpha n_\mu(1\pm n_{\alpha'})(1\pm n_{\mu'})-n_{\alpha'}n_{\mu'}(1\pm n_\alpha)(1\pm n_\mu)\}. \tag{23.61}$$

Carrying out in (23.61) the integration over time, taking into account the relation (16.32), and noting that the integrals in the sense of the principal value give no contribution, we obtain

$$\langle\dot H_1\rangle=\sum_{\alpha\mu\alpha'\mu'}E_\mu w_{\alpha\mu}^{\alpha'\mu'}\times$$
$$\times\{n_\alpha n_\mu(1\pm n_{\alpha'})(1\pm n_{\mu'})-n_{\alpha'}n_{\mu'}(1\pm n_\alpha)(1\pm n_\mu)\}, \tag{23.62}$$

where

$$w_{\alpha\mu}^{\alpha'\mu'}=\frac{2\pi}{\hbar}|\langle\alpha\mu|\Phi|\alpha'\mu'\rangle|^2\delta(E_\alpha+E_\mu-E_{\alpha'}-E_{\mu'}) \tag{23.62a}$$

is the probability per unit time of a transition in the Born approximation.

We note that in going from (23.61) to (23.62) the factor $\beta_1-\beta_2$ cancelled, but there remains the nonlinear effect of the dependence on β_1 and β_2, because

n_α and $n_{\alpha'}$ depend on β_1, while n_μ and $n_{\mu'}$ depend on β_2.

For a nondegenerate gas with $\mu_1=\mu_2$ we have

$$n_\alpha n_\mu(1 \pm n_{\alpha'})(1 \pm n_{\mu'}) - n_{\alpha'} n_{\mu'}(1 \pm n_\alpha)(1 \pm n_\mu) \cong$$
$$\cong n_\alpha n_\mu \left(1 - \frac{n_{\alpha'} n_{\mu'}}{n_\alpha n_\mu}\right) = n_\alpha n_\mu \left(1 - e^{-(\beta_1-\beta_2)(E_\mu-E_{\mu'})}\right),$$

where the fact that energy is conserved in a collision has been taken into account,

$$E_\alpha + E_\mu = E_{\alpha'} + E_{\mu'}.$$

Consequently,
$$\langle \dot{H}_1 \rangle = \sum_{\alpha\mu\alpha'\mu'} E_\mu w_{\alpha\mu}^{\alpha'\mu'} n_\alpha n_\mu \left(1 - e^{-(\beta_1-\beta_2)(E_\mu-E_{\mu'})}\right). \tag{23.62b}$$

Thus, we have obtained an expression for the energy current which is nonlinear in the thermodynamic forces $\beta_1-\beta_2$ which agrees with the result which follows from the kinetic equation.

The connection of the kinetic equation with equation (23.62) is obvious, because the latter equation can be written in the form

$$\langle \dot{H}_1 \rangle = -\langle \dot{H}_2 \rangle = -\sum_\mu E_\mu \frac{\partial n_\mu}{\partial t}, \tag{23.63}$$

where
$$\frac{\partial n_\mu}{\partial t} = -\sum_{\alpha\alpha'\mu'} w_{\alpha\mu}^{\alpha'\mu'} \{n_\alpha n_\mu(1 \pm n_{\alpha'})(1 \pm n_{\mu'}) - n_{\alpha'} n_{\mu'}(1 \pm n_\alpha)(1 \pm n_\mu)\} \tag{23.64}$$

is the kinetic equation for the occupation numbers. The right hand side of equation (23.64) is the collision integral.

The kinetic equation (23.64) can be deduced directly, if one averages the operator

$$\dot{n}_\mu = \frac{\partial}{\partial t}(b_\mu^+ b_\mu)$$

over the statistical distribution (23.54), which is expanded in powers of the small interaction, as was done for the calculation of $\langle \dot{H}_1 \rangle$.

From equation (23.63) it can be seen that in the nonlinear theory instead of the product of thermodynamic forces with currents a sum of the products of the subsystem energies with the collision integrals is used.

For small $\beta_1-\beta_2$, expanding the exponential in (23.62b) in a series in $\beta_1-\beta_2$ with an accuracy up to the linear terms, we obtain a linear relationship between the thermodynamic force and the current:

$$\langle \dot{H}_1 \rangle = L_{\dot{H}_1\dot{H}_1}(\beta_1-\beta_2), \tag{23.65}$$

where

$$L_{\dot{H}_1\dot{H}_1} = \sum_{\alpha\mu\alpha'\mu'} \frac{1}{2}(E_\mu - E_{\mu'})^2 w_{\alpha\mu}^{\alpha'\mu'} n_\alpha n_\mu \tag{23.65a}$$

is the kinetic coefficient for the rate of transfer of energy.

The rate of transfer of energy (23.58) is easily calculated also in the case of small particle density (or small density of elementary excitations). In order to obtain an explicit expansion of the expression (23.58), it is necessary to calculate the Green function (23.59) for small density. Differentiating (23.59) with respect to t, we obtain an equation for the Green function (23.60):

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} G^{\alpha\mu\alpha'\mu'}_{\alpha'_1\mu'_1\alpha_1\mu_1}(t) + \sum_{\alpha_2\mu_2} \Big\{ \langle \alpha'_1\mu'_1 | H^{(2)} | \alpha_2\mu_2 \rangle G^{\alpha\mu\alpha'\mu'}_{\alpha_2\mu_2\alpha_1\mu_1}(t) - \\ - G^{\alpha\mu\alpha'\mu'}_{\alpha'_1\mu'_1\alpha_2\mu_2}(t) \langle \alpha_2\mu_2 | H^{(2)} | \alpha_1\mu_1 \rangle \Big\} + F^{\alpha\mu\alpha'\mu'}_{\alpha'_1\mu'_1\alpha_1\mu_1}(t) = \\ = \delta(t)\, \delta_{\alpha\alpha'_1} \delta_{\mu\mu'_1} \delta_{\alpha'\alpha_1} \delta_{\mu'\mu_1} K_{\alpha\mu\alpha'\mu'}, \end{aligned} \tag{23.66}$$

where $H^{(2)}$ is the two particle Hamiltonian, F(t) is a term which contains Green functions of a higher order, which we shall not write out explicitly, and K is the average commutator of the operators $a^+_\alpha b^+_\mu b_{\mu'} a_{\alpha'}$ and $a^+_{\alpha'} b^+_{\mu'} b_\mu a_\alpha$.

We shall consider the limiting case of a gas with small density, when we can restrict ourselves to the approximation of pair collisions. Then the term F(t) which describes the higher order collisions can be omitted, thereby breaking the chain of equations for the Green functions. The average commutator K in this approximation is equal to

$$\begin{aligned} K_{\alpha\mu\alpha'\mu'} = i\hbar G^{\alpha\mu\alpha'\mu'}_{\alpha\mu\alpha'\mu'}(+0) \simeq \\ \simeq n_\alpha n_\mu (1 \pm n_{\alpha'})(1 \pm n_{\mu'}) - n_{\alpha'} n_{\mu'} (1 \pm n_\alpha)(1 \pm n_\mu). \end{aligned} \tag{23.67}$$

In our approximation $n_\alpha \ll 1$, $n_\mu \ll 1$ one can consider the distributions to be Boltzmann distributions.

The solution of the equations (23.66) has the form

$$G^{\alpha\mu\alpha'\mu'}_{\alpha'_1\mu'_1\alpha_1\mu_1}(t) = \frac{1}{i\hbar}\,\theta(t)\left\langle \alpha'\mu' \left| e^{-\frac{i}{\hbar}H^{(2)}t} \right| \alpha_1\mu_1 \right\rangle \left\langle \alpha'_1\mu'_1 \left| e^{\frac{i}{\hbar}H^{(2)}t} \right| \alpha\mu \right\rangle K_{\alpha\mu\alpha'\mu'}. \qquad (23.68)$$

Substituting (23.68) into (23.58), we obtain

$$\langle \dot{H}_1 \rangle = -\int_{-\infty}^{0} dt\, e^{\varepsilon t}(\beta_1 - \beta_2)\frac{1}{(i\hbar)^2} \sum_{\substack{\alpha\mu\alpha'\mu' \\ \alpha_1\mu_1\alpha'_1\mu'_1}} \left\langle \alpha\mu \left| \Phi e^{\frac{i}{\hbar}H^{(2)}t} \right| \alpha'\mu' \right\rangle \times$$
$$\times \langle \alpha'\mu' | (h_2(-t) - E_\mu) f_{\alpha\mu}(h_1(-t), h_2(-t)) | \alpha_1\mu_1 \rangle \times$$
$$\times \left\langle \alpha_1\mu_1 \left| \Phi e^{-\frac{i}{\hbar}H^{(2)}t} \right| \alpha'_1\mu'_1 \right\rangle \times \langle \alpha'_1\mu'_1 | h_2(t) - E_{\mu_1} | \alpha\mu \rangle, \qquad (23.69)$$

where

$$H^{(2)} = h_1 + h_2 + \Phi, \qquad (23.70)$$

h_1 and h_2 are the single particle Hamiltonians of the particles of the first and second type, their time argument denoting the Heisenberg representation, and

$$f_{\alpha\mu}(E_{\alpha'}, E_{\mu'}) = K_{\alpha\mu\alpha'\mu'}[\beta_1(E_\alpha - E_{\alpha'}) + \beta_2(E_\mu - E_{\mu'})]^{-1}. \qquad (23.71)$$

We note that in the matrix elements

$$\langle \alpha'\mu' | (h_2(-t) - E_\mu) f_{\alpha\mu}(h_1(-t), h_2(-t)) | \alpha_1\mu_1 \rangle$$
$$\langle \alpha'_1\mu'_1 | h_2(t) - E_{\mu_1} | \alpha\mu \rangle$$

one can omit the dependence on t, which is equivalent to neglecting terms of the order of $v^3t^3/V=(vt/L)^3$ in comparison with unity, where v is the relative velocity of the colliding particles, and $V=L^3$ is the volume of the system (see [214]).

Indeed, because of the factor $e^{\varepsilon t}$ the integrand in (23.69) is noticeably different from zero only for times $t \sim \varepsilon^{-1}$, and therefore $v^3t^3/V \sim v^3/V\varepsilon^3$, from which it follows that for the correct order of the limiting transitions, when first $V \to \infty$ and then $\varepsilon \to 0$, the dependence of the matrix elements on time can be neglected in our case. At the same time this automatically excludes waves reflected from the boundaries of the volume. A similar procedure is discussed in the formal theory of scattering of Gell-Mann and Goldberger [84] (see Appendix I).

From the formal theory of scattering it follows that for large times, significantly larger than the collision time τ_c, the matrix elements of the operator of the pairwise interaction with the two particle evolution operator $\Phi e^{\pm(i/\hbar)H^{(2)}t}$ can be expressed through the scattering matrix [85], and in particular, for $|t| \gg \tau_c$

$$\left\langle \alpha\mu \middle| \Phi e^{\pm\frac{i}{\hbar}H^{(2)}t} \middle| \alpha'\mu' \right\rangle = \\ = e^{\pm\frac{i}{\hbar}(E_{\alpha'}+E_{\mu'})t} \begin{cases} \langle\alpha\mu|T|\alpha'\mu'\rangle \text{ for } & +, \\ \langle\alpha\mu|T^{+}|\alpha'\mu'\rangle \text{ for } & -, \end{cases} \tag{23.72}$$

where $\langle\alpha\mu|T|\alpha'\mu'\rangle$ are the matrix elements of the scattering T-matrix. Substituting in (23.69) the asymptotic expressions for the matrix elements and integrating over time, we obtain the previous equation (23.62), but with the transition probability expressed in terms of the T-matrix:

$$w_{\alpha\mu}^{\alpha'\mu'} = \frac{2\pi}{\hbar} |\langle\alpha\mu|T|\alpha'\mu'\rangle|^2 \delta(E_\alpha + E_\mu - E_{\alpha'} - E_{\mu'}). \tag{23.73}$$

Therefore all the derivations of the previous section are preserved also for the case of small density.

In particular, n_μ also satisfies the kinetic equation (23.64), but in the equation the probability of transition corresponds to small density (23.73), rather than to a small interaction as before.

The positivity of the production of entropy was demonstrated earlier only for linear dissipative processes. We shall consider the production of entropy for the nonlinear process of exchange of energy between subsystems.

In accordance with the general definition of entropy (20.13) it is in our case equal to

$$S = -\langle \ln \rho_l \rangle_l = -\langle \ln \rho_l \rangle,$$

i.e.,

$$S = \sum_i \beta_i \langle H_i \rangle + \ln Q_l. \qquad (23.74)$$

(23.75)

After differentiating with respect to time and taking into account the fact that

$$\frac{d \ln Q_l}{dt} = -\sum_i \dot{\beta}_i \langle H_i \rangle, \qquad (23.76)$$

we obtain

$$\frac{dS}{dt} = \sum_i \beta_i \langle \dot{H}_i \rangle = (\beta_1 - \beta_2) \langle \dot{H}_1 \rangle. \qquad (23.77)$$

We shall show that

$$\frac{dS}{dt} = (\beta_1 - \beta_2)^2 \int_{-\infty}^{0} e^{\varepsilon t}\, dt \int_0^1 d\tau \langle \dot{H}_1 e^{-\tau B} \dot{H}_1(t) e^{\tau B} \rangle_l > 0. \qquad (23.78)$$

The inequality (23.78) has already been used earlier for the case in which the averaging is carried out over an equilibrium distribution.

Taking into account (23.62) we write the production of entropy (23.77) in the form

$$\frac{dS}{dt} = \frac{1}{2} \sum_{\alpha\mu\alpha'\mu'} (\beta_1 - \beta_2)(E_\mu - E_{\mu'})\, \omega_{\alpha\mu}^{\alpha'\mu'} \times$$
$$\times \{ n_\alpha n_\mu (1 \pm n_{\alpha'})(1 \pm n_{\mu'}) - n_{\alpha'} n_{\mu'} (1 \pm n_\alpha)(1 \pm n_\mu) \}; \qquad (23.79)$$

consequently,

$$\frac{dS}{dt} = \frac{1}{2} \sum_{\alpha\mu\alpha'\mu'} \omega_{\alpha\mu}^{\alpha'\mu'} n_\alpha n_\mu (1 \pm n_{\alpha'})(1 \pm n_{\mu'}) \times$$
$$\times (\beta_1 - \beta_2)(E_\mu - E_{\mu'}) \left(1 - e^{-(\beta_1 - \beta_2)(E_\mu - E_{\mu'})}\right) \geqslant 0, \qquad (23.80)$$

since for arbitrary x

$$x(1 - e^{-x}) \geqslant 0 \qquad (23.81)$$

and all the remaining terms in (23.80) are positive.

And thus, it is shown that in the nonlinear process considered above the production of entropy is positive.

23.5. Rate of Chemical Reactions.

Chemical reactions in a homogeneous phase are an example of nonlinear irreversible processes, similar to relaxation processes, in which the method of the nonequilibrium statistical operator can be very easily applied.

We shall assume that the chemical reactions take place sufficiently slowly such that a spatially homogeneous state with identical temperatures for the reagents and the products of the reaction is established in the volume in which the reaction is taking place. We shall consider the simplest reactions in such a system.

Assume that in the system there takes place only a single binary reaction between the molecules A and B with the formation of the molecules C and D, i.e.,

$$A + B \rightleftarrows C + D. \tag{23.82}$$

For simplicity we shall assume that the reaction takes place in the gas phase.

We take the Hamiltonian of the system to be of the form

$$H = \sum_{i=1}^{4} H_i + u, \tag{23.83}$$

where H_1, H_2 are the Hamiltonians of the reagents, H_3, H_4 are the Hamiltonians of the products of the reaction, and u is the interaction which drives the reaction. For it we use a model form of the type

$$u = \sum_{\alpha_1 \alpha_2 \alpha_1' \alpha_2'} \left\{ \Phi^{\alpha_1' \alpha_2'}_{\alpha_1 \alpha_2} a^{+}_{\alpha_1} b^{+}_{\alpha_2} c_{\alpha_1'} d_{\alpha_2'} + \Phi^{\alpha_1' \alpha_2'}_{\alpha_1 \alpha_2} d^{+}_{\alpha_2'} c^{+}_{\alpha_1'} b_{\alpha_2} a_{\alpha_1} \right\}, \tag{23.84}$$

where $a^{+}_{\alpha_1}, b^{+}_{\alpha_2}, c^{+}_{\alpha_1'}, d^{+}_{\alpha_2'}$ are the creation operators for the molecules A,B,C,D in the states $\alpha_1, \alpha_2, \alpha_1', \alpha_2'$, and $a_{\alpha_1}, b_{\alpha_2}, c_{\alpha_1'}, d_{\alpha_2'}$ are the destruction operators for the corresponding states. Thus, the second term in (23.84) describes the direct reaction (23.82), and the second term describes the inverse reaction. The operator (23.84) is analogous to the corresponding operator for the excitation of internal degrees of freedom (23.52), which was considered in section 23.4 of this chapter.

The Hamiltonian (23.83) is a model Hamiltonian by virtue of the fact that we assume that the matrix elements are known from quantum mechanical calculations. Such a Hamiltonian is applicable for the theory of chemical reactions in the gas phase only, because in a liquid upon collisions of the molecules of the reagents part of the energy will be transferred to the liquid in the form of elementary excitations, and it is necessary to take this process into account in the interaction operator.

The operator for the total particle number

$$N = \sum_{i=1}^{4} N_i, \tag{23.85}$$

where

$$N_1 = \sum_{\alpha} a_{\alpha}^{+} a_{\alpha}, \quad N_2 = \sum_{\alpha} b_{\alpha}^{+} b_{\alpha}, \qquad N_3 = \sum_{\alpha} c_{\alpha}^{+} c_{\alpha}, \quad N_4 = \sum_{\alpha} d_{\alpha}^{+} d_{\alpha}, \tag{23.85a}$$

is conserved in time, because

$$\dot{N} = \frac{1}{i\hbar} [N, H] = 0, \tag{23.86}$$

but N_i changes in time as a consequence of the reaction,

$$\dot{N}_i = \frac{1}{i\hbar} [N_i, H] \qquad (i = 1, 2, 3, 4). \tag{23.87}$$

All of these currents are expressed through a single rate of reaction operator

$$J = \dot{N}_1 = \sum_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2} \frac{1}{i\hbar} \left\{ \Phi_{\alpha_1 \alpha_2}^{\alpha'_1 \alpha'_2} a_{\alpha_1}^{+} b_{\alpha_2}^{+} c_{\alpha'_1} d_{\alpha'_2} - \Phi_{\alpha_1 \alpha_2}^{\alpha'_1 \alpha'_2} d_{\alpha'_2}^{+} c_{\alpha'_1}^{+} b_{\alpha_2} a_{\alpha_1} \right\}, \tag{23.88}$$

$$\dot{N}_1 = J, \quad \dot{N}_2 = J, \quad \dot{N}_3 = -J, \quad \dot{N}_4 = -J \tag{23.89}$$

or

$$\dot{N}_i = \nu_i J, \tag{23.89a}$$

where the v_i are the stoichiometric numbers in the equation for the reaction, i.e., $v_1=v_2=1$, $v_3=v_4=-1$.

The conservation law (23.89a) corresponds to the statistical operator

$$\rho = Q^{-1}\exp\left\{-\beta\left(H-\sum_i \mu_i\tilde{N}_i\right)\right\} =$$
$$= Q^{-1}\exp\left\{-\beta\left(H-\sum_i \mu_i N_i + \sum_i \int_{-\infty}^{0} e^{\varepsilon t}\mu_i \dot{N}_i(t)\,dt\right)\right\}, \tag{23.90}$$

where μ_1,μ_2 are the chemical potentials of the reagents, and μ_3,μ_4 are the chemical potentials of the reaction products. Taking into account (23.89a) we write (23.90) in the form

$$\rho = Q^{-1}\exp\left\{-\beta\left(H-\sum_i \mu_i N_i + \sum_i \mu_i \nu_i \int_{-\infty}^{0} e^{\varepsilon t} J(t)\,dt\right)\right\} =$$
$$= Q^{-1}\exp\left\{-\beta\left(H-\sum_i \mu_i N_i - A\int_{-\infty}^{0} e^{\varepsilon t} J(t)\,dt\right)\right\}, \tag{23.91}$$

where

$$A = -\sum_i \mu_i \nu_i \tag{23.92}$$

is the chemical affinity in the terminology of de Donde [27], which plays the role of the thermodynamic force in the linear approximation.

The operator J contains a small parameter - the matrix elements of the transition which accompanies the chemical reaction.

We average the reaction rate (23.88) over the distribution (23.91) and expand the statistical operator in terms of the small parameter contained in (23.88). We obtain

$$\langle J\rangle = \langle \dot{N}_1\rangle = A\beta \int_{-\infty}^{0} d\tau\, e^{\varepsilon t} \int_{0}^{1} d\tau \langle \dot{N}_1 e^{-\tau B} \dot{N}_1(t)\, e^{\tau B}\rangle_l, \tag{23.93}$$

where $\langle\ldots\rangle_l$ denotes an averaging over the quasi-equilibrium distribution

$$\rho_l = Q_l^{-1} e^{-B}, \quad B = \beta\left(H - \sum_i \mu_i N_i\right). \tag{23.94}$$

If we replace in (23.93) the averaging over a quasi-equilibrium state by an averaging over an equilibrium state, then we obtain the linear relationship between the reaction rate and the affinity:

$$\langle \dot{N}_1 \rangle = \beta A L_{\dot{N}_1 \dot{N}_1}, \tag{23.93a}$$

where

$$L_{\dot{N}_1 \dot{N}_1} = \beta^{-1} \int_{-\infty}^{0} \int_{0}^{\beta} e^{\varepsilon t} \langle \dot{N}_1 \dot{N}_1 (t + i\hbar\tau) \rangle_0 \, dt \, d\tau, \tag{23.93b}$$

i.e., the relation obtained by Yamamoto [129,130].

We shall expand formula (23.93) for the case of a small interaction, but for arbitrary A.

Taking into account the fact that

$$e^{-B\tau} a_\alpha e^{B\tau} = e^{\beta (E_\alpha - \mu_1) \tau} a_\alpha,$$
$$e^{-B\tau} a_\alpha^+ e^{B\tau} = e^{-\beta (E_\alpha - \mu) \tau} a_\alpha^+,$$

we obtain

$$e^{-B\tau} a_{\alpha_1}^+ b_{\alpha_2}^+ c_{\alpha_1'} d_{\alpha_2'} e^{B\tau} =$$
$$= \exp\left\{ -\beta \left[\left(E_{\alpha_1} + E_{\alpha_2} - E_{\alpha_1'} - E_{\alpha_2'} \right) + A \right] \tau \right\} a_{\alpha_1}^+ b_{\alpha_2}^+ c_{\alpha_1'} d_{\alpha_2'}. \tag{23.95}$$

In the Heisenberg representation for the operator $\dot{N}_1(t)$ one can neglect the interaction, because in (23.93) there is already a factor of second order in the interaction; therefore, averages are easily calculated using Wick's theorem making use of (23.95). Carrying out in (23.93) an integration over τ and t, as in the expansion of formula (23.55), we obtain for the rate of a chemical reaction the expression

$$\langle J \rangle = \langle \dot{N}_1 \rangle = \sum_{\alpha_1 \alpha_2 \alpha_1' \alpha_2'} w_{\alpha_1 \alpha_2}^{\alpha_1' \alpha_2'} \left\{ n_{\alpha_1} n_{\alpha_2} \left(1 \pm n_{\alpha_1'} \right) \left(1 \pm n_{\alpha_2'} \right) - \right.$$
$$\left. - n_{\alpha_1'} n_{\alpha_2'} \left(1 \pm n_{\alpha_1} \right) \left(1 \pm n_{\alpha_2} \right) \right\}, \tag{23.96}$$

where
$$w_{\alpha_1\alpha_2}^{\alpha_1'\alpha_2'} = \frac{2\pi}{\hbar}\left|\Phi_{\alpha_1\alpha_2}^{\alpha_1'\alpha_2'}\right|^2 \delta\left(E_{\alpha_1} + E_{\alpha_2} - E_{\alpha_1'} - E_{\alpha_2'}\right) \qquad (23.97)$$

is the probability per unit time of a reaction.

On the right hand side of equation (23.96) is the summed collision integral of the kinetic equation (23.64) with the probabilities of transition (23.97). It is easily verified, as in the preceding section, that the occupation numbers satisfy the kinetic equation.

For a non-degenerate gas $n_\alpha \ll 1$, and the reaction rate is equal to

$$\langle \dot N_1 \rangle = (1 - e^{-\beta A}) \sum_{\alpha_1\alpha_2\alpha_1'\alpha_2'} w_{\alpha_1\alpha_2}^{\alpha_1'\alpha_2'} n_{\alpha_1} n_{\alpha_2}, \qquad (23.98)$$

where A is the chemical affinity (23.92).

If the system is close to a state of statistical equilibrium, i.e.,

$$\beta |A| \ll 1, \qquad (23.99)$$

then the reaction rate is equal to

$$\langle \dot N_1 \rangle = L_{\dot N_1 \dot N_1} \beta A, \qquad (23.100)$$

where
$$L_{\dot N_1 \dot N_1} = \sum_{\alpha_1\alpha_2\alpha_1'\alpha_2'} w_{\alpha_1\alpha_2}^{\alpha_1'\alpha_2'} n_{\alpha_1} n_{\alpha_2} \qquad (23.101)$$

is the kinetic coefficient, which has the meaning of the rate of the direct reaction. Thus, by the condition (23.99) the total rate of the chemical reaction is proportional to the chemical affinity, and A is a thermodynamic force.

