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Lectures on statistical physics

by

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LECTURES ON STATISTICAL PHYSICS

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translated from the Russian and edited by D. Leites

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Author's Preface

I read this lecture course in 1966–67 at the Department of Mechanics and Mathematics of the Moscow State University. Currently statistical physics is more than 90% heuristic science. This means that the facts established in this science are not proved, as a rule, in the mathematical meaning of this word although the arguments leading to them are quite convincing.

A few rigorous results we have at the moment usually justify heuristic arguments. There is no doubt that this situation will continue until rigorous mathematical methods will embrace the only branch of statistical physics physicists do not represent sufficiently clearly namely the theory of phase transitions.

I think that at the moment statistical physics has not yet found an adequate mathematical description. Therefore I believe that the classical heuristic arguments developed starting with Maxwell and Gibbs did not lose their value. The rigorous results obtained nowadays are only worthy I think only if they can compete in the simplicity and naturalness with the heuristic arguments they are called to replace. The classical statistical physics has such results: first of all these are theorems due to Van Hove, and Lee and Yang on the existence of thermodynamical potential and Bogolyubov–Khatset–Ruelle theorem on existence of correlation functions. The quantum statistical physics has no similar results yet.

The above point of view was the cornerstone of this course. I tried to present the material based on the classical heuristic arguments paying particular attention to the logical sequence. The rigorous results are only given where they are obtained by sufficiently natural methods. Everywhere the rigorous theorems are given in the assumptions that maximally simplify the proof. The course is by no means an exhaustive textbook on statistical physics. I hope however, that it will be useful to help the reader to comprehend the journal and monographic literature.

The initial transcription of the lectures was performed by V. Roitburd to whom I am sincerely thankful. Thanks are also due to R. Minlos, who wrote at my request Appendix 3 with a review of rigorous results.

F. Berezin, 1972

Editor's preface

It was for a long time that I wanted to see these lectures published: To me, they are more lucid than other books on the same topic and much shorter. The recent lectures by Minlos [M1] is the only exception and, what is unexpected and nice for the reader, these two books practically do not intersect and both are up to date.

In the original preprint (1972), bibliographical references were absent. I appended the book with the necessary (to my mind) minimum, in particular, the latest works (mainly books). I also cited a report from Math. Reviews clearly illustrating that a number of open problems tackled in this book is left to the reader.

In a recent book by V. V. Kozlov [Koz], where in a lively and user-friendly way there are discussed the ideas of Gibbs and Poincaré not much understood (or not understood at all) during the past 100 years since they had been published, these notes of Berezin's lectures are given their due. In particular, Kozlov gives a reference (reproduced here) to an answer to one of Berezin's questions obtained 30 years after it was posed.

On notations. Although some of Berezin's notations are not conventional now (the English tr for trace pushed out the German sp for Spur) I always kept in mind, while editing, an anecdote on a discussion of F. M. Dostoevsky with his editor:

"Fedor Mikhailovich! You wrote here: 'In the room stood a round table of oval form'. This is not quite... You know..."

Dostoevsky mused and retorted:

"Yes, you are right. However, leave, as it is."

Therefore, although in modern texts the notation $\{f_n\}$ denotes, or should denote, the set consisting of one element — f_n — only and not of all vectors f_n for all possible n, whereas in Berezin's lectures, it is just the other way round, I did not edit this: the geniuses has right to insist on their own style. Few similar shortcomings of the lecture style that still remain in this transcript, should not, I think, deter the reader.

D. Leites, 2006

Part I

CLASSICAL STATISTICAL PHYSICS

§ 1. Background from Classical Mechanics

1.1. Properties of trajectories of mechanical systems. We will only consider so-called *conservative systems*, i.e., the ones whose energy does not depend on time. Each state of a mechanical dynamical system with n degrees of freedom is described by a point of a $2n$-dimensional phase space. The customary notations of the coordinates of the phase space are usually denoted by $p = (p_1, \dots, p_n)$ (*generalized momenta*) and $q = (q_1, \dots, q_n)$ (*generalized positions*). To each physical quantity (more precisely, to each time independent physical quantity) there corresponds a function $f(p, q)$ in the phase space. In what follows, speaking about a physical quantity we always have in mind the corresponding function.

The energy whose function is usually denoted by $H(p, q)$ plays a particular role. The function $H(p, q)$ is called the *Hamiltonian function* or *Hamiltonian*. The evolution of the system with time is given by the differential equations

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H}{\partial p}. \tag{1.1}$$

Hereafter we assume that the existence and uniqueness theorem for any initial conditions and any t holds for the system (1.1). The following

properties of the system (1.1) will be needed in what follows:

1) Let $p(t, p^0, q^0)$, $q(t, p^0, q^0)$ be a solution of the system (1.1) with the initial conditions

$$p(0, p^0, q^0) = p^0, \quad q(0, p^0, q^0) = q^0. \tag{1.2}$$

Let further $f(p, q)$ be a function constant along the trajectories of the system, i.e.,

$$f(p(t, p^0, q^0), q(t, p^0, q^0)) = f(p^0, q^0). \tag{1.3}$$

Physical quantities possessing this property are called *conserved* ones or *integrals of motion*.

If f is differentiable, then differentiating equality (1.3) with respect to t and taking (1.1) into account we deduce that f satisfies the partial differential equation

$$\sum_i \Big(\frac{\partial f}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial f}{\partial q_i} \frac{\partial H}{\partial p_i} \Big) = 0. \tag{1.4}$$

The expression in the left-hand side of this equation is called the *Poisson bracket* and denoted [1] by $[f, H]$. The functions satisfying condition (1.4), i.e., such that $[f, H] = 0$, are said to be *commuting* with H. It is easy to verify that condition (1.4) is not only necessary but also sufficient for the differentiable function f be an integral of motion.

Obviously, if f is an integral of motion, then the trajectory of a system possessing at least one common point with the surface $f(p, q) = \text{const}$ entirely belongs to this surface. Each conservative dynamical system possesses at least one integral of motion. The energy $H(p, q)$ is such an integral. For the proof, it suffices to verify, due to the above, that the Poisson bracket $[H, H]$ vanishes. Therefore each trajectory of the system lies on a certain surface of constant energy $H(p, q) = E$. These surfaces play a most important role in statistical physics.

2) Solutions of the system (1.1) form a one-parametric family of self-maps of the phase space:

$$(p^0, q^0) \mapsto (p(t, p^0, q^0), q(t, p^0, q^0)). \tag{1.5}$$

The existence and uniqueness theorem implies that the map (1.5) is one-to-one at every t. Since H does not depend on t, and therefore so do the functions $\dfrac{\partial H}{\partial q}$ and $\dfrac{\partial H}{\partial p}$ in the right-hand side of (1.1), it follows that the maps (1.5) constitute a one-parameter group:

$$\begin{aligned} p(t, p(\tau, p^0, q^0), q(\tau, p^0, q^0)) &= p(t + \tau, p^0, q^0), \\ q(t, p(\tau, p^0, q^0), q(\tau, p^0, q^0)) &= q(t + \tau, p^0, q^0). \end{aligned}$$

3) The Jacobian of the map (1.5) is equal to 1:

$$\frac{D(p(t, p^0, q^0), q(t, p^0, q^0))}{D(p^0, q^0)} = 1. \tag{1.6}$$

This equality means that the maps (1.5) preserve the volume element

$$dp\, dq = dp^0\, dq^0,$$

[1] Also by $\{f, H\}$.

where

$$dp\,dq = \prod_{i=1}^{n} dp_i\,dq_i \quad \text{and} \quad dp^0\,dq^0 = \prod_{i=1}^{n} dp_i^0\,dq_i^0.$$

The condition (1.6) is equivalent to the fact that, for any integrable function $f(p,q)$, we have

$$\int f(p(t,p^0,q^0),q(t,p^0,q^0))\,dp^0\,dq^0 = \int f(p,q)\,dp\,dq.$$

Properties 2) and 3) follow from the general theorems of the theory of differential equations. Let us recall these theorems. For a system of equations

$$\frac{dx_i}{dt} = f_i(x_1,\dots,x_n), \tag{1.7}$$

where the f_i do not depend on t, we have

1) The solutions $x_i = x_i(t,x_1^0,\dots,x_n^0)$ such that $x_i(0,x_1^0,\dots,x_n^0) = x_i^0$ form a one-parameter transformation group of the n-dimensional space

$$x_i^0 \mapsto x_i(t,x_1^0,\dots,x_n^0).$$

2) The Jacobian of the map (1.7) is equal to

$$\left|\frac{\partial x_i}{\partial x_j^0}\right| = e^{\int_0^t \sum \frac{\partial f_i}{\partial x_i}\,dt}$$

(*Liouville's theorem*).

For the Hamiltonian systems, we have

$$\sum \frac{\partial f_i}{\partial x_i} = \sum\Big(\frac{\partial^2 H}{\partial p_i \partial q_i} - \frac{\partial^2 H}{\partial p_i \partial q_i}\Big) = 0,$$

and therefore the maps (1.5) preserve the volume.

1.2. An invariant measure on the surfaces of constant energy. Denote by S_E the surface of constant energy $H(p,q) = E$, let ξ be a point on S_E and $\xi(t,\xi_0)$ a trajectory through ξ_0.

A measure $d\xi$ on S_E is said to be *invariant* if, for any integrable function $f(\xi)$ and any t, the function $f(\xi(t,\xi_0))$ is integrable with respect to ξ_0 and

$$\int f(\xi(t,\xi_0))\,d\xi_0 = \int f(\xi)\,d\xi. \tag{1.8}$$

An *equivalent definition*: A measure is said to be *invariant* if, for any measurable set A and any t, the set A_t obtained from A under the action of the dynamical system 1.7 through time t, and measures of A and A_t are equal.

To see that the second definition follows from the first one, take for $f(\xi)$ the characteristic function of A. The first definition directly follows from the second one by the definition of Lebesgue's integral.

Suppose that the surface of constant energy S_E is a manifold. Then it can be covered by a system of neighborhoods U_α, each of which is homeomorphic to a ball in a $(2n-1)$-dimensional Euclidean space. Let $\xi_1, \dots, \xi_{2n-1}$ be local coordinates in U_α. If the measure in each U_α is of the form

$$d\xi = \omega(\xi)\, d\xi_1 \dots d\xi_{2n-1},$$

where $\omega(\xi)$ is a Lebesgue-integrable in U_α function, then the measure $d\xi$ in S_E will be referred to *absolutely continuous with respect to Lebesgue measure*. If the measure in S_E is absolutely continuous with respect to Lebesgue measure, then it is invariant if (1.8) holds only for continuous functions with compact support. Moreover, it suffices to consider functions that are non-zero only within a coordinate patch. This follows from the fact that if the measure is absolutely continuous with respect to Lebesgue measure, then such functions are dense in $L_1(S_E)$.

The following is the main theorem of this section.

1.3. Theorem. *If the Hamiltonian function $H(p,q)$ is continuously differentiable, then the non-singular surface of constant energy is a manifold and it possesses an invariant measure absolutely continuous with respect to Lebesgue measure.*

Recall that the surface $H(p,q) = E$ is said to be *non-singular*, if $\dfrac{\partial H}{\partial p_i}$, $\dfrac{\partial H}{\partial q_i}$ do not vanish anywhere on the surface for all i.

The fact that under these conditions the surface S_E is a manifold follows from the implicit function theorem. Each point $\xi \in S_E$ possesses a neighborhood U_ξ in which the equation $H(p,q) = E$ is solvable for one of the coordinates. Let, for definiteness' sake, this coordinate be p_1. Then, in U_ξ, the equation of S_E takes the form

$$p_1 = f(p_2, \dots, p_n, q_1, \dots, q_n),$$

where $p_2, \dots, p_n,\ q_1, \dots, q_n$ are local coordinates in U_ξ. Let $f(p,q)$ be a continuous function, $\varphi(\xi)$ — its value on S_E. Consider the integral

$$I_h = \frac{1}{h} \int\limits_{E \le H(p,q) \le E+h} f(p,q)\, dp\, dq, \tag{1.9}$$

over the part of the phase space confined between S_E and S_{E+h}. Let us show that the limit $\lim\limits_{h\to 0} I_h$ exists. For this, in the phase space, in a neighborhood of S_E, introduce new coordinates E and ξ, where ξ is a point on the surface S_E (this can be performed since S_E is non-singular.) In new coordinates the integral (1.9) takes the form

$$I_h = \frac{1}{h}\int\limits_E^{E+h}\left(\int\limits_{S_E} f(\xi,\varepsilon)\omega(\xi,\varepsilon)\,d\xi_1\ldots d\xi_{2n-1}\right)d\varepsilon,$$

where ξ_i are coordinates of the part of S_E outside which $\varphi(\xi)=0$, and $\omega(\xi,\varepsilon)$ is the Jacobian. Since S_E is non-singular, it follows that $\omega(\xi,\varepsilon)$ is a continuous function.

Due to continuity of the integrand the integral I_h has a limit as $h\to 0$. This limit is equal to

$$I = \int f(\xi,E)\omega(\xi,E)\,d\xi_1\ldots d\xi_{2n-1} = \int \varphi(\xi)\,d\xi. \tag{1.10}$$

It follows from (1.10) that I is an integral with respect to a measure on S_E which is absolutely continuous with respect to Lebesgue measure.

Observe that, thanks to invariance of the measure $dp\,dq$ and surfaces S_E and S_{E+h}, the integral (1.9) possesses a property similar to (1.8):

$$\frac{1}{h}\int\limits_{E\le H(p,q)\le E+h} f(p(t,p^0,q^0),q(t,p^0,q^0))\,dp^0\,dq_0 = \\ = \frac{1}{h}\int\limits_{E\le H(p,q)\le E+h} f(p,q)\,dp\,dq. \tag{1.11}$$

Passing in this equality to the limit as $h\to 0$ we deduce that the integral (1.10) also possesses property (1.8). Therefore the measure $d\xi$ defined from (1.10) is invariant.

One can also express the integral (1.10) in the initial coordinates p and q:

$$I = \int f(p,q)\delta(H(p,q)-E)\,dp\,dq, \tag{1.12}$$

where δ is Dirac's δ-function. The expression of this integral in the form (1.12) is very convenient and will be constantly used in what follows (the formal properties of δ-function easily imply that (1.12) and (1.10) coincide.)

One can absolutely analogously prove that if $K_1, \dots, K_\alpha$ is an arbitrary set of independent continuously differentiable first integrals of the system and the surface singled out by the system of equations

$$K_1 = k_1, \ \dots, \ K_\alpha = k_\alpha$$

is non-singular, then there exists an invariant measure absolutely continuous with respect to Lebesgue measure, and the integral with respect to this measure can be expressed in the form

$$\int f(p,q)\delta(K_1(p,q) - k_1) \dots \delta(K_\alpha(p,q) - k_\alpha)\, dp\, dq.$$

1.4. Ergodic hypothesis. Let on a set M with measure μ a one-parameter group G of measure preserving transformations act. The triple (M, μ, G) is called a *dynamical system*. A dynamical system is called *ergodic* if every invariant measurable subset of M is either of measure zero or differs from the whole M by a set of measure zero.

Let M be the surface singled out by the system of equations

$$K_1 = k_1, \ \dots, \ K_\alpha = k_\alpha,$$

where the $K_i(p,q)$ are the first integrals of the mechanical system. By the above, if M is non-singular, then it possesses an invariant measure and therefore a dynamical system arises.

Question. *Is it ergodic?*

To answer this question it is extremely important to justify equilibrium statistical physics. The assumption on ergodicity of M is called the *ergodic hypothesis*.

Obviously, the most important is the case where $M = S_E$ is the surface of constant energy. We will discuss relations of the ergodic hypothesis with justification of statistical physics in the next section.

1.5. A relation of the mean with respect to time and the mean over the surface of constant energy (microcanonical mean). First of all, let us formulate the physical hypothesis concerning the properties of the devices that investigate the systems consisting of microscopic subsystems.

Our devices do not measure the instant values of physical quantities but rather their mean values

$$\frac{1}{T}\int_0^T f(q(t,p^0,q^0), p(t,p^0,q^0))\, dt, \tag{1.13}$$

where $\big(q(t,p^0,q^0),p(t,p^0,q^0)\big)$ is the trajectory of the system passing through the point (p^0,q^0) at $t=0$. The time T of relaxation of the devices is essentially greater than the lifespan of the processes, so the mean (1.13) can be replaced by the limit

$$\lim_{T\to\infty}\frac{1}{T}\int\limits_0^T f(p(t,p^0,q^0),q(t,p^0,q^0))\,dt, \tag{1.14}$$

which is called *the mean of f with respect to time*.

A mathematical discussion is possible starting from here.

Suppose that a dynamical system that appears on the surface of constant energy S_E is ergodic and for any E the surface S_E possesses a finite measure. In this case the *von Neumann's ergodic theorem* implies that the mean with respect to time (1.14) is equal to the mean over the surface S_E on which this trajectory lies. Let us formulate von Neumann's theorem.

Theorem. *Let there be given an ergodic dynamical system on a set M with finite measure $\mu(M)<\infty$ and let $x(y,t)$ be a trajectory of this system passing through a point y. Then, for any function $f\in L^2(M,\mu)$, there exists a limit (with respect to $L^2(M,\mu)$-convergence) of functions $f_T(y)=\frac{1}{T}\int\limits_0^T f(x(y,t))\,dt$, equal to*

$$\lim_{T\to\infty}\frac{1}{T}\int\limits_0^T f(x(y,t))\,dt=\frac{1}{\mu(M)}\int\limits_M f(x)\,d\mu(x).$$

The limit does not depend on the initial point y.

In our conditions this theorem implies that, for a given ergodic system, we have [2)]

$$\lim_{T\to\infty}\frac{1}{T}\int\limits_0^T f(p(t,p^0,q^0),q(t,p^0,q^0))\,dt=\frac{\int f(p,q)\delta(H(p,q)-E)\,dp\,dq}{\int\delta(H(p,q)-E)\,dp\,dq}. \tag{1.15}$$

The right-hand side of (1.15) is the mean of f on the surface of constant energy. According to the accepted physical terminology this mean is called the *microcanonic* one.

[2)] Recall that, by a hypothesis above, we have

$$\int\delta(H(p,q)-E)\,dp\,dq<\infty.$$

Chapter 1

THE ENSEMBLE OF MICROSCOPIC SUBSYSTEMS

This chapter is devoted to the study of mechanical systems consisting of a huge number N of weakly interacting identical microscopic subsystems. Unlike the whole system, each subsystem is described by few parameters. We suppose that no subsystem interacts with any objects outside the system. *Microscopic nature of an individual subsystem* means that it does not depend on the total number N of subsystems in the ensemble. The study of ensembles of microscopic subsystems is mainly of methodological value. The most popular in statistical physics ensembles (real gases) consist of macroscopic subsystems. For an example of ensemble of microscopic subsystems (with certain reservations discussed in § 5)), we can take an ideal gas confined in a macroscopic vessel, e.g., in a closed thermos. For an individual microscopic subsystem we can take a molecule of the gas. The number of subsystems [1)] is of the order of magnitude of the Avogadro number $\sim 10^{27}$.

§ 2. Physical assumptions. Further discussion of Ergodic Hypothesis. Gibbs's distribution

2.1. The microcanonical mean. We will use the following notation: We denote the total set of all phase variables of the system by $(\mathcal{P}, \mathcal{Q})$, whereas the set of phase variables describing the α-th subsystem will be denoted by $(p^{(\alpha)}, q^{(\alpha)})$. Therefore,

$$(p^{(\alpha)}, q^{(\alpha)}) = \big\{(p_i^{(\alpha)}, q_i^{(\alpha)})\big\}, \text{ where } i = 1, \dots, n.$$

[1)] Let us give one more definition of the microscopic subsystem which apparently better describes the physical nature of the situation. The subsystem is said to be *microscopic* if the number of its degrees of freedom does not depend on the total number of subsystems in the ensemble. Under such a definition the ideal gas becomes the ensemble of microscopic subsystems without any reservations.

I did not use this definition since I do not know how to generalize it to the quantum case. I thought that different definitions of microscopic subsystem for the classical and quantum cases would violate the uniformity of my narrative.

In this notation, $(\mathcal{P}, \mathcal{Q}) = \{(p_i^{(\alpha)}, q_i^{(\alpha)})\}$, where $\alpha = 1, \dots, N$, $i = 1, \dots, n$. Let $d\mathcal{P}\, d\mathcal{Q}$ denote the volume element in the phase space of the system

$$d\mathcal{P}\, d\mathcal{Q} = \prod_{i,\alpha} dp_i^{(\alpha)} dq_i^{(\alpha)}.$$

In this notation, the Hamiltonian of the system takes the form

$$\mathcal{H}_\varepsilon(\mathcal{P}, \mathcal{Q}) = \sum_{\alpha=1}^{N} H(p^{(\alpha)}, q^{(\alpha)}) + v_\varepsilon(\mathcal{P}, \mathcal{Q}), \tag{2.1}$$

where $H(p^{(\alpha)}, q^{(\alpha)})$ is the Hamiltonian of an individual subsystem and $v_\varepsilon(\mathcal{P}, \mathcal{Q})$ is the interaction energy of subsystems which is supposed to be very small. The parameter ε is introduced for our convenience in such a way that $\lim\limits_{\varepsilon \to 0} v_\varepsilon(\mathcal{P}, \mathcal{Q}) = 0$. Let

$$\mathcal{H} = \sum_{\alpha=1}^{N} H(p^{(\alpha)}, q^{(\alpha)}) \tag{2.2}$$

denote the Hamiltonian obtained from $\mathcal{H}_\varepsilon$ as $\varepsilon \to 0$. The function $\mathcal{H}$ is the Hamiltonian of the system consisting of non-interacting subsystems. This system is not ergodic [2)].

We will make the following two assumptions:

1) There exists a limit of means with respect to time as $\varepsilon \to 0$

$$\lim_{\varepsilon \to 0} \lim_{T \to \infty} \frac{1}{T} \int_0^T f(\mathcal{P}_\varepsilon(t), \mathcal{Q}_\varepsilon(t))\, dt, \tag{2.3}$$

where $\mathcal{P}_\varepsilon(t)$ and $\mathcal{Q}_\varepsilon(t)$ are trajectories of the system with Hamiltonian $\mathcal{H}_\varepsilon$ (our assumption that the interaction between the subsystems is"small" means that the mean $\lim\limits_{T \to \infty} \frac{1}{T} \int\limits_0^T f(\mathcal{P}_\varepsilon(t), \mathcal{Q}_\varepsilon(t))\, dt$ is, with high accuracy, equal to the limit (2.3).

2) The system is ergodic for $\varepsilon \neq 0$. Therefore

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T f(\mathcal{P}_\varepsilon(t), \mathcal{Q}_\varepsilon(t))\, dt = \frac{\int f(\mathcal{P}, \mathcal{Q}) \delta(\mathcal{H} - E)\, d\mathcal{P}\, d\mathcal{Q}}{\int \delta(\mathcal{H} - E)\, d\mathcal{P}\, d\mathcal{Q}}. \tag{2.4}$$

[2)] Obviously, for the system with Hamiltonian (2.2), the functions $H_\alpha = H(p^{(\alpha)}, q^{(\alpha)})$ are integrals of motion. The surface of constant energy S_E is fibrated into invariant sets singled out by the equations $H(p^{(\alpha)}, q^{(\alpha)}) = h_\alpha$ $(\alpha = 1, \dots, N)$. Therefore S_E possesses invariant subsets of non-zero and non-full measure. For example, the subset of points $(\mathcal{P}, \mathcal{Q}) \in S_E$, such that $a < H(p^{(1)}, q^{(1)}) < b$ for an appropriate choice of a and b.

The right-hand side of (2.4) is continuous with respect to ε at $\varepsilon = 0$, and therefore

$$\lim_{\varepsilon\to 0}\lim_{T\to\infty}\frac{1}{T}\int\limits_0^T f(\mathcal{P}_\varepsilon(t),\mathcal{Q}_\varepsilon(t))\,dt = \frac{\int f(\mathcal{P},\mathcal{Q})\delta(\mathcal{H}-E)\,d\mathcal{P}\,d\mathcal{Q}}{\int \delta(\mathcal{H}-E)\,d\mathcal{P}\,d\mathcal{Q}}, \tag{2.5}$$

where $\mathcal{H}$ is the Hamiltonian of the (non-ergodic!) system consisting of non-interacting subsystems.

Thus the mean with respect to time of f is replaced by its microcanonic mean (2.5) with Hamiltonian function $\mathcal{H}$ that generate highly non-ergodic system.

2.2. Gibbs's distribution. Highly interesting for statistical physics are the mean values of quantities that behave similarly to energy. (Such quantities are sometimes called *summatory*):

$$\mathcal{F}^{(N)}(\mathcal{P},\mathcal{Q}) = \frac{1}{N}\sum f(p^{(\alpha)},q^{(\alpha)}). \tag{2.6}$$

Let $\varepsilon = \dfrac{E}{N}$ be the mean energy of the subsystem. In what follows we pass to the limit as $N\to\infty$. It is essential that ε does not depend on N. The microcanoniocal mean of $\mathcal{F}(\mathcal{P},\mathcal{Q})$ is equal to

$$\overline{\mathcal{F}}_E^{(N)} = \frac{\int \mathcal{F}(\mathcal{P},\mathcal{Q})\delta(\mathcal{H}(\mathcal{P},\mathcal{Q})-N_\varepsilon)\,d\mathcal{P}\,d\mathcal{Q}}{\int \delta(\mathcal{H}(\mathcal{P},\mathcal{Q})-N_\varepsilon)\,d\mathcal{P}\,d\mathcal{Q}}.$$

Taking into account the form of $\mathcal{F}_E^{(N)}$, we see that

$$\overline{\mathcal{F}}_E^{(N)} = \int f(p,q)\rho_N(p,q)\,dp\,dq, \tag{2.7}$$

where

$$\rho_N(p,q) = \frac{\int \delta\Bigl(\sum\limits_{\alpha=1}^{N-1} H(p^{(\alpha)},q^{(\alpha)}) + H(p,q) - N_\varepsilon\Bigr)\prod\limits_{\alpha=1}^{N-1} dp^{(\alpha)}\,dq^{(\alpha)}}{\int \delta\Bigl(\sum\limits_{\alpha=1}^{N-1} H(p^{(\alpha)},q^{(\alpha)}) - N_\varepsilon\Bigr)\prod\limits_{\alpha=1}^{N-1} dp^{(\alpha)}\,dq^{(\alpha)}}. \tag{2.8}$$

It turns out there exists a limit $\rho(p,q) = \lim\limits_{N\to\infty}\rho_N(p,q)$. Since N is very big, it follows that the mean (2.7) coincides, with good accuracy, with its limit at $N\to\infty$ which is equal to [3)]

$$\overline{\mathcal{F}}_{\text{microcan.}} = \overline{f}_{\text{Gibbs}} = \int f(p,q)\rho(p,q)\,dp\,dq.$$

[3)] in § 4 we will estimate the rate of convergence of $\int f\rho_N\,dp\,dq$ to its limit

The function $\rho(p,q)$ is the density of the probability distribution called *Gibbs's distribution* or *the canonical distribution*. We will compute this function in what follows. It turns out to be equal to

$$\rho(p,q) = \frac{e^{-\beta H(p,q)}}{\int e^{-\beta H(p,q)}\, dp\, dq},$$

where the parameter β is determined from the equation

$$\varepsilon = \frac{\int H e^{-\beta H}\, dp\, dq}{\int e^{-\beta H}\, dp\, dq}.$$

The described above passage to the limit as $N \to \infty$ is often called"*thermodynamical*", and various quantities obtained under passage to this limit are called"*thermodynamical limits*". In case where the subsystem possesses apart from energy the first integrals $K_1, \dots, K_s$ and the interaction v'_ε is such that the quantities

$$\mathcal{K}_i = K_i(p_1, q_1) + K_i(p_2, q_2) + \dots$$

are preserved and on the surfaces $\mathcal{K}_i = Nk_i$ the ergodic dynamical systems appear, the microcanonic mean (2.5) is replaced by

$$\overline{\mathcal{F}}^{(N)}_{E,K_2,\dots,K_S} = \frac{\int \mathcal{F}\delta(\mathcal{H} - N_\varepsilon)\delta(\mathcal{K}_1 - N_{k_1}) \dots \delta(\mathcal{K}_s - N_{k_s})\, d\mathcal{P}\, d\mathcal{Q}}{\int \delta(\mathcal{H} - N_\varepsilon)\delta(\mathcal{K}_1 - N_{k_1}) \dots \delta(\mathcal{K}_s - N_{k_s})\, d\mathcal{P}\, d\mathcal{Q}}.$$

The corresponding density of the Gibbs's distribution is equal to

$$\rho(p,q) = \frac{e^{-\beta(H(p,q)+\mu_1 K_1(p,q)+\dots+\mu_S K_S(p,q))}}{\int e^{-\beta(H(p,q)+\mu_1 K_1(p,q)+\dots+\mu_S K_S(p,q))}\, dp\, dq},$$

where the parameters β and μ_i are determined from the equations

$$\int H(p,q)\rho\, dp\, dq = \varepsilon, \quad \int K_i \rho\, dp\, dq = k_i.$$

2.3. Discussion of hypotheses. First of all, we note that the system under the study is very close to a non-ergodic one and it is precisely this definitely non-ergodic system consisting of non-interacting subsystems that plays the main role for us. The nature of interactions between subsystems is irrelevant, only the fact that it is"small" is important. Therefore theorems on ergodicity of a certain concrete dynamical system are immaterial [4)].