The condition of chemical equilibrium is that the rate of the chemical reaction be zero, i.e., the equality to zero of the chemical affinity:

$$A = -\sum_i \mu_i \nu_i = 0. \qquad (23.102)$$

For a mixture of ideal gases the chemical potential is equal to [92]

$$\mu_i = \beta^{-1} \ln p_i + \chi_i, \tag{23.103}$$

where

$$p_i = pc_i \tag{23.103a}$$

is the partial pressure of the ith component, $c_i = N_i/N$ is the concentration of particles of the ith component, and χ_i is a function of temperature, which is easily calculated from the statistical sum for an ideal gas. Taking into account (23.103) the condition of chemical equilibrium takes on the form of the law of mass action:

$$\prod_i p_i^{\nu_i} = e^{-\beta \sum_i \nu_i \chi_i} = K, \tag{23.104}$$

where K is a constant of the chemical equilibrium, depending only on the temperature.

Taking into account (23.104) the kinetic coefficient (23.101) can be written in the form

$$L_{\dot{N}_1 \dot{N}_1} = \varkappa c_1 c_2, \tag{23.105}$$

where

$$\varkappa = e^{\beta(\chi_1 + \chi_2)} p^2 \sum_{\alpha_1 \alpha_2 \alpha'_1 \alpha'_2} w_{\alpha_1 \alpha_2}^{\alpha'_1 \alpha'_2} e^{-\beta(E_{\alpha_1} + E_{\alpha_2})} \tag{23.106}$$

is the constant of the rate of the direct reaction. The relation (23.105) expresses the kinetic law of mass action.

Using (23.89a) the linear relation (23.100) between the reaction rate and the chemical affinity can be written in the form

$$\frac{\langle \dot{N}_i \rangle}{\nu_i} = \frac{d\xi}{dt} = L_{\dot{N}_1 \dot{N}_1} \beta A, \tag{23.107}$$

where we have introduced the parameter

$$\xi = \frac{\langle N_i \rangle - \langle N_i \rangle_0}{\nu_i} \tag{23.108}$$

which is the completeness, or the degree of development of the chemical reaction, and $\langle N_i \rangle_0$ is the equilibrium concentration of the product i.

The chemical affinity A can be expressed in terms of the derivative of the entropy with respect to the completeness of the reaction ξ:

$$S = \ln Q_l + \beta \langle H \rangle - \beta \sum_l \mu_l \langle N_l \rangle. \tag{23.109}$$

In fact,

$$\frac{\partial S}{\partial t} = -\beta \sum_l \mu_l \langle \dot{N}_l \rangle = \beta A \frac{d\xi}{dt}, \tag{23.110}$$

because the derivatives of $\ln Q_e$ with respect to β and μ_i cancel, and we assume that $\langle H \rangle$ is constant. Consequently,

$$A = T \left(\frac{\partial S}{\partial \xi} \right)_{\langle H \rangle}. \tag{23.111}$$

In a state of statistical equilibrium A=0, because the reaction rate is zero. We expand A in the neighborhood of equilibrium with respect to the small deviation of ξ from the equilibrium value ξ_0:

$$A = T \left(\frac{\partial^2 S}{\partial \xi^2} \right)_{\xi=0} (\xi - \xi_0). \tag{23.112}$$

Substituting (23.112) into (23.107), we obtain a relaxation equation for the completeness of the reaction

$$\frac{d\xi}{dt} = -\frac{\xi - \xi_0}{\tau}, \tag{23.113}$$

where

$$\tau = -\frac{1}{L_{\dot{N}_1 \dot{N}_1} \left(\frac{\partial^2 S}{\partial \xi^2} \right)_{\xi=0}} > 0 \tag{23.114}$$

is the time of relaxation of the reaction. Integrating (23.113), we obtain the time dependence of the completeness of the reaction:

$$\xi - \xi_0 = (\xi(0) - \xi_0) e^{-t/\tau}, \tag{23.115}$$

i.e., the completeness of the reaction tends exponentially to the equilibrium value ξ_0.

The relaxation time, introduced in (23.114), corresponds to constant energy and constant particle number. Analogous relations can be obtained also for other thermodynamic conditions [27,131].

In the general case the rate of a chemical reaction is nonlinear with respect to the affinity, i.e.,

$$\langle \dot N_1 \rangle = L_{\dot N_1 \dot N_1}(1 - e^{-\beta A}). \tag{23.116}$$

The discussion presented above is valid also for an arbitrary number of components, among which different chemical reactions are possible. Then

$$\langle \dot N_i \rangle = \sum_m L_{\dot N_i \dot N_m}(1 - e^{-\beta A_m}), \tag{23.117}$$

where

$$L_{\dot N_i \dot N_m} = \sum_{\alpha_1\alpha_2\ldots\alpha_1'\alpha_2'\ldots} w_{\alpha_1\alpha_2\ldots}^{\alpha_1'\alpha_2'\ldots}(i, m)\, n_{\alpha_1} n_{\alpha_2}\ldots \tag{23.118}$$

is the kinetic coefficient,

$$A_m = -\sum_i \mu_i \nu_{im} \tag{23.119}$$

is the chemical affinity, and ν_{im} are the stoichiometric coefficients, with which the substance i enters into the m^{th} reaction.

The condition of chemical equilibrium

$$A_m = -\sum_i \mu_i \nu_{im} = 0 \tag{23.120}$$

takes on the form, taking into account (23.103),

$$\prod_i p_i^{\nu_{im}} = e^{-\beta \sum_i \nu_{im} \chi_i} = K_m, \tag{23.121}$$

where K_m is the constant of chemical equilibrium of the m^{th} reaction.

The kinetic law of mass action in this case takes on the form

$$L_{\dot{N}_l \dot{N}_m} = \varkappa_l \prod_m c_m^{\nu_{lm}}, \qquad (23.122)$$

where

$$\varkappa_l = e^{\beta \sum_m \nu_{lm} \chi_l} p^{\sum_m \nu_{lm}} \sum_{\alpha_1 \alpha_2 \dots \alpha'_1 \alpha'_2 \dots} \omega_{\alpha_1 \alpha_2 \dots}^{\alpha'_1 \alpha'_2 \dots} e^{-\beta \sum_m \nu_{lm} E_{\alpha_m}} \qquad (23.122a)$$

and everywhere $\nu_{lm} > 0$, i.e., only positive stoichiometric coefficients are taken into account.

Let us consider the production of entropy in chemical reactions in a homogeneous system for the nonlinear case.

The entropy for such a system is equal to (23.109), and taking into account (23.89a) the production of entropy is equal to

$$\frac{dS}{dt} = -\beta \sum_{l=1}^{4} \mu_l \nu_l \langle J \rangle = \beta A \langle J \rangle. \qquad (23.123)$$

Substituting here the expression (23.116) for the average reaction rate, we obtain for the production of entropy the expression

$$\frac{dS}{dt} = L_{\dot{N}_l \dot{N}_l} \beta A (1 - e^{-\beta A}) \geqslant 0, \qquad (23.124)$$

which follows from the inequality (23.81). Consequently, the production of entropy in a chemical reaction is positive.

Until now we have considered only equations of balance for particles in chemical reactions. One can consider analogously the balance of energy. Although this is essential for chemical reactions (see [132]), we shall not make here such a generalization. The goal of this paragraph was to demonstrate that the method of the nonequilibrium statistical operator can describe even nonlinear processes in chemical kinetics.

§ 24. Statistical Operator of a Relativistic System and Relativistic Hydrodynamics

24.1. Relativistic Statistical Operator.

The phenomenological nonequilibrium thermodynamics for the relativistic case was developed by Eckart [133] for a single-component liquid (or gas) and was generalized for a mixture by Kluitenberg, de Groot, and Mazur [134]. An account is given, for example, in [82].

We shall apply the method of constructing nonequilibrium statistical operators, presented in § 21 to a relativistic system, following [5]. Taking into account relativity only simplifies the problem, because it makes it possible to construct easily invariant quantities while the statistical operator and the entropy which it defines must in the relativistic case be invariant with respect to a Lorentz transformation [135].

The law of conservation of energy-momentum in the relativistic case has the form

$$\sum_{\mu=1}^{4} \frac{\partial T_{\mu\nu}(x, t)}{\partial x_\mu} = 0, \tag{24.1}$$

where $\mathbf{x}$ is the set of coordinates x_1, x_2, x_3, a $x_4 = ict$, and $T_{\mu\nu}(\mathbf{x}, t)$ is the relativistic expression for the symmetric energy-momentum density tensor, which is assumed to be known. We shall consider a system which is characterized only by this conservation law, and in particular a system without electrical charge and spin.

The conservation law (24.1) corresponds to the local integral of motion

$$\widetilde{T_{4\nu}(x)} = T_{4\nu}(x) - \int_{-\infty}^{0} e^{\epsilon t}\, \dot{T}_{4\nu}(x, t)\, dt =$$
$$= T_{4\nu}(x) + \sum_{\mu=1}^{3} \int_{-\infty}^{0} e^{\epsilon t} \frac{\partial T_{\mu\nu}(x, t)}{\partial x_\mu}\, ic\, dt. \tag{24.2}$$

In (24.2) we have selected the retarded solution, i.e., we have made use of the causality condition.

Using (24.2) one can discuss stationary processes, but we shall discuss immediately nonstationary processes, because a discussion of these processes in the relativistic case is even simpler because of the symmetry between space and time coordinates.

By the usual method, but taking into account the conservation law (24.1), we construct operators, which depend on time only through some parameters $F_\nu(x,t)$ ($\nu=1,\dots,4$), and which define the macroscopic state of the system:

$$
\begin{aligned}
B_{4\nu}(\boldsymbol{x},t) &= -F_\nu(\boldsymbol{x},t)\,T_{4\nu}(\boldsymbol{x}) = -F_\nu(x,t)\,T_{4\nu}(\boldsymbol{x}) + \\
&+ \int_{-\infty}^{0} e^{\varepsilon t_1}\left\{F_\nu(\boldsymbol{x},t+t_1)\,\dot{T}_{4\nu}(\boldsymbol{x},t_1) + \frac{\partial F_\nu(\boldsymbol{x},t+t_1)}{\partial t_1}\,T_{4\nu}(\boldsymbol{x},t_1)\right\}dt_1 = \\
&= -F_\nu(\boldsymbol{x},t)\,T_{4\nu}(\boldsymbol{x}) + \int_{-\infty}^{0} e^{\varepsilon t_1}\left\{-F_\nu(\boldsymbol{x},t+t_1)\,ic\sum_{\mu=1}^{3}\frac{\partial T_{\mu\nu}(\boldsymbol{x},t_1)}{\partial x_\mu} + \right. \\
&\qquad\left. + \frac{\partial F_\nu(\boldsymbol{x},t+t_1)}{\partial t_1}\,T_{4\nu}(\boldsymbol{x},t_1)\right\}dt_1. \qquad (24.3)
\end{aligned}
$$

The parameters $F_\nu(x,t)$, the physical meaning of which we shall explain later, are selected such that the expression

$$\sum_\nu \int B_{4\nu}(\boldsymbol{x})\,d\boldsymbol{x}$$

is Lorentz invariant. Dropping the surface integrals, we obtain for this quantity the expression

$$
\begin{aligned}
\sum_\nu \int B_{4\nu}(\boldsymbol{x},t)\,d\boldsymbol{x} &= -\sum_\nu \int F_\nu(\boldsymbol{x},t)\,T_{4\nu}(\boldsymbol{x})\,d\boldsymbol{x} + \\
&+ \sum_{\mu,\nu=1}^{4}\int\int_{-\infty}^{0} e^{\varepsilon t_1}\frac{\partial F_\nu(\boldsymbol{x},t+t_1)}{\partial x_\mu}\,T_{\mu\nu}(\boldsymbol{x},t_1)\,d\boldsymbol{x}\,ic\,dt_1. \qquad (24.4)
\end{aligned}
$$

Following the usual approach, we construct the statistical operator

$$
\begin{aligned}
\rho &= Q^{-1}\exp\left\{-\sum_\nu \int B_{4\nu}(\boldsymbol{x},t)\,d\boldsymbol{x}\right\} = Q^{-1}\exp\left\{\sum_\nu \int F_\nu(\boldsymbol{x},t)\,T_{4\nu}(\boldsymbol{x})\,d\boldsymbol{x} - \right. \\
&\left. -\sum_{\mu,\nu}\int\int_{-\infty}^{0} e^{\varepsilon t_1}\frac{\partial F_\nu(\boldsymbol{x},t+t_1)}{\partial x_\mu}\,T_{\mu\nu}(\boldsymbol{x},t_1)\,d\boldsymbol{x}\,ic\,dt_1\right\}, \qquad (24.5)
\end{aligned}
$$

where the parameters $F_\nu(\mathbf{x},t)$ are defined from the conditions

$$\langle T_{4\nu}(\mathbf{x})\rangle = \langle T_{4\nu}(\mathbf{x})\rangle_l, \qquad (24.6)$$

where

$$\rho_l = Q_l^{-1}\exp\left\{\sum_\nu \int F_\nu(\mathbf{x},t)\,T_{4\nu}(\mathbf{x})\,d\mathbf{x}\right\} \qquad (24.7)$$

is the relativistic local equilibrium statistical operator.

24.2. Thermodynamic Equalities.

We shall now explain the physical meaning of the parameters $F_\nu(\mathbf{x},t)$. We put

$$F_\nu(\mathbf{x},t) = -\beta(\mathbf{x},t)\,iu_\nu(\mathbf{x},t), \qquad (24.8)$$

where u_ν is the four dimensional velocity, i.e.,

$$\sum_\nu u_\nu^2(x,t) = -1. \qquad (24.8a)$$

This guarantees the Lorentz invariance of the statistical operator (24.5), because $\int T_{4\nu}(\mathbf{x})d\mathbf{x}$ transforms like a 4-vector, if the field is non-zero only in a finite region of space [136].

Let us consider the local equilibrium state (24.7)

$$\rho_l = Q_l^{-1}\exp\left\{-\sum_\nu \int \beta(\mathbf{x},t)\,iu_\nu(\mathbf{x},t)\,T_{4\nu}(\mathbf{x})\,d\mathbf{x}\right\}, \qquad (24.9)$$

where

$$Q_l = \mathrm{Sp}\exp\left\{-\sum_\nu \int \beta(\mathbf{x},t)\,iu_\nu(\mathbf{x},t)\,T_{4\nu}(x)\,dx\right\}. \qquad (24.9a)$$

Let us go over into a moving system in which the spatial components of the 4-vector u_ν are equal to zero, $u_1'=u_2'=u_3'=0$, $u_4'=i$, i.e.,

$$u'_\nu = i\delta_{\nu 4}, \tag{24.10}$$

which satisfies the condition (24.8a). Here and in what follows we shall denote by primes the components of vectors and tensors in this moving system.

In this co-moving system the statistical operator (24.9) has the usual, nonrelativistic form

$$\rho_l = Q_l^{-1} \exp\left\{ - \int \beta(x, t)\, H'(x)\, dx \right\}, \tag{24.11}$$

where

$$H'(x) = - T'_{44}(x) \tag{24.11a}$$

is the Hamiltonian density in the moving system. Formulas (24.11) and (24.11a) confirm the correctness of the definition (24.9).

We choose u_ν such that the variation of $\ln Q_l$ with respect to u_1, u_2, or u_3 is equal to zero, i.e.,

$$\frac{\delta \ln Q_l}{\delta u_\nu(x, t)} = 0 \qquad (\nu = 1, 2, 3). \tag{24.12}$$

We have already made use of a similar condition in § 20, where we considered an ordinary velocity, rather than a four-dimensional velocity. This condition insured the choice of the parameter v(x,t) as the average mass velocity, which was required for the fulfillment of the thermodynamic equalities. The condition (24.12) implies that we are defining the densities of mechanical quantities, on which the statistical operator depends, in a local system, which moves together with the element of liquid.

We calculate the variation of (24.9a), taking into account (24.8a):

$$\delta \ln Q_l = - i \sum_\nu \int \beta(x, t) \left\{ \langle T_{4\nu}(x) \rangle - \langle T_{44}(x) \rangle \frac{u_\nu(x, t)}{u_4(x, t)} \right\} \delta u_\nu(x, t)\, dx,$$

because

$$\sum_{\nu=1}^{3} u_\nu \delta u_\nu + u_4 \delta u_4 = 0 \qquad (\nu = 1, 2, 3).$$

From the condition (24.12) we obtain

$$\frac{u_\nu(x,t)}{u_4(x,t)} = \frac{\langle T_{4\nu}(x)\rangle}{\langle T_{44}(x)\rangle} = -ic\frac{\langle G_\nu(x)\rangle}{\langle H(x)\rangle}, \tag{24.13}$$

where

$$G_\nu(x) = \frac{1}{ic}T_{4\nu}(x), \qquad H(x) = -T_{44}(x) \tag{24.14}$$

are the densities of momentum and energy, respectively.

If one introduces the ordinary, three-dimensional local velocity

$$v_\nu(x,t) = c^2\frac{\langle G_\nu(x)\rangle}{\langle H(x)\rangle} = ic\frac{\langle T_{4\nu}(x)\rangle}{\langle T_{44}(x)\rangle} \qquad (\nu = 1, 2, 3), \tag{24.15}$$

then the relation (24.13) can be written in the form

$$\frac{u_\nu(x,t)}{u_4(x,t)} = -\frac{iv_\nu(x,t)}{c}, \tag{24.16}$$

or taking into account (24.8a)

$$u_\nu(x,t) = \frac{v_\nu(x,t)}{c\sqrt{1-\frac{v^2(x,t)}{c^2}}}, \qquad u_4(x,t) = \frac{i}{\sqrt{1-\frac{v^2(x,t)}{c^2}}}. \tag{24.16a}$$

Thus, for the local velocities $v_\nu(x,t)$ and $u_\nu(x,t)$ we obtain well-known relativistic relations.

There remains to explain the meaning of the parameter $\beta(x,t)$. We calculate for this the variation of the statistical sum (24.9a) with respect to $\beta(x,t)$ for constant $u_\nu(x,t)$:

$$\frac{\delta \ln Q_t}{\delta\beta(x,t)} = -\sum_{\nu=1}^{4} u_\nu(x,t)\langle T_{4\nu}(x)\rangle, \tag{24.17}$$

from which we obtain, taking into account (24.13), (24.8a), (24.16a), and (24.14), the thermodynamic equality

$$\frac{\delta \ln Q_t}{\delta\beta(x,t)} = \langle T_{44}(x)\rangle\sqrt{1-\frac{v^2(x,t)}{c^2}} = -\langle H(x)\rangle\sqrt{1-\frac{v^2(x,t)}{c^2}}, \tag{24.17a}$$

which is analogous to the first of the equations of the system (20.21a), and which goes over into it in the nonrelativistic limit $v(x,t) \ll c$ and for a zero value of the chemical potential μ.

From (24.17) it follows that $\beta^{-1}(x,t)$ plays the role of an invariant "proper" temperature, while the quantity

$$\beta^{-1}(x,t)\left(1-\frac{v^2(x,t)}{c^2}\right)^{-1/2}$$

plays the role of an ordinary, noninvariant temperature.

24.3. Relativistic Hydrodynamic Equations.

The statistical operator (24.5) allows one to obtain the equations of relativistic hydrodynamics. For this we obtain linear relations between the average energy-momentum tensor and the thermodynamic forces $\partial F_\nu/\partial x_\mu$, assuming that the latter are small:

$$\langle T_{\mu\nu}(x)\rangle = \\ =\langle T_{\mu\nu}(x)\rangle_l - \sum_{\mu_1\nu_1}\int\int_{-\infty}^{0} e^{\varepsilon t_1}\,(T_{\mu\nu}(x), T_{\mu_1\nu_1}(x',t_1))\,\frac{\partial F_{\nu_1}(x',t+t_1)}{\partial x'_{\mu_1}}\,dx'\,ic\,dt_1, \tag{24.18}$$

where $(T_{\mu\nu}, T_{\mu_1\nu_1})$ is the quantum correlation function, and $\langle\ldots\rangle_l$ denotes an averaging over the local equilibrium distribution (24.9).

Expression (24.18) unites all irreversible processes which can take place in a system with a single conservation law of energy-momentum, i.e., thermal conductivity and shear and second viscosity, but for an isotropic medium it is inconvenient, because processes of different tensor rank are not separated in it. Below we shall give another, less general, but correspondingly more convenient expression for irreversible currents in an isotropic medium.

In order to construct operators which describe irreversible currents, it is necessary to separate out from the tensor $T_{\mu\nu}$ the part which describes convective motion with a hydrodynamic velocity u_μ; we have already defined this velocity by the condition (24.12).

We note that any vector F_μ can be divided into a sum of vectors, one of which is parallel to u_μ, and the other of which is perpendicular to it, i.e.,

$$F_\mu = f u_\mu + f_\mu. \tag{24.19}$$

From the condition of orthogonality of f_μ to u_μ

$$\sum_\mu f_\mu u_\mu = 0 \tag{24.19a}$$

we find, taking into account (24.8a),

$$f = \left(\sum_\mu u_\mu F_\mu\right)\left(\sum_\mu u_\mu^2\right)^{-1} = -\sum_\mu u_\mu F_\mu. \tag{24.19b}$$

We express the vector f_μ in terms of the tensor (24.20)

$$\Delta_{\mu\nu} = \delta_{\mu\nu} + u_\mu u_\nu,$$

where $\delta_{\mu\nu}$ is the Kronecker symbol. The tensor $\Delta_{\mu\nu}$ is orthogonal to u_μ:

$$\sum_\mu u_\mu \Delta_{\mu\nu} = 0. \tag{24.21}$$

Assuming that

$$f_\mu = \sum_\nu \Delta_{\mu\nu} F_\nu, \tag{24.22}$$

we verify that this vector is indeed the component of F_μ perpendicular to u_μ. In this connection, multiplying (24.19) by $\Delta_{\mu\nu}$ and summing over μ, we obtain with the use of (24.21) the expression (24.22).

The tensor $\Delta_{\mu\nu}$ plays the same role in relativistic theory as does the Kronecker symbol in the nonrelativistic theory. To make clear the meaning of this tensor we go over into a system of coordinates moving with the hydrodynamic velocity (24.10). The tensor $\Delta_{\mu\nu}$ in this system has a very simple form

$$\Delta'_{\mu\nu} = \delta_{\mu\nu} - \delta_{\mu 1}\delta_{\nu 1}, \tag{24.22a}$$

or in matrix form

$$\Delta' = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{24.22b}$$

Such a separation into characteristic components with respect to the hydrodynamic motion can be carried out for any tensor, and in particular for $T_{\mu\nu}$:

$$T_{\mu\nu} = \varepsilon u_\mu u_\nu + P_\mu u_\nu + P_\nu u_\mu + P_{\mu\nu},$$

where

$$\sum_\mu P_\mu u_\mu = 0, \qquad \sum_\nu P_{\mu\nu} u_\nu = 0. \tag{24.23}$$

(24.23a)

The coefficients of the decomposition (24.23) are equal to

$$\begin{aligned} \varepsilon &= \sum_{\mu,\lambda} u_\mu T_{\mu\lambda} u_\lambda, \\ P_\mu &= -\sum_{\nu\lambda} \Delta_{\mu\nu} T_{\nu\lambda} u_\lambda = c^{-1} q_\mu, \\ P_{\mu\nu} &= \sum_{\mu_1\nu_1} \Delta_{\mu\mu_1} T_{\mu_1\nu_1} \Delta_{\nu_1\nu}, \end{aligned} \tag{24.24}$$

which can be verified directly. We shall omit the arguments x and t whereever this leads to no confusion.

The quantities (24.24) have a simple physical meaning: ε is the density of internal energy, which is not related to the convective motion; $P_\mu c = q_\mu$ is the heat current; $P_{\mu\nu}$ is the stress tensor. All of these quantities are operators or dynamical variables.

In order to elucidate the physical meaning of the expressions (24.24), we write them in a system moving with the hydrodynamic velocity. Making use of (24.10) and (24.22), we obtain

$$\begin{aligned} \varepsilon &= -T'_{44}, \\ P'_\mu &= -iT'_{\mu 4} + \delta_{\mu 4} i T'_{44}, \\ P'_{\mu\nu} &= T'_{\mu\nu} - \delta_{\mu 4} T'_{4\nu} - \delta_{\nu 4} T'_{\mu 4} + \delta_{\mu 4}\delta_{\nu 4} T'_{44}. \end{aligned} \tag{24.24a}$$

Taking into account (24.14) these relations can be written in the form

$$\begin{aligned} \varepsilon &= H', \\ P'_\mu &= cG'_\mu \quad (\mu = 1, 2, 3), \qquad P'_4 = 0, \\ P'_{\mu\nu} &= T'_{\mu\nu} \quad (\mu, \nu = 1, 2, 3), \qquad P'_{\nu 4} = 0. \end{aligned} \tag{24.24b}$$

In a system moving with the hydrodynamic velocity all quantities must coincide with their nonrelativistic expressions. Thus, indeed, ε has the meaning of an energy density, P_μ is the energy current in the co-moving system, i.e., the heat current divided by c, and $P_{\mu\nu}$ is the stress tensor.

We introduce the viscous shear stress tensor $\pi_{\mu\nu}$, which, like $P_{\mu\nu}$, is orthogonal to u_μ, but which has zero trace:

$$P_{\mu\nu} = \pi_{\mu\nu} + p\Delta_{\mu\nu}, \tag{24.25}$$

where

$$p = \frac{1}{3}\sum_\mu P_{\mu\mu}. \tag{24.25a}$$

Then

$$\sum_\mu \pi_{\mu\nu} u_\nu = 0, \tag{24.26}$$

and, in addition,

$$\sum_\mu \pi_{\mu\mu} = 0, \tag{24.26a}$$

because

$$\sum_\mu \Delta_{\mu\mu} = \sum_\mu (1 + u_\mu^2) = 3.$$

Using (24.25) we write the decomposition of the tensor $T_{\mu\nu}$ into characteristic components (24.23) in the form

$$T_{\mu\nu} = \varepsilon u_\mu u_\nu + p\Delta_{\mu\nu} + P_\mu u_\nu + P_\nu u_\mu + \pi_{\mu\nu}. \tag{24.27}$$

Thus, we have divided the tensor $T_{\mu\nu}$ into three parts, having scalar, tensor, and vector character with respect to the operators ε, p, P_μ and $\pi_{\mu\nu}$. This division, which is applied in phenomenological relativstic hydrodynamics [133,134], enables us to separate scalar, vector, and tensor processes.