To justify the passage from the mean with respect to time to the mean over the surface of constant energy ,the following type of theorem is sufficient:

[4)] In what follows, we will see that the systems consisting of macroscopic subsystems is a totally different matter.

2.3.1. Hypothesis (Conjecture). *Consider dynamical systems with Hamiltonian functions of the form $H = H_0 + V$, where H_0 is a fixed function and V is a variable function running over a topological space. For an everywhere dense set of functions V, the dynamical systems with Hamiltonian $H = H_0 + V$ are ergodic.*

Even a more rough question is of interest.

Question. *Is it true that, in a natural topology in the space of dynamical systems, the ergodic systems constitute a dense set?*

Returning to the above formulated hypothesis, let us give an example of Hamiltonian functions interesting from this point of view:

$$\begin{aligned} &H = H_0 + \varepsilon V(q), \quad \text{where } \varepsilon > 0, \\ &H_0 = (q_1^0 + \omega p_1^2) + \ldots + (q_n^2 + \omega p_n^2), \end{aligned} \tag{2.9}$$

and $V(q) \geq 0$ is a 4-th degree polynomial in totality of the variables $q_1, \ldots, q_n$. The coefficients of non-negative 4-th degree polynomials constitute a set $\mathcal{D}$ in the finite-dimensional space of the coefficients of all 4-th degree polynomials in n variables.

2.3.2. Question. *Is it true that, for all points of $\mathcal{D}$, except a set of Lebesgue measure zero (or perhaps the set consisting of the union of manifolds of smaller dimension), the systems are ergodic?* [5)]

2.3.3. Hypothesis. *In the microcanonical mean (2.4) one can pass to the limit as $\varepsilon \to 0$, and the microcanonical mean (2.5) is the limit.*

This hypothesis is a precise mathematical equivalent of the physical assumption that the interactions are "small". The hypothesis can be justified for appropriate potentials with the help of usual theorems on passage to the limit under the integral sign. For example, for Hamiltonian functions of the form (2.9), such a passage is definitely possible.

The above described point of view on the relation between the mean with respect to time and over the surface of constant energy is traditional though it is very seldom expressed with sufficient clarity.

In this relation a principal question arises: Assume that our system can be approximated by ergodic systems. Consider the mean with respect to

[5)] For the answer obtained 30 years after Berezin posed the question, see [U]; for an interpretation, see [Koz]. — *Ed.*

time

$$\varphi(p,q,T)=\frac{1}{T}\int\limits_0^T F(p(t),q(t))\,dt,$$

where $(p(t),q(t))$ is the trajectory of the system corresponding to the parameter ε. Will the rate with which φ tends to the limit as $T\to\infty$ decay fast as $\varepsilon\to 0$? If this were so for the systems with Hamiltonians of the form (2.1) and function F of the form (2.6) then the above arguments would lose a good deal of their physical meaning.

§ 3. An heuristic deduction of the Gibbs distribution

3.1. A combinatorial problem. Our nearest goal is the proof of existence of the limit $\rho(p,q)=\lim\limits_{N\to\infty}\rho_N(p,q)$ and the equality

$$\rho(p,q)=\frac{e^{-\beta H(p,q)}}{\int e^{-\beta H(p,q)}\,dp\,dq},\tag{3.1}$$

where ρ_N is given by formula (2.8).

In this section, we use simple graphic arguments; in the next one we give a rigorous proof.

Let us split the phase space of the subsystem into cubic cells with side l. We will only consider the states of subsystems for which the points depicting them lie strictly inside a cell. To each such system we assign a state whose point coincides with the center of the cell.

In this way, we obtain an auxiliary lattice subsystem. It is intuitively clear that the auxiliary system consisting of such subsystems turns into the initial one as $l\to 0$.

Hereafter and to the end of the section, (p,q) denotes a point of the lattice whose vertices are the centers of the cells.

Let $(\mathcal{P},\mathcal{Q})=(p^{(1)},\dots,p^{(N)},q^{(1)},\dots,q^{(N)})$ be a state of the total system and let among the coordinates $p^{(\alpha)}$, $q^{(\alpha)}$ there be $N(p,q)$ equal with each other and equal to p and q, respectively.

The occupation number $N(p,q)$ is equal to the number of subsystems whose states are depicted by the points lying inside the cell centered at (p,q). Obviously

$$\sum N(p,q)=N.\tag{3.2}$$

Further, if the point $(\mathcal{P},\mathcal{Q})$ lies on the surface S_E, then its occupation number satisfies, in addition to (3.2), the relation

$$\sum N(p,q)H(p,q)=N_\varepsilon,\tag{3.3}$$

obtained from the equation $\sum H(p^{(\alpha)}, q^{(\alpha)}) = E$ of the surface S_E by simplification. The parameter $\varepsilon = \dfrac{E}{N}$ can be interpreted as the *mean energy of the subsystem*.

The set $\{N(p,q)\}$ of non-negative integers satisfying conditions (3.2) and (3.3) is said to be *admissible*.

Obviously, each admissible set $\{N(p,q)\}$ is the set of occupation numbers for a certain state $(\mathcal{P}, \mathcal{Q}) \in S_E$.

The mean of a function $\mathcal{F}$ over the surface S_E is equal to

$$\overline{\mathcal{F}}_E = \frac{\sum\limits_{(\mathcal{P},\mathcal{Q})\in S_E} \mathcal{F}(\mathcal{P},\mathcal{Q})}{\sum\limits_{\mathcal{P},\mathcal{Q}\in S_E} 1}. \tag{3.4}$$

If $\mathcal{F} = \mathcal{F}^{(N)}(\mathcal{P},\mathcal{Q}) = \dfrac{1}{N}\sum f(p^{(\alpha)}, q^{(\alpha)})$, then after simplification we get

$$\mathcal{F}^{(N)}(\mathcal{P},\mathcal{Q}) = \frac{1}{N}\sum_{p,q} N(p,q) f(p,q), \tag{3.5}$$

where $N(p,q)$ are the occupation numbers corresponding to the point $(\mathcal{P},\mathcal{Q})$.

Obvious combinatorial considerations make it obvious that the number of distinct states $(\mathcal{P},\mathcal{Q})$ with the same set $\{N(p,q)\}$ of occupation numbers is equal to $\dfrac{N!}{\prod\limits_{p,q} N(p,q)!}$. Therefore

$$\sum_{(\mathcal{P},\mathcal{Q})\in S_E} \mathcal{F}^{(N)}(\mathcal{P},\mathcal{Q}) = \frac{1}{N}\sum_{\{N(p,q)\}} \frac{N!}{\prod\limits_{p,q} N(p,q)!} \sum N(p,q) f(p,q). \tag{3.6}$$

The outer sum in the right-hand side of (3.6) runs over all admissible sets of non-negative integers. Applying (3.6) to the case where $f(p,q) \equiv 1$, we find $\sum\limits_{\mathcal{P},\mathcal{Q}\in S_E} 1$ and

$$\overline{\mathcal{F}}_E^{(N)} = \frac{\sum\limits_{\{N(p,q)\}} \dfrac{N!}{\prod\limits_{p,q} N(p,q)!} \sum\limits_{(p,q)} \dfrac{N(p,q)}{N} f(p,q)}{\sum\limits_{\{N(p,q)\}} \dfrac{N!}{\prod\limits_{p,q} N(p,q)!}}, \tag{3.7}$$

where the outer sum in the numerator and the sum in the denominator runs over all admissible sets $\{N(p,q)\}$ of non-negative integers.

Our goal is to find the limit of the mean values (3.4) and (3.7).

3.2. A solution of the combinatorial problem. The following transformations of equation (3.7) are related with its probabilistic interpretation. Observe that (3.7) is the mathematical expectation of the random quantity

$$\varphi = \sum \frac{N(p,q)}{N} f(p,q), \tag{3.8}$$

in which the admissible set of numbers $N(p,q)$ depends on chance and the probability of the set $\{N(p,q)\}$ is equal to

$$\frac{\dfrac{N!}{\prod\limits_{p,q} N(p,q)!}}{\sum\limits_{\{N(p,q)\}} \dfrac{N!}{\prod\limits_{p,q} N(p,q)!}}. \tag{3.9}$$

Observe although this is inessential in what follows that the quantity φ itself for a fixed set $N(p,q)$ is also the mathematical expectation of the function $f(p,q)$ depending on a random point (p,q) distributed with probability $\dfrac{N(p,q)}{N}$.

In what follows, we will find the most probable set $\{N(p,q)\}$, i.e., such that (3.9) attains its maximum and replace the mean of (3.8) over all sets by the value of φ for the most probable set.

Obviously, the expression (3.9) and its numerator attain their maximum for the same values of $N(p,q)$. Taking logarithm of the numerator of (3.9) and using the Stirling formula for $N(p,q)!$, we find $N(p,q)$ from the equations

$$\frac{\partial}{\partial N(p,q)} \Big(\Big(\ln N! - \sum N(p,q)(\ln N(p,q) - 1) \Big) - \beta \sum N(p,q) H(p,q) - \mu \sum N(p,q) \Big) = 0, \tag{3.10}$$

where β and μ are the Lagrange multipliers corresponding to (3.2)) and (3.3).

Equation (3.10) has the only solution

$$N(p,q) = Ce^{-\beta H(p,q)}, \quad \text{where } C = e^{\mu}. \tag{3.11}$$

The fact that the expression (3.11) determines the maximum of the function we are interested in and not any other extremal is obvious, in a sense, since the equation (3.10) has the only solution.

We find the constants C and β from equations (3.2) and (3.3):

$$\frac{\sum H(p,q)e^{-\beta H(p,q)}}{\sum e^{-\beta H(p,q)}} = \varepsilon, \quad C = \frac{N}{\sum e^{-\beta H(p,q)}}. \tag{3.11 a}$$

Having replaced in (3.7) the sum over all admissible sets $N(p,q)$ by the value of φ for the most probable set we find:

$$\overline{\mathcal{F}}_E = \sum \frac{e^{-\beta H(p,q)}}{\sum e^{-\beta H(p,q)}} f(p,q). \tag{3.12}$$

Multiplying the numerator and denominator in (3.11) and (3.12) by l^n (the volume of the cell) we see that all sums in these formulas are integral ones. Passing to the limit as $l \to 0$ we finally obtain

$$\varepsilon = \frac{\int H(p,q)e^{-\beta H(p,q)}\, dp\, dq}{\int e^{-\beta H(p,q)}\, dp\, dq}, \tag{3.13}$$

$$\overline{\mathcal{F}}_E = \int f(p,q)\rho(p,q)\, dp\, dq, \tag{3.14}$$

where

$$\rho(p,q) = \frac{e^{-\beta H(p,q)}}{\int e^{-\beta H(p,q)}\, dp\, dq}. \tag{3.15}$$

The mathematically flawless deduction of the Gibbs distribution based on the considerations developed in this section is hardly possible [6)]. Therefore, the complete deduction (given shortly) is based on another idea which is not so graphic.

§ 4. A complete deduction of the Gibbs distribution

4.1. Formulation of the main theorem. In this section we will prove the existence of the limit as $N \to \infty$ of the functions $\rho_N(p,q)$, cf. (2.8):

$$\rho_N(p,q) = \frac{\int \delta\left(\sum\limits_{\alpha=1}^{N-1} H(p^{(\alpha)}, q^{(\alpha)}) + H(p,q) - N_\varepsilon\right) \prod\limits_{\alpha=1}^{N-1} dp^{(\alpha)}\, dq^{(\alpha)}}{\int \delta\left(\sum\limits_{\alpha=1}^{N} H(p^{(\alpha)}, q^{(\alpha)}) - N_\varepsilon\right) \prod\limits_{\alpha=1}^{N} dp^{(\alpha)}\, dq^{(\alpha)}}. \tag{4.1}$$

[6)] The main difficulty is the reduction to the combinatorial problem, i.e., to formula (3.7). Contrariwise the solution of combinatorial problem (i.e., the proof of the relation $\lim\limits_{N\to\infty} \overline{\mathcal{F}}_E^{(N)} = \overline{\mathcal{F}}_E$, where $\overline{\mathcal{F}}_E^{(N)}$ is determined by (3.7) and $\overline{\mathcal{F}}_E$ is determined by (3.14)) can be made quite rigorous under broad assumptions concerning $H(p,q)$ and $f(p,q)$. For this, one can use Laplace transformation in the same way we apply it in the next section.

and compute it. In what follows it is convenient to denote the area of the surface of constant energy of the subsystem by

$$\omega(\varepsilon) = \int \delta(H(p,q) - \varepsilon)\, dp\, dq. \tag{4.2}$$

4.1.1. Theorem. *Let $H(p,q)$ satisfy the conditions*

1) $H(p,q) \geq 0$,
2) $\omega(\varepsilon)$ *is monotonically non-decreasing and differentiable,*
3) $\omega(\varepsilon) \sim \varepsilon^p$, *where* $p > 0$ *as* $\varepsilon \to 0$,
4) $\omega(\varepsilon) \sim \varepsilon^q$, *where* $q > 0$ *as* $\varepsilon \to +\infty$,
5) *The function* $e^{-\beta\varepsilon}\omega'(\varepsilon)$ *is integrable for any* $\beta > 0$.

Then

1) *The sequence* $\rho_N(p,q)$ *tends to*

$$\rho(p,q) = \frac{e^{-\beta H(p,q)}}{\int e^{-\beta H(p,q)}},$$

where $\beta = \beta(\varepsilon) > 0$ *is the only root of the equation*

$$\frac{\int H(p,q) e^{-\beta H(p,q)}\, dp\, dq}{\int e^{-\beta H(p,q)}\, dp\, dq} = \varepsilon; \tag{4.3}$$

2) *for any measurable function* $f(p,q)$ *such that*

$$\int |f| e^{-\beta H}\, dp\, dq < \infty, \quad \int |f| H e^{-\beta H}\, dp\, dq < \infty,$$

the limit exists

$$\lim_{N\to\infty} \int f \rho_N\, dp\, dq = \int f \rho\, dp\, dq.$$

Proof. Denote by $a_N(p, q \mid \varepsilon)$ the numerator of (4.1) and $\Omega_N(\varepsilon)$ the denominator of (4.1). Let us study the asymptotics of these functions as $N \to \infty$. Since $\Omega_N = \int a_N\, dp\, dq$, it suffices to consider a_N. Observe that $\Omega_1(\varepsilon) = \omega(\varepsilon)$ is given by (4.2). Further,

$$\delta\Bigg(\sum_{\alpha=1}^{N} H(p^{(\alpha)}, q^{(\alpha)}) - x\Bigg) =$$

$$= \int_{-\infty}^{\infty} \delta(H(p^{(N)}, q^{(N)}) - y)\, \delta\Bigg(\sum_{\alpha=1}^{N-1} H(p^{(\alpha)}, q^{(\alpha)}) - (x-y)\Bigg)\, dy.$$

Integrating this equation against $\prod_{\alpha=1}^{N} dp^{(\alpha)}\,dq^{(\alpha)}$ and $\prod_{\alpha=1}^{N-1} dp^{(\alpha)}\,dq^{(\alpha)}$ and using the fact that $\Omega_N(\varepsilon)=0$ for $\varepsilon<0$ we deduce:

$$\Omega_N\Big(\frac{x}{N}\Big)=\int\limits_{-\infty}^{\infty}\omega(y)\Omega_{N-1}\Big(\frac{x-y}{N-1}\Big)\,dy=\int\limits_{0}^{x}\omega(y)\Omega_{N-1}\Big(\frac{x-y}{N-1}\Big)\,dy,$$

$$a_N\Big(\xi,\eta\,|\,\frac{x}{N}\Big)=\int\limits_{-\infty}^{\infty}\delta(H(\xi,\eta)-y)\Omega_{N-1}\Big(\frac{x-y}{N-1}\Big)\,dy=\Omega_{N-1}\Big(\frac{x-H(\xi,\eta)}{N-1}\Big).$$

Thus the functions Ω_N and a_N are expressed in terms of ω by means of multiple convolutions. Therefore, to study them, the Laplace transformation [7)] is convenient. Using the formulas found and the condition of the theorem we find by the induction that the function $a_N(\xi,\eta\,|\,\varepsilon)$ grows as a power of ε for fixed ξ, η. Therefore the Laplace transform of $a_N(\xi,\eta\,|\,\varepsilon)$ exists. Denote the Laplace transform of a_N by A_N:

$$A_N(\xi,\eta\,|\,t)=\int\limits_{0}^{\infty}a_N(\xi,\eta\,|\,\varepsilon)e^{-t\varepsilon}\,d\varepsilon=$$

$$=\int\limits_{0}^{\infty}\int\delta\Big(\sum_{\alpha=1}^{N-1}H(p^{(\alpha)},q^{(\alpha)})+H(\xi,\eta)-N_\varepsilon\Big)\prod_{\alpha=1}^{N-1}dp^{(\alpha)}\,dq^{(\alpha)}e^{-t\varepsilon}\,d\varepsilon=$$

$$=\frac{1}{N}\int e^{-\left(\sum\limits_{\alpha=1}^{N-1}H(p^{(\alpha)},q^{(\alpha)})+H(\xi,\eta)\right)\frac{t}{N}}\prod_{\alpha=1}^{N-1}dp^{(\alpha)}\,dq^{(\alpha)}=$$

$$=\frac{1}{N}e^{-\frac{t}{N}H(\xi,\eta)}\left(\int e^{-\frac{t}{N}H(p,q)}\,dp\,dq\right)^{N-1}.$$

The inverse transform is equal to

$$a_N(\xi,\eta\,|\,\varepsilon)=\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}A_N(\xi,\eta\,|\,N(\lambda+i\tau))e^{N(\lambda+i\tau)\varepsilon}\,d\tau=$$

$$=\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}\psi(\xi,\eta\,|\,\tau)e^{(N-1)\varphi(\tau)}\,d\tau,\quad(4.4)$$

[7)] For the necessary background on Laplace transformations, see § 7

where

$$\begin{aligned}\psi(\xi,\eta\,|\,\tau) &= e^{-(\lambda+i\tau)(H(\xi,\eta)-\varepsilon)},\\ \varphi(\tau) &= \ln\int e^{-(\lambda+i\tau)(H(\xi,\eta)-\varepsilon)}\,dp\,dq.\end{aligned}\tag{4.5}$$

It turns out that the functions ψ and φ satisfy the following conditions:

$\psi(\xi,\eta\,|\,\tau)$ is bounded and continuously differentiable with respect to τ;

φ is three times continuously differentiable, moreover

a) $\varphi(0)$ is real,

b) $\varphi'(0)=0$,

c) $\varphi''(0)$ is real and $\varphi''(0)=-\alpha<0$,

d) for any $\delta>0$, there exists $K=K(\delta)>0$ such that

$$\int\limits_{|t|>\delta} e^{N\mathrm{Re}\ (\varphi(t)-\varphi(0))}\,dt < K^N.$$

We only have to prove, obviously, properties a)–d) of φ. We will postpone this proof to the end of the section where we will also establish that the property b) is satisfied for the only value $\lambda=\beta$ which is a solution of equation (4.3).

Properties a)–c) coincide with the properties a)–c) of Theorem 7 and the property d) above guarantees fulfillment of the property d) of Theorem 7 with the constant $\sigma=1$. Thus, we can apply Theorem 7. By this theorem, for a sufficiently large N, we have

$$a_N(\xi,\eta\,|\,\varepsilon)=\frac{1}{2\pi}\sqrt{\frac{\pi}{N\alpha}}\Big(\psi(0)\Big(1+\frac{c(N)}{\sqrt{N}}\Big)+\frac{b(N)}{\sqrt{N}}\Big),\tag{4.6}$$

where $c(N)$ and $b(N)$ satisfy

$$\begin{aligned}|c(N)| &\le 2\max_{|t|<\delta}\Big|\frac{\varphi(0)-\alpha t^2}{\alpha t^3}\Big|,\\ |b(N)| &\le 2\sup_t|\psi(t)|+\max_{|t|<\delta}\Big|\frac{\psi(t)-\psi(0)}{t}\Big|.\end{aligned}$$

Observe that, in our case, for $\lambda=\beta$, we have

$$\begin{aligned}|\psi| &= e^{-\beta(H(\xi,\eta)-\varepsilon)},\\ \Big|\frac{\psi(t)-\psi(0)}{t}\Big| &= \Big|\frac{e^{-(\beta+it)(H-\varepsilon)}-e^{-\beta(H-\varepsilon)}}{t}\Big| =\\ &= 2e^{-\beta(H-\varepsilon)}\Big|\frac{\sin\frac{t(H-\varepsilon)}{2}}{t}\Big| \le |H(\xi,\eta)-\varepsilon|e^{-\beta(H-\varepsilon)}.\end{aligned}$$

Thus, for a sufficiently large N, the function $a_N(\xi, \eta \mid \varepsilon)$ is representable in the form

$$a_N(\xi, \eta \mid \varepsilon) = \tilde{a}_N(\xi, \eta \mid \varepsilon) \frac{1}{2\pi} \sqrt{\frac{\pi}{N\alpha}} e^{N\varphi(0)+\beta\varepsilon},$$

where

$$\tilde{a}_N(\xi, \eta \mid \varepsilon) = e^{-\beta H(\xi,\eta)} \Big(1 + \frac{c'(N) + H(\xi,\eta) d(N)}{\sqrt{N}}\Big), \tag{4.7}$$

$d(N)$ and $c'(N)$ are bounded by constants independent of N, ξ, η. Obviously,

$$\rho_N(\xi, \eta) = \frac{\tilde{a}_N(\xi, \eta)}{\int \tilde{a}_N(\xi, \eta)\, d\xi\, d\eta}.$$

Unlike a_N, the function $\tilde{a}_N$ possesses a limit as $N \to \infty$:

$$\lim_{N\to\infty} \tilde{a}_N(\xi, \eta \mid \varepsilon) = e^{-\beta H(\xi,\eta)}. \tag{4.8}$$

Let a function $f(\xi, \eta)$ be such that

$$\begin{aligned} &\int |f(\xi,\eta)| H(\xi,\eta) e^{-\beta H(\xi,\eta)}\, d\xi\, d\eta < \infty, \\ &\int |f(\xi,\eta)| e^{-\beta H(\xi,\eta)}\, d\xi\, d\eta < \infty. \end{aligned} \tag{4.9}$$

(Observe that $f(\xi, \eta) \equiv 1$ satisfies these conditions.) Consider a sequence of functions $f_N = \tilde{a}_N f$, where each f_N is bounded by an integrable function

$$\Big| f(\xi,\eta) e^{-\beta H(\xi,\eta)} \Big(1 + \frac{c'(N) + d(N) H(\xi,\eta)}{\sqrt{N}}\Big) \Big| < \Big| f(\xi,\eta) e^{-\beta H(\xi,\eta)} \Big(1 + c' + d H(\xi,\eta)\Big) \Big|,$$

and where c' and d are functions that bind $c'(N)$ and $d(N)$ ($|c'(N)| \le c'$ and $|d(N)| \le d$). Let, moreover, the sequence $f_N(\xi, \eta)$ converge to $f(\xi, \eta) e^{-\beta H(\xi,\eta)}$. We can apply Lebesgue's theorem. Therefore there exists the limit of integrals $\int f \tilde{a}_N\, d\xi\, d\eta$ equal to

$$\lim_{N\to\infty} \int f(\xi,\eta) \tilde{a}_N(\xi,\eta)\, d\xi\, d\eta = \int f(\xi,\eta) e^{-\beta H(\xi,\eta)}\, d\xi\, d\eta.$$

In particular, for $f \equiv 1$, we get

$$\lim_{N\to\infty} \int \tilde{a}_N(\xi,\eta)\, d\xi\, d\eta = \int e^{-\beta H(\xi,\eta)}\, d\xi\, d\eta.$$

Taking (4.8) into account we deduce the existence of the limit of the ρ_N as $N \to \infty$ and the equality

$$\lim_{N\to\infty} \rho_N(\xi,\eta) = \frac{e^{-\beta H(\xi,\eta)}}{\int e^{-\beta H(p,q)}\,dp\,dq}.$$

Therefore, for the function f satisfying conditions (4.9), we have

$$\lim_{N\to\infty} \int \rho_N(\xi,\eta) f(\xi,\eta)\,d\xi\,d\eta = \int f(\xi,\eta)\rho(\xi,\eta)\,d\xi\,d\eta.$$

To complete the proof of the theorem, it suffices to verify that φ satisfies conditions a)–d).

It is obvious that $\varphi(0)$ is real. Further,

$$\varphi'(\tau) = -i\frac{\int (H(p,q)-\varepsilon)e^{-(\lambda+i\tau)(H(p,q)-\varepsilon)}\,dp\,dq}{\int e^{-(\lambda+i\tau)(H(p,q)-\varepsilon)}\,dp\,dq} = -i(\overline{H}_{\lambda+i\tau} - \varepsilon), \quad (4.10)$$

where

$$\overline{H}_{\lambda+i\tau} = \frac{\int H(p,q)e^{-(\lambda+i\tau)H(p,q)}\,dp\,dq}{\int e^{-(\lambda+i\tau)H(p,q)}\,dp\,dq}.$$

Let us show that, for $\tau = 0$, we have

$$\frac{d}{d\lambda}\overline{H}_\lambda < 0,$$

Indeed:

$$\frac{d\overline{H}_\lambda}{d\lambda} = \frac{\left(\int He^{-\lambda H}\,dp\,dq\right)^2 - \int H^2 e^{-\lambda H}\,dp\,dq \int e^{-\lambda H}\,dp\,dq}{\left(\int e^{-\lambda H}\,dp\,dq\right)^2}.$$

Now apply the Cauchy inequality:

$$\left(\int He^{-\lambda H}\,dp\,dq\right)^2 = \left(\int He^{-\frac{1}{2}\lambda H}e^{-\frac{1}{2}\lambda H}\,dp\,dq\right)^2 \le$$
$$\le \int H^2 e^{-\lambda H}\,dp\,dq \int e^{-\lambda H}\,dp\,dq.$$

The equality can only happen when $He^{-\frac{\lambda H}{2}}$ is proportional to $e^{-\frac{\lambda H}{2}}$; this is impossible. Therefore, we always have a strict inequality

$$\frac{d\overline{H}_\lambda}{d\lambda} < 0. \quad (4.11)$$

Hence $\overline{H}_\lambda$ strictly monotonically decays.