After an averaging with respect to local equilibrium the first two terms in (24.27) have the meaning of the energy-momentum tensor of an ideal liquid and describe non-dissipative processes. The two following terms give the heat current, and the last term gives the viscous momentum current. These parts describe irreversible processes.

For a local equilibrium state the average values only of the first two terms are non-zero:

$$\langle T_{\mu\nu}\rangle_l = (\langle\varepsilon\rangle_l + \langle p\rangle_l)\, u_\mu u_\nu + \langle p\rangle_l\, \delta_{\mu\nu}, \tag{24.28}$$

because in the co-moving system the average values of vectors and of the non-diagonal elements of tensors are equal to zero (see section 20.5),

$$\langle P_\mu \rangle_l = 0, \qquad \langle \pi_{\mu\nu} \rangle_l = 0. \tag{24.29}$$

We represent the statistical operator (24.5) in such a form that scalar, vector, and tensor processes will be separated in it. Taking into account (24.27) and the orthogonality of $\partial u_\mu / \partial x_\nu$ to u_μ,

$$\sum_\mu \frac{\partial u_\mu}{\partial x_\nu} u_\mu = 0, \tag{24.30}$$

which follows from (24.8a), we obtain

$$\begin{gathered}
\sum_{\mu\nu} T_{\mu\nu} \frac{\partial \beta u_\mu}{\partial x_\nu} = \\
= \beta \sum_{\mu\nu} \pi_{\mu\nu} \frac{\partial u_\mu}{\partial x_\nu} - \sum_\mu \beta P_\mu \left(\beta^{-1} \frac{\partial \beta}{\partial x_\mu} - \frac{1}{c} D u_\mu \right) - \frac{1}{c} \varepsilon D\beta + \beta p \operatorname{div} \boldsymbol{u}, \\
\operatorname{div} \boldsymbol{u} = \sum_\mu \frac{\partial u_\mu}{\partial x_\mu},
\end{gathered} \tag{24.31}$$

where

$$D = c \sum_\mu u_\mu \frac{\partial}{\partial x_\mu} \tag{24.32}$$

is a scalar operator, having the meaning of the total derivative in relativistic theory. In this connection, in the moving system (24.10) the operator D coincides with the time derivative,

$$D = \frac{\partial}{\partial t'}. \tag{24.32a}$$

In the expression (24.31) which goes into the exponential of the statistical operator, terms containing operators of different tensor rank are separated. Taking into account (24.31), we write the statistical operator in the form

$$\rho = Q^{-1} \exp\Big\{ -\sum_{\nu} \int \beta(\boldsymbol{x}, t)\, iu_{\nu}(\boldsymbol{x}, t)\, T_{4\nu}(\boldsymbol{x})\, d\boldsymbol{x} -$$
$$- \int \int_{-\infty}^{0} e^{\varepsilon t_1} c\beta(\boldsymbol{x}, t + t_1) \Big[\sum_{\mu\nu} \pi_{\mu\nu}(\boldsymbol{x}, t_1) \frac{\partial u_{\mu}(\boldsymbol{x}, t + t_1)}{\partial x_{\nu}} - \sum_{\mu} P_{\mu}(\boldsymbol{x}, t_1) \times$$
$$\times \Big(\beta^{-1}(\boldsymbol{x}, t + t_1) \frac{\partial \beta(\boldsymbol{x}, t + t_1)}{\partial x_{\mu}} - \frac{1}{c} Du_{\mu}(\boldsymbol{x}, t + t_1) \Big) +$$
$$+ p(\boldsymbol{x}, t_1) \operatorname{div} \boldsymbol{u}(\boldsymbol{x}, t + t_1) - \frac{1}{c} \varepsilon(\boldsymbol{x}, t_1) \beta^{-1}(\boldsymbol{x}, t + t_1) D\beta(\boldsymbol{x}, t + t_1) \Big] d\boldsymbol{x}\, dt_1 \Big\}. \tag{24.33}$$

The quantities

$$\frac{\partial u_{\mu}}{\partial x_{\nu}}, \quad \beta^{-1} \frac{\partial \beta}{\partial x_{\mu}} - \frac{1}{c} Du_{\mu}, \quad \operatorname{div} \boldsymbol{u}$$

play the role of thermodynamic forces, associated with the currents

$$\langle \pi_{\mu\nu}(\boldsymbol{x}) \rangle, \quad \langle P_{\mu}(\boldsymbol{x}) \rangle, \quad \langle p(\boldsymbol{x}) \rangle - \langle p(\boldsymbol{x}) \rangle_l,$$

while the quantity $D\beta$ can be expressed in terms of div$\boldsymbol{u}$ by using the equations of ideal hydrodynamics. In this connection, in accordance with (24.28) for a local equilibrium state we have for the energy-momentum tensor

$$\langle T_{\mu\nu}(\boldsymbol{x}) \rangle_l = hu_{\mu}u_{\nu} + p\delta_{\mu\nu}, \tag{24.34}$$

where

$$h = \langle \varepsilon \rangle_l + \langle p \rangle_l \tag{24.34a}$$

is the thermal function or enthalpy per unit volume, and

$$p = \langle p \rangle_l \tag{24.34b}$$

is the pressure. Equating to zero the four-dimensional divergence of (24.34)

$$\frac{\partial}{\partial x_{\nu}} \langle T_{\mu\nu}(\boldsymbol{x}) \rangle_l = 0, \tag{24.35}$$

we obtain the hydrodynamic equation of a relativistic system, neglecting dissipation processes:

$$u_\mu \frac{\partial h u_\nu}{\partial x_\nu} + h u_\nu \frac{\partial u_\mu}{\partial x_\nu} + \frac{\partial p}{\partial x_\mu} = 0, \qquad (24.36)$$

where a summation over repeated indices is assumed. Taking the scalar product of this equation with u_μ and making use of (24.8a), we find

$$-\frac{\partial h u_\nu}{\partial x_\nu} + u_\mu \frac{\partial p}{\partial x_\mu} = 0, \qquad (24.37)$$

or in the notation of (24.32)

$$-ch\,\mathrm{div}\,\boldsymbol{u} + D(p-h) = 0. \qquad (24.38)$$

In our case p and h are functions of β, and consequently,

$$D\beta = \left(\frac{\partial(p-h)}{\partial\beta}\right)^{-1} hc\,\mathrm{div}\,\boldsymbol{u} = \beta\frac{\partial p}{\partial\varepsilon}\,c\,\mathrm{div}\,\boldsymbol{u}, \qquad (24.39)$$

because

$$p - h = -\varepsilon, \quad h = -\beta\frac{\partial p}{\partial\beta}. \qquad (24.39a)$$

Consequently, one can eliminate the quantity $D\beta$ in the exponential of the statistical operator (24.33):

$$\begin{aligned}\rho = Q^{-1}\exp\Big\{ & -\sum_\nu \int \beta(\boldsymbol{x}, t)\, i u_\nu(\boldsymbol{x}, t)\, T_{4\nu}(\boldsymbol{x})\, d\boldsymbol{x} - \\ & - \int \int_{-\infty}^{0} e^{\varepsilon t_1} c\beta(\boldsymbol{x}, t+t_1)\Big[\sum_{\mu\nu} \pi_{\mu\nu}(\boldsymbol{x}, t_1)\frac{\partial u_\mu(\boldsymbol{x}, t+t_1)}{\partial x_\nu} - \\ & - \sum_\mu P_\mu(\boldsymbol{x}, t_1)\Big(\beta^{-1}(\boldsymbol{x}, t+t_1)\frac{\partial\beta(\boldsymbol{x}, t+t_1)}{\partial x_\mu} - \frac{1}{c} D u_\mu(\boldsymbol{x}, t+t_1)\Big) + \\ & + p'(\boldsymbol{x}, t_1)\,\mathrm{div}\,\boldsymbol{u}(\boldsymbol{x}, t+t_1)\Big] d\boldsymbol{x}\, dt_1\Big\},\end{aligned} \qquad (24.40)$$

where

$$p'(\boldsymbol{x}, t) = p(\boldsymbol{x}, t) - \frac{\partial p}{\partial\varepsilon}\varepsilon(\boldsymbol{x}, t).$$

We shall now obtain linear relations between the average currents and the thermodynamic forces, assuming that the forces are small; we shall limit our attention to linear terms and make use of the Curie theorem [27], according to which only currents of the same tensor rank can be connected:

$$\langle \pi_{\mu\nu}(x)\rangle = -\sum_{\mu_1,\nu_1}\int\int_{-\infty}^{0} e^{\varepsilon t_1}(\pi_{\mu\nu}(x), \pi_{\mu_1\nu_1}(x', t_1))\beta(x', t+t_1) \times \frac{\partial u_{\mu_1}(x', t+t_1)}{\partial x'_{\nu_1}} c\, dx'\, dt_1, \tag{24.41a}$$

$$\begin{gathered}\langle P_\mu(x)\rangle = c^{-1}\langle q_\mu(x, t)\rangle = \sum_{\nu}\int\int_{-\infty}^{0} e^{\varepsilon t_1}(P_\mu(x), P_\nu(x', t_1))\beta(x', t+t_1) \times \\ \times\left(\beta^{-1}(x', t+t_1)\frac{\partial\beta(x', t+t_1)}{\partial x'_\nu} - \frac{1}{c}Du_\nu(x', t+t_1)\right)c\, dx'\, dt_1,\end{gathered} \tag{24.41b}$$

$$\langle p(x)\rangle - \langle p(x)\rangle_l = -\int\int_{-\infty}^{0} e^{\varepsilon t_1}(p'(x), p'(x', t_1))\beta(x', t+t_1)\operatorname{div} u(x', t+t_1)\, c\, dx'\, dt_1. \tag{24.41c}$$

We shall make use of the property of spatial isotropy of the system to simplify the expressions for the correlation functions which appear in the relations (24.41a) and (24.41b).

In the moving system the tensors (P', P') and (π', π') have the usual form:

$$\begin{gathered}(P'_\mu, P'_\nu) = L_p\delta_{\mu\nu},\\ (\pi'_{\mu\nu}, \pi'_{\mu_1\nu_1}) = L_\pi\frac{1}{2}\left\{\delta_{\mu\mu_1}\delta_{\nu\nu_1} + \delta_{\mu\nu_1}\delta_{\nu\mu_1} - \frac{2}{3}\delta_{\mu\nu}\delta_{\mu_1\nu_1}\right\},\end{gathered} \tag{24.42}$$

where L_p, L_π are scalar constants, and $\mu, \nu, \mu_1, \nu_1 = 1, 2, 3$, while the time components are equal to zero; then $\delta_{\mu\nu} = \Delta'_{\mu\nu}$, where the prime denotes the function (24.20) in the moving system.

Returning to the original system, we obtain

$$\begin{gathered}(P_\mu, P_\nu) = L_p\Delta_{\mu\nu},\\ (\pi_{\mu\nu}, \pi_{\mu_1\nu_1}) = L_\pi\frac{1}{2}\left\{\Delta_{\mu\mu_1}\Delta_{\nu\nu_1} + \Delta_{\mu\nu_1}\Delta_{\nu\mu_1} - \frac{2}{3}\Delta_{\mu\nu}\Delta_{\mu_1\nu_1}\right\}.\end{gathered} \tag{24.43}$$

The tensors (24.43) satisfy the conditions of orthogonality to the 4-velocity, which follow from (24.23a), condition (24.26a), and spatial isotropy.

Calculating the complete contraction of the left and right hand sides of (24.43), we find the scalars L_p and L_π:

$$L_P(x, x', t) = \frac{1}{3}\,(P(x)\cdot P(x', t)),$$
$$L_\pi(x, x', t) = \frac{1}{5}\,(\pi(x) : \pi(x', t)). \qquad (24.44)$$

In deriving the second of the relations (24.44) we have made use of the fact that

$$\mathrm{Sp}\Delta^2 = \mathrm{Sp}\Delta = 3,$$

because

$$\sum_\lambda \Delta_{\mu\lambda}\Delta_{\lambda\nu} = \Delta_{\mu\nu}.$$

Taking into account (24.43), we write the relations (24.41a-c) in the form

$$\langle\pi_{\mu\nu}(x)\rangle = -\sum_{\mu_1\nu_1}\int\int_{-\infty}^{0} e^{\varepsilon t_1} L_\pi(x, x', t_1)\beta(x', t+t_1)\times$$
$$\times\frac{1}{2}\left\{\Delta_{\mu\mu_1}\Delta_{\nu\nu_1}\left(\frac{\partial u_{\mu_1}(x', t+t_1)}{\partial x'_{\nu_1}} + \frac{\partial u_{\nu_1}(x', t+t_1)}{\partial x'_{\mu_1}}\right) - \right.$$
$$\left. - \frac{2}{3}\Delta_{\mu\nu}\Delta_{\mu_1\nu_1}\frac{\partial u_{\mu_1}(x', t+t_1)}{\partial x'_{\nu_1}}\right\} c\,dx'\,dt_1,$$

$$\langle P_\mu(x)\rangle = \sum_\nu\int\int_{-\infty}^{0} e^{\varepsilon t_1} L_P(x, x', t_1)\beta(x', t+t_1)\times$$
$$\times\Delta_{\mu\nu}\left(\beta^{-1}(x', t+t_1)\frac{\partial\beta(x', t+t_1)}{\partial x'_\nu} - \frac{1}{c}Du_\nu(x', t+t_1)\right)c\,dx'\,dt_1,$$

$$\langle p(x)\rangle - \langle p(x)\rangle_l =$$
$$= -\int\int_{-\infty}^{0} e^{\varepsilon t_1} L_p(x, x', t_1)\beta(x', t+t_1)\,\mathrm{div}\,u(x', t+t_1)\,c\,dx'\,dt_1, \quad (24.45)$$

(24.45)

where

$$L_p(x, x', t_1) = (p'(x), p'(x', t_1)). \qquad (24.45a)$$

If one neglects the retardation and spatial dispersion in (24.45), then these relations go over into the linear relations of relativistic hydrodynamics:

$$\begin{aligned}
\langle \pi_{\mu\nu} \rangle &= -\eta c \sum_{\mu_1\nu_1} \frac{1}{2} \left\{ \Delta_{\mu\mu_1}\Delta_{\nu\nu_1} \left(\frac{\partial u_{\mu_1}}{\partial x_{\nu_1}} + \frac{\partial u_{\nu_1}}{\partial x_{\mu_1}} \right) - \frac{2}{3} \Delta_{\mu\nu}\Delta_{\mu_1\nu_1} \frac{\partial u_{\mu_1}}{\partial x_{\nu_1}} \right\}, \\
\langle P_\mu \rangle &= c^{-1} \langle q_\mu \rangle = \lambda c \sum_{\nu} \Delta_{\mu\nu} \left(\beta^{-1} \frac{\partial \beta}{\partial x_\nu} - \frac{1}{c} D u_\nu \right), \\
\langle p \rangle - \langle p \rangle_l &= -\zeta c \operatorname{div} \boldsymbol{u},
\end{aligned} \tag{24.46}$$

which were obtained, except the last relation, by Eckart [133] (see also [82]) by the method of phenomenological nonequilibrium thermodynamics. In statistical nonequilibrium thermodynamics one obtains in addition to these relations explicit expressions for the kinetic coefficients - shear viscosity η, second viscosity ζ, and thermal conductivity:

$$\begin{aligned}
\eta &= \frac{\beta}{5} \int \int_{-\infty}^{0} e^{\varepsilon t} (\pi(x) : \pi(x', t))\, dx'\, dt, \\
\lambda &= \frac{\beta}{3} \int \int_{-\infty}^{0} e^{\varepsilon t} (\boldsymbol{P}(x) \cdot \boldsymbol{P}(x', t))\, dx'\, dt, \\
\zeta &= \beta \int \int_{-\infty}^{0} e^{\varepsilon t} (p'(x), p'(x', t))\, dx'\, dt.
\end{aligned} \tag{24.47}$$

Expression (24.46) for the heat current contains the relativistic term $\frac{1}{c}Du_\nu$, which shows that the heat current in a single-component system is caused not only by a temperature gradient, but also by an acceleration.

24.4. Charge Transfer Processes.

Up to this time we have considered only the conservation of energy-momentum. In the relativistic region the number of particles is not conserved, and if one considers the transfer of a number of particles, then one must take into account their formation as a consequence of various reactions, i.e., in the equations of balance for particle number one must add source terms, as in the theory of chemical reactions (see section 23.5).

Besides energy-momentum charges of various types are conserved in relativistic theory (electrical, baryon, lepton, etc.). We shall consider the conservation law for charge of a single type (the generalization to different types of charge presents no difficulties):

$$\sum_{\nu=1}^{4} \frac{\partial j_\nu(x, t)}{\partial x_\nu} = 0, \tag{24.48}$$

where $j_\nu(x)$ is the density of 4-vector current with spatial components j_1, j_2, j_3 (the three-dimensional current) and time component $j_4 = -ic\rho$, where ρ is the charge density.

The conservation law (24.48) corresponds to the local integral of motion

$$\widetilde{j_4(x)} = j_4(x) + ic \sum_{\nu=1}^{3} \int_{-\infty}^{0} e^{\varepsilon t} \frac{\partial j_\nu(x, t)}{\partial x_\nu} dt, \tag{24.49}$$

which transforms like the fourth component of a vector.

We construct the quantity $B_4(x,t)$, which transforms also like $\widetilde{j_4(x)}$, but which contains the parameters $\varphi(x,t)$ - some auxiliary scalar field, and $\beta(x,t)$ - the inverse temperature:

$$\begin{aligned} B_4(x, t) &= -\widetilde{i\beta(x, t)\varphi(x, t) j_4(x)} = -i\beta(x, t)\varphi(x, t) j_4(x) + \\ &\quad + i \int_{-\infty}^{0} e^{\varepsilon t_1} \frac{d}{dt_1} \beta(x, t + t_1)\varphi(x, t + t_1) j_4(x, t_1)\, dt_1 = \\ &= -i\beta(x, t)\varphi(x, t) j_4(x) + i \int_{-\infty}^{0} e^{\varepsilon t_1} \Big\{ j_4(x, t_1) \frac{\partial}{\partial t_1} \beta(x, t + t_1)\varphi(x, t + t_1) - \\ &\quad - ic\beta(x, t + t_1)\varphi(x, t + t_1) \sum_{\nu=1}^{3} \frac{\partial j_\nu(x, t_1)}{\partial x_\nu} \Big\} dt_1. \end{aligned} \tag{24.50}$$

The operator $B_4(x,t)$ is a solution of the Liouville equation for $\varepsilon \to 0$. It corresponds to the invariant

$$\begin{aligned} \int B_4(x, t)\, dx &= -\int \beta(x, t)\varphi(x, t)\, i j_4(x)\, dx + \\ &+ i \sum_\nu \int \int_{-\infty}^{0} e^{\varepsilon t_1} j_\nu(x, t_1) \frac{\partial}{\partial x_\nu} (\beta(x, t + t_1)\varphi(x, t + t_1))\, ic\, dx\, dt_1, \end{aligned} \tag{24.51}$$

where surface integrals are omitted.

In the statistical operator (24.5) one must also take into account the invariant (24.51):

$$\rho = Q^{-1} \exp\left\{ -\int \left(\sum_{\nu} B_{4\nu}(x, t) + \frac{1}{c} B_4(x, t) \right) dx \right\}. \tag{24.52}$$

The nonequilibrium statistical operator (24.52) can be applied to the study of transfer processes of energy-momentum and charge in a spatially homogeneous system. We write it in the explicit form:

$$\begin{aligned} \rho = Q^{-1} \exp\Bigg\{ & \int \beta(x, t) \left(-\sum_{\nu} u_{\nu}(x, t)\, iT_{4\nu}(x) + \frac{i}{c} \varphi(x, t)\, j_4(x) \right) dx - \\ & - \int \int_{-\infty}^{0} e^{\varepsilon t_1} \left(\sum_{\mu\nu} T_{\mu\nu}(x, t_1) \frac{\partial F_{\nu}(x, t + t_1)}{\partial x_{\mu}} + \right. \\ & \left. + j_{\nu}(x, t_1) \frac{\partial}{\partial x_{\nu}} \beta(x, t + t_1) \frac{i}{c} \varphi(x, t + t_1) \right) ic\, dx\, dt_1 \Bigg\}. \end{aligned} \tag{24.53}$$

The quantities $\partial F_{\nu}/\partial x_{\mu}$ and $\partial\beta\varphi/\partial x_{\mu}$ play the role of thermodynamic forces. If they are small, then for the average current of energy, momentum, and charge we obtain linear relations of the type (24.41a-c). Here, as earlier, it is convenient to separate the convective motion in $T_{\mu\nu}$ with the help of (24.23) and analogously in j_{ν}. If the particles have spin, then in addition to the conservation of energy-momentum (24.1) and charge (24.48) one must also take into account the conservation of angular momentum, which can be done by the same method.

For ordinary gases the quantum hydrodynamic effects are very small. Quantum hydrodynamics finds application in a different area - in the theory of multiple production of particles in collisions of fast nucleons with nuclei [137,138].

§ 25. Kinetic Equations

25.1. Generalized Kinetic Equations.

Up to this time we have considered transfer equations for the hydrodynamic regime, in which the nonequilibrium state can be described macroscopically by a small number of hydrodynamic (or thermodynamic) parameters: temperatures and chemical potentials of the components, mass velocity, etc. In considering strongly nonequilibrium processes for systems with a small interaction in the spatially homogeneous case (sections 23.4, 23.5) it turned out that the average occupation numbers satisfied the kinetic equation (see equation (23.64)). We shall show that this is not accidental and that the method of the nonequilibrium statistical operator can be applied, following the work of L. A. Pokrovskiy [56,191], also to the kinetic stage, if the parameters describing the state of the system are chosen in an appropriate manner. (For a discussion of the meaning of the kinetic and hydrodynamic stages see page 323).

Let us consider a quantum mechanical system with a Hamiltonian

$$H = H_0 + H_1, \tag{25.1}$$

where H_0 is the Hamiltonian of the free particles or quasi-particles, and H_1 is the Hamiltonian of the interaction, which we shall consider to be small.

We shall assume that the set of quantities $\langle P_k \rangle$ is sufficient to describe the nonequilibrium state for time scales which are not too small, where the brackets denote a nonequilibrium averaging. For example, for a spatially homogeneous state of a gas one can choose

$$P_k = a_k^+ a_k, \tag{25.2}$$

and then

$$\langle P_k \rangle = \langle a_k^+ a_k \rangle \tag{25.3}$$

is the distribution function for the states k. For a spatially inhomogeneous case one can choose

$$P_k = a_{k+q}^+ a_k, \tag{25.4}$$

and then

$$\langle a_{k+q}^+ a_k \rangle \tag{25.5}$$

is the distribution function, characterizing a spatially inhomogeneous state of a gas. Thus, the distribution function $\langle P_k \rangle$ is considered as a thermodynamic parameter, which allows one to extend the general scheme of nonequilibrium thermodynamics to kinetic processes. As the kinetic equation is in general nonlinear, it is necessary to consider a nonlinear variant of the theory.

We note that the operators P_k often satisfy simple commutation relations with the Hamiltonian of the free particles

$$[H_0, P_k] = \sum_l a_{kl} P_l, \tag{25.6}$$

where the α_{kl} are some numerical coefficients, which define the free evolution of the operators P_k. In the article by S. V. Peletminskiy and A. A. Yatsenko [36] a generalized kinetic equation has been constructed for the average values of such operators.

In the particular case in which the P_k are chosen in accordance with (25.4), and

$$H_0 = \sum_k E_k a_k^+ a_k, \tag{25.7}$$

we have

$$[H_0, a_{k+q}^+ a_k] = (E_{k+q} - E_k)\, a_{k+q}^+ a_k. \tag{25.8}$$

For the choice of (25.2) we have $\alpha_{kl}=0$.

In the majority of problems it is sufficient to consider only operators which satisfy the condition (25.6), although it is sometimes convenient to include in the discussion operators which do not satisfy this condition; we shall not consider such cases.

The operators P_k obey the equations of motion

$$\frac{\partial P_k}{\partial t} = \frac{1}{i\hbar}[P_k, H] = -\frac{1}{i\hbar}\sum_l \alpha_{kl} P_l + \frac{1}{i\hbar}[P_k, H_1]. \tag{25.9}$$

To the equations of motion (25.9) corresponds the nonequilibrium statistical operator, constructed according to the usual rules (see § 21), which in the limit $\varepsilon \to 0$ satisfies the Liouville equation

$$\begin{aligned} \rho = Q^{-1} \exp\left\{ -\sum_k \widetilde{F_k(t) P_k} \right\} = \\ = Q^{-1} \exp\left\{ -\sum_k \varepsilon \int_{-\infty}^{0} e^{\varepsilon t_1} F_k(t+t_1)\, P_k(t_1)\, dt_1 \right\}, \end{aligned} \tag{25.10}$$

or

$$\begin{aligned} \rho = Q^{-1} \exp\Bigg\{ -\sum_k F_k(t)\, P_k + \\ + \int_{-\infty}^{0} dt_1\, e^{\varepsilon t_1} \sum_k \left(F_k(t+t_1)\, \dot{P}_k(t_1) + \frac{dF_k(t+t_1)}{dt} P_k(t_1) \right) \Bigg\}, \end{aligned} \tag{25.11}$$

where the $F_k(t)$ are some parameters related to $\langle P_k \rangle$. This dependence is defined from the auxiliary conditions

$$\langle P_k \rangle = \langle P_k \rangle_q, \tag{25.12}$$

where we denote by

$$\langle \ldots \rangle = \mathrm{Sp}(\rho \ldots) \tag{25.13}$$

an averaging with the nonequilibrium statistical operator (25.11), and by

$$\langle \ldots \rangle_q = \mathrm{Sp}(\rho_q \ldots) \tag{25.14}$$

an averaging with the quasi-equilibrium statistical operator

$$\rho_q = Q_q^{-1} \exp\left\{-\sum_k F_k(t) P_k\right\}, \tag{25.14a}$$

$$Q_q = \mathrm{Sp}\exp\left\{-\sum_k F_k(t) P_k\right\}. \tag{25.14b}$$

The quasi-equilibrium statistical operator (25.14a) is constructed analogously to the local equilibrium statistical operator (20.10), which was discussed in § 20, but the statistical operator (25.14a) can describe strongly nonequilibrium states and is not related to the concept of local temperature.

For the nonequilibrium statistical operator (25.11) the relations

$$\frac{\partial \ln Q_q}{\partial F_k} = \frac{\partial \Phi}{\partial F_k} = -\langle P_k \rangle_q = -\langle P_k \rangle. \tag{25.15}$$

serve as an analog of the thermodynamic equalities, where

$$\Phi = \Phi(\ldots F_k \ldots) = \ln Q_q \tag{25.16}$$

is the analog of the Massieu-Planck function. If k takes on a continuous set of values, then in (25.14a) the sums go over into integrals, and the functions go over into functionals.

The thermodynamic equalities can also be represented in the form

$$\frac{\partial S}{\partial \langle P_k \rangle} = F_k(t), \tag{25.17}$$

where

$$S = \Phi + \sum_k \langle P_k \rangle F_k(t) \tag{25.18}$$

is the entropy of the nonequilibrium state.

The production of entropy is equal to

$$\dot{S} = \sum_k \langle \dot{P}_k \rangle F_k(t), \tag{25.19}$$

because

$$\dot{\Phi} = -\sum_k \langle P_k \rangle \dot{F}_k(t). \tag{25.20}$$

The fact that the relations (25.15)-(25.18) have the same form as the thermodynamic equalities does not imply that the nonequilibrium state which is described by the statistical operator (25.11) is close to a state of statistical equilibrium.

The average value of (25.9), calculated with the operator (25.11),

$$\frac{\partial \langle P_k \rangle}{\partial t} = -\frac{1}{i\hbar} \sum_k a_{kl} \langle P_l \rangle + \frac{1}{i\hbar} \langle [P_k, H_1] \rangle, \tag{25.21}$$

is a generalized kinetic equation for $\langle P_k \rangle$, because the average commutator of P_k with the interaction operator is expressed in terms of $\langle P_k \rangle$ with the help of (25.11), (25.12). The first term on the right hand side of (25.21) expresses the free, collisionless evolution of the distribution function $\langle P_k \rangle$, while the second term expresses the collision integral.

We shall eliminate in the exponential of the statistical operator (25.11) the time derivatives of the parameters $F_k(t+t_1)$. We have

$$\begin{aligned} \frac{dF_k(t)}{dt} &= \sum_l \frac{\partial F_k}{\partial \langle P_l \rangle} \langle \dot{P}_l \rangle = \\ &= -\frac{1}{i\hbar} \sum_{lm} \frac{\partial F_k}{\partial \langle P_l \rangle} a_{lm} \langle P_m \rangle + \sum_l \frac{\partial F_k}{\partial \langle P_l \rangle} \frac{1}{i\hbar} \langle [P_l, H_1] \rangle. \end{aligned} \tag{25.22}$$

Further, we note that

$$\sum_{k,l} F_k a_{kl} \langle P_l \rangle = \left\langle \left[H_0, \sum_k F_k P_k \right] \right\rangle_q \equiv 0, \tag{25.23}$$

because $\sum_k F_k P_k$ commutes with ρ_q. Differentiating the identity (25.23) with respect to F_k, we obtain

$$\sum_{m}\alpha_{km}\langle P_m\rangle+\sum_{ml}F_m\alpha_{ml}\frac{\partial\langle P_l\rangle}{\partial F_k}=0. \tag{25.24}$$

Taking into account that

$$\frac{\partial\langle P_l\rangle}{\partial F_k}=-\frac{\partial^2\ln Q_q}{\partial F_k\,\partial F_l}=\frac{\partial\langle P_k\rangle}{\partial F_l}, \tag{25.25}$$

we multiply (25.24) by $\partial F_i/\partial\langle P_k\rangle$ and sum over k. As a result we obtain

$$\sum_{k,\,l}\frac{\partial F_l}{\partial\langle P_k\rangle}\alpha_{kl}\langle P_l\rangle+\sum_{m}F_m\alpha_{ml}=0. \tag{25.26}$$

Using (25.26), we bring (25.22) to the form

$$\frac{dF_k(t)}{dt}=\frac{1}{i\hbar}\sum_{l}\alpha_{lk}F_l(t)+\sum_{l}\frac{\partial F_k}{\partial\langle P_l\rangle}\,\frac{1}{i\hbar}\,\langle[P_l,\ H_1]\rangle. \tag{25.27}$$

This equation can be considered as a kinetic equation in the variables F_k.

Substituting (25.9) and (25.27) into (25.11), we write the nonequilibrium statistical operator in the form

$$\begin{aligned}\rho=Q^{-1}\exp\Big\{-\sum_{k}F_k(t)\,P_k+\\ +\int_{-\infty}^{0}dt_1\,e^{\varepsilon t_1}\sum_{k}\frac{1}{i\hbar}\Big([P_k(t_1),\ H_1(t_1)]\,F_k(t+t_1)+\\ +\sum_{l}\frac{\partial F_k(t+t_1)}{\partial\langle P_l\rangle}\langle[P_l,\ H_1]\rangle^{t+t_1}\,P_k(t_1)\Big)\Big\},\end{aligned} \tag{25.28}$$

where the superscript $t+t_1$ on the averaging sign implies that it is carried out with the statistical operator (25.11), taken at the instant $t+t_1$. From (25.28) it is evident that the integral term in the exponential is of at least first order of smallness in the interaction.

We shall seek an expansion of the collision integral

$$S_k = \frac{1}{i\hbar} \langle [P_k, H_1] \rangle \tag{25.29}$$

in a series in powers of the interaction. Since the operator which is being averaged (25.29) is of first order in the interaction, in an expansion of the exponential (25.28) (see section 22.2) one need keep only first order terms in order to obtain an expansion which is accurate through second order terms. The expansion of (25.29) begins with terms of the first order and has the form

$$S_k(\ldots \langle P_i \rangle \ldots) = S_k^{(1)} + S_k^{(2)} + \ldots, \tag{25.30}$$

where

$$S_k^{(1)} = \frac{1}{i\hbar} \langle [P_k, H_1] \rangle_q, \tag{25.31}$$

$$S_k^{(2)} = S_k'^{(2)} + S_k''^{(2)}, \tag{25.32}$$

$$S_k'^{(2)} = -\sum_l \frac{1}{\hbar^2} \int_{-\infty}^{0} dt_1 \, e^{\varepsilon t_1} ([H_1, P_k], [H_1(t_1), P_l(t_1)]) F_l(t + t_1), \tag{25.33}$$

$$\begin{aligned} S_k''^{(2)} = -\sum_{m,l} \frac{1}{\hbar^2} \int_{-\infty}^{0} dt_1 \, e^{\varepsilon t_1} ([H_1, P_k], P_l(t_1)) \times \\ \times \frac{\partial F_l(t + t_1)}{\partial \langle P_m \rangle} \langle [H_1(t_1), P_m(t_1)] \rangle_q \end{aligned} \tag{25.34}$$

and the usual notation for the quantum correlation functions has been introduced:

$$(B, C) = \int_0^1 d\tau \langle B(e^{-\tau A} C e^{\tau A} - \langle C \rangle_q) \rangle_q, \tag{25.35}$$

$$A = \sum_k F_k(t) P_k. \tag{25.36}$$

Formulas (25.31)-(25.34) already give the collision integral of the generalized kinetic equation with an accuracy through second order in the interaction, but they can be further simplified. In the collision integrals (25.33) and (25.34) one can omit the interaction in the Heisenberg representations for the operators, because in these formulas there is already a factor of second order in the interaction. In addition, in (25.33) one can put

$$\sum_l F_l(t + t_1) P_l(t_1) = \sum_l F_l(t) P_l, \tag{25.37}$$

because this sum is an integral of motion when the interaction is neglected. Indeed, (25.28) is an integral of motion for $\varepsilon \to 0$, and the integral terms in its exponential are proportional to the interaction. Noting also that

$$\sum_l e^{-\tau A}[H_1(t_1),\ P_l F_l(t)]e^{\tau A} = \frac{d}{d\tau} e^{-\tau A} H_1(t_1) e^{\tau A}, \tag{25.38}$$

and carrying out an integration over τ, we obtain

$$S_k^{\prime(2)} = -\frac{1}{\hbar^2} \int_{-\infty}^{0} dt\, e^{\varepsilon t} \langle [H_1(t),\ [H_1,\ P_k]] \rangle_q, \tag{25.39}$$

i.e., this part of the collision integral is proportional to the Fourier component of the retarded Green function with $\omega = i\varepsilon$, or to the spectral intensity of the time correlation function for zero frequency (see § 16).

We now transform $S_k^{\prime\prime(2)}$, writing it in explicit form:

$$\begin{aligned} S_k^{\prime\prime(2)} = -\sum_{l,m} \frac{1}{\hbar^2} \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \int_0^1 d\tau \, \langle [H_1,\ P_k] e^{-\tau A} \frac{\partial F_l(t+t_1)}{\partial \langle P_m \rangle} \times \\ \times \langle [H_1(t_1),\ P_m(t_1)] \rangle_q (P_l(t_1) - \langle P_l(t_1) \rangle_q) e^{\tau A} \rangle_q. \end{aligned} \tag{25.40}$$

We shall show that

$$\frac{d}{dt_1} \sum_{l,m} \left[\frac{\partial F_l(t+t_1)}{\partial \langle P_m \rangle} \langle [H_1(t_1'),\ P_m(t_1)] \rangle_q (P_l(t_1) - \langle P_l(t_1) \rangle_q) \right] = 0, \tag{25.41}$$

from which it follows that in (25.40) one can put $t_1 = 0$ everywhere except $H(t_1)$.

Neglecting the interaction, we calculate the time derivative of the matrix

$$\frac{\partial \langle P_k \rangle}{\partial F_n} = -\frac{\partial^2 \ln Q_q}{\partial F_n \partial F_k} = -\int_0^1 d\tau \langle P_k e^{-\tau A} (P_n - \langle P_n \rangle_q) e^{\tau A} \rangle_q. \tag{25.42}$$

We have

$$\begin{aligned} \frac{d}{dt} \frac{\partial \langle P_k \rangle}{\partial F_n} &= -\sum_m \frac{\partial^3 \ln Q_q}{\partial F_n \partial F_k \partial F_m} \frac{dF_m}{dt} = \\ &= -\sum_{m,j} \frac{1}{i\hbar} \frac{\partial^3 \ln Q_q}{\partial F_n \partial F_k \partial F_m} \alpha_{jm} F_j. \end{aligned} \tag{25.43}$$

Differentiating the identity (25.23) with respect to F_n and F_k, we find

$$\sum_{l,m} \frac{\partial^3 \ln Q_q}{\partial F_n \partial F_k \partial F_m} \alpha_{lm} F_l + \sum_m \frac{\partial^2 \ln Q_q}{\partial F_n \partial F_m} \alpha_{km} + \sum_m \frac{\partial^2 \ln Q_q}{\partial F_k \partial F_m} \alpha_{nm} = 0. \tag{25.44}$$

With the help of (25.44), (25.43), and (25.42), we obtain

$$\frac{d}{dt} \frac{\partial \langle P_k \rangle}{\partial F_n} = -\frac{1}{i\hbar} \sum_m \left(\frac{\partial \langle P_m \rangle}{\partial F_n} \alpha_{kn} + \frac{\partial \langle P_k \rangle}{\partial F_m} \alpha_{nm} \right). \tag{25.45}$$

Taking the derivative with respect to t of the identity

$$\sum_n \frac{\partial F_n}{\partial \langle P_m \rangle} \frac{\partial \langle P_m \rangle}{\partial F_k} = \delta_{nk}, \tag{25.46}$$

multiplying the result by $\partial F_k/\partial \langle P_l \rangle$, and summing over k, we find

$$\frac{d}{dt} \frac{\partial F_n}{\partial \langle P_l \rangle} = \frac{1}{i\hbar} \sum_k \alpha_{kn} \frac{\partial F_k}{\partial \langle P_l \rangle} + \frac{1}{i\hbar} \sum_m \alpha_{ml} \frac{\partial F_n}{\partial \langle P_m \rangle}, \tag{25.47}$$

from which, by making use of (25.9), we obtain (25.41). Therefore in (25.40) one can omit t_1 everywhere except $H_1(t_1)$.

Noting also that

$$\int_0^1 d\tau \langle [H_1, P_k] e^{-\tau A} (P_n - \langle P_n \rangle_q) e^{\tau A} \rangle_q = i\hbar \frac{\partial S_k^{(1)}}{\partial F_n}, \tag{25.48}$$

we write (25.40) in the form

$$S_k''^{(2)} = -\frac{i}{\hbar} \int_{-\infty} dt\, e^{\varepsilon t} \left\langle \left[H_1(t), \sum_m P_m \frac{\partial S_k^{(1)}}{\partial \langle P_m \rangle} \right] \right\rangle_q, \tag{25.49}$$

or, combining (25.39) and (25.49), we obtain

$$S_k^{(2)} = -\frac{1}{\hbar^2}\int_{-\infty}^{0} dt\, e^{\varepsilon t}\left\langle\left[H_1(t),\ [H_1,\ P_k] + i\hbar\sum_m P_m \frac{\partial S_k^{(1)}}{\partial\langle P_m\rangle}\right]\right\rangle_q. \tag{25.50}$$

Formulas (25.31) and (25.50) give an expansion of the collision integral in powers of the interaction with an accuracy up to terms of second order. They were obtained in this form in the article by S. V. Peletminskiy and A. A. Yatsenko [36] by a different method, which is close to the method of Mori [30].

25.2. Non-ideal Quantum Gases.

As a simple example we shall consider the construction of the kinetic equations for non-ideal quantum gases. In this case the Hamiltonian of the free particles is

$$H_0 = \sum_k E_k a_k^+ a_k, \qquad E_k = \frac{\hbar^2 k^2}{2m}, \tag{25.51}$$

and the interaction Hamiltonian is

$$H_1 = \frac{1}{2V}\sum_{\substack{k_1 k_2 k_1' k_2' \\ k_1 + k_2 = k_1' + k_2'}} \Phi(k_1 k_2 | k_1' k_2')\, a_{k_1}^+ a_{k_2}^+ a_{k_1'} a_{k_2'}, \tag{25.52}$$

where

$$\Phi(k_1 k_2 | k_1' k_2') = \frac{1}{2}\left(\nu(k_1 - k_1') \pm \nu(k_1 - k_2')\right) \tag{25.53}$$

is the matrix element of the interaction, and

$$\nu(k) = \int \Phi(x)\, e^{i(kx)}\, dx \tag{25.54}$$

is the Fourier component of the interaction potential.

The matrix element (25.53) is symmetrized for Bose statistics and antisymmetrized for Fermi statistics. This is convenient to do, because for Bose statistics an interchange of the operators $\alpha_{k_1'}$ and $\alpha_{k_2'}$, whch is equivalent to an interchange of the indices k_1' and k_2', does not change the sign of the product, while for Fermi statistics it does change the sign. If one does not perform this symmetrization (or antisymmetrization), then in the final results similar combinations of the Fourier components will appear just the same.

We choose as the basic operators

$$P_k = a_k^+ a_k = n_k, \tag{25.55}$$

and then

$$[H_0, n_k] = 0 \tag{25.56}$$

and in relations (25.6) we have $\alpha_{kl} = 0$.

The commutator of the interaction operator with n_k is equal to

$$[H_1, n_k] = \frac{1}{V} \sum_{\substack{k_1 k_2 k_1' \\ k_1 + k_2 = k_1' + k}} \Phi(k_1 k_2 | k_1' k)\left(a_{k_1}^+ a_{k_2}^+ a_{k_1'} a_k - a_k^+ a_{k_1'}^+ a_{k_2} a_{k_1}\right), \tag{25.57}$$

where the symmetry (or antisymmetry) properties of the matrix elements (25.53) have been taken into account.

It is now easy to calculate the collision integral (25.39), using Wick's theorem and formula (16.32)

$$\begin{aligned} S_k'^{(2)} &= -\frac{1}{\hbar^2} \int_{-\infty}^{0} dt\, e^{\varepsilon t} \langle [H_1(t), [H_1, n_k]] \rangle_q = \\ &= \sum_{\substack{k_1 k_2 k_1' \\ k_1 + k_2 = k_1' + k}} w(k_1 k_2 | k_1' k) \left\{ \bar{n}_{k_1} \bar{n}_{k_2} \left(1 \mp \bar{n}_{k_1'}\right)(1 \mp \bar{n}_k) - \right. \\ &\qquad \left. - \left(1 \mp \bar{n}_{k_1}\right)\left(1 \mp \bar{n}_{k_2}\right) \bar{n}_{k_1'} \bar{n}_k \right\}, \end{aligned} \tag{25.58}$$

where

$$w(k_1 k_2 | k_1' k) = \frac{4\pi}{\hbar} |\Phi(k_1 k_2 | k_1' k)|^2 \delta\left(E_{k_1} + E_{k_2} - E_{k_1'} - E_k\right) \tag{25.59}$$

is the probability of a transition per unit time in the Born approximation, and

$$\bar{n}_k = \langle n_k \rangle_q \tag{25.60}$$

are the average occupation numbers of the state k. The remaining collision operators (25.31) and (25.49) are equal to zero,

$$S_k^{(1)} = S_k''^{(2)} = 0.$$

We finally obtain the kinetic equation for the quantum Bose or Fermi gas in the form

$$\frac{dn_k}{dt} = -\sum_{k_1 k' k_1'} w(kk_1|k'k_1')\left\{\bar{n}_k\bar{n}_{k_1}\left(1 \mp \bar{n}_{k'}\right)\left(1 \mp \bar{n}_{k_1'}\right) - \right.$$
$$\left. - \left(1 \mp \bar{n}_k\right)\left(1 \mp \bar{n}_{k_1}\right)\bar{n}_{k'}\bar{n}_{k_1'}\right\}, \qquad (25.61)$$

where the plus sign refers to a Bose gas, and the minus sign refers to a Fermi gas.

A third approximation for the collision operator for quantum gases was obtained by N. N. Bogolyubov and K. P. Gurov [139] (see the monograph [140]), and a fourth approximation was obtained by V. G. Bar'yakhtar, S. V. Peletminskiy, and A. A. Yatsenko [141].

The kinetic equation for quantum gases with the collision operator (25.61) was first obtained by G. Uhlenbeck and E. Uehling [142]. This problem was considered later by many authors [143-145], who began with the mixed coordinate-momentum representation of Wigner (see section 14.2). More detail on the derivation of the quantum kinetic equation can be seen in the monograph by Fudzita [146] and in the articles [147-149].

Kinetic equations of the type (25.61) are applied to nondegenerate quantum gases. For degenerate gases the kinetic equation must be constructed for the distribution functions of the elementary excitations, rather than for the distribution functions of the particles. For example, for the elementary excitations in a non-ideal Bose gas the kinetic equation was obtained by N. N. Bogolyubov [150].

For a non-ideal degenerate Bose gas the distribution functions (25.3) are not sufficient; it is necessary to consider also the functions $\langle \alpha_k \alpha_{-k} \rangle$, i.e.,

$$P_k = \{a_k^+ a_k,\ a_k a_{-k}\}.$$

This scheme is carried out in the article [151]. An analogous situation exists in the theory of superconductivity.

25.3. Kinetic Equation for Electrons in a Metal.

Let us consider one more example of a quantum kinetic equation - the Bloch equation for electrons in a metal. In this case

$$H = H_0 + H_1, \tag{25.62}$$

where

$$H_0 = \sum_{k,\sigma} E_{k\sigma} a^+_{k\sigma} a_{k\sigma} + \sum_q \hbar\omega_q b^+_q b_q \tag{25.62a}$$

is the Hamiltonian of the free electrons and phonons, and

$$H_1 = \frac{1}{\sqrt{V}} \sum_{\substack{k,k_1,q,\sigma \\ k_1-k=q}} v_q \left(\frac{\hbar}{2\omega_q}\right)^{1/2} (b_q + b^+_{-q})\, a^+_{k_1\sigma} a_{k\sigma} \tag{25.62b}$$

is the interaction Hamiltonian of the electrons with the lattice phonons (see the footnote on page 176).

To derive the kinetic equation for electrons in the spatially homogeneous case we choose

$$P_k = a^+_{k\sigma} a_{k\sigma} n_{k\sigma}. \tag{25.63}$$

The kinetic equation for $\langle n_{k\sigma}\rangle$ has the form

$$\frac{\partial \langle n_{k\sigma}\rangle}{\partial t} = \frac{1}{i\hbar} \langle [n_{k\sigma}, H_1]\rangle = S^{(1)}_k + S^{(2)}_k + \tag{25.64}$$

Noting that

$$S^{(1)}_k = \frac{1}{i\hbar} \langle [n_{k\sigma}, H_1]\rangle_q = 0,$$

we write the kinetic equation (25.64) in the form

$$\begin{aligned}\frac{\partial \bar{n}_k}{\partial t} &= -\frac{1}{\hbar^2} \int_{-\infty}^{0} dt\, e^{\varepsilon t} \langle [H_1(t), [H_1, n_{k\sigma}]]\rangle_q = \\ &= \frac{1}{V} \sum_{\substack{k_1, q \\ k_1-k=q}} \frac{\pi}{\omega_q} |v_q|^2 \{(\bar{N}_q + 1)\, \bar{n}_{k_1} (1 - n_k) - \bar{N}_q (1 - \bar{n}_{k_1})\, \bar{n}_k\} \times \\ &\times \delta(E_{k_1} - E_k - \hbar\omega_q) - \frac{1}{V} \sum_{\substack{k_1, q \\ k_1-k=-q}} \frac{\pi}{\omega_q} |v_q|^2 \times \\ &\times \{(\bar{N}_q + 1)\, \bar{n}_k (1 - \bar{n}_{k_1}) - \bar{N}_q n_k (1 - \bar{n}_k)\}\, \delta(E_{k_1} - E_k + \hbar\omega_q),\end{aligned} \tag{25.65}$$

where

$$\bar{n}_k = \langle n_{k\sigma}\rangle_q, \qquad \bar{N}_q = \langle N_q\rangle_q = \langle b^+_q b_q\rangle_q \tag{25.66}$$

are the distribution functions for electrons and phonons.

Equation (25.65) is the well-known Bloch equation, on which the theory of electrical conductivity and thermal conductivity of metals and semiconductors is constructed [152-155].

In the same way one can derive the kinetic equation for the phonon distribution function:

$$\frac{\partial\langle N_q\rangle}{\partial t}=\frac{1}{i\hbar}\langle[N_q,\ H_1]\rangle, \tag{25.67}$$

where the right hand side is easily expanded using perturbation theory. This equation is considered in the book [153].

One can obtain just as simply other kinetic equations, for example, the Peierls equation for phonons in a lattice [156], where collisions are caused by anharmonicity effects.

The equation for a small subsystem, interacting with a large system which is in an equilibrium state (thermostat), is a special case of the kinetic equations. For such a subsystem the probability of a direct transition is not equal to the probability of the inverse transition, because upon transition an exchange of energy with the thermostat is possible. Therefore the probability of the transition is not simply the square of the matrix element of the perturbation, as in (25.59), but rather it must depend on the temperature. The method of the nonequilibrium statistical operator is convenient for obtaining equations of this type, as was shown in the article of L. A. Pokrovskiy [157]. In this article is considered also the particular case of the derivation of the equations for spin systems taking into account the nondiagonal terms (the Redfield equations [158]) and the equations for the average spin operators, i.e., the Bloch equations [158] (see also [211]).

An important area for the application of the kinetic equation is a completely or partially ionized plasma and plasma-like media. To construct the theory of transfer processes in such systems it is necessary to go beyond the bounds of the ordinary perturbation theory of the small interaction and to take into account the effects of polarization of the medium; otherwise divergences appear in the kinetic equation. The kinetic equation for a plasma taking into account polarization was first derived by Balescu [176,177] by the method of Prigogine [178] and Lenard [179] by the method of Bogolyubov [1]. A sufficiently simple and completely rigorous method of deriving this equation was given by Yu. L. Klimontovich [163]. The statistical theory of inelastic processes in a plasma was developed by him using the same method [180].

The kinetic theory of the electron liquid in metals was worked out by V. P. Silin [181,182], who predicted spin waves in nonferromagnetic metals.

In this book we shall not be concerned with the theory of transfer processes in a plasma, because this is a large and independent subject. In addition, the method of the nonequilibrium statistical operator [2-5] up to the present time has not been applied to a plasma, although this is possible.