Let us investigate the behavior of $\overline{H}_\lambda$ as $\lambda \to 0$ and $\lambda \to \infty$. We have

$$\overline{H}_\lambda = \frac{\int H(p,q)e^{-\lambda H(p,q)}\,dp\,dq}{\int e^{-\lambda H(p,q)}\,dp\,dq} = \frac{\int\limits_0^\infty \varepsilon e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon}{\int\limits_0^\infty e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon}.$$

Recall that from the very beginning we required that $H(p,q)$ should be such that the function $\omega(\varepsilon)$ grows polynomially as $\varepsilon \to \infty$ and decays polynomially as $\varepsilon \to 0$.

First, consider the case $\lambda \to \infty$. We have

$$\int\limits_0^\infty e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon = \int\limits_0^a e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon + \int\limits_a^\infty e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon. \tag{4.12}$$

The number a is selected so that $|\omega(\varepsilon) - r\varepsilon^p| < \delta\varepsilon^p$ for $0 < \varepsilon < a$ and certain r and δ. We also have

$$\int\limits_0^a e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon < (r+\delta)\int\limits_0^a \varepsilon^p e^{-\lambda\varepsilon}\,d\varepsilon \approx \frac{r+\delta}{\lambda^{p+1}}\Gamma(p+1) \quad \text{as } \lambda \to \infty.$$

Let us estimate the second summand in (4.12):

$$\int\limits_a^\infty e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon = e^{-\lambda\varepsilon_0}\int\limits_a^\infty e^{-\lambda(\varepsilon-\varepsilon_0)}\omega(\varepsilon)\,d\varepsilon < Ce^{-\lambda\varepsilon_0}, \quad \text{where } \varepsilon_0 < a.$$

Thus

$$\int\limits_0^\infty e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon \approx \frac{C_1}{\lambda^{p+1}} \quad \text{as } \lambda \to \infty.$$

Similar estimates show that

$$\int\limits_0^\infty \varepsilon e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon \approx \frac{C_2}{\lambda^{p+2}} \quad \text{as } \lambda \to \infty.$$

Hence

$$\overline{H}_\lambda \to 0 \quad \text{as } \lambda \to \infty.$$

It is the integral $\int\limits_a^\infty$ that gives the main contribution to $\int\limits_0^\infty e^{-\lambda\varepsilon}\omega(\varepsilon)\,d\varepsilon$ as $\lambda \to 0$ (and not the integral $\int\limits_0^a$, as is the case as $\lambda \to \infty$). Easy estimates show that $\overline{H}_\lambda \to \infty$ not more slow than $C_3\lambda^{-1}$ as $\lambda \to 0$.

Thus $\overline{H}_\lambda$ strictly monotonically decays and, moreover, $\lim\limits_{\lambda\to 0} \overline{H}_\lambda = +\infty$, $\lim\limits_{\lambda\to\infty} \overline{H}_\lambda = 0$. Therefore the equation $\overline{H}_\lambda - \varepsilon = 0$ possesses a unique root β. Thus we have established that property b) holds for a unique value $\lambda = \beta$.

Further, due to (4.11) and (4.10) we have

$$\varphi''(0) = \frac{d\overline{H}_\lambda}{d\lambda} < 0$$

for all λ.

Let us pass to the proof of property d). Set

$$\tilde{\psi}(\tau) = \int \psi(\xi, \eta \mid \tau)\, d\xi\, d\eta = e^{+(\beta+\tau i)\varepsilon} \int\limits_0^\infty e^{(\beta+\tau i)x}\omega(x)\, dx.$$

Since $\varphi(\tau) = \ln \tilde{\psi}(\tau)$, it follows that

$$e^{N\mathrm{Re}\ (\varphi(\tau)-\varphi(0))} = \Big|\frac{\tilde{\psi}(\tau)}{\tilde{\psi}(0)}\Big|^N.$$

Let us rewrite $\tilde{\psi}(\tau)$:

$$\int\limits_0^\infty e^{-(\beta+i\tau)x}\omega(x)\, dx = -\frac{1}{\beta+i\tau}\int\limits_0^\infty \frac{d}{dx}\Big(e^{-(\beta+i\tau)x}\Big)\omega(x)\, dx = \\ = \frac{e^{-(\beta+i\tau)x}\omega(x)}{\beta+i\tau}\Big|_0^\infty + \frac{1}{\beta+i\tau}\int\limits_0^\infty e^{-(\beta+i\tau)x}\omega'(x)\, dx. \tag{4.13}$$

By assumption on $\omega(x)$ the integrated term vanishes. Using (4.13) we deduce that

$$\frac{\tilde{\psi}(\tau)}{\tilde{\psi}(0)} = \frac{\beta}{\beta+i\tau}\,\frac{\int\limits_0^\infty e^{-(\beta+i\tau)x}\omega'(x)\, dx}{\int e^{-\beta x}\omega'(x)\, dx}.$$

Since $\omega'(x) \geq 0$, it follows that $\left|\int e^{-(\beta+i\tau)x}\omega'(x)\,dx\right| \leq \int e^{-\beta x}\omega'(x)\,dx$. Hence

$$\left|\frac{\tilde{\psi}(\tau)}{\tilde{\psi}(0)}\right| \leq \left|\frac{\beta}{\beta+i\tau}\right| = \frac{1}{\sqrt{1+\frac{\tau^2}{\beta^2}}}.$$

Further, making the change of variables $x = \ln\left(1+\frac{\tau^2}{\beta^2}\right)$, we find (the last inequality holds only for a sufficiently large N):

$$\int_\delta^\infty \left|\frac{\tilde{\psi}(\tau)}{\tilde{\psi}(0)}\right|^N d\tau \leq \int_\delta^\infty \frac{d\tau}{\left(1+\frac{\tau^2}{\beta^2}\right)^{1/2}} = \int_\delta^\infty e^{-\frac{N}{2}\ln\left(1+\frac{\tau^2}{\beta^2}\right)}\,d\tau =$$

$$= \frac{\beta}{2}\int_{\ln\left(1+\frac{\delta^2}{\beta^2}\right)}^\infty e^{-\frac{N}{2}x}\frac{e^x}{\sqrt{e^x-1}}\,dx \leq \frac{\beta}{2\frac{\delta}{\beta}}\int_{\ln\left(1+\frac{\delta^2}{\beta^2}\right)}^\infty e^{-\left(\frac{N}{2}-1\right)x}\,dx =$$

$$= \frac{\beta^2}{2\delta}\frac{e^{-\left(\frac{N}{2}-1\right)\ln\left(1+\frac{\delta^2}{\beta^2}\right)}}{\frac{N}{2}-1} \leq K^N,$$

where $K = \frac{1}{\sqrt{1+\delta^2/\beta^2}}$. □

Let us return to eq. (4.6). Integrating (4.6) over ξ and η we obtain for Ω_N an expression similar to (4.6):

$$\Omega_N(\varepsilon) = \frac{1}{2\pi}\sqrt{\frac{\pi}{N\alpha}}e^{N\varphi(0)}\left(\varphi(0)\left(1+\frac{\tilde{c}(N)}{\sqrt{N}}\right)+\frac{\tilde{b}(N)}{\sqrt{N}}\right), \tag{4.14}$$

where $|\tilde{c}(N)|$ and $\tilde{b}(N)|$ are bounded by constants that do not depend on N. We will use formula (4.14) in § 6.

§ 5. Relation to thermodynamics

In phenomenological thermodynamics, the main properties that characterize macroscopic state of bodies are temperature, heat, pressure and entropy. In this section we will give formal definitions of these quantities and relate them with the Gibbs distribution.

5.1. Temperature. The Gibbs distribution depends on a parameter β completely determined by the mean energy. *The absolute temperature* of the system is given by the formula

$$T = \frac{1}{k\beta}, \tag{5.1}$$

where k is *the Boltzmann constant*. We will postpone for a while the discussion of a relation between thus formally defined temperature and more conventional definitions.

5.2. Pressure and generalized pressure. In addition to the generalized coordinates q and p, the Hamiltonian of a subsystem can depend on exterior parameters λ_i (for example, for a gas in a vessel of variable volume V, the Hamiltonian can depend on this volume).

The Hamiltonian of the system consisting of subsystems that depend on exterior parameters $\lambda_1, \ldots, \lambda_S$ is of the form

$$\mathcal{H} = \sum_\alpha H(p^{(\alpha)}, q^{(\alpha)}; \lambda_1, \ldots, \lambda_S),$$

where the parameters λ_i assume the same value for all subsystems.

As the parameter λ_i varies, a force equal to $-\dfrac{\partial \mathcal{H}}{\partial \lambda_i}$ acts on the system. The mean value of $-\dfrac{\partial \mathcal{H}}{\partial \lambda_i}$ over the ensemble is called the *generalized pressure*. Using the Gibbs distribution we find that the generalized pressure is equal to

$$p_i = -N \frac{\int \frac{\partial H}{\partial \lambda_i} e^{-\beta H}\, dp\, dq}{\int e^{-\beta H}\, dp\, dq} = \frac{N}{\beta} \frac{\partial \ln z}{\partial \lambda_i}, \tag{5.2}$$

where

$$z = \int e^{-\beta H}\, dp\, dq. \tag{5.3}$$

Observe that the generalized pressure is denoted by the same symbol as the momentum. Do not confuse!

If $\lambda_i = V$ is the volume occupied by the system, then $p_i = p$ is the *usual pressure*.

Observe that the formula similar to (5.2) expresses the *mean energy of the subsystem*:

$$\overline{\mathcal{E}} = -\frac{\partial \ln z}{\partial \beta}.$$

Therefore the function z enables to compute the main physical characteristics of the system. It is called *the statistical integral*, whereas $\ln z$ is called the *thermodynamical potential*. The set of parameters $\mathcal{E}$, $\lambda_1, \ldots, \lambda_S$ (or which is the same β, $\lambda_1, \ldots, \lambda_S$ determines what is called *the thermodynamical state of the system* and the functions $f(\mathcal{E}, \lambda_1, \ldots, \lambda_S)$ (or $f(\beta, \lambda_1, \ldots, \lambda_S)$) are called the *state functions*. The equations (5.2), where $p_i = p_i(\beta, \lambda_1, \ldots, \lambda_S)$, are called *the equations of state*.

Observe that, if the subsystem depends on exterior parameters, we cannot, strictly speaking, consider it a microscopic one. Indeed, the right-hand

side of (5.2) contains a factor N. At the same time the generalized pressure does not tend to ∞ as $N \to \infty$. Obviously, this is only possible if the exterior parameters λ_i depend on N, i.e., if the system is not microscopic.

In particular, as we will see in what follows, if the system is an ideal gas and the parameter is the volume V, then $V = Nv$, where $v = \dfrac{V}{N}$ is *the specific volume* that does not depend on N. Therefore one can only consider the ideal gas as an ensemble of microscopic subsystems only for a fixed volume. If we would like to consider the volume as a variable parameter we are forced to consider the ideal gas as an ensemble of macroscopic subsystems.

Observe by the way, that the volume, as a parameter, characterizes the vessel in which the gas is contained rather than the gas itself: All physical characteristics of the gas in the whole volume, and any part of it, are the same. Therefore the characteristic of the gas having a physical meaning is not the volume V itself but rather *the specific volume* v or the *density* $\rho = \dfrac{1}{v}$.

5.3. Heat and entropy. The exterior forces applied to the system perform an action. According to the general principles of mechanics, under small alterations of parameters λ_i, an action is performed over the system, and this action is equal to

$$-\sum \frac{\partial \mathcal{H}}{\partial \lambda_i} d\lambda_i = -\sum \frac{\partial H(p^{(\alpha)}, q^{(\alpha)})}{\partial \lambda_i} d\lambda_i.$$

The difference between the increment of the energy of the system and the mean of the actions performed by exterior forces over the ensemble is called *the increment of the heat of the system* and is denoted by dQ:

$$dQ = N\left(d\mathcal{E} + \frac{\sum\left(\int \frac{\partial H}{\partial \lambda_i} e^{-\beta H}\, dp\, dq\right) d\lambda_i}{\int e^{-\beta H}\, dp\, dq}\right) = (d\mathcal{E} - \sum p_i d\lambda_i)N, \qquad (5.4)$$

where $\mathcal{E}$ is the mean energy of the subsystem, p_i is the mean pressure, and N is the number of macroscopic subsystems. The differential dQ is not the total differential of any function of state (i.e., function in $\lambda_1, \ldots, \lambda_S, \beta$).

Closely related with heat is the *entropy* S, which is a function of state. In the phenomenological thermodynamics, the entropy is determined in terms of its differential

$$dS = \beta dQ.$$

5.3.1. Theorem. *$dS = \beta dQ$ is the total differential of the function*

$$S(\beta, \lambda_1, \ldots, \lambda_S) = N(\ln z + \beta\mathcal{E}) + \text{const}. \qquad (5.5)$$

Proof reduces to the computation of partial derivatives of the function S:

$$\frac{1}{N}\frac{\partial S}{\partial \beta} = \frac{\partial \ln z}{\partial \beta} + \mathcal{E} + \beta\frac{\partial \mathcal{E}}{\partial \beta} = -\mathcal{E} + \mathcal{E} + \beta\frac{\partial \mathcal{E}}{\partial \beta} = \beta\frac{\partial \mathcal{E}}{\partial \beta},$$
$$\frac{1}{N}\frac{\partial S}{\partial \lambda_i} = \frac{\partial \ln z}{\partial \lambda_i} + \beta\frac{\partial \mathcal{E}}{\partial \lambda_i} = -\beta\lambda_i + \beta\frac{\partial \mathcal{E}}{\partial \lambda_i}.$$

Now, let us compute dS:

$$dS = N\Big(\beta\frac{\partial \mathcal{E}}{\partial \beta}d\beta + \sum \beta\Big(\frac{\partial \mathcal{E}}{\partial \lambda_i} - p_i\Big)d\lambda_i\Big) =$$
$$N\beta(d\mathcal{E} - \sum p_i d\lambda_i) = \beta dQ. \quad \square \tag{5.6}$$

Note that the entropy is only determined up to an additive constant. the following question naturally arises:

Question. *Is it possible to define this constant in a physically justified way, for example, setting entropy equal to zero at the zero temperature.*

This question is discussed in § 6. We will see that, in the classical statistical physics, it is impossible to do so. For a given ensemble consisting of microscopic subsystems, it is natural to set

$$S = N(\ln z + \beta\mathcal{E});$$

and the function $S' = \ln z + \beta\mathcal{E}$ inside the parentheses will be sometimes called the *entropy of a particular subsystem.*

5.4. How to measure temperature. The one-atom ideal gas. Let us show that our definition of the temperature is consistent with the conventional understanding of it. Let us consider a one-atom ideal gas in a vessel of variable volume V. A gas is called *one-atom* and *ideal* if its particles are non-interacting with each other massive points. An individual particle of the gas possesses only kinetic energy and its Hamiltonian is equal to

$$h(p,q) = \frac{p^2}{2m}, \quad \text{where } p^2 = p_1^2 + p_2^2 + p_s^2,$$

and where m is the mass of the particle [8)].