§ 26. Kramers-Fokker-Planck Equations

In many problems of nonequilibrium statistical mechanics (Brownian motion of a particle in a liquid, relaxation in a system of oscillators, the theory of homogeneous nucleation, etc.) the evolution of a small subsystem in contact with a large thermodynamically equilibrium subsystem, hereinafter called the thermostat, is considered. In the case of a weak interaction between the subsystems this evolution is described by the Kramers-Fokker-Planck kinetic equation, which was first derived by Kramers [161] using the theory of Markov processes, and proceeding from the Langevin equation with a phenomenological friction constant. Later this equation was obtained by Kirkwood [13] for the particular case of Brownian motion in a liquid. In this Kirkwood succeeded in deriving an expression for the coefficient of friction in terms of the autocorrelation function of the forces acting on the Brownian particle. The Fokker-Planck equation was obtained from the equations of mechanics (classical and quantum), and expressions for its coefficients in terms of the correlation functions of the perturbing forces were first obtained already in 1939 in an article by N. N. Bogolyubov and N. M. Krylov [169] (see also the work of N. N. Bogolyubov [169a]) long before the article by Kirkwood [13]. Unfortunately, these important articles were published in an almost inaccessible publication and because of this did not receive sufficient recognition at the time.

In this paragraph we give a derivation of the Kramers-Fokker-Planck equation for the case of classical statistical mechanics using the method discussed in § 21, following the work of A. G. Bashkirov and the author [162].

26.1. General Method.

Let there be N identical subsystems in contact with a thermostat, and not interacting with each other. The total Hamiltonian of such a system has the form

$$H = \sum_i H_1(p_i, q_i) + H_2(P, Q) + \sum_i U(p_i, q_i, P, Q), \tag{26.1}$$

where $H_1(p_i,q_i)$ is the Hamiltonian of the i^{th} small subsystem with dynamical variables p_i,q_i, $H_2(P,Q)$ is the Hamiltonian of the thermostat, P and Q being the collection of its dynamical variables, and $U(p_i,q_i,P,Q)$ is the interaction potential between the i^{th} subsystem and the thermostat.

The macroscopic state of the total system is characterized, besides by the thermodynamic variables of the thermostat, also by the distribution function of the subsystems f(p,q,t) in phase space. To this quantity corresponds a dynamical variable - the composite density of systems in phase space

$$n(p, q) = \sum_i \delta(p - p_i)\,\delta(q - q_i), \tag{26.2}$$

such that

$$f(p, q, t) = \langle n(p, q) \rangle, \tag{26.3}$$

where <...> is an averaging with some nonequilibrium distribution function, which will be considered below. We note that the integral of (26.2) over the phase variables p and q is equal to the total number of the small subsystems $\int n(p,q)\,dp\,dq = N$. In the particular case in which the small subsystems are, for example, spherically symmetric Brownian particles, p_i and q_i are the ordinary momenta and coordinates of the i^{th} Brownian particle $\mathbf{p}_i$ and $\mathbf{q}_i$, and the expression (26.2) defines the density in the six-dimensional phase space

$$n(\mathbf{p}, \mathbf{q}) = \sum_i \delta(\mathbf{p} - \mathbf{p}_i)\,\delta(\mathbf{q} - \mathbf{q}_i), \tag{26.2a}$$

which has been widely used by Yu. L. Klimontovich for constructing kinetic equations in the theory of the nonequilibrium plasma [163].

We shall consider first the general case when (26.2) is the density in a multi-dimensional phase space, the dimension of which is defined by the number of canonically conjugate dynamical variables p_i, q_i of a single small subsystem.

The composite density (26.2) satisfies the equation of motion

$$\dot{n}(p, q) = \{n(p, q), H\} = -\frac{\partial}{\partial q} j_1(p, q) - \frac{\partial}{\partial p} j_2(p, q), \tag{26.4}$$

where {...} is a classical Poisson bracket (2.10),

$$j_1(p, q) = \left(\frac{\partial H_1(p, q)}{\partial p} + \frac{\partial U(p, q, P, Q)}{\partial p}\right) n(p, q), \tag{26.5a}$$

$$j_2(p, q) = -\left(\frac{\partial H_1(p, q)}{\partial q} + \frac{\partial U(p, q, P, Q)}{\partial q}\right) n(p, q). \tag{26.5b}$$

In accordance with the general method of constructing the nonequilibrium distribution function, the conservation law (26.4) corresponds to the nonequilibrium distribution function

$$\rho = Q^{-1}\exp\left\{-\beta H + \beta\int dp\,dq\,\varepsilon\int_{-\infty}^{0} dt_1\,e^{\varepsilon t_1}\varphi(p,q,t+t_1)\,n(p,q,t_1)\right\} =$$

$$= Q^{-1}\exp\Big\{-\beta H + \beta\int dp\,dq\,\varphi(p,q,t)\,n(p,q) -$$

$$-\beta\int dp\,dq\int_{-\infty}^{0} dt_1\,e^{\varepsilon t_1}[\varphi(p,q,t+t_1)\,\dot{n}(p,q,t_1) +$$

$$+\dot{\varphi}(p,q,t+t_1)\,n(p,q,t_1)]\Big\} \tag{26.6a}$$

or taking into account (26.4)

$$\rho = Q^{-1}\exp\Big\{-\beta H + \beta\int dp\,dq\,\varphi(p,q,t)\,n(p,q) -$$

$$-\beta\int dp\,dq\int_{-\infty}^{0} dt_1\,e^{\varepsilon t_1}\Big[\frac{\partial\varphi(p,q,t+t_1)}{\partial q}\,j_1(p,q,t_1) +$$

$$+\frac{\partial\varphi(p,q,t+t_1)}{\partial p}\,j_2(p,q,t_1) + \dot{\varphi}(p,q,t+t_1)\,n(p,q,t_1)\Big]\Big\}, \tag{26.6b}$$

where $\varphi(p,q,t)$ is a function of $\langle n(p,q)\rangle$; this function will later be eliminated and will not enter into the final result. This function is defined from the condition

$$\langle n(p,q)\rangle = \langle n(p,q)\rangle_l, \tag{26.7}$$

where <...> is an averaging with the total distribution function (26.6b), and $\langle\ldots\rangle_l$ is an averaging with a local equilibrium or quasi-equilibrium distribution function.

$$\rho_l = Q_l^{-1}\exp\left\{-\beta H + \beta\int dp\,dq\,\varphi(p,q,t)\,n(p,q)\right\}. \tag{26.8}$$

To eliminate the derivative $\dot{\varphi}(p,q,t)$ from (26.6b) we differentiate both sides of the equation (26.7) with respect to time. Then for the left hand side we obtain

$$\frac{d}{dt}\langle n(p,q)\rangle = -\frac{\partial}{\partial q}\langle j_1(p,q)\rangle - \frac{\partial}{\partial p}\langle j_2(p,q)\rangle \cong$$

$$\cong -\frac{\partial H_1(p,q)}{\partial p}\,\frac{\partial}{\partial q}\langle n(p,q)\rangle + \frac{\partial H_1(p,q)}{\partial q}\,\frac{\partial}{\partial p}\langle n(p,q)\rangle \cong$$

$$\cong\left(-\frac{\partial H_1(p,q)}{\partial p}\,\frac{\partial\varphi}{\partial q} + \frac{\partial H_1(p,q)}{\partial q}\,\frac{\partial\varphi}{\partial p}\right)\beta\langle n(p,q)\rangle_l, \tag{26.9a}$$

where we have neglected terms of the type

$$\left\langle\frac{\partial U(p, q, P, Q)}{\partial p}\right\rangle \text{ and } \left\langle\frac{\partial U(p, q, P, Q)}{\partial q}\right\rangle$$

and we have made use of the equality (26.4) (see (26.24)). We now differentiate the right hand side of (26.7):

$$\begin{aligned}\frac{d}{dt}\langle n(p, q)\rangle_t &= \\ &=\beta\left\langle\int dp'\,dq'\,\dot{\varphi}(p', q', t)\left[n(p, q)\left(n(p', q')-\langle n(p', q')\rangle_t\right)\right]\right\rangle_t = \\ &=\beta\left(\dot{\varphi}(p, q)-\bar{\dot{\varphi}}\right)\langle n(p, q)\rangle_t \cong \beta\dot{\varphi}(p, q, t)\langle n(p, q)\rangle_t,\end{aligned} \tag{26.9b}$$

where we have neglected the term

$$\bar{\dot{\varphi}} = \int dp\,dq\,\dot{\varphi}(p, q, t)\langle n(p, q)\rangle_t, \tag{26.10}$$

which has the order of magnitude of the average force in the local equilibrium state.

Equating (26.9a) and (26.9b), we obtain the collisionless kinetic equation

$$\dot{\varphi}(p, q, t) = -\frac{\partial H_1(p, q)}{\partial p}\frac{\partial\varphi(p, q, t)}{\partial q}+\frac{\partial H_1(p, q)}{\partial q}\frac{\partial\varphi(p, q, t)}{\partial p}, \tag{26.11}$$

which we could have written down immediately, by assuming that φ(p,q,t) is a function of the single particle distribution function <n(p,q)>, for which such an equation is evident.

Substituting (26.11) into (26.6b), we obtain

$$\begin{aligned}\rho = Q^{-1}\exp\Big\{&-\beta H+\beta\int dp\,dq\,\varphi(p, q, t)\,n(p, q)- \\ &-\beta\int dp\,dq\int_{-\infty}^{0} dt_1\,e^{\varepsilon t_1}\Big[\frac{\partial\varphi(p, q, t+t_1)}{\partial q}j_1'(p, q, t_1) + \\ &\qquad+\frac{\partial\varphi(p, q, t+t_1)}{\partial q}j_2'(p, q, t_1)\Big]\Big\}\end{aligned} \tag{26.12}$$

or in the approximation which is linear in the interaction between the subsystem and the thermostat

$$\rho=\rho_l-\rho_l\beta\int dp\,dq\int_{-\infty}^{0}dt_1 e^{\varepsilon t_1}\Big[\frac{\partial\varphi(p,q,t+t_1)}{\partial q}\big(j_1'(p,q,t_1)-\langle j_1'(p,q,t_1)\rangle_l\big)+$$
$$+\frac{\partial\varphi(p,q,t+t_1)}{\partial p}\big(j_2'(p,q,t_1)-\langle j_2'(p,q,t_1)\rangle_l\big)\Big], \qquad (26.13)$$

where

$$j_1'(p,q)=j_2(p,q)-\frac{\partial H_1(p,q)}{\partial p}n(p,q)=$$
$$=\frac{\partial U(p,q,P,Q)}{\partial p}n(p,q), \qquad (26.14a)$$

and

$$j_2'(p,q)=j_2(p,q)+\frac{\partial H_1(p,q)}{\partial q}n(p,q)=$$
$$=-\frac{\partial U(p,q,P,Q)}{\partial q}n(p,q). \qquad (26.14b)$$

We shall now proceed to the derivation of the equation for the distribution function f(p,q,t)=<n(p,q)>. For this we average the exact mechanical equation of motion (26.4) over all dynamical variables of the system, which gives

$$\frac{\partial f}{\partial t_1}+\frac{\partial H_1(p,q)}{\partial p}\frac{\partial f}{\partial q}-\frac{\partial H_1(p,q)}{\partial q}\frac{\partial f}{\partial p}=$$
$$=-\frac{\partial}{\partial q}\langle j_1'(p,q)\rangle-\frac{\partial}{\partial p}\langle j_2'(p,q)\rangle. \qquad (26.15)$$

This equation is none other than the Bogolyubov chain [1] for the distribution functions. Indeed, on the left hand side of (26.15) is the distribution function in the phase space of the subsystem, while on the right hand side is the distribution function of a higher order in the phase space both of the dynamical variables of the subsystem and of the thermostat. To uncouple this equation we make use, on the right hand side, of the distribution function obtained earlier (26.13). Then,

$$\langle j_1'(p,q)\rangle=\langle j_1'(p,q)\rangle_l-\beta\int dp'\,dq'\int_{-\infty}^{0}dt_1 e^{\varepsilon t_1}\Big[\frac{\partial\varphi(p',q',t+t_1)}{\partial q'}\times$$
$$\times\langle j_1'(p,q)\big(j_1'(p',q',t_1)-\langle j_1'(p',q',t_1)\rangle_l\big)\rangle_l+$$
$$+\frac{\partial\varphi(p',q',t+t_1)}{\partial p'}\langle j_1'(p,q)\big(j_2'(p',q',t_1)-\langle j_2'(p',q',t_1)\rangle_l\big)\rangle_l\Big]. \qquad (26.16)$$

Let us investigate the second term on the right hand side of (26.16):

$$-\beta \int dp'\,dq' \int_{-\infty}^{0} dt_1\, e^{\varepsilon t_1} \frac{\partial\varphi(p', q', t+t_1)}{\partial q'} \Big\langle \frac{\partial U(p, q, P, Q)}{\partial p} n(p, q) \times$$

$$\times \Big(\frac{\partial U(p', q', P, Q, t_1)}{\partial p'} n(p', q', t_1) - \langle j_1'(p', q', t_1)\rangle_l\Big)\Big\rangle_l =$$

$$= -\beta \int_{-\infty}^{0} dt_1\, e^{\varepsilon t_1} \Big[\frac{\partial\varphi(p, q, t+t_1)}{\partial q} f(p, q, t) \Big\langle \frac{\partial U(p, q, P, Q)}{\partial p} \frac{\partial U(p, q, P, Q, t_1)}{\partial p}\Big\rangle_0 -$$

$$- f(p, q, t) \Big\langle \frac{\partial U(p, q, P, Q)}{\partial p}\Big\rangle_0 \Big\langle \overline{\frac{\partial\varphi(t+t_1)}{\partial q} \frac{\partial U(p, q, P, Q, t_1)}{\partial p}}\Big\rangle_0\Big] \simeq$$

$$\simeq -\beta \int_{-\infty}^{0} dt_1\, e^{\varepsilon t_1} \frac{\partial\varphi(p, q, t+t_1)}{\partial q} f(p, q, t) \times$$

$$\times \Big\langle \frac{\partial U(p, q, P, Q)}{\partial p} \frac{\partial U(p, q, P, Q, t_1)}{\partial p}\Big\rangle_0, \tag{26.17a}$$

where we have neglected the correlation between different small subsystems, the correlation corresponding to a higher order of the small interaction U.

We replace the local equilibrium averaging $\langle\ldots\rangle_l$ of quantities small with respect to U by an averaging over the equilibrium conditional distribution:

$$\langle \ldots n(p, q)\rangle_l \simeq f(p, q, t)\langle\ldots\rangle_0, \tag{26.18}$$

$$\langle\ldots\rangle_0 \equiv \int dP\,dQ \ldots \frac{e^{-\beta H_0}}{\int dP\,dQ\, e^{-\beta H_0}}, \tag{26.19}$$

where

$$H_0 = H_1(p, q) + H_2(P, Q) + U(p, q, P, Q); \tag{26.19a}$$

the bar above the quantities in (26.17a) denotes the averaging (26.10). In addition, we have neglected terms of second order with respect to the "average forces"

$$\Big\langle \frac{\partial U(p, q, P, Q)}{\partial q}\Big\rangle_0 \text{ and } \Big\langle \frac{\partial U(p, q, P, Q)}{\partial p}\Big\rangle_0,$$

which are very small.

In particular, if, for example, the potential depends on q only through the difference Q-q, and the Hamiltonian (26.1) is an even function of Q, then the average force

$$\left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \right\rangle_0$$

is exactly zero, which is the case, for example, for a Brownian particle in a liquid.

These arguments can be used also to calculate the local equilibrium current

$$\langle j_1'(p, q)\rangle_l = \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} n(p, q) \right\rangle_l = \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \right\rangle_0 f(p, q, t), \tag{26.20}$$

which may also be equal to zero, but which in the general case is a small quantity; as will be shown below, taking this quantity into account leads to a renormalization of the energy of the subsystem $H_1 \rightarrow H_1 + \langle U\rangle_0$.

In an analogous way one can investigate the third term on the right hand side of (26.16). It is equal to

$$\beta f(p, q, t) \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \frac{\partial \varphi(p, q, t+t_1)}{\partial p} \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \frac{\partial U(p, q, P, Q, t_1)}{\partial q} \right\rangle_0 \tag{26.17b}$$

in the same approximation as for (26.17a).

Thus,

$$\begin{aligned} j_1'(p, q)\rangle = {} & \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \right\rangle_0 f(p, q, t) - \\ & - \beta f(p, q, t) \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \frac{\partial \varphi(p, q, t+t_1)}{\partial q} \times \\ & \times \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \frac{\partial U(p, q, P, Q, t_1)}{\partial p} \right\rangle_0 + \\ & + \beta f(p, q, t) \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \frac{\partial \varphi(p, q, t+t_1)}{\partial p} \times \\ & \times \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \frac{\partial U(p, q, P, Q, t_1)}{\partial q} \right\rangle_0 \end{aligned} \tag{26.21}$$

and analogously

$$
\begin{aligned}
\langle j_2'(p, q)\rangle = & -\left\langle \frac{\partial U(p, q, P, Q)}{\partial q} \right\rangle_0 f(p, q, t) + \\
& + \beta f(p, q, t) \int_{-\infty}^{0} dt_1 e^{\varepsilon t_1} \frac{\partial \varphi(p, q, t+t_1)}{\partial q} \left\langle \frac{\partial U(p, q, P, Q)}{\partial q} \times \right. \\
& \times \left. \frac{\partial U(p, q, P, Q, t_1)}{\partial p} \right\rangle_0 - \beta f(p, q, t) \int_{-\infty}^{0} dt_1 e^{\varepsilon t} \times \\
& \times \frac{\partial \varphi(p, q, t+t_1)}{\partial p} \left\langle \frac{\partial U(p, q, P, Q)}{\partial q} \frac{\partial U(p, q, P, Q, t_1)}{\partial q} \right\rangle_0 .
\end{aligned}
$$

(26.22)

We shall now eliminate the derivatives ∂φ/∂q and ∂φ/∂p from (26.21) and (26.22). For this one needs only the zeroth order in the interaction potential, putting

$$f(p, q, t) = f_l(p, q, t) \cong Q_l^{-1} \exp\{-\beta(H_1(p, q) - \varphi(p, q, t))\}, \tag{26.23}$$

from which

$$
\begin{aligned}
\frac{\partial \varphi(p, q, t+t_1)}{\partial p} &= \frac{\partial H_1(p, q)}{\partial p} + kT \frac{\partial \ln f(p, q, t+t_1)}{\partial p}, \\
\frac{\partial \varphi(p, q, t+t_1)}{\partial q} &= \frac{\partial H_1(p, q)}{\partial q} + kT \frac{\partial \ln f(p, q, t+t_1)}{\partial q}.
\end{aligned} \tag{26.24}
$$

Substituting into the right hand side of (26.15) the expressions (26.21) and (26.22), and taking into account (26.24), we obtain

$$\begin{aligned}
&\frac{\partial f}{\partial t}+\frac{\partial\left(H_1(p,q)+\langle U(p,q,P,Q)\rangle_0\right)}{\partial p}\frac{\partial f}{\partial q}-\frac{\partial\left(H_1(p,q)+\langle U(p,q,P,Q)\rangle_0\right)}{\partial q}\frac{\partial f}{\partial p}= \\
&=-\frac{\partial}{\partial q}\Bigg[-\beta f(p,q,t)\int_{-\infty}^{0}dt_1\,e^{\varepsilon t_1}\left(\frac{\partial H_1(p,q)}{\partial q}+kT\,\frac{\partial\ln f(p,q,t+t_1)}{\partial q}\right)\times \\
&\qquad\times\left\langle\frac{\partial U(p,q,P,Q)}{\partial p}\,\frac{\partial U(p,q,P,Q,t_1)}{\partial p}\right\rangle_0+ \\
&\quad+\beta f(p,q,t)\int_{-\infty}^{0}dt_1\,e^{\varepsilon t_1}\left(\frac{\partial H_1(p,q)}{\partial p}+kT\,\frac{\partial\ln f(p,q,t+t_1)}{\partial p}\right)\times \\
&\qquad\times\left\langle\frac{\partial U(p,q,P,Q)}{\partial p}\,\frac{\partial U(p,q,P,Q,t_1)}{\partial q}\right\rangle_0\Bigg]- \\
&-\frac{\partial}{\partial p}\Bigg[\beta f(p,q,t)\int_{-\infty}^{0}dt_1\,e^{\varepsilon t_1}\left(\frac{\partial H_1(p,q)}{\partial q}+kT\,\frac{\partial\ln f(p,q,t+t_1)}{\partial q}\right)\times \\
&\qquad\times\left\langle\frac{\partial U(p,q,P,Q)}{\partial q}\,\frac{\partial U(p,q,P,Q,t_1)}{\partial p}\right\rangle_0- \\
&\quad-\beta f(p,q,t)\int_{-\infty}^{0}dt_1\,e^{\varepsilon t_1}\left(\frac{\partial H_1(p,q)}{\partial p}+kT\,\frac{\partial\ln f(p,q,t+t_1)}{\partial p}\right)\times \\
&\qquad\times\left\langle\frac{\partial U(p,q,P,Q)}{\partial q}\,\frac{\partial U(p,q,P,Q,t_1)}{\partial q}\right\rangle_0\Bigg].
\end{aligned}\tag{26.25}$$

This equation describes the evolution of the distribution function of a subsystem which has coordinates p and q, and which is in contact with a thermostat; it can be considered as the Liouville equation for an open system. The right hand side (the collision integral) shows that the evolution of the distribution function f(p,q,t) at the moment of time t depends on the state of the system at the preceding moments of time $-\infty < t+t_1 \leq 0$. It is customary to refer to equations of this type as not being Markov. A Markov equation is obtained from (26.25) in the particular case in which the time correlation functions

$$\left\langle\frac{\partial U}{\partial p}\,\frac{\partial U(t_1)}{\partial p}\right\rangle_0,\quad\left\langle\frac{\partial U}{\partial p}\,\frac{\partial U(t_1)}{\partial q}\right\rangle_0\ \text{etc.},$$

die out so rapidly that the terms which stand in front of them of the type

$$\frac{\partial H_1}{\partial q}+kT\,\frac{\partial\ln f(t+t_1)}{\partial q}$$

do not have time to change significantly and can be taken outside of the integral over time. In the Markov approximation (26.25) has the form

$$\begin{aligned} \frac{\partial f}{\partial t} &+ \frac{\partial (H_1(p, q) + \langle U(p, q, P, Q)\rangle_0)}{\partial p} \frac{\partial f}{\partial q} - \\ &- \frac{\partial (H_1(p, q) + \langle U(p, q, P, Q)\rangle_0)}{\partial q} \frac{\partial f}{\partial p} = \\ &= \frac{\partial}{\partial q}\left[L_{11}(p, q)\left(\frac{\partial H_1(p, q)}{\partial q} f(p, q, t) + kT \frac{\partial f(p, q, t)}{\partial q}\right) - \right. \\ &\left. - L_{12}(p, q)\left(\frac{\partial H_1(p, q)}{\partial p} f(p, q, t) + kT \frac{\partial f(p, q, t)}{\partial p}\right)\right] - \\ &- \frac{\partial}{\partial p}\left[L_{21}(p, q)\left(\frac{\partial H_1(p, q)}{\partial q} f(p, q, t) + kT \frac{\partial f(p, q, t)}{\partial q}\right) - \right. \\ &\left. - L_{22}(p, q)\left(\frac{\partial H_1(p, q)}{\partial p} f(p, q, t) + kT \frac{\partial f(p, q, t)}{\partial p}\right)\right], \end{aligned} \tag{26.26}$$

where the following kinetic coefficients have been introduced:

$$\begin{aligned} L_{11}(p, q) &= \beta \int_{-\infty}^{0} dt\, e^{\varepsilon t} \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \frac{\partial U(p, q, P, Q, t)}{\partial p} \right\rangle_0, \\ L_{12}(p, q) &= \beta \int_{-\infty}^{0} dt\, e^{\varepsilon t} \left\langle \frac{\partial U(p, q, P, Q)}{\partial p} \frac{\partial U(p, q, P, Q, t)}{\partial q} \right\rangle_0, \\ L_{21}(p, q) &= \beta \int_{-\infty}^{0} dt\, e^{\varepsilon t} \left\langle \frac{\partial U(p, q, P, Q)}{\partial q} \frac{\partial U(p, q, P, Q, t)}{\partial p} \right\rangle_0, \\ L_{22}(p, q) &= \beta \int_{-\infty}^{0} dt\, e^{\varepsilon t} \left\langle \frac{\partial U(p, q, P, Q)}{\partial q} \frac{\partial U(p, q, P, Q, t)}{\partial q} \right\rangle_0. \end{aligned} \tag{26.27}$$

The resulting equation (26.26) is the Kramers-Fokker-Planck equation, which describes the behavior of a small subsystem in a thermostat. It can be regarded as the generalization of the Liouville equation to the case of an unisolated system. This equation has been obtained by many authors [161, 164-168] using the theory of stochastic processes, for which the kinetic coefficients are expressed through the transition probability, which is considered to be a given characteristic of the random process.

Application of the method of the nonequilibibirum statistical operator to the given problem allows one not only to derive the Kramers-Fokker-Planck equation, but also to obtain expressions for the kinetic coefficients (26.27) which enter into the equation in terms of the correlation functions of the forces which act on the subsystem.

26.2. Special Cases.

The simplest example of the problem which is being considered is that of the Brownian motion of a heavy particle in a gas or liquid, where the small interaction between the particle and the liquid results from the large difference in the mass of the Brownian particle M and a particle of the liquid m.

The Hamiltonian in this case has the form

$$H = \sum_i \frac{p_i^2}{2M} + H_2(P, Q) + \sum_{i,j} U(|q_i - Q_j|). \tag{26.28}$$

For the density (26.2a) we obtain an equation of motion of the type (26.4) with currents

$$\begin{aligned} j_1(p, q) &= \frac{p}{M}\, n(p, q), \\ j_2(p, q) &= -\sum_j \frac{\partial U(q - Q_j)}{\partial q}\, n(p, q). \end{aligned} \tag{26.29}$$

The nonequilibrium statistical operator (26.13) in our case takes on the form

$$\rho = \rho_l - \rho_l \beta \int dp\, dq \int_{-\infty}^{0} dt_1\, e^{\varepsilon t_1} \frac{\partial q(p, q, t + t_1)}{\partial p}\, j_2(p, q, t_1); \tag{26.30}$$

here the average local current $\langle j_2 \rangle_l$ is equal to zero, because the liquid is considered to be in equilibrium.