[8)] The properties of any real gas are close to the properties of the ideal gas if the temperature is large and the density is small (see the next chapter).

Let us compute the statistical integral

$$z = \int e^{-\beta h(p,q)}\, dp\, dq = V\left(\int_{-\infty}^{\infty} e^{-\beta \frac{p^2}{2m}}\, dp\right)^3 = V\left(\frac{2\pi m}{\beta}\right)^{3/2}. \tag{5.7}$$

We find that the pressure of the ideal gas is equal to

$$p = \frac{N}{\beta}\frac{\partial \ln z}{\partial V} = \frac{N}{\beta V} = \frac{1}{\beta v}.$$

We have deduced the equation of state

$$pV = \frac{N}{\beta} \quad \text{or} \quad pv = \frac{1}{\beta}. \tag{5.8}$$

On the other hand, in thermodynamics the behaviour of the ideal gas based on the experiments is described by the following equation (*Klapeiron's equation*)

$$pV = NkT, \tag{5.9}$$

where p is the pressure, V is the volume, N is the number of particles, T is the absolute temperature, $k = 1{,}38 \cdot 10^{-16}$erg/grad is Boltzman's constant.

Comparing (5.8) and (5.9) we see that, indeed, for the ideal gas, we have

$$T = \frac{1}{k\beta}. \tag{5.10}$$

In order to verify that (5.10) holds also for an arbitrary system, we use the following property of the temperature well-known from the phenomenological thermodynamics (in other words, from experiments).

If two systems in equilibrium and at the same temperature are made to contact, then the united system is also in equilibrium and its temperature coincides with the temperature of the initial systems and the mean energies of particles of each type are the same.

Thus, let us mix an ideal gas at temperature $T = \frac{1}{k\beta}$ with an arbitrary system consisting of microscopic subsystems with Hamiltonian $H(p,q)$ at the same temperature and the parameter β' in the Gibbs distribution. Let us take, for convenience, as many systems of the auxiliary ideal gas as there are subsystems in our system. Let us show that $\beta' = \beta$. Consider a new system, each of whose subsystems consists of one particle of gas and the initial subsystem. The Hamiltonian of the new subsystem is equal to

$$H'(p,p',q,q') = H(p,q) + h(p',q'),$$

where $h(p', q') = \dfrac{(p')^2}{2m}$ is the Hamiltonian of the particle of the ideal gas.

The density of the Gibbs distribution in the new system is equal to $\dfrac{e^{-\beta_0 H'}}{z(\beta_0)}$. The mean energy of the particle of gas is equal to

$$\mathcal{E}(\beta_0) = \frac{\int h(p,q) e^{-\beta_0 (H(p',q')+h(p,q))}\, dp\, dp'\, dq\, dq'}{\int e^{-\beta_0 (H+h)}\, dp\, dp'\, dq\, dq'} = \frac{\int h(p,q) e^{-\beta_0 h(p,q)}\, dp\, dq}{\int e^{-\beta_0 h}\, dp\, dq}.$$

On the other hand, the mean energy of the particle of gas remains equal to $\mathcal{E}(\beta) = \dfrac{\int h e^{-\beta h}\, dp\, dq}{\int e^{-\beta h}\, dp\, dq}$. We know that the mean energy uniquely determines β. Hence $\beta_0 = \beta$. By the same arguments $\beta_0 = \beta'$. Thus, $\beta' = \beta$,and the temperature of the system is equal to $\dfrac{1}{k\beta}$.

5.5. The second law of thermodynamics. Suppose we are given two systems (1) and (2) at distinct temperatures $T_2 > T_1$. Let us mix these systems and wait till the equilibrium is established. Then:

1) the temperature T of the obtained system C is strictly between T_1 and T_2,

2) the mean energy of each subsystem that earlier entered the system (1) has increased whereas the mean energy of each subsystem which earlier entered the system (2) has diminished.

These two statements constitute the *second law of thermodynamics*. It is briefly formulated as follows: The energy flows from a more heated body to a cooler one.

For simplicity, consider first the case where both systems consist of the same number of subsystems. Let the Hamiltonian functions of subsystems of the systems (1) and (2) be equal to $H_1(p', q')$ and $H_2(p'', q'')$, respectively. Let us unite somehow the subsystems of the first and second systems into pairs and let us assume that these pairs are subsystems which constitute the system C obtained as a result of joining the initial systems. The Hamiltonian of the mixture is equal to $H(p,q) = H_1(p', q') + H_2(p'', q'')$, where $p = (p', p'')$, $q = (q', q'')$. The densities of the Gibbs distribution of the initial subsystems and of the mixture are equal to, respectively,

$$\frac{e^{-\beta_1 H_1(p',q')}}{z_1(\beta_1)}, \quad \frac{e^{-\beta_2 H_2(p'',q'')}}{z_2(\beta_2)}, \quad \frac{e^{-\beta H(p,q)}}{z(\beta)}.$$

Since the subsystems do not interact, it follows that

$$z = \int e^{-\beta H(p,q)}\, dp\, dq = z_1(\beta) \cdot z_2(\beta).$$

The mean energy of the mixture is equal to $\mathcal{E}(\beta) = \mathcal{E}_1(\beta_1) + \mathcal{E}_2(\beta_2)$, where $\mathcal{E}_i(\beta_i)$ is the mean energy of the initial subsystem.

On the other hand,

$$\mathcal{E}(\beta) = \frac{\int H(p,q)e^{-\beta H(p,q)}\,dp\,dq}{z} = \mathcal{E}_1(\beta) + \mathcal{E}_2(\beta). \tag{5.11}$$

Now recall that $\dfrac{\partial \mathcal{E}}{\partial \beta} < 0$, therefore, if $T \le T_1 < T_2$ and $\beta_2 < \beta_1 \le \beta$, then $\mathcal{E}_1(\beta) + \mathcal{E}_2(\beta) < \mathcal{E}_1(\beta_1) + \mathcal{E}_2(\beta_2)$ which contradicts to the equality $\mathcal{E}_1(\beta_1) + \mathcal{E}_2(\beta_2) = \mathcal{E}_1(\beta) + \mathcal{E}_2(\beta)$. By a similar reason the inequality $T_1 < T_2 \le T$ is also impossible. Hence

$$T_1 < T < T_2. \tag{5.12}$$

Since $\mathcal{E}(\beta)$ is monotonically decaying function, eq. (5.12) implies that

$$\mathcal{E}_1(\beta_1) < \mathcal{E}_1(\beta), \quad \mathcal{E}_2(\beta_2) > \mathcal{E}_2(\beta). \tag{5.13}$$

In the general case, where the number of particles N_1 and N_2 of the systems to be mixed are not equal, we consider an auxiliary system K consisting of N copies of the system C (the mixture of (1) with (2)). In the system K, the system C plays the role of a subsystem. The Hamiltonian of C is equal to

$$\mathcal{H}(P,Q) = \sum_{\alpha=1}^{N_1} H_1(p^{(\alpha)}, q^{(\alpha)}) + \sum_{\beta=1}^{N_2} H_2(p^{(\beta)}, q^{(\beta)}).$$

The mean energy of C (as a subsystem of K) is equal to

$$E(\beta) = \frac{\int H(P,Q)e^{-\beta H(\mathcal{P},\mathcal{Q})}\,d\mathcal{P}\,d\mathcal{Q}}{\int e^{-\beta \mathcal{H}(\mathcal{P},\mathcal{Q})}\,d\mathcal{P}\,d\mathcal{Q}} = N_1\mathcal{E}_1(\beta) + N_2\mathcal{E}_2(\beta).$$

The total energy of K is equal to $NE(\beta)$.

On the other hand, the conservation of energy implies that $NE(\beta) = N(N_1\mathcal{E}_1(\beta_1) + N_2\mathcal{E}_2(\beta_2))$. Therefore

$$\gamma_1\mathcal{E}_1(\beta) + \gamma_2\mathcal{E}_2(\beta) = \gamma_1\mathcal{E}_1(\beta_1) + \gamma_2\mathcal{E}_2(\beta_2), \tag{5.14}$$

where $\gamma_i = \dfrac{N_i}{N_1 + N_2}$. Here γ_i is the portion of particles of the i-th type in the system C. As earlier, we deduce from (5.14) that $T_1 < T < T_2$ and (5.13).

We can use equation (5.14) for an actual calculation of the temperature of the mixture.

5.6. A remark on the mixing of gases. In the latest two items of this section we intermixed various systems in equilibrium — the favorite pastimes of phenomenological thermodynamicists. Let us discuss how such mixing can be performed physically. Let, in accordance with traditions, the initial systems be a gas A and a gas B. Usually, their mixing is considered to be performed as follows. There is a vessel K divided by a partition on one side of which, K_A, the gas A is placed and on the other one, K_B, the gas B is placed, both in equilibrium. Then the partition is removed and the gases become intermixed.

Such scenario of intermixing is not quite realistic.

Figure 1.1

Indeed, before the partition is removed, a particle of gas A has Hamiltonian $H_A(p,q)$, where q runs over K_A. For a fixed p, the Hamiltonian $H_A(p,q)$ is defined nowhere except K_A. After the partition is removed, q runs over the whole K that is the Hamiltonian $H_A(p,q)$ becomes extended onto the whole K by an unknown way.

The situation is not better if the gas is an ideal one and remains same after the partition is removed. In this case both before and after the partition is removed we have $H_A = \dfrac{p^2}{2m_A}$. However, the independence of $H_A(p,q)$ of q in this case is an imaginary one: Before the partition is removed q runs over K_A whereas after it is removed it runs over K and this is essential, for example, in computing z_A and the pressure.

Therefore, the gas A (same as B) is in distinct thermodynamical states before and after the partition is removed. The initial state of gas A (same as gas B) under the intermixing that was assumed in the above two subsections was the state when the gas occupied **the whole volume** K, that is the state **after the partition had been removed**.

Therefore the intermixing of gases in a vessel should be considered as follows. Let, first, the vessel be occupied by gases A and B so that between the particles of the gas A, same as between the particles of the gas B, the interaction were"small" (that is, on the one hand, the interaction establishes ergodicity but, on the other hand, is so small that we can ignore it computing microcanonical mean, see § 2). We also assume that particles of gas A **do not interact** at all with particles of gas B. Gas A existed in K as if gas B did not exist at all.

Next, we introduce"small interaction" between particles of gas A and B. As a result, we have intermixing which eventually leads to an equilibrium state of the mixture.

The partition is not needed at all! Of course, we can let it be to stir our physical intuition. Then the picture will be as follows: at step 1 we remove the partition but gases A and B do not interact with each other. Thus we prepare the initial states of gases A and B. And at step 2 we switch on the small interaction between gases.

The picture described in the above paragraph is physically justified if gases A and B are distinct. [9)]. The next section is devoted to the case where the gases A and B coincide.

5.7. The principle of indistinguishability of the particles. If the gases A and B consist of identical particles, the above described picture is counterintuitive: In this case, if A and B are at the same temperatures and density, it is impossible to imagine that, after the partition is removed, these gases will, first,"assume the initial position" and spread all over the vessel ignoring each other and only afterwards start intermixing. The intermediary stage seems to be unjustified. This is due to the fact that our intuition automatically takes into account the principle of indistinguishability of particles.

The principle of indistinguishability of the particles. *Let the dynamical system consist of N non-interacting identical subsystems. In this case, the states of the system which are obtained from each other by permutation of coordinates $(p^{(\alpha)}, q^{(\alpha)})$ of the subsystems are indistinguishable.*

The precise meaning of the word"indistinguishable" is that all the physical quantities at our disposal are symmetric with respect to the permutations of the coordinates of the subsystems [10)] and therefore assume the same values at the points with interchanged coordinates.

Taking into account the indistinguishability of the particles the intermixing of gases can be imagined as follows.

The initial position. The system consists of a gas A confined in the volume K_A and having N_A particles and a gas B confined in the volume

[9)] Under appropriate conditions (gases A and B are sufficiently rarefied and their particles are somehow marked; for example, are of different color) one can actually observe such a picture: during the first moments after the partition is removed only the particles near the boundary regions of gases A and B interact. The gases spread all over the whole vessel almost ignoring each other. Later on, ever larger number of particles of these gases become close to each other and interact and the intermixing starts. It goes without saying that it is impossible to study the details of this picture remaining in the framework of the equilibrium statistical physics. The next section is devoted to the case where the gases A and B coincide.

[10)] Recall that all of them are *summatory* ones $\mathcal{F}(P,Q) = \frac{1}{N}\sum f(p^{(\alpha)}, q^{(\alpha)})$.

K_B and having N_B particles. Both gases are in the same thermodynamical state [11]. After the partition is removed the particles of gases A and B situated in the direct vicinity of the partition started to"weakly interact" and this had immediately led to the unification of the gases — they turned into the united gas that occupied the total volume of K. It is meaningless to consider the penetration of particles of gas A in the domain K_B: This domain is occupied by the particles of gas B which are indistinguishable from particles of gas A! Since the equilibrium only depends in this case on the behavior of the boundary particles it is established practically immediately, in any case much faster than in the case where the gases A and B are distinct and to establish the equilibrium in the mixture the participation of all particles of these gases is necessary.