As a consequence of the large mass difference (M>>m) the Markov approximation (26.26) is completely adequate for the motion of the Brownian particles:

$$\frac{\partial f}{\partial t} + \frac{p}{M} \cdot \frac{\partial f}{\partial q} = \frac{\partial}{\partial p} \cdot \zeta(q) \left(\frac{p}{M} f + kT \frac{\partial f}{\partial p} \right), \tag{26.31}$$

where

$$\zeta(q) = \beta \int_{-\infty}^{0} dt\, e^{\varepsilon t} \sum_{ij} \left\langle \frac{\partial U(q - Q_i)}{\partial q} \frac{\partial U(q - Q_j, t)}{\partial q} \right\rangle_0 \tag{26.32}$$

is the coefficient of friction, expressed in terms of the correlator of the forces which act on the Brownian particle.

By the same method one can obtain the Kramers-Fokker-Planck equation for Brownian motion in a liquid with an inhomogeneous temperature distribution [57].

Another interesting example is the relaxation of a harmonic oscillator which is weakly interacting with an equilibrium system of oscillators similar to itself.

The Hamiltonian of the total system in angle-action variables (α, J) has the form

$$H = \omega \sum_i J_i + U(\alpha_1, \ldots, \alpha_n, J_1, \ldots, J_n). \tag{26.33}$$

A distinctive feature of this system is the dependence of the interaction potential U on both the generalized coordinates α_i and on the generalized momenta J_i.

The density (26.2) in the angle-action space has the form

$$n(\alpha, J) = \sum_i \delta(\alpha - \alpha_i)\, \delta(J - J_i). \tag{26.34}$$

Applying the general scheme to the system (26.33), we obtain the corresponding Kramers-Fokker-Planck equation [161] (for more detail see [162]; for a generalization of the method see [204]).

§ 27. Extremal Properties of a Nonequilibrium Statistical Operator

The equilibrium distribution functions and statistical operators for all of the Gibbs ensembles correspond to a maximum of the information entropy for various, given, external conditions, as was shown in §§ 4 and 10. The local equilibrium distribution also corresponds to a maximum of the information entropy for given distributions of energy, momentum, and particle number as functions of position and time. In §§ 21-26 we constructed nonequilibrium statistical operators from quasi-integrals of motion, not connecting such distributions with an extremum of the information entropy.

Attempts have been made repeatedly to construct a nonequilibrium statistical operator from the extremum of the information entropy [71,72]; however, one usually obtains in this way only quasi-equilibrium distributions, which do not describe irreversible processes. In this paragraph we shall show, following the work of the author and V. P. Kalashnikov [170,189], that from the extremum of the information entropy one can obtain a statistical operator which describes irreversible processes, if one requires the extremum of the information entropy for fixed thermodynamic coordinates not only for a given moment of time, but also for all past moments of time. It turns out that this statistical operator coincides with the nonequilibrium statistical operator which was obtained on the basis of quasi-integrals of motion in §§ 21-26.

27.1. Extremal Properties of a Quasi-Equilibrium Distribution.

Our further discussion will pertain both to the hydrodynamic and to the kinetic stages of the nonequilibrium process; therefore we shall consider from the beginning the extremal properties of the quasi-equilibrium distribution which describes such states.

Let the nonequilibrium state be defined by the collection of average values of some operators P_m, where m is an index which may take on continuous and discrete values. To describe the hydrodynamic stage of the nonequilibrium process one must choose for the P_m the densities of energy, momentum, and particle number (21.3a) or their Fourier components. To describe the kinetic stage one may choose as the P_m the occupation numbers of the single particle states (25.4).

The quasi-equilibrium (or local equilibrium) operator is defined from the extremum of the information entropy (10.1)

$$S_u = -\mathrm{Sp}(\rho \ln \rho) \tag{27.1}$$

with the auxiliary conditions of the constancy of

$$\mathrm{Sp}(\rho P_m) = \langle P_m \rangle_q^t \tag{27.2}$$

and conservation of the normalization

$$\mathrm{Sp}\rho = 1. \tag{27.3}$$

In fact, the conditional extremum of the functional (27.1) corresponds to the unrestricted extremum of the functional

$$L(\rho) = -\mathrm{Sp}(\rho \ln \rho) - \sum_m F_m \,\mathrm{Sp}(\rho P_m) - (\Phi - 1)\,\mathrm{Sp}\,\rho, \tag{27.4}$$

where F_m and $\Phi-1$ are Lagrange multipliers. From the condition

$$\delta L(\rho) = -\mathrm{Sp}\left\{\left(\ln\rho + \Phi + \sum_m P_m F_m(t)\right)\delta\rho\right\} = 0 \tag{27.5}$$

it follows that the extremum corresponds to the quasi-equilibrium statistical operator

$$\begin{aligned} \rho_q &= \exp\left\{-\Phi - \sum_m P_m F_m(t)\right\} \equiv \exp\{-S(t, 0)\}, \\ \Phi &= \ln \mathrm{Sp} \exp\left\{-\sum_m P_m F_m(t)\right\}. \end{aligned} \tag{27.6}$$

In the particular case of the hydrodynamic regime the parameters F_m have the meaning of the thermodynamic parameters (21.6a), which depend on time and space coordinates. In this case in the formula (27.6) the summation over m implies also an integration over x. In the case of the kinetic regime P_m can be chosen in accordance with (25.3) or (25.4), and then the summation over m goes over into an integration over momentum.

The quasi-equilibrium statistical operator (27.6) is not a solution of the Liouville equation and cannot give a correct description of irreversible processes; nevertheless, the properties of the nonequilibrium statistical operator are closely connected to the properties of the quasi-equilibrium operator (27.6) (see section 27.3 and Appendix III).

In the case of statistical equilibrium the quasi-equilibrium distribution (27.6) goes over into the Gibbs distribution

$$\rho_0 = \exp\left\{-\Phi_0 - \sum_m F_m^0 P_m\right\}, \tag{27.6a}$$

where

$$\begin{aligned} P_0 &= \int H(\boldsymbol{x})\,d\boldsymbol{x} = H, & F_0^0 &= \beta, \\ P_1 &= \int \boldsymbol{p}(\boldsymbol{x})\,d\boldsymbol{x} = \boldsymbol{P}, & F_1^0 &= -\beta\boldsymbol{v}, \\ P_2 &= \int n(\boldsymbol{x})\,d\boldsymbol{x} = N, & F_2^0 &= -\beta\left(\mu - \frac{m}{2}v^2\right), \end{aligned}$$

which not only corresponds to an extremum of the information entropy, but which is also a solution of the Liouville equation.

The thermodynamic entropy and the logarithm of the statistical sum (the

Massieu-Planck functional) of the distribution (27.6) are connected by the relation

$$S = \Phi + \sum_m \langle P_m\rangle_q^t F_m(t), \quad \langle \ldots \rangle_q^t = \mathrm{Sp}\,(\rho_q \ldots), \tag{27.7}$$

which can be considered as a generalization to the quasi-equilibrium case of the Legendre transformation of equilibrium thermodynamics. Varying the normalization condition for the operator (27.6) and making use of the relation (27.7), we obtain

$$\delta\Phi = -\sum_m \langle P_m\rangle_q^t \,\delta F_m(t), \quad \delta S = \sum_m F_m(t)\,\delta\langle P_m\rangle_q^t, \tag{27.8}$$

from which follow the thermodynamic equalities

$$\langle P_m\rangle_q^t = -\frac{\delta\Phi}{\delta F_m(t)}, \tag{27.9}$$

$$F_m(t) = \frac{\delta S}{\delta\langle P_m\rangle_q^t} \tag{27.10}$$

and the Gibbs-Helmholtz relations

$$S = \Phi - \sum_m F_m(t)\frac{\delta\Phi}{\delta F_m(t)}, \quad \Phi = S - \sum_m \langle P_m\rangle_q^t \frac{\delta S}{\delta\langle P_m\rangle_q^t}. \tag{27.11}$$

The relations (27.7)-(27.11) differ from the equilibrium thermodynamic equalities only in the replacement of the partial derivatives by functional derivatives, if m is a continuous index.

We shall find the connection between the second functional derivatives of S and Φ and the quantum correlation functions in a quasi-equilibrium state; differentiating the equalities (27.9) and (27.10):

$$\frac{\delta \langle P_m \rangle_q^t}{\delta F_n(t)} = -\frac{\delta^2 \Phi}{\delta F_m(t)\,\delta F_n(t)} = \frac{\delta \langle P_n \rangle_q^t}{\delta F_m(t)} = -(P_n, P_m)^t, \tag{27.12}$$

$$\frac{\delta F_m(t)}{\delta \langle P_n \rangle_q^t} = \frac{\delta^2 S}{\delta \langle P_n \rangle_q^t\,\delta \langle P_m \rangle_q^t} = \frac{\delta F_n(t)}{\delta \langle P_m \rangle_q^t}, \tag{27.13}$$

$$\sum_{m'} \frac{\delta^2 \Phi}{\delta F_m(t)\,\delta F_{m'}(t)} \frac{\delta^2 S}{\delta \langle P_{m'} \rangle_q^t\,\delta \langle P_n \rangle_q^t} = -\delta_{mn}, \tag{27.14}$$

where the correlation functions $(P_n, P_m)^t$ have the form

$$(P_n, P_m)^t = \int_0^1 d\tau \langle P_n (e^{-\tau S(t,0)} P_m e^{\tau S(t,0)} - \langle P_m \rangle_q^t) \rangle_q^t. \tag{27.15}$$

Relations (27.14) have already been used in § 6 (see (6.24)).

27.2. Derivation of a Nonequilibrium Statistical Operator from the Extremum of Information Entropy.

The quasi-equilibrium statistical operator (27.6) corresponds to the extremum of the information entropy (27.1) for fixed $\langle P_m \rangle^t$ and at a fixed time t. Consequently, the operator is a function of $F_m(t)$ (if m is a discrete index) for a given moment of time t, and it does not take into account "memory" effects, i.e., the possible functional dependence of ρ on $F_m(t+t')$ at past moments of time $-\infty < t' \leqslant 0$. Irreversible processes are often characterized by such retardation, which leads to dispersion of the kinetic coefficients.

We shall show that the nonequilibrium statistical operator which we applied in §§ 21-26 can be defined from the extremum of the information entropy (27.1) with the auxiliary conditions that the values of

$$\mathrm{Sp}(\rho P_m(t')) = \langle P_m \rangle^{t+t'} \tag{27.16}$$

are specified in the interval $-\infty < t' \leqslant 0$, i.e., not only for the given moment t, but also for all past moments of time, and with conservation of the normalization

$$\mathrm{Sp}\rho = 1. \tag{27.17}$$

In (27.16) $P_m(t')$ implies the Heisenberg representation, i.e., the evolution of the system in time in accordance with the Liouville equation. Thus, the auxiliary condition (27.16) has a dynamical character and includes information about the evolution of the system, while the auxiliary condition (27.2) has a statistical character and includes information only about the state of the system at a given moment.

This conditional extremum with the "memory" effect corresponds to the unrestricted extremum of the functional

$$L(\rho) = -\operatorname{Sp}(\rho \ln \rho) - (\tilde{\tilde{\Phi}} - 1)\operatorname{Sp}\rho - \int_{-\infty}^{0} dt' \sum_m G_m(t, t')\operatorname{Sp}(\rho P_m(t')), \qquad (27.18)$$

where $\tilde{\tilde{\Phi}}-1$ and $G_m(t,t')$ are Lagrange multipliers. From the extremum condition for the functional (27.18) it follows that

$$\delta L(\rho) = -\operatorname{Sp}\left\{\left[\ln\rho + \tilde{\tilde{\Phi}} + \sum_m \int_{-\infty}^{0} dt'\, G_m(t, t')\, P_m(t')\right]\delta\rho\right\} = 0, \qquad (27.19)$$

from which we find

$$\rho = \exp\left\{-\tilde{\tilde{\Phi}} - \int_{-\infty}^{0} dt' \sum_m G_m(t, t')\, P_m(t')\right\}. \qquad (27.20)$$

The Lagrange multipliers are defined from the condition (27.16) and the normalization (27.17). Varying the normalization condition with respect to $G_m(t,t')$ and taking into account (27.16), we obtain

$$\frac{\delta\tilde{\tilde{\Phi}}}{\delta G_m(t, t')} = -\langle P_m(t')\rangle^t = -\langle P_m\rangle^{t+t'}. \qquad (27.21)$$

If the P_m are integrals of motion, then $P_m(t')=P_m$ and the statistical operator (27.20) must go over into the Gibbs distribution (27.6a), i.e., the integral

$$\int_{-\infty}^{0} G_m(t, t')\, dt'$$

must converge to the constant value F_m^0. This can be achieved by putting

$$G_m(t, t') = F_m^0 \frac{d}{dt'} e^{\varepsilon t'} = \varepsilon e^{\varepsilon t'} F_m^0 \qquad (\varepsilon > 0).$$

Taking into account this property and relation (27.21), the Lagrange multipliers are conveniently chosen in the form

$$G_m(t, t') = \varepsilon e^{\varepsilon t'} F_m(t + t'), \tag{27.22}$$

where the $F_m(t+t')$ are the parameters conjugate with $\langle P_m \rangle^{t+t'}$. Then we obtain the statistical operator

$$\rho = \exp\left\{ -\tilde{\Phi} - \varepsilon \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \sum_m F_m(t + t')\, P_m(t') \right\}, \tag{27.23}$$

which coincides with the nonequilibrium statistical operator which was obtained earlier (21.10a), (25.10)[1]. The parameter $\varepsilon > 0$ approaches zero after the thermodynamic limit is taken in the calculation of the averages.

Thus, it is shown that the nonequilibrium statistical operator (27.23) corresponds to the extremum (maximum) of the information entropy for fixed average $\langle P_m \rangle^{t_1}$ at any past moment of time t_1 in the interval $-\infty < t_1 \leq t$.

The nonequilibrium statistical operator can be written in the more compact form:

$$\begin{gathered} \rho = \exp\left\{ -\tilde{\Phi} - \sum_m \widetilde{P_m F_m(t)} \right\}, \\ \tilde{\Phi} = \ln \operatorname{Sp} \exp\left\{ -\sum_m \widetilde{P_m F_m(t)} \right\}, \end{gathered} \tag{27.24}$$

where we have introduced the operation of taking the invariant (or quasi-invariant) part of an operator with respect to motion with the Hamiltonian H, which is denoted, as always, by a wavy line over the operators:

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[1] Earlier in §§ 21,22 we denoted the normalizing factor for the distribution (27.23), $Q = \exp\tilde{\Phi}$, by means of $Q = \exp\Phi$.

$$\widetilde{P_m F_m(t)} \equiv \varepsilon \int_{-\infty}^{0} dt' \, e^{\varepsilon t'} P_m(t') F_m(t+t') =$$

$$= P_m F_m(t) - \int_{-\infty}^{0} dt' \, e^{\varepsilon t'} \{\dot{P}_m(t') F_m(t+t') + P_m(t') \dot{F}_m(t+t')\},$$

$$P_m(t) = e^{\frac{itH}{\hbar}} P_m e^{-\frac{itH}{\hbar}}, \qquad (27.25)$$

$$\dot{P}_m = \frac{1}{i\hbar} [P_m, H], \quad \dot{F}_m(t) = \frac{dF_m(t)}{dt}.$$

In the final results $\varepsilon \to +0$ after the volume of the system has become infinite. The operators $\widetilde{P_m F_m}(t)$ satisfy the Liouville equation

$$\frac{\partial}{\partial t} (\widetilde{P_m F_m(t)}) + \frac{1}{i\hbar} [(\widetilde{P_m F_m(t)}), H] =$$

$$= \varepsilon \int_{-\infty}^{0} dt' \, e^{\varepsilon t'} \{\dot{P}_m(t') F_m(t+t') + P_m(t') \dot{F}_m(t+t')\} \qquad (27.26)$$

where $\varepsilon \to +0$. Therefore we call (27.25) the invariant (or quasi-invariant) part of the product $P_m F_m(t)$ with respect to the evolution with the Hamiltonian H. These products are thus integrals of motion for $\varepsilon \to +0$. It is evident that in this limit the statistical operator (27.24), constructed from the operators (27.25), will also be a solution of the Liouville equation. The operation of taking the invariant part, which smoothes the oscillatory terms, is used in the formal theory of scattering to impose boundary conditions which exclude the advanced solutions of the Schroedinger equation [84] (see Appendix I); we shall also use this operation in order to choose the Lagrange multipliers (27.22) such that the nonequilibrium statistical operator (27.23) is a retarded solution of the Liouville equation.

The parameters $F_m(t)$ of the nonequilibrium statistical operator are chosen such that $F_m(t)$ and $\langle P_m \rangle^t$ are thermodynamically conjugate parameters, which is achieved if one imposes on $F_m(t)$ the conditions

$$\langle P_m \rangle^t = \langle P_m \rangle^t_q, \qquad (27.27)$$

where

$$\langle P_m \rangle^t_q = \mathrm{Sp}(\rho_q P_m) = \mathrm{Sp}(e^{-S(t,0)} P_m).$$

Indeed, in that case

$$\frac{\delta \Phi}{\delta F_m(t)} = -\langle P_m \rangle^t_q = -\langle P_m \rangle^t, \qquad (27.28)$$

and thus,

$$\delta \Phi = -\sum_m \langle P_m \rangle^t \, \delta F_m(t). \qquad (27.29)$$

By definition the entropy is equal to

$$S = -\operatorname{Sp}(\rho_q \ln \rho_q) = \Phi + \sum_m \langle P_m \rangle^t F_m(t), \tag{27.30}$$

from which follow, taking into account (27.29), the thermodynamic equalities

$$\delta S = \sum_m F_m(t)\, \delta \langle P_m \rangle^t, \tag{27.31}$$

$$F_m(t) = \frac{\delta S}{\delta \langle P_m \rangle^t}, \tag{27.31a}$$

the same as for the quasi-equilibrium distribution (27.10).

27.3. Connection Between Nonequilibrium and Quasi-Equilibrium Statistical Operators.

The nonequilibrium statistical operator (27.24) is intimately connected with the quasi-equilibrium statistical operator (27.6). The nonequilibrium operator can be constructed from the quasi-equilibrium operator, if one takes the quasi-invariant part of the logarithm of the latter:

$$\rho = \exp\{\widetilde{\ln \rho_q}\} = \exp\left\{\varepsilon \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} e^{\frac{it'H}{\hbar}} \ln \rho_q(t+t')\, e^{-\frac{it'H}{\hbar}}\right\} = \exp\{-\widetilde{S(t, 0)}\}, \tag{27.32}$$

or

$$\rho = \exp\left\{-\varepsilon \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} S(t+t', t')\right\} = \exp\left\{-S(t, 0) + \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \dot{S}(t+t', t')\right\}, \tag{27.32a}$$

where

$$S(t, 0) = \Phi + \sum_m P_m F_m(t) \tag{27.33}$$

is the entropy operator, and

$$\dot{S}(t,0)=\frac{\partial S(t,0)}{\partial t}+\frac{1}{i\hbar}[S(t,0),H],$$
$$\dot{S}(t,t')=e^{it'H/\hbar}\dot{S}(t,0)e^{-it'H/\hbar} \tag{27.34}$$

is the entropy production operator.

The argument t+t′ in $\rho_q(t+t')$ implies a time dependence through the parameters $F_m(t+t')$; in $S(t+t',t')$ the first argument implies a time dependence through the parameters, while the second argument implies a time dependence through the Heisenberg representation of the operators $P_m(t')$.

We shall require that from the normalization (27.6) it follow that (27.32) also be normalized. The relation (27.32) defines the following connection between the logarithms of the normalizing factors of the quasi-equilibrium (27.6) and nonequilibrium (27.24) operators:

$$\tilde{\Phi}=\varepsilon\int_{-\infty}^{0}dt'\,e^{\varepsilon t'}\Phi(t+t')=\Phi(t)-\int_{-\infty}^{0}dt'\,e^{\varepsilon t'}\dot{\Phi}(t+t'), \tag{27.35}$$

if the conditions (27.27) are imposed on the function $F_m(t)$.

Actually, the variations of the left and right hand sides of the formula (27.35) with respect to the functions $F_m(t+t')$ are equal to, respectively,

$$\delta\tilde{\Phi}=-\varepsilon\int_{-\infty}^{0}dt'\,e^{\varepsilon t'}\sum_m\langle P_m(t')\rangle^t\,\delta F_m(t+t'), \tag{27.36}$$

$$\varepsilon\delta\int_{-\infty}^{0}dt'\,e^{\varepsilon t'}\Phi(t+t')=-\varepsilon\int_{-\infty}^{0}dt'\,e^{\varepsilon t'}\sum_m\langle P_m\rangle_q^{t+t'}\,\delta F_m(t+t'). \tag{27.36a}$$

By virtue of the equalities (27.27) these variations must coincide. In addition, for a concrete choice of the functions $F_m(t)$, corresponding to the statistical equilibrium distribution (27.6a), namely $F_m(t)=F_m^0$, we have

$$\rho=\rho_q=\rho_0,\qquad \tilde{\Phi}=\Phi=\Phi_0.$$

This then proves the relation (27.35).

The entropy production operator (27.34) can be written in the form

$$\dot{S}(t,\ 0)=\sum_m\{\dot{P}_mF_m(t)+P_m\dot{F}_m(t)\}+\dot{\Phi}=$$
$$=\sum_m\{\dot{P}_mF_m(t)+(P_m-\langle P_m\rangle^t)\,\dot{F}_m(t)\}. \qquad (27.37)$$

For this the average production of entropy $\dot{S}$ is written in the following way:

$$\dot{S}=\langle\dot{S}(t,\ 0)\rangle^t=\sum_m\langle\dot{P}_m\rangle^tF_m(t). \qquad (27.38)$$

From (27.38) it follows that the quantities $F_m(t)$ play the role of the thermodynamic forces, while the $\langle\dot{P}_m\rangle^t$ are the conjugate currents. As we verified in section 22.3, the positivity of the production of entropy is connected with the choice of the retarded form of the integrals of motion (27.25).

In a quasi-equilibrium state we have

$$\langle\dot{S}(t,\ 0)\rangle_l=\sum_m\langle\dot{P}_m\rangle_qF_m(t)=\mathrm{Sp}\left\{\frac{1}{i\hbar}[S(t,\ 0),\ H]\,e^{-S(t,\ 0)}\right\}=0, \qquad (27.38a)$$

where we have made a cyclic permutation of the operators under the spur sign. Consequently, the entropy production operator (27.37) can be written in the form

$$\dot{S}(t,\ 0)=\Delta\sum_m\{\dot{P}_mF_m(t)+P_m\dot{F}_m(t)\}, \qquad (27.37a)$$

where

$$\Delta\dot{P}_m=\dot{P}_m-\langle\dot{P}_m\rangle_q,\qquad \Delta P_m=P_m-\langle P_m\rangle_l.$$

It is easy to verify that the nonequilibrium statistical operator (27.32) is a solution of the Liouville equation for $\varepsilon\to0$. Indeed, we have

$$\frac{\partial\rho}{\partial t} + \frac{1}{i\hbar}[\rho, H] =$$
$$= -\varepsilon \int_{-\infty}^{0} dt' \, e^{\varepsilon t'} \int_{0}^{1} d\tau \, e^{-\tau \widetilde{S(t,0)}} \sum_{m} \{(\dot{P}_m(t') - \langle \dot{P}_m(t')\rangle^t) F_m(t+t') +$$
$$+ (P_m(t') - \langle P_m(t')\rangle^t) \dot{F}_m(t+t')\} e^{\tau \widetilde{S(t,0)}} \rho, \qquad (27.39)$$

(27.39)

where $\varepsilon \to +0$ after the approach of the system volume V to infinity. For the indicated sequence of calculation of the limits there exist the relations [186]

$$\lim_{\varepsilon\to 0,\ V\to\infty} \langle P_m(t')\rangle^t = \langle P_m\rangle^{t+t'},$$
$$\lim_{\varepsilon\to 0,\ V\to\infty} \langle \dot{P}_m(t')\rangle^t = \langle \dot{P}_m\rangle^{t+t'}. \qquad (27.40)$$

Essentially, we do not require that the operator ρ satisfy exactly the Liouville equation; rather it is sufficient that the properties (27.40) be satisfied for any operator.

The introduction of the quasi-integrals of motion (27.25) can be regarded, in connection with the ideas of N. N. Bogolyubov on "quasi-averages" [171, 172], as the introduction of infinitesimal sources in the Liouville equation, which then tend to zero in the calculation of averages after the volume of the system has approached infinity (see Appendix III and the articles [186, 187]).

27.4. Generalized Transfer Equations.

In nonequilibrium statistical mechanics for a description of the time evolution of a nonequilibrium state it is necessary to know, besides the thermodynamic equalities, the equations of motion of the average values of dynamical quantities - generalized transfer equations (or generalized kinetic equations). We have already considered such equations in § 25 for the kinetic regime and in §§ 21-24 for the hydrodynamic regime.

One can obtain generalized transfer equations describing the time evolution of the averages $\langle P_m\rangle^t$ or of the related functions $F_m(t)$ by averaging over the nonequilibrium distribution (27.24) the equations of motion for the operators P_m, which together with the conditions (27.27) gives

$$\frac{d}{dt}\langle P_m\rangle^t = \frac{d}{dt}\langle P_m\rangle^t_q = \sum_{m'} \frac{\delta\langle P_m\rangle^t_q}{\delta F_{m'}(t)} \dot{F}_{m'}(t) = \langle P_m\rangle^t = \frac{1}{i\hbar}\langle [P_m, H]\rangle^t. \qquad (27.41)$$

We call these equations generalized transfer equations, including in this concept all possible equations of balance of the theory of irreversible processes, for example, the kinetic equations for various particles or quasi-particles (§§ 25, 26), equations for the balance of energy, particle number, or momentum (§ 22), relaxation equations (§ 23), etc. If there is a small parameter, the right hand side of equation (27.41) can be expanded in a series in powers of this parameter, which leads, in general, to integral equations for $F_m(t)$ or $\langle P_m\rangle^t$. To obtain hydrodynamic equations one uses as the small parameters the gradients of the thermodynamic parameters (§ 22), to obtain relaxation equations one uses the differences of the thermodynamic parameters (§ 23), and to obtain kinetic equations one uses as the small parameter the interaction between particles or quasi-particles (§ 25).

For the conclusion of this section we shall expand the generalized transfer equations for a simple particular case in which the Hamiltonian has the form

$$H = H_0 + V, \tag{27.42}$$

where V is a small perturbation. We have already considered this case in § 25, following the work [56]. We return to this example in order to demonstrate the convenience of the use of the entropy production operator (27.34) and to write in explicit form the generalized transfer equation (27.41).

We shall assume, as in § 25, that the equations of motion for the operators P_m have the form

$$\dot P_m = \frac{1}{i\hbar}[P_m, H_0 + V] = -\frac{1}{i\hbar}\sum_n \alpha_{mn} P_n + \dot P_{m\,(V)}, \tag{27.43}$$

where α_{mn} is a matrix of c-numbers, which are defined by the commutation relations (25.6), and

$$\dot P_{m\,(V)} = \frac{1}{i\hbar}[P_m, V]. \tag{27.44}$$

In this case the entropy production operator (27.37) can be written, taking into account (25.22), in the form

$$\begin{aligned}\dot S(t, 0) = \sum_m \Big\{ \dot P_{m\,(V)} F_m(t) + \sum_l P_m \frac{\delta F_m(t)}{\delta \langle P_l\rangle^t} \langle \dot P_{l\,(V)}\rangle^t + \\ + \left(\frac{i}{\hbar}\sum_l \alpha_{ml} F_m(t) P_l + \frac{i}{\hbar}\sum_{ll'} P_m \frac{\delta F_l(t)}{\delta \langle P_m\rangle^t} \alpha_{ll'} \langle P_{l'}\rangle^t\right)\Big\}.\end{aligned} \tag{27.45}$$

The expansion of the operator $\dot{S}(t,0)$ in powers of V begins with terms of the first order in V, because the sum of terms in the round brackets in (27.45) is identically equal to zero, because of the identity (25.23). Consequently,

$$\dot{S}(t,0) = \sum_{m}\left\{ \dot{P}_{m(V)} F_{m}(t) + \sum_{l} P_{m} \frac{\delta F_{n}(t)}{\delta \langle P_{l}\rangle^{t}} \langle \dot{P}_{l(V)}\rangle^{t} \right\}. \qquad (27.46)$$

Thus, the integral term in the exponent of the exponential in the expression for the nonequilibrium statistical operator (27.32a) is small, and ρ can be expanded in powers of this term:

$$\rho = \exp\{-\widetilde{S(t,0)}\} =$$
$$= \left\{ 1 + \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \int_{0}^{1} d\tau\, e^{-\tau S(t,0)} \dot{S}(t+t',t')\, e^{\tau S(t,0)} + \dots \right\} e^{-S(t,0)}. \qquad (27.47)$$

It is now possible to obtain explicit expressions for the right hand side of the generalized transfer equation (27.41) with an accuracy through terms of second order in V:

$$\langle \dot{P}_{m}\rangle^{t} = \frac{i}{\hbar} \sum_{n} a_{mn} \langle P_{n}\rangle^{t} + \langle \dot{P}_{m(V)}\rangle_{q}^{t} +$$
$$+ \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \sum_{n} (\dot{P}_{m(V)}, \dot{P}_{n(V)}(t'))^{t} F_{n}(t+t') +$$
$$+ \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \sum_{nl} (P_{m(V)}, P_{n}(t'))^{t} \frac{\delta F_{n}(t+t')}{\delta \langle P_{l}\rangle^{t+t'}} \langle \dot{P}_{l(V)}\rangle_{q}^{t+t'} + \dots, \qquad (27.48)$$

where the brackets $(\dots, \dots)^{t}$ denote the correlation functions (27.15).

In the important particular case in which $\langle \dot{P}_{n(V)}\rangle_{q}^{t} = 0$, the generalized transfer equation (27.48) takes on the form

$$\frac{d}{dt}\langle P_{m}\rangle = -\sum_{n} (P_{m}, P_{n})^{t} \dot{F}_{n}(t) =$$
$$= \sum_{n} \left\{ \frac{i}{\hbar} a_{mn} \langle P_{n}\rangle^{t} + \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} (\dot{P}_{m(V)}, \dot{P}_{n(V)}(t'))^{t} F_{n}(t+t') \right\}. \qquad (27.49)$$

On the right hand side of equation (27.49) are the time correlation functions of the currents, calculated with respect to a quasi-equilibrium state. They define either the collision operator of the kinetic equation or the kinetic coefficients.

We remark that expansions of the type (27.47) make it possible to write approximately the production of entropy in the following simple form

$$\dot S = \int_{-\infty}^{0} dt' e^{\varepsilon t'} (\dot S(t, 0),\ \dot S(t+t', t'))^t. \tag{27.50}$$

Thus, the production of entropy is defined by the correlation functions for the entropy production operators.

27.5. Generalized Transfer Equations and Evolution Criteria of Prigogine and Glansdorf Macroscopic Systems.

We shall consider what restrictions are imposed by the requirement of maximum entropy in a quasi-equilibrium state, and we shall show, following [170], that this stipulation gives the criteria, which were established by Prigogine and Glansdorf [173,174], for the evolution of macroscopic systems, and in the particular case in which the kinetic coefficients are constant, it leads to the theorem of Prigogine on the minimum production of entropy [175, 27] (see also [227]).

We shall consider the time derivatives of the functionals $\dot S$ (see (27.38)) and Φ:

$$\dot\Phi = -\sum_m \langle P_m\rangle^t \dot F_m(t). \tag{27.51}$$

We obtain

$$\ddot S = \sum_m \{\langle \dot P_m\rangle^t \dot F_m(t) + \langle \ddot P_m\rangle^t F_m(t)\}, \tag{27.52}$$

$$\ddot\Phi = -\sum_m \{\langle \dot P_m\rangle^t \dot F_m(t) + \langle P_m\rangle^t \ddot F_m(t)\}. \tag{27.53}$$

Making use of (27.49), (27.9), (27.10), and (27.12), the first terms on the right hand sides of formulas (27.52) and (27.53) can be taken to the form

$$\frac{d_F\dot{S}}{dt} = \sum_{m} \langle \dot{P}_m \rangle^t F_m(t) = - \sum_{m,\, n} \frac{\delta^2 \Phi}{\delta F_m(t)\, \delta F_n(t)} \dot{F}_m(t)\, \dot{F}_n(t) =$$

$$= - \sum_{m,\, n} (P_m,\ P_n)^t \dot{F}_m(t)\, \dot{F}_n(t), \qquad (27.54)$$

$$\frac{d_P\dot{\Phi}}{dt} = - \sum_{m,\, n} \frac{\delta^2 S}{\delta \langle P_m \rangle^t\, \delta \langle P_n \rangle^t} \langle \dot{P}_m \rangle^t \langle \dot{P}_n \rangle^t = - \frac{d_F\dot{S}}{dt}. \qquad (27.55)$$

They have the meaning of the rate of change of the production of entropy, caused by the change of the thermodynamic forces, and the rate of change of $\dot{\Phi}$, caused by the change of $\langle P_m \rangle^t$.

The condition of maximum entropy in the quasi-equilibrium state implies that the quadratic form $\delta^2 S$ is negative definite, i.e.,

$$\sum_{m,\, n} \frac{\delta^2 S}{\delta \langle P_m \rangle^t\, \delta \langle P_n \rangle^t} \delta \langle P_m \rangle^t\, \delta \langle P_n \rangle^t < 0. \qquad (27.56)$$

From here it follows, taking into account (27.55) and (27.54), that

$$\frac{d_F\dot{S}}{dt} < 0, \qquad \frac{d_P\dot{\Phi}}{dt} > 0. \qquad (27.57)$$

The first of these relations constitutes the general evolution criterion for macroscopic systems [173,174] (the Glansdorf-Prigogine theorem), which says that in a real irreversible process there takes place a decrease of part of the production of entropy $d_F\dot{S}/dt$.

The second of relations (27.57) is another formulation of the general evolution criterion, according to which in a real irreversible process there takes place an increase of $d_P\dot{\Phi}/dt$. This theorem is established in [170].

We shall now show that in the approximation which is linear in the thermodynamic forces the generalized transfer equations satisfy the relations

$$\ddot{S} \equiv \frac{d_F\dot{S}}{dt} + \frac{d_P\dot{S}}{dt} = 2\,\frac{d_F\dot{S}}{dt} < 0, \qquad (27.58)$$

$$\ddot{\Phi} \equiv \frac{d_P\dot{\Phi}}{dt} + \frac{d_F\dot{\Phi}}{dt} = 2\,\frac{d_P\dot{\Phi}}{dt} > 0, \qquad (27.59)$$

i.e., in other words these processes are accompanied by a decrease of the production of entropy and an increase in the time rate of change of the functional Φ.

The relation (27.58) is the Prigogine theorem on the minimum production of entropy [175,27]. The theorem (27.59) on the maximum of the functional $\dot{\Phi}$ is proved in [170].

Assume that the deviations of the thermodynamic forces $F_m(t)$ from their equilibrium values F_m^0

$$\Delta F_m = F_m(t) - F_m^0 \tag{27.60}$$

are small, and that the connection between ΔF_m and ΔP_m

$$\Delta P_m = \langle P_m \rangle^t - \langle P_m \rangle_0 \tag{27.61}$$

can be considered linear, i.e.,

$$\Delta \langle P_m \rangle = -\sum_n \frac{\delta^2 \Phi_0}{\delta F_m(t)\, \delta F_n(t)} \Delta F_n, \tag{27.62}$$

$$\Delta F_m = \sum_n \frac{\delta^2 S_0}{\delta \langle P_m \rangle^t\, \delta \langle P_n \rangle^t} \Delta \langle P_n \rangle. \tag{27.63}$$

The subscript 0 on the quantities S_0 and Φ_0 implies that after taking the functional derivatives one must put $F_m(t) = F_m^0$ in the resulting correlation functions; the $\langle P_m \rangle_0$ denote averages over an equilibrium state.

Further, it is evident that

$$\sum_m \dot{P}_m F_m^0 = 0 \text{ and } \sum_m \langle \dot{P}_m \rangle^t F_m^0 = 0, \tag{27.64}$$

where we assume $H = \sum_m P_m F_m^0$, and for weakly equilibrium states there exists a linear connection between the currents and the thermodynamic forces:

$$\langle \dot{P}_m \rangle^t = \sum_n L_{mn}^F \Delta F_n, \tag{27.65}$$

where L^F_{mn} are the kinetic coefficients, from which it follows that the production of entropy (27.38) is equal to

$$\dot S = \sum_m F_m \langle \dot P_m \rangle^t = \sum_{m,n} L^F_{mn} \Delta F_m \Delta F_n. \tag{27.66}$$

There exist also linear relations for the rates of change of the thermodynamic forces $\dot F_m$ and the increases $\Delta\langle P_n\rangle$:

$$\dot F_m = \sum_n L^P_{mn} \Delta \langle P_n \rangle, \tag{27.67}$$

where the L^P_{mn} are kinetic coefficients, connected to the L^F_{mn} by the relations

$$\begin{aligned} L^P_{mn} &= \sum_{m',n'} \frac{\delta^2 S_0}{\delta\langle P_m\rangle^t \delta\langle P_{m'}\rangle^t} L^F_{m'n'} \frac{\delta^2 S_0}{\delta\langle P_{n'}\rangle^t \delta\langle P_n\rangle^t}, \\ L^F_{mn} &= \sum_{m',n'} \frac{\delta^2 \Phi}{\delta F_m(t)\, \delta F_{m'}(t)} L^P_{m'n'} \frac{\delta^2 \Phi}{\delta F_{n'}(t)\, \delta F_n(t)} \end{aligned} \tag{27.68}$$

and satisfying the Onsager reciprocity relations

$$L^F_{mn} = L^F_{nm}, \qquad L^P_{mn} = L^P_{nm}. \tag{27.69}$$

Making use of the relations (27.65) and (27.69), we obtain

$$\begin{aligned} \frac{d_F S}{dt} &= \sum_m \dot F_m(t) \langle \dot P_m \rangle^t = \sum_{mn} L^F_{mn} \Delta \dot F_m \Delta F_n, \\ \frac{d_P \dot S}{dt} &= \sum_m F_m(t) \langle \ddot P_m \rangle^t = \sum_{mn} L^F_{mn} \Delta F_m \Delta \dot F_n = \frac{d_F \dot S}{dt}, \end{aligned} \tag{27.70}$$

which together with formulas (27.57) prove the first of the inequalities (27.58). Analogously, making use of (27.63) and (27.69), we obtain

$$\frac{d_P\Phi}{dt} = -\sum_{m} \langle \dot{P}_m \rangle^t \dot{F}_m(t) = -\sum_{mn} L^P_{mn} \Delta \langle \dot{P}_m \rangle \Delta \langle P_n \rangle,$$
$$\frac{d_F\dot{\Phi}}{dt} = -\sum_{m} \langle P_m \rangle^t \ddot{F}_m(t) = -\sum_{mn} L^P_{mn} \Delta \langle P_m \rangle \Delta \langle \dot{P}_n \rangle = -\frac{d_P\dot{\Phi}}{dt}, \qquad (27.71)$$

which together with (27.57) proves the second of the inequalities (27.58).

Thus, the generalized transfer equations satisfy the evolution criteria of nonequilibrium phenomenological thermodynamics.

APPENDICES

Appendix 1

FORMAL THEORY OF SCATTERING IN QUANTUM MECHANICS

The formal theory of scattering is discussed in many textbooks and monographs [1-3], but in these for the most part the important question of effecting the limiting transitions - the approach of the dimensions of the system L to infinity and the approach to zero of the parameter ε, which characterizes the switching on of the interaction - is not considered sufficiently explicitly. It is very significant that the result depends on the order of effecting these limiting transitions. This question is elucidated completely explicitly in the article by Gell-Mann and Goldberger [4], a short account of which we shall present, because the question of the order of the limiting transitions is basic also in nonequilibrium statistical mechanics (see § 21).

For the quantum mechanical description of the scattering the total Hamiltonian of the colliding particles H is divided into two parts K and V, where K is the Hamiltonian of the noninteracting particles, and V is the interaction between them. It is assumed that V approaches zero sufficiently rapidly as the particles are separated. The probability of a transition per unit time from one free particle state into another is sought.

The total system is described by the Schroedinger equation

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = (K + V)\Psi(t). \tag{I.1}$$

An essential, distinctive feature of the problem consists in the fact that the interaction V exists at any moment of time, although the scattering process takes place between states without any interaction.

In the absence of the interaction the Schroedinger equation has the form

$$i\hbar \frac{\partial\Phi(t)}{\partial t} = K\Phi(t), \qquad (I.2)$$

and the stationary solution is

$$\Phi_i(t) = \Phi_i e^{-\frac{iE_i}{\hbar}t}. \qquad (I.3)$$

It is required to calculate the effective differential cross section for the scattering from the state Φ_j into the state Φ_i under the influence of the interaction V. The initial state Φ_j is used to characterize the actual state Ψ_j of the real system. Knowing $\Psi_j(t)$, we can find the probability that by the time t the system will make a transition into one of its final states Φ_i.

We shall now discuss the question of formulating correctly the boundary conditions for scattering in the Schroedinger equation (I.1). Suppose that we observe the scattering process at the instant t=0. It is necessary to formulate mathematically the physical procedure for preparing the quantum mechanical state Ψ_j by the time of the transition t=0, i.e., for t<0 (fixing the energy and the direction of the beam).

If one assumes simply that at some distant moment of time t=T, preceding the collision, the wave function Ψ_j was equal to the wave function of a free state

$$\Psi_j(t) = e^{-\frac{iH}{\hbar}(t-T)}\Phi_j(T), \qquad H = K + V,$$

then such a boundary condition introduces the unphysical element of "instantaneously" switching on of the interaction V at t=T. In reality the interaction is switched on gradually; therefore such boundary conditions are inconvenient.

One can impose the boundary conditions differently, representing the incoming wave train as the average over some time interval τ in the past

$$\frac{1}{\tau}\int_{-\tau}^{0} e^{-\frac{i}{\hbar}H(t-T)}\Phi_j(T)\,dT$$

and allowing τ to become infinite at the end of the calculations, i.e., to carry out the operation of "smoothing" in time. Such a boundary condition is also inconvenient, because it leads to expressions which are not sufficiently well defined, and which require additional procedures to make precise their meaning.

The most convenient boundary condition consists in assuming that for $t<0$ the wave function Ψ_j is equal to

$$\Psi_j^{(\varepsilon)}(t) = \varepsilon \int\limits_{-\infty}^{0} e^{\varepsilon T} e^{-\frac{i}{\hbar} H(t-T)} \Phi_j(T)\, dT, \qquad (I.4)$$

where $\varepsilon \to +0$ at the end of the calculations. In this we are also carrying out a "smoothing" in time, because

$$\varepsilon \int\limits_{-\infty}^{0} e^{\varepsilon T}\, dT = 1,$$

but the factor $e^{\varepsilon T}$ separates out the "past", and therefore the averaging (I.4) has a "causal" character.

One must, however, take precautions, because in addition to $\varepsilon \to 0$ it is necessary to effect also another limiting transition $L \to \infty$ (the functions ϕ_i are normalized to unity in the large volume L^3). The time of switching on the interaction τ is of the order of magnitude ε^{-1}, and cannot be larger than the time of spreading of the wave packet to the length L, i.e., it cannot be larger than the magnitude L/v, where v is the group velocity

$$\varepsilon^{-1} \ll L/v;$$

consequently, the quantity $\varepsilon^{-1}L^{-3}$ approaches zero as $L^{-3} \to 0$ and $\varepsilon^{-1} \to \infty$. This implies that first one must make the limiting transition $L^3 \to \infty$, and then $\varepsilon \to 0$.

Condition (I.4) together with the rule indicated above for the limiting transitions $L \to \infty$, $\varepsilon \to 0$ guarantees the choice of the correct retarded, causal solutions of the Schroedinger equation. In this connection, for $\varepsilon^{-1} < L/v$ waves reflected from the boundaries of the system, i.e., converging waves, are excluded, because the length of the beam of waves in time ε^{-1} is shorter than the time necessary for its propagation over the length L. The great convenience of the boundary condition (I.4) compared with the Sommerfeld condition consists in that the causality condition is imposed more automatically, without a detailed analysis of the diverging waves. The boundary condition (I.4) can be justified by the method of wave packets [5]. A boundary condition analogous to (I.4) is applied in § 21 of this book to the Liouville equation. It is evident that part of the significance of this boundary condition consists in the fact that it selects retarded solutions (see Appendix III).

We shall now calculate the probability of a quantum transition between states as a function of time. The probability that a system which is described by the wave function $\Psi_j(t)$ will be found at the time t in the state ϕ_i is equal to, in accordance with the basic rules of quantum mechanics,

$$w_{ij}(t) = |f_{ij}(t)|^2 N_j^{-1}, \qquad \text{(I.5)}$$

where

$$f_{ij}(t) = \left(\Phi_i^*(t)\,\Psi_j(t)\right) \qquad \text{(I.5a)}$$

is the probability amplitude of the transition, and

$$N_j = \left(\Psi_j^*(t)\,\Psi_j(t)\right) \qquad \text{(I.5b)}$$

is the normalization constant, which is independent of time because of the hermiticity of the Hamiltonian.

Taking into account (I.3), the equation (I.4) can be written in the form

$$\Psi_j(t) = e^{-\frac{iHt}{h}}\,\varepsilon \int_{-\infty}^{0} e^{\varepsilon T} e^{\frac{i}{h}(H-E_j)T}\,\Phi_j\,dT \qquad \text{(I.6)}$$

or, after carrying out an integration over T,

$$\Psi_j(t) = e^{-\frac{i}{h}Ht}\,\frac{\varepsilon}{\varepsilon + \frac{i}{h}(H - E_j)}\,\Phi_j. \qquad \text{(I.7)}$$

The function Φ_j satisfies the equation

$$(H - E_j)\,\Phi_j = V\Phi_j, \qquad \text{(I.8)}$$

and therefore for t=0 the equation (I.7) can be written in the form

$$\Psi_j(0) = \Phi_j + \frac{1}{(E_j - H) + i\varepsilon h}\,V\Phi_j. \qquad \text{(I.9)}$$

Instead of the explicit expression for $\Psi_j(0)$ (I.9) one can write for it the equivalent equation

$$\Psi_j(0) = \Phi_j + \frac{1}{(E_j - K) + i\varepsilon h}\,V\Psi_j(0), \qquad \text{(I.10)}$$

which is called the Lippmann-Schwinger equation. Iterating equation (I.10) gives a series in powers of V. The factor

$$G^{+}(E_j) = \lim_{\varepsilon \to +0} \frac{1}{(E_j - K) + i\varepsilon\hbar}$$

is the retarded Green function.

With the help of (I.10) we obtain for the transition amplitude the expression

$$f_{ij}(0) = \delta_{ij} + \frac{1}{(E_j - E_i) + i\varepsilon\hbar} R_{ij}(\varepsilon), \qquad \text{(I.11)}$$

$$R_{ij}(\varepsilon) = \left(\Phi_i^{*} V \Psi_j(0)\right) \qquad \text{(I.12)}$$

is the reaction matrix. Equation (I.11) is convenient because it points out explicitly the existence of a singularity in f_{ij} for $E_i = E_j$ and $\varepsilon \to 0$.

The operator $R_{ij}(\varepsilon)$ is a smooth function of energy after the transition to the limit; each singularity is contained in a factor

$$\frac{1}{(E_j - E_i) + i\varepsilon\hbar}.$$

However the limiting transition $L^3 \to \infty$ can still not be applied to $R_{ij}(\varepsilon)$, because it is proportional to L^{-3}, as a consequence of the normalization of Φ_i to unity in the volume L^3. Therefore it is convenient to introduce the operator

$$\lim_{\substack{L \to \infty \\ \varepsilon \to +0}} R_{ij}(\varepsilon) L^3 = \mathfrak{R}_{ij}, \qquad \text{(I.13)}$$

which already has no singularity at $E_i = E_j$.

In order to calculate the derivative of f_{ij} for t=0 we write (I.5a) in the form

$$f_{ij}(t) = \left(\Phi_i^{*} e^{\frac{i}{\hbar}(E_i - H)t} \Psi_j(0)\right), \qquad \text{(I.14)}$$

from which it follows that

$$\dot{f}_{ij}(0) = \frac{i}{\hbar}\left(\Phi_i^*(E_i - H)\Psi_j(0)\right). \tag{I.15}$$

or, making use of (I.8),

$$\dot{f}_{ij}(0) = -\frac{i}{\hbar}\left(\Phi_i^* V \Psi_j(0)\right) = -\frac{i}{\hbar} R_{ij}(\varepsilon). \tag{I.15a}$$

This relation justifies the use of the name reaction matrix for R_{ij}, because it is proportional to the rate of change of the transition amplitude f_{ij}.

From (I.11) and (I.15a) follows an expression for the rate of change of the modulus of the transition amplitude:

$$\left[\frac{d}{dt}|f_{ij}(t)|^2\right]_{t=0} = \frac{1}{\hbar} 2\delta_{ij} \operatorname{Im} R_{jj} + \frac{2\varepsilon}{(E_j - E_i)^2 + \varepsilon^2\hbar^2}|R_{ij}(\varepsilon)|^2. \quad \text{(I. 16)} \tag{I.16}$$

There remains to calculate the normalization constant N_j. Making use of (I.5a) and the completeness property of the system of functions Φ_j, it follows that

$$\sum_i |f_{ij}|^2 = N_j. \tag{I.17}$$

From (I.16) and (I.17) it follows, taking into account that the normalization constant N_j is time independent, that

$$\frac{2}{\hbar} \operatorname{Im} R_{jj}(\varepsilon) + \sum_i \frac{2\varepsilon}{(E_j - E_i)^2 + \varepsilon^2\hbar^2}|R_{ij}(\varepsilon)|^2 = 0. \tag{I.18}$$

From (I.17) and (I.11) we obtain for N_j the expression

$$N_j = 1 + \frac{2}{\varepsilon\hbar} \operatorname{Im} R_{jj}(\varepsilon) + \sum_i \frac{1}{(E_j - E_i)^2 + \varepsilon^2\hbar^2}|R_{ij}(\varepsilon)|^2 \tag{I.19}$$

or taking into account (I.18)

$$N_j = 1 + \frac{1}{\varepsilon\hbar} \operatorname{Im} R_{jj}(\varepsilon) \tag{I.19a}$$

Noticing that R_{ij} is of the order of L^{-3}, we find that for our double limiting transition N_j approaches unity.