A situation is possible when, with respect to certain physical quantities, the particles of gases A and B behave as indistinguishable, but are distinct with respect to other parameters. For example, they can possess identical mechanical properties (form, elasticity, and so on) but be colored differently. In this case, the values of physical parameters that do not depend on their color will be established in accordance with the indistinguishability principle practically identically and will be the same as the values of these quantities for each gas separately before mixing. But the mixture attains homogeneity of the color much later and the color of the mixture will be distinct from the initial colorations of the gases. In other words, the physical quantities that characterize the interaction of the gases with the light will relax much slower than mechanical ones and, by the way, unlike the mechanical ones, they have to change their values since these values were distinct for the initial gases).

Let us make several remarks of purely mathematical nature.

Remarks. 1) The group of G of permutation of coordinates of subsystems $(p^{(\alpha)}, q^{(\alpha)})$ acts in the phase space of the system consisting of identical subsystems. The subspace of the phase space singled out by the equation $P = 0$ is, obviously, invariant with respect to G. Let T be the fundamental domain [12] for G in this subspace. Then the points of the form (P, Q), where $Q \in T$, constitute a fundamental domain for G in the whole space. We will call it *the effective part* of the phase space and denote by Γ. If $\mathcal{F}(P, Q)$ is a

[11] In other words, at the same temperature and density if we are talking about the ideal gases. Recall that the density is the only exterior parameter of initial gases.

[12] That is a domain possessing the following properties: 1) If $Q \in T$, then $gQ \notin T$ for any $g \in G$ distinct from the unity, 2) any point of the space $P = 0$ can be represented in the form gQ for some $g \in G$ and $Q \in T$, where gQ denotes the result of the action of the element g on the point Q.

function invariant with respect to G, then, obviously,

$$\frac{1}{N!}\int \mathcal{F}(P,Q)\,dP\,dQ = \int\limits_{\Gamma} \mathcal{F}(P,Q)\,dP\,dQ.$$

In the left-hand side, the integral is taken over the total phase space.

In § 6, we will have a chance to observe particular importance of integrals of certain functions over the effective part Γ of the phase space.

2) We can consider the gases A and B before the partition between them was removed and they had been intermixed as a united system whose phase space L_1 is the product of phase spaces L_A and L_B of gases A and B. Obviously, L_1 is a part of the phase space L of the system obtained from gases A and B as a result of removing the partition and intermixing:

$$\begin{aligned} &L = \{(p^{(\alpha)}, q^{(\alpha)}) \mid q^{(\alpha)} \in K\},\\ &L_1 = \{(p^{(\alpha)}, q^{(\alpha)}) \mid q^{(\alpha)} \in K_A \ \text{ or } \ q^{(\alpha)} \in K_B\},\\ &K = K_A \cup K_B. \end{aligned}$$

The group $S_1 = S_A \times S_B$, consisting of the permutations of coordinates of particles of gases A and B separately, acts in the space L_1. Let T_1 be the fundamental domain for S_1 in L_1. Obviously, $T_1 = T_A \times T_B$, where T_A and T_B are the fundamental domains in L_A and L_B for the groups S_A and S_B, respectively.

3) Let the gases A and B consist of indistinguishable particles and the specific volumes of the gases before the partition is removed were equal. It is of interest to estimate the portion of the space L contained in L_1. Both spaces are the products of the common subspace $\{p^{(\alpha)}, 0\}$ by the domain $\{0, q^{(\alpha)}\}$ which, in the first case, coincides with K^N and, in the second case, with $K_A^{N_A} \times K_B^{N_B}$. Their respective volumes are equal to V^N and $V_A^{N_A} V_B^{N_B}$. Obviously, $V^N \gg V_A^{N_A} V_B^{N_B}$. (For example, if $V_A = V_B = \frac{1}{2}V$, then $V^N = 2^N V_A^{N_A} V_B^{N_B}$.)

With the volumes of fundamental domains T and T_1 the situation is quite different. Denote them by $V_{\text{eff.}}$ and $V_{1\,\text{eff.}}$, respectively. Applying the Stirling formula we deduce that

$$\begin{aligned} V_{\text{eff.}} &= \frac{1}{N!} V^{N_A+N_B} \approx e^{N_A+N_B} \left(\frac{V}{N_A+N_B}\right)^{N_A+N_B},\\ V_{1\,\text{eff.}} &= \frac{V_A^{N_A}}{N_A!}\,\frac{V_B^{N_B}}{N_B!} \approx e^{N_A+N_B} \left(\frac{V_A}{N_A}\right)^{N_A} \left(\frac{V_B}{N_B}\right)^{N_B}. \end{aligned}$$

Since the specific volumes of gases were equal, i.e., $v = \dfrac{V_A}{N_A} = \dfrac{V_B}{N_B}$, we have $v = \dfrac{V_A + V_B}{N_A + N_B} = \dfrac{V}{N_A + N_B}$, and therefore

$$\lim_{N\to\infty} \frac{V_{\text{eff.}}}{V_{1\,\text{eff.}}} = 1.$$

The result obtained apparently demonstrates that although the part of L complementary to L_1 might be huge, it is"a hick town", hardly essential for the statistical properties of the system. Therefore, the systems before and after intermixing are close and nothing essential happens after partition is removed. The equilibrium takes place practically instantly.

§ 6. Properties of the entropy

6.1. The maximum principle. The entropy of the individual subsystem $S'(\beta)$ can be expressed in terms of the Gibbs distribution by a simple formula

$$S' = \int \rho(p,q) \ln \rho(p,q)\, dp\, dq. \tag{6.1}$$

To prove it, one should substitute $\rho = \dfrac{e^{-\beta H(p,q)}}{\int e^{-\beta H}}$ into (6.1) and compare the result obtained with the definition (formula (5.6).

Formula (6.1) is remarkable: With its help we can determine the entropy for an arbitrary distribution $\rho(p,q)$. The Gibbs distribution is singled out from the set of all distributions by the following *maximum principle*.

6.1.1. Theorem. *Consider distributions ρ such that $\int H(p,q)\rho(p,q)\, dp\, dq = \mathcal{E}$. On this set, the entropy has the only maximum attained on the Gibbs distribution.*

Proof. To prove the maximum principle, we compute the first variation of the entropy and show that the entropy possesses the only stationary point — the Gibbs distribution, and the second variation is negative at this point.

Thus, we are looking for the stationary points of the functional

$$S = -\int \rho(p,q) \ln \rho(p,q)\, dp\, dq$$

such that

$$\int H(p,q)\rho(p,q)\, dp\, dq = \mathcal{E},$$

$$\int \rho(p,q)\, dp\, dq = 1.$$

As always, while seeking the conditional extremum we consider the functional

$$\mathcal{F} = S - \lambda \int H(p,q)\rho(p,q)\,dp\,dq - \mu \int \rho(p,q)\,dp\,dq.$$

and compute its variational derivative $\mathcal{F}$

$$\frac{\delta \mathcal{F}}{\delta \rho(p,q)} = -\ln \rho(p,q) - 1 - \lambda H(p,q) - \mu,$$

wherefrom $\rho(p,q) = Ce^{-\lambda H(p,q)}$. Denote by β the solution of the equation

$$\frac{1}{\int e^{-\lambda H}\,dp\,dq} \int H(p,q)e^{-\lambda H(p,q)}\,dp\,dq = \mathcal{E}.$$

In § 4 we have shown that this equation has a unique solution. As a result, we obtain that the only stationary point of our variational problem is the Gibbs distribution.

Now, let us compute the second variational derivative:

$$\frac{\delta^2 S}{\delta\rho(p,q)\delta\rho(p',q')} = -\frac{\delta(p-p')\delta(q-q')}{\rho(p,q)}.$$

Thus,the second variation is strictly negative.

Clearly, we can do without delta functions as well: Just look at

$$S(\rho + h) = S(\rho) - \int h(p,q)(\ln \rho(p,q) + 1)\,dp\,dq - \frac{1}{2}\int \frac{h^2(p,q)}{\rho(p,q)}\,dp\,dq + \dots$$

From this expansion we also deduce that the second variation is strictly negative. The maximum principle is proved. □

6.2. The Nernst theorem. Let us now find out how the entropy depends on β or, which is the same, on the temperature T. In order to simplify the formulas, we ignore the inessential, at this stage, parameter N and, instead of the entropy of the whole system S, we consider the function $S'(\beta) = \ln z + \beta\mathcal{E}$. (Recall that $S = NS' + C$.) Observe that

$$\frac{\partial S'}{\partial \beta} = \frac{\partial \ln z}{\partial \beta} + \mathcal{E} + \beta\frac{\partial \mathcal{E}}{\partial \beta} = \beta\frac{\partial \mathcal{E}}{\partial \beta},$$

since $\mathcal{E} = -\dfrac{\partial \ln z}{\partial \beta}$. In § 3, we showed that $\dfrac{\partial \mathcal{E}}{\partial \beta} < 0$, and therefore $\dfrac{\partial S}{\partial \beta} < 0$.

Let us investigate the behavior of the entropy as $T \to 0$ $(\beta \to \infty)$. We will assume (as in § 3) that the volume of the surface of constant energy $\omega(h)$ decays as $h \to 0$ as a polynomial function

$$\omega(h) = \int \delta(H(p,q) - h)\,dp\,dq = h^\alpha \omega_0(1 + o(1)) \quad \text{as} \quad h \to 0.$$

We will simplify the problem further, and assume that

$$\omega(h) = \omega_0 h^\alpha (1 + \omega_1(h) h^\alpha), \quad \text{where } |\omega_1(h)| < C,\ \gamma > 0. \tag{6.2}$$

Let us transform the integral that determines z as follows:

$$z = \int e^{-\beta H(p,q)}\, dp\, dq = \int_0^\infty e^{-\beta h} \delta(h - H(p,q))\, dp\, dq\, dh = \int_0^\infty e^{-\beta h} \omega(h)\, dh.$$

Set

$$z = z_1 + z_2, \quad \text{where} \quad z_1 = \int_0^1 e^{-\beta h} \omega(h)\, dh, \quad z_2 = \int_1^\infty e^{-\beta h} \omega(h)\, dh.$$

Let us find the asymptotic of each summand separately. Let us evaluate z_1 taking (6.2) into account:

$$z_1 = \omega_0 \int_0^1 e^{-\beta h} h^\alpha (1 + h^\gamma \omega_1(h))\, dh =$$

$$= \frac{\omega_0}{\beta^{\alpha+1}} \int_0^\beta e^{-S} S^\alpha\, dS + \frac{\omega_0}{\beta^{\alpha+1+\gamma}} \int_0^\beta e^{-S} S^{\alpha+\gamma} \omega_1\Big(\frac{S}{\beta}\Big)\, dS.$$

As $\beta \to \infty$ we have

$$\frac{\omega_0}{\beta^{\alpha+1}} \int_0^\beta e^{S} S^\alpha\, dS \sim \Gamma(\alpha+1) \frac{\omega_0}{\beta^{\alpha+1}},$$

$$\frac{\omega_0}{\beta^{\alpha+1+\gamma}} \int_0^\beta e^{S} S^{\alpha+\gamma} \omega\Big(\frac{S}{\beta}\Big)\, dS \sim \frac{\text{const}}{\beta^{\alpha+1+\gamma}}.$$

Thus,

$$z_1 \sim \omega_0 \frac{\Gamma(\alpha+1)}{\beta^{\alpha+1}} \quad \text{as } \beta \to \infty.$$

The asymptotics of z coincides with the asymptotics of z_1 since

$$z_2 = \int_1^\infty e^{-\beta h} \omega(h)\, dh = e^{-\frac{\beta}{2}} \int_1^\infty e^{-\beta(h-\frac{1}{2})} \omega(h)\, dh < \text{const} \times e^{-\frac{\beta}{2}}.$$

Therefore

$$\ln z \sim C - (\alpha+1)\ln\beta.$$

Now let us investigate $\mathcal{E}$. We have

$$\mathcal{E} = \frac{\int He^{-\beta h}\,dp\,dq}{z} = \frac{\int\limits_0^\infty he^{-\beta h}\omega(h)\,dh}{\int\limits_0^\infty e^{-\beta h}\omega(h)\,dh} \sim \frac{\omega_0\dfrac{\Gamma(\alpha+2)}{\beta^{\alpha+2}}}{\omega_0\dfrac{\Gamma(\alpha+1)}{\beta^{\alpha+1}}} = \frac{C_1}{\beta},$$

i.e., at large β (small T) the energy is proportional to T. The final result is

$$S' \sim -C - (\alpha+1)\ln\beta = -C + (\alpha+1)\ln T. \tag{6.3}$$

Thus, $S(T) \to -\infty$ as $T \to 0$ in the same way as $\ln T$. The result obtained contains the negative answer to the question of § 5: Is it possible to select a constant in the definition of entropy so that $S(0) = 0$? In the framework of classical mechanics, there is no way to select such a constant.

The result obtained contradicts the wide-spread but imprecise formulation of the *Nernst theorem* according to which

there exists a constant C such that the entropy $S = N(\ln z + \beta E) + C$ vanishes at $T = 0$.

In the classical statistical physics, this is impossible. In the quantum statistical physics, as we will see in due course, this is, however, possible. In conclusion, observe that from"genuinely physical" point of view the above common formulation of the Nernst theorem is not, however, too imprecise since, at the temperatures close to the absolute zero, quantum statistical physics operates, not the classical one.

6.3. The Boltzmann formula. Let us return to formula (4.14). According to this formula, there exists a limit $\lim\limits_{N\to\infty}\dfrac{1}{N}\ln\Omega_N(E)$, where

$$\Omega_N(E) = \int \delta(\mathcal{H}(P,Q) - E)\,dP\,dQ$$

is the volume of the surface of constant energy in the phase space of the whole system. According to (4.14) this limit is equal to

$$\lim_{N\to\infty}\frac{1}{N}\ln\Omega_N(E) = \varphi(0), \tag{6.4}$$

where

$$\varphi(0) = \ln\int e^{-\beta(H(p,q)-\mathcal{E})}\,dp\,dq = \ln z + \beta\mathcal{E} = S'$$

is the specific entropy. In a somewhat weaker form the result obtained can be expressed as an asymptotic equality

$$\Omega_N(E) = e^{NS} \approx e^S. \tag{6.5}$$

Formula (6.5) is known as **the Boltzmann formula**. Boltzmann considered it one of his greatest achievements.