The effective differential cross section for the transition $j \rightarrow i$ ($i \neq j$) is equal to the probability of transition per unit time (I.16), divided by the current vL^{-3}, where v is the relative velocity of the colliding systems. Therefore from (I.16) it follows that

$$\sigma_{ij} = \lim_{\varepsilon \rightarrow +0} \lim_{L \rightarrow \infty} \frac{2\varepsilon}{(E_j - E_i)^2 + \varepsilon^2 h^2} \, | R_{ij} (\varepsilon) |^2 L^3 v^{-1}. \tag{I.20}$$

The factor

$$\frac{2\varepsilon}{(E_j - E_i)^2 + \varepsilon^2 h^2}$$

approaches $2\pi/\hbar \, \delta(E_j - E_i)$ in the limit $\varepsilon \rightarrow 0$. The final states j are in the continuous spectrum; thus, transitions are observed not into a given state i, but into a small interval of final states, and therefore it is necessary to average (I.20) over a small interval of final states. This operation corresponds to the "coarse structure" coarsening in statistical mechanics. In such an averaging $\delta(E_j - E_i)$ is removed, and in its place appears $\rho(E_j)L^3$ - the density of states in momentum space in the volume V per unit interval of energy at the energy E_j. Finally

$$\sigma_{ij} = 2\pi \, | \mathfrak{R}_{ij} |^2 \rho (E_j) \, v^{-1}, \tag{I.21}$$

where σ_{ij} is already calculated on the small interval of final states, usually on an element of solid angle.

Until this time we have assumed that $j \neq i$, that is, that the initial state does not coincide with the final state. It is evident that a single state can have no effect on the transition probability calculated above, but the change of w_{jj} in time is essential for calculating the change of the population of the initial level.

From equation (I.16) for i=j it follows that

$$N_j \frac{d}{dt} w_{jj} \Big|_{t=0} = \frac{2}{h} \mathrm{Im} \, R_{jj} (\varepsilon) + \frac{2}{\varepsilon h} \, | R_{jj} (\varepsilon) |^2. \tag{I.22}$$

Now on the other hand, in the limit $L \rightarrow \infty$, $\varepsilon \rightarrow +0$ the second term in (I.22) is vanishingly small compared with the first term.

Going over in (I.18) to the limit $\varepsilon \rightarrow +0$, we obtain

$$\frac{-2\,\mathrm{Im}\,\mathfrak{R}_{ii}}{L^3} = \frac{1}{L^3}\sum_{i\neq j}\frac{2\pi}{L^3}\,|\mathfrak{R}_{ji}|^2\,\delta(E_j - E_i), \tag{I.23}$$

i.e., the relation

$$\sum_{i\neq j}\sigma_{ij} = -\frac{2}{v}\,\mathrm{Im}\,\mathfrak{R}_{ii}, \tag{I.23a}$$

giving the connection between the imaginary part of the scattering matrix and the total effective cross section. This relation, which follows from the conservation of the normalization, is called the optical theorem.

The boundary conditions for the quantum mechanical collision problem can be formulated by introducing infinitesimally small sources, which pick out the retarded solutions of the Schroedinger equation [6].

We note that the Schroedinger equation (I.1) is invariant with respect to the transformation of time reversal, i.e., with respect to the replacements t→-t, i→-i and the reversal of the sign of the magnetic field. In addition, the solution of the equation (I.1) is sensitive to the introduction of an infinitesimal source which breaks this symmetry.

The boundary conditions which select the retarded solutions of the Schroedinger equation in the formal theory of scattering, in the variant of Gell-Mann — Goldberger [4], can be obtained, if, following [6], one introduces in (I.1) for t≤0 an infinitesimal source, which breaks the symmetry of the Schroedinger equation with respect to time reversal:

$$\frac{\partial\Psi_\varepsilon(t)}{\partial t} - \frac{1}{i\hbar}H\Psi_\varepsilon(t) = -\varepsilon\left(\Psi_\varepsilon(t) - \Phi(t)\right), \tag{I.24}$$

where ε→+0 after the approach of the volume of the system to infinity, and Φ(t) is the wave function of free motion of particles with the Hamiltonian K. The infinitesimal source (I.24) is introduced in such a way that it is equal to zero for Ψ(t)=Φ(t), i.e., in the absence of interaction. It indeed violates the symmetry of the Schroedinger equation with respect to time reversal, because in this transformation the left hand side of equation (I.24) changes sign, while the right hand side remains unchanged. The sign of ε is chosen so as to obtain the retarded, and not the advanced solutions.

We write equation (I.24) in the form

$$\frac{d}{dt}\left(e^{\varepsilon t}\,\Psi_\varepsilon(t,t)\right) = \varepsilon e^{\varepsilon t}\,\Phi(t,t), \tag{I.25}$$

where

$$\Psi_\varepsilon(t,t) = e^{-Ht/i\hbar}\,\Psi_\varepsilon(t), \quad \Phi(t,t) = e^{-Ht/i\hbar}\,\Phi(t). \tag{I.25a}$$

Integrating (I.25) from -∞ to t, we have

$$\Psi_\varepsilon(t) = \varepsilon \int_{-\infty}^{t} e^{\varepsilon(t_1 - t)} e^{-H(t_1 - t)/i\hbar} \Phi(t_1)\, dt_1 = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t'} e^{-Ht'/i\hbar} \Phi(t + t')\, dt'. \qquad (I.26)$$

Putting in (I.26) t=0, we obtain the boundary condition for scattering theory in the form of Gell-Mann — Goldberger

$$\Psi_\varepsilon(0) = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t} e^{-Ht/i\hbar} \Phi(t)\, dt, \qquad (I.27)$$

which we have already considered above.

Appendix II

STATISTICAL THEORY OF TRANSFER PROCESSES ACCORDING TO McLENNAN

The construction of a statistical theory of transfer processes according to McLennan [1,2] is based on the introduction of external forces of a non-potential character, which describe the influence of the surroundings or the thermostat on a given system, i.e., the influence of reservoirs of energy and particles and movable pistons, which are in contact with the system. We shall describe briefly this method, because it is close to the method of the non-equilibrium statistical operator [3-6], an account of which is given in § 21, and it leads to the same results. A comparison of these two methods enables one to consider the same questions from different points of view and to better clarify their physical meaning.

We shall consider classical systems with total Hamiltonian H_u - the Hamiltonian of the universe in the terminology of McLennan. One must not attribute a great significance to this term; we shall, as before, be interested in the evolution of a small subsystem, accessible to our measurements, and we shall not be concerned with questions of the construction of the universe. We have

$$H_u = H + H_s + U, \qquad (II.1)$$

where H is the Hamiltonian of the system being considered, H_s is the Hamiltonian of the surroundings, and U is the Hamiltonian of the interaction of the system with the surroundings.

The distribution function of the total system f_u obeys the Liouville equation (2.11)

$$\frac{\partial f_u}{\partial t} + \{f_u, H_u\} = 0, \tag{II.2}$$

where {...} denotes the classical Poisson brackets (2.10). The distribution functions for the system under consideration and the surroundings are respectively equal to

$$f = \int f_u \, d\Gamma_s, \quad g = \int f_u \, d\Gamma, \tag{II.3}$$

where $d\Gamma_s$ and $d\Gamma$ are elements of phase volume for the surroundings and the given system. If f_u is normalized, then f and g are also normalized:

$$\begin{gathered} \int f \, d\Gamma = 1, \quad \int g \, d\Gamma_s = 1, \\ \int f_u \, d\Gamma \, d\Gamma_s = 1. \end{gathered} \tag{II.4}$$

We obtain an equation for f, integrating (II.2) over the phase space of the surroundings $d\Gamma_s$:

$$\frac{\partial f}{\partial t} + \{f, H\} + \int \{f_u, H_s\} \, d\Gamma_s + \int \{f_u, U\} \, d\Gamma_s = 0, \tag{II.5}$$

because H depends only on the variables of the system under consideration. The third term in this equation is zero, because the integrand is a divergence in the phase space of the surroundings. The last term can be simplified, if one introduces the function X, which describes the correlation of the system with the surroundings:

$$f_u = fgX. \tag{II.6}$$

Then,

$$\frac{\partial f}{\partial t} + \{f, H\} + \frac{\partial (fF_\alpha)}{\partial p_\alpha} = 0, \tag{II.7}$$

where

$$F_\alpha = -\int gX \frac{\partial U}{\partial q_\alpha} d\Gamma_s, \tag{II.8}$$

q_α and p_α are the coordinates and momenta of the system, and in (II.7) a summation over α is assumed. The quantity F_α has the meaning of a "force", which represents the action of the surroundings on the system. If there is no correlation between the system and the surroundings, i.e., X=1, then

$$F_\alpha = -\frac{\partial}{\partial q_\alpha}\int gU\,d\Gamma_s,$$

i.e., the force F_α is a potential type force and its action can be represented by an additional term in the Hamiltonian. In the general case the force F_α is nonpotential.

We note that the derivation of equation (II.7) from equation (II.2) is analogous to obtaining the chain of coupled equations in the method of Bogolyubov-Born-Green-Kirkwood-Ivon (B-B-G-K-I) [7].

We introduce the negative of the logarithm of the distribution function $\eta = -\ln f$:

$$f = e^{-\eta}. \tag{II.9}$$

Then equation (II.7) can be written in the form

$$\frac{\partial \eta}{\partial t} + \{\eta, H\} + F_\alpha \frac{\partial \eta}{\partial p_\alpha} = \frac{\partial F_\alpha}{\partial p_\alpha}, \tag{II.10}$$

or, if one introduces the total derivative of the dynamical variable η,

$$\frac{d\eta}{dt} = \frac{\partial \eta}{\partial t} + \{\eta, H\} + F_\alpha \frac{\partial \eta}{\partial p_\alpha}. \tag{II.11}$$

then equation (II.10) can be rewritten in the form

$$\frac{d\eta}{dt} = \frac{\partial F_\alpha}{\partial p_\alpha}. \qquad \text{(II.12)}$$

From this equation it is obvious that if the forces F_α depend on the momenta, then the total derivative of η is non-zero.

For what follows it is necessary to establish the form of the external forces which appear on the right hand side of equation (II.12). We shall consider that they are defined by thermodynamic variables - the temperature, the chemical potential, and the velocity, which characterize the surroundings, and not by the details of the microscopic state of the system. In this case the term $\partial F_\alpha/\partial p_\alpha$ in equation (II.10) is connected with the entropy current, which flows into the system. One can assume for it the expression

$$\frac{\partial F_\alpha}{\partial p_\alpha} = - \oint j_S(x)\, ds, \qquad \text{(II.13)}$$

where $j_S(x)$ is the entropy current density (including the work which is carried out on the system), ds is an element of the surface which bounds the system, for which

$$j_S(x) = \beta(x, t)\left[j_H(x) - \left(\mu(x, t) - \frac{1}{2} m v^2(x)\right) j(x) - v(x, t) \cdot T(x)\right]. \qquad \text{(II.14)}$$

where $j_H(x)$, j(x), and T(x) are the dynamical variables of the currents of energy, particle number, and momentum (see § 19).

One can give arguments which motivate this choice for the sources of entropy, considering a system of discrete sources [8], but essentially this is the basic assumption of the McLennan theory: the assumption that the influence of the surroundings can be characterized by the functions $\beta(x,t)$, $\mu(x,t)$, and $v(x,t)$. In the expression (II.14) the first term corresponds to the contribution of the energy current, the second term to the contribution of the particle current , and the third term is caused by the work done.

In what follows for simplicity we shall first consider the case in which the only process is exchange of energy with a thermostat, i.e., the case in which the equation for η has the form

$$\frac{d\eta}{dt} = - \oint \beta(x, t)\, j_H(x) \cdot ds. \qquad \text{(II.15)}$$

We transform the surface integral in (II.15) into a volume integral by taking into account the law of conservation of energy (19.16):

$$\frac{\partial H(x)}{\partial t} + \nabla \cdot j_H(x) = 0. \tag{II.16}$$

We obtain after an integration by parts

$$\frac{d\eta}{dt} = \frac{d}{dt} \int \beta(x, t) H(x)\, dx - \int \left\{ j_H(x) \cdot \nabla\beta(x) + H(x) \frac{\partial\beta(x, t)}{\partial t} \right\} dx. \tag{II.17}$$

This equation for η has many solutions, because one can always add a solution of the homogeneous equation

$$\frac{d\eta}{dt} = 0. \tag{II.18}$$

In order to obtain the particular solution which interests us, it is necessary to give in addition an initial condition. We shall assume that at t=-∞ the system is found in statistical equilibrium and is described by the Gibbs canonical ensemble:

$$\eta|_{t=-\infty} = \alpha + \beta H. \tag{II.19}$$

The initial condition (II.19) corresponds to the usual situation, in which one proceeds from an equilibrium state of the system and takes it to a non-equilibrium state with the help of an external influence, as in the indirect methods of the theory of the linear reaction (see the beginning of Chapter IV). One can verify that the solution of equation (II.17) with the initial condition (II.19) has the form

$$\eta(t) = \alpha + \int \beta(x, t) H(x)\, dx - \\ - \int \int_{-\infty}^{t} \left[j_H(x, t'-t) \cdot \nabla\beta(x, t') + H(x, t'-t) \frac{\partial\beta(x, t')}{\partial t'} \right] dx\, dt'. \tag{II.20}$$

It is assumed that $\beta(x,t) \to \beta$ for $t \to -\infty$ sufficiently rapidly for the convergence of the integrals. The function

$$f = e^{-\eta} \qquad (II.21)$$

is the required distribution function.

In the more general case, when one takes into account also the exchange of particles and momenta with the surroundings, one obtains formula (21.10e) of Chapter IV.

Thus, the McLennan method [1,2] and the method of the nonequilibrium statistical operator [3-6] lead to identical expressions for the distribution function.

Appendix III

BOUNDARY CONDITIONS FOR STATISTICAL OPERATORS IN THE THEORY OF NONEQUILIBRIUM PROCESSES AND QUASI-AVERAGE METHOD

In the theory of nonequilibrium processes one considers the solutions of the quantum Liouville equation for the statistical operator ρ

$$\frac{\partial \rho}{\partial t} + \frac{1}{i\hbar}[\rho, H] = 0, \qquad (III.1)$$

or of the classical Liouville equation for the distribution function f

$$\frac{\partial f}{\partial t} + \{f, H\} = 0, \qquad (III.2)$$

where {..., ...} denotes the classical Poisson brackets. We shall show, following [1], how to formulate the boundary conditions for the Liouville equation with the help of infinitesimal sources. In what follows we shall discuss the boundary conditions only for the quantum case, because the classical case is analogous to it.

It is very simple to find a formal solution of the Liouville equation (III.1):

$$\rho(t) = U(t, t_0)\, \rho(t_0)\, U^{+}(t, t_0), \qquad (III.3)$$

where $\rho(t_0)$ is an arbitrary statistical operator at the initial moment of time t_0, and $U(t,t_0)$ is the evolution operator. However the formal solution (III.3) is useful only in the case when the initial statistical operator $\rho(t_0)$ is well chosen. For example, if the state is close to statistical equilibrium, then in the Kubo theory one chooses $t_0=-\infty$ and $\rho(-\infty)$ in the form of an equilibrium statistical operator. In the general case the formal solution (III.3) is of little use in describing a nonequilibrium process. Consequently, the fundamental problem of nonequilibrium statistical mechanics is not to find formal exact solutions of the Liouville equation, but to choose correct boundary conditions for the equation, and to construct solutions in the sense of quasi-averages, as in the quantum theory of collisions.

A state with specified average values $\langle P_m \rangle$ can be described by the quasi-equilibrium statistical operator

$$\rho_q = \exp\left\{-\Phi - \sum_m P_m F_m(t)\right\} = \exp\{-S(t,0)\}, \tag{III.4}$$

where

$$\Phi = \ln \mathrm{Sp} \exp\left\{-\sum_m P_m F_m(t)\right\} \tag{III.5}$$

is the Massieu Planck function, and the $F_m(t)$ are the parameters which are conjugate to the average values

$$\langle P_m \rangle_q^t = \mathrm{Sp}(\rho_q P_m). \tag{III.6}$$

The quasi-equilibrium statistical operator (III.4) guarantees satisfaction of the thermodynamic equalities for its parameters Φ, $F_m(t)$, and $S=-\langle \ln \rho_q \rangle_q$, namely

$$\frac{\delta \Phi}{\delta F_m(t)} = -\langle P_m \rangle_q^t, \quad \frac{\delta S}{\delta \langle P_m \rangle_q^t} = F_m(t), \tag{III.7}$$

i.e., the parameters $F_m(t)$ and $\langle P_m \rangle_q^t$ are indeed thermodynamically conjugate[1]. However, the statistical operator (III.4) does not satisfy the Liouville equation and does not describe irreversible processes. As we shall verify below, this operator can be used to formulate the boundary conditions for the Liouville equation (III.1), in a manner which is similar to the way in which the wave function of free particles is used to formulate the boundary

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[1] If the index m takes on discrete values, then the variational derivatives in (III.7) go over into ordinary partial derivatives.

conditions for the Schroedinger equation in the quantum theory of scattering.

The quantum Liouville equation (III.1), as well as the classical (III.2), is symmetric with respect to the transformation of time reversal (in the classical case this implies the replacement t→-t, reversal of the momenta of all particles, and reversal of the direction of the magnetic field). However, the solution of the Liouville equation is unstable with respect to small perturbations which break this symmetry.

We introduce, following [1], into the Liouville equation an infinitesimally small source, satisfying the following requirements:

1) The source breaks the symmetry of the Liouville equation with respect to time reversal, or in other words, it breaks the total isolation of the system. In addition, it approaches zero as $\varepsilon \to 0$, where this limiting transition is carried out after taking the thermodynamic limit.

2) The source picks out the retarded solutions of the Liouville equation. This condition defines the sign of ε; i.e., if one introduces a source as in (I.24), then $\varepsilon > 0$ and $\varepsilon \to +0$. The advanced solutions would give a decrease rather than an increase in entropy [2].

3) The source is equal to zero when ρ is equal to the quasi-equilibrium statistical operator ρ_q (III.4). In the particular case of statistical equilibrium the source must be absent.

Two methods can be proposed to introduce into the Liouville equation infinitesimally small sources which satisfy these requirements.

The first method consists in introducing an infinitesimal source into the right hand side of the Liouville equation (III.1)

$$\frac{\partial \rho_\varepsilon}{\partial t} + \frac{1}{i\hbar}[\rho_\varepsilon, H] = -\varepsilon(\rho_\varepsilon - \rho_q), \tag{III.8}$$

where $\varepsilon \to +0$ after the thermodynamic limiting transition for the calculation of averages. Equation (III.8) is analogous to equation (I.24) of the quantum theory of collisions. This is the only form which satisfies the requirement that the source be linear with respect to ρ_ε and also conditions 1-3. The infinitesimal source in (III.8) indeed breaks the symmetry of equation (III.1) with respect to time reversal, because in this transformation the left hand side of equation (III.8) changes sign, while the right hand side remains unchanged.

We write equation (III.3) in the form

$$\frac{d}{dt}\left(e^{\varepsilon t}\rho_\varepsilon(t, t)\right) = \varepsilon e^{\varepsilon t}\rho_q(t, t), \tag{III.9}$$

where

$$\rho_\varepsilon(t, t) = U^+(t, 0)\,\rho_\varepsilon(t, 0)\,U(t, 0),$$

$$\rho_q(t, t) = U^+(t, 0)\,\rho_q(t, 0)\,U(t, 0),$$

$$U(t, 0) = \exp\left\{\frac{Ht}{i\hbar}\right\} \tag{III.10}$$

(H is independent of time), and the notations

$$\rho_\varepsilon = \rho_\varepsilon(t, 0), \qquad \rho_q = \rho_q(t, 0). \tag{III.11}$$

have been introduced. Integrating equation (III.9) from -∞ to t and assuming that

$$\lim_{t\to-\infty} e^{\varepsilon t}\rho(t, t) = 0,$$

we obtain

$$\rho_\varepsilon(t, t) = \varepsilon \int_{-\infty}^{t} e^{\varepsilon(t_1 - t)}\rho_q(t_1, t_1)\,dt_1 = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t'}\rho_q(t + t', t + t')\,dt'. \tag{III.12}$$

Consequently, the required nonequilibrium statistical operator has the form

$$\rho_\varepsilon = \rho_\varepsilon(t, 0) = \widetilde{\rho_q(t, 0)} = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t'}\rho_q(t + t', t')\,dt', \tag{III.13}$$

where the wavy line above an operator denotes the operation of taking the quasi-invariant part. The statistical operator (III.13) was obtained earlier from other considerations in the article by V. P. Kalashnikov and the author [3]. The nonequilibrium statistical operator (III.13) with an integration by parts can be written conveniently in the form [3]

$$\rho_\varepsilon = \rho_q + \int_{-\infty}^{0} dt'\,e^{\varepsilon t'} \int_{0}^{1} d\tau\, e^{-\tau S(t+t', t')}\,\dot{S}(t + t', t')\,e^{(\tau-1)S(t+t', t')}, \tag{III.14}$$

where

$$\dot{S}(t, 0) = \frac{\partial S(t, 0)}{\partial t} + \frac{1}{i\hbar}[S(t, 0), H],$$

$$\dot{S}(t, t') = U^+(t', 0)\,\dot{S}(t, 0)\,U(t', 0) \tag{III.15}$$

is the entropy production operator.

We choose the parameters $F_m(t)$, which enter into the expression for the entropy operator, from the condition that the averages of the quantities P_m, calculated with the nonequilibrium statistical operator (III.13), coincide with the averages of the same quantities calculated with respect to the quasi-equilibrium statistical operator (III.4):

$$\langle P_m\rangle^t = \langle P_m\rangle^t_q, \tag{III.16}$$

where

$$\langle\ldots\rangle^t = \lim_{\varepsilon\to+0} \mathrm{Sp}\,(\rho_\varepsilon \ldots). \tag{III.17}$$

Then $\langle P_m\rangle^t$ and $F_m(t)$ become conjugate parameters, because

$$\frac{\delta\Phi}{\delta F_m(t)} = -\langle P_m\rangle^t_q = -\langle P_m\rangle^t. \tag{III.18}$$

With the help of the nonequilibrium statistical operator (III.13) one can calculate the average value of any operator A:

$$\langle A\rangle = \lim_{\varepsilon\to+0} \mathrm{Sp}\,(\rho_\varepsilon A) = \prec A\succ. \tag{III.19}$$

Such averages in the terminology of N. N. Bogolyubov [4,5] are called quasi-averages. If one applies the averaging operation (III.19) to the operators $\dot{P}_m$, then, taking into account (III.16), one obtains the transfer equations

$$\frac{\partial}{\partial t}\langle P_m\rangle^t_q = \langle \dot{P}_m\rangle^t = \lim_{\varepsilon\to+0} \mathrm{Sp}\,(\rho_\varepsilon \dot{P}_m) = \prec \dot{P}_m\succ. \tag{III.20}$$

Consequently, the transfer equations are equations for quasi-averages.

The second method of introducing infinitesimal sources is based on the fact that the logarithm of a statistical operator, which satisfies the Liouville equation, also satisfies the Liouville equation

$$\frac{\partial \ln\rho}{\partial t} + \frac{1}{i\hbar}[\ln\rho, H] = 0. \tag{III.21}$$

The parameters $F_m(t)$, which enter into the expression for the entropy operator $S(t,0)$ and the entropy production operator $\dot{S}(t,0)$, are defined, as earlier, from conditions (III.16).

The nonequilibrium statistical operator (III.25) corresponds to the extremum of the information entropy with the additional conditions that the quantities

$$(P_m(t_1))^t = \mathrm{Sp}(\rho P_m(t_1))$$

are fixed for any past moment of time $-\infty < t_1 \leqslant 0$ and that the normalization be preserved (see [7] and § 27 of this book).

The statistical operator (III.25) bears a similarity to the statistical operator of McLennan [8]. The latter may be obtained from (III.25) after an integration by parts, taking into account the conservation laws and discarding surface integrals. The difference between this method and the method of McLennan is that in this method one considers infinitesimal perturbations of the Liouville equation, rather than finite, real perturbations, caused by the thermostat, as are considered by McLennan. One might say that the introduction of boundary conditions for the Liouville equation takes into account in an idealized, conditional way the influence of the thermostat.

which is related to the properties of both the quantum and the classical Poisson brackets. Consequently, infinitesimal sources can be introduced not only in (III.1), but also in (III.21).

If we require that the infinitesimal source satisfy conditions 1-3, and in addition, that it be linear with respect to lnρ, we obtain

$$\frac{\partial \ln \rho_\varepsilon}{\partial t} + \frac{1}{i\hbar}\left[\ln \rho_\varepsilon, H\right] = -\varepsilon\left(\ln \rho_\varepsilon - \ln \rho_q\right), \qquad \text{(III.22)}$$

where ε→+0 after taking the thermodynamic limit. Indeed, the source in (III.22) violates the symmetry of equation (III.21) with respect to time reversal, and it conforms with conditions 1-3. We write equation (III.22) in the form

$$\frac{d}{dt}\left(e^{\varepsilon t} \ln \rho_\varepsilon(t, t)\right) = \varepsilon e^{\varepsilon t} \ln \rho_q(t, t). \qquad \text{(III.23)}$$

Integrating (III.23) from -∞ to t, we obtain

$$\ln \rho_\varepsilon(t, t) = \varepsilon \int_{-\infty}^{t} e^{\varepsilon(t_1 - t)} \ln \rho_q(t_1, t_1)\, dt_1 = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t'} \ln \rho_q(t + t', t + t')\, dt', \qquad \text{(III.24)}$$

and, consequently, the required nonequilibrium statistical operator has the form

$$\rho_\varepsilon = \rho_\varepsilon(t, 0) = \exp\left\{\widetilde{\ln \rho_q(t, 0)}\right\} = \exp\left\{-\varepsilon \int_{-\infty}^{0} dt'\, e^{\varepsilon t'} \ln \rho_q(t + t', t')\right\}, \qquad \text{(III.25)}$$

where ε→+0 after taking the thermodynamic limit for the calculation of averages.

The nonequilibrium statistical operator (III.25) was obtained earlier in articles by the author [2-6] from other considerations. It is convenient to write this operator, after an integration by parts, in the form

$$\rho_\varepsilon = \exp\left\{-\widetilde{S(t, 0)}\right\} = \exp\left\{-S(t, 0) + \int_{-\infty}^{0} dt'\, e^{\varepsilon t'}\, \dot{S}(t + t', t')\right\}. \qquad \text{(III.26)}$$