6.4. The Gibbs paradox. Let us compute the entropy of one-atom ideal gas confined in a vessel of volume V at temperature $T = \dfrac{1}{k\beta}$. In § 5, we have already computed the statistical integral

$$z = V\Big(\frac{2\pi m}{\beta}\Big)^{3/2}.$$

From this we deduce that

$$S = N(\ln z + \beta\mathcal{E}) + C = N\ln V + \frac{3}{2}N\ln\Big(\frac{2\pi m}{\beta}\Big) + \beta N\mathcal{E} + C, \tag{6.6}$$

where $\mathcal{E}$ is the mean energy of the molecule. It is easy to calculate that

$$\mathcal{E} = \frac{\int \dfrac{1}{2m}\sum\limits_{i=1}^{3} p_i^2 e^{-\frac{\beta}{2m}\sum\limits_{i=1}^{3} p_i^2}\, d^3p\, d^3q}{\int e^{-\frac{\beta}{2m}\sum\limits_{i=1}^{3} p_i^2}\, d^3p\, d^3q} = \frac{3}{2\beta} = \frac{3}{2}kT. \tag{6.7}$$

Suppose that the constant C that enters the definition of entropy is somehow fixed and does not depend on N.

Now assume that the vessel is obtained by joining two vessels whose volumes are V_1 and V_2 and which contained the same ideal gas at the same equilibrium state (i.e., at the same temperature and with the same density). Let us calculate the change of specific entropy occasioned by mixing the gases:

$$\frac{1}{N}\Delta S = \frac{1}{N}(S - S_1 - S_2) = \frac{1}{N}(N\ln V - N_1\ln V_1 - N_2\ln V_2) = \\ = \frac{N_1}{N}\ln\frac{V}{V_1} + \frac{N_2}{N}\ln\frac{V}{V_2} > 0.$$

Thus, under mixing of identical gases at the same equilibrium state, the mean entropy of one particle increases which does not make sense since, as a result of intermixing, we obtain the gas in the same equilibrium state at the initial components. This is the contents of *the Gibbs paradox*.

To resolve the paradox, we should concede that C must depend on N. And since we would like to consider the ideal gas in the vessel of variable volume V, we must consider it as an ensemble of macroscopic subsystems and set $V = Nv$, where v is the specific volume that does not depend on N (see. **??**). Recall that it is specific volume, not the total volume, which is a physical characteristic of the system.

Set $C = -N \ln N$ and use the equality $\mathcal{E}\beta = \dfrac{3}{2}$ (see (6.7)). As a result, we obtain an expression of the entropy in terms of the specific volume that does not lead to paradoxes:

$$S = N\Big(\ln v + \frac{3}{2} \ln \frac{2\pi m}{\beta} + \frac{3}{2}\Big). \tag{6.8}$$

The expression in parentheses can be interpreted as the specific entropy. In conclusion, observe that one can deduce expression (6.8), or rather its version, with the last summand replaced by $\dfrac{5}{2}$ in the following way. In the phase space of the whole system, consider the function

$$\Phi = e^{-\beta(\mathcal{H}(P,Q)-E)},$$

where $\mathcal{H}(P, Q)$ is the Hamiltonian of the whole system and $E = N\mathcal{E}$ is the total energy of the system. The integral of Φ over the effective part of the phase space is asymptotically equal to

$$\frac{1}{N!} \int \Phi \, dP \, dQ \approx e^S = e^{NS'}, \tag{6.9}$$

where S' is the expression in the parentheses of (6.6) modified as indicated. We should understand the equality (6.9) as the statement on the existence of the limit

$$S' = \lim_{N\to\infty} \frac{1}{N} \left(\ln \frac{1}{N!} \int \Phi \, dP \, dQ \right).$$

Indeed, set

$$I_N = \frac{1}{N!} \int \Phi \, dP \, dQ = \frac{z^N}{N!} e^{N\beta\mathcal{E}}.$$

Then

$$\frac{1}{N} \ln I_N = \ln z + \beta\mathcal{E} - \frac{\ln N!}{N} = \ln V + \frac{3}{2} \ln \frac{2\pi m}{\beta} + \beta\mathcal{E} - \frac{\ln N!}{N}.$$

The Stirling formula implies that $\dfrac{\ln N!}{N} \approx \ln N - 1$. Therefore

$$\lim_{N\to\infty} \frac{1}{N} \ln I_N = \ln \frac{V}{N} + \frac{3}{2} \ln \frac{2\pi m}{\beta} + \frac{5}{2} = S'.$$

In our transformations we used the fact that $\beta\mathcal{E} = \frac{3}{2}$. Formula (6.9) is remarkable: It is an exact analogue of the corresponding formula of the quantum statistical physics and can be obtained from the latter by passing to the limit as $h \to 0$, where h is the Planck constant.

§ 7. Analytical appendix to Chapter 1

Let $f(x)$ be locally integrable on $(0, \infty)$ and $|f(x)| < Cx^N$ for x large. Its *Laplace transform* is the function

$$F(t) = \int_0^\infty e^{-tx} f(x)\, dx.$$

For the Laplace transform, the inversion formula holds:

$$f(x) = \lim_{b\to\infty} \frac{1}{2\pi} \int_{-b}^{b} F(\lambda + it) e^{(\lambda+it)x}\, dt = \lim_{b\to\infty} \frac{1}{2\pi i} \int_{\lambda-ib}^{\lambda+ib} F(p) e^{px}\, dp \quad \text{as } \lambda > 0.$$

(The limit in the right-hand side does not depend on λ).

Proof does not differ from the proof of the inversion formula for the Fourier transform and we will omit it.

In order to introduce the Gibbs distribution we have to know the asymptotic behavior of the integral

$$R(N) = \int_{-\infty}^{\infty} \psi(t) e^{N\varphi(t)}\, dt \quad \text{as } N \to \infty. \tag{7.1}$$

7.1. Theorem. *Let the function $\psi(t)$ be bounded and differentiable, let $\varphi(t)$ be three times continuously differentiable and satisfy the following conditions*:

a) $\varphi(0)$ *is real;* ;

b) $\varphi'(0) = 0$;

c) $\varphi''(0)$ *is real and* $\varphi''(0) = -\alpha < 0$;

d) *for any* $\delta > 0$ *and sufficiently large* N, *we have*

$$\int_{|t|>\delta} e^{N\,Re\,(\varphi(t)-\varphi(0))}\, dt < \frac{\sigma}{N}, \quad \textit{where } \sigma = \sigma(\delta).$$

Then the function $R(N)$ can be expressed, for sufficiently large N, in the form

$$R(N) = \sqrt{\frac{\pi}{N\alpha}} e^{N\varphi(0)} \Big(\Big(1 + \frac{c(N)}{\sqrt{N}}\Big)\psi(0) + \frac{b(N)}{\sqrt{N}} \Big),$$

where [13)]

$$|c(N)| \le \max_{|t|<\delta} \frac{\varphi(0) - t^2\alpha}{t^3\alpha},$$

$$|b(N)| \le \sup_t |\psi(t)| + \max_{|t|<\delta} \Big| \frac{\psi(t) - \psi(0)}{t} \Big|.$$

Proof. Let us present the integral (7.1) as the sum:

$$\int_{-\infty}^{\infty} \psi(t) e^{N\varphi(t)}\, dt = \int_{|t|<\delta} \psi(t) e^{N\varphi(t)}\, dt + \int_{|t|>\delta} \psi(t) e^{N\varphi(t)}\, dt. \tag{7.2}$$

Let us first estimate the second integral in (7.2):

$$\Big| \int_{|t|>\delta} \psi(t) e^{N\varphi(t)}\, dt \Big| \le \sup_t |\psi(t)| \int_{|t|>\delta} e^{N\mathrm{Re}\ \varphi(t)}\, dt =$$

$$= e^{N\varphi(0)} \sup_t |\psi(t)| \int_{|t|>\delta} e^{N\mathrm{Re}\ (\varphi(t)-\varphi(0))}\, dt \le e^{N\varphi(0)} \sup_t |\psi(t)| \frac{\sigma}{N},$$

where σ is determined by condition d) of the theorem. We finally see that, for N sufficiently large, we have

$$\int_{|t|>\delta} \psi(t) e^{N\varphi(t)}\, dt = e^{N\varphi(0)} \frac{c_1}{N}, \quad \text{where } |c_1| \le \sigma \sup_t |\psi(t)|. \tag{7.3}$$

Let us pass to the first integral in (7.2):

$$\int_{-\delta}^{\delta} \psi(t) e^{N\varphi(t)}\, dt = \psi(0) \int_{-\delta}^{\delta} e^{N\varphi(t)}\, dt + \int_{-\delta}^{\delta} [\psi(t) - \psi(0)] e^{N\varphi(t)}\, dt. \tag{7.4}$$

Thanks to conditions a), b) and c), for a sufficiently small δ and $|t| < \delta$, the function φ is of the form

$$\varphi(t) = \varphi(0) - t^2\alpha + t^3\alpha[\varphi_1(t) + i\varphi_2(t)],$$

[13)] If $\psi(t)$ is real, then we have a more convenient estimate of $b(N)$:

$$|b(N)| \le \sup_t |\psi(t)| + \max_{|t|<\delta} |\psi'(t)|.$$

where φ_1 and φ_2 are continuous.

Let us select δ so that, for $|t| < \delta$, we have

$$1 - t\varphi_1(t) > \varkappa > 0, \quad 1 - \frac{t}{2}\varphi_1(t) > \varkappa > 0. \tag{7.5}$$

Let us rewrite the integral $\int\limits_{-\delta}^{\delta} e^{N\varphi(t)}\,dt$:

$$\int\limits_{-\delta}^{\delta} e^{N\varphi(t)}\,dt = e^{N\varphi(0)} \int\limits_{-\delta}^{\delta} e^{-Nt^2\alpha(1-t[\varphi_1(t)+i\varphi_2(t)])}\,dt =$$

$$= e^{N\varphi(0)} \int\limits_{-\delta}^{\delta} e^{-Nt^2\alpha}\,dt + e^{N\varphi(0)} \int\limits_{-\delta}^{\delta} e^{-Nt^2\alpha}\big(e^{Nt^3\alpha(\varphi_1+i\varphi_2)} - 1\big)\,dt.$$

It is easy to estimate the first summand:

$$\int\limits_{-\delta}^{\delta} e^{-Nt^2\alpha}\,dt = \frac{1}{\sqrt{N\alpha}} \int\limits_{-\delta\sqrt{N\alpha}}^{\delta\sqrt{N\alpha}} e^{-S^2}\,dS = \sqrt{\frac{\pi}{N\alpha}}(1 + c_N), \tag{7.6}$$

where $c_N = 2 \int\limits_{\delta\sqrt{N\alpha}}^{\infty} e^{-S^2}\,dS \sim e^{-\delta^2 N\alpha}$.

In order to estimate $\int\limits_{-\delta}^{\delta} e^{-Nt^2\alpha}\big(e^{Nt^3\alpha(\varphi_1+i\varphi_2)} - 1\big)\,dt$, observe that

$$|e^{a+ib} - 1|^2 = 1 + e^{2a} - 2e^a\cos b = 1 + e^{2a} - 2e^a + 2e^a(1 - \cos b) =$$

$$= (1 - e^a)^2 + 4e^a \sin^2\frac{b}{2} \le (ae^a)^2 + 4e^a \sin^2\frac{b}{2} \le$$

$$\le (ae^a)^2 + b^2 e^a \le (|a|e^a + |b|e^{a/2})^2.$$

This implies

$$|e^{a+ib} - 1| \le |a|e^a + |b|e^{a/2}.$$

Let us use this inequality and (7.5):

$$\Big|\int\limits_{-\delta}^{\delta} e^{-Nt^2\alpha}\big(e^{Nt^3\alpha(\varphi_1+i\varphi_2)}-1\big)\,dt\Big| \le \int\limits_{-\delta}^{\delta} e^{-Nt^2\alpha}N|t|^3\alpha(|\varphi_1|e^{Nt^3\alpha\varphi_1}+$$

$$+|\varphi_2|e^{Nt^3\alpha\frac{\varphi_1}{2}})\,dt \le \int\limits_{-\delta}^{\delta} N|t|^3\alpha(|\varphi_1|+|\varphi_2|)e^{-Nt^2\alpha\varkappa}\,dt \le$$

$$\le cN\alpha\int\limits_{-\delta}^{\delta} e^{-\varkappa t^2N\alpha}|t|^3\,dt = \frac{cN\alpha}{(N\alpha\varkappa)^2}\int\limits_{-\delta\sqrt{N\varkappa\alpha}}^{\delta\sqrt{N\varkappa\alpha}} e^{-S^2}|S|^3\,dS =$$

$$= \frac{C}{N\alpha\varkappa^2}(1+c_1(N)), \quad (7.7)$$

where

$$c=\max_{|t|<\delta}(|\varphi_1(t)|+|\varphi_2(t)|), \quad c_1(N)=2\int\limits_{\delta\sqrt{N\varkappa\alpha}}^{\infty} S^3e^{-S^2}\,dS\to 0 \quad \text{as } N\to\infty.$$

Taking into account (7.6) and (7.7) we get

$$\int\limits_{-\delta}^{\delta} e^{N\varphi(t)}\,dt = \sqrt{\frac{\pi}{N\alpha}}\Big(1+\frac{a'(N)}{\sqrt{N\alpha}}\Big)e^{N\varphi(0)}, \quad (7.8)$$

where

$$a'(N)\le \max_{|t|<\delta}(|\varphi_1(t)|+|\varphi_2(t)|)+c'(N)\le$$

$$\le \sqrt{2}\max_{|t|<\delta}|\varphi_1(t)+i\varphi_2(t)|+c'(N)=\sqrt{2}\max_{|t|<\delta}\Big|\frac{\varphi-\varphi(0)+t^2\alpha}{t^3\alpha}\Big|+c'(N),$$

and $c'(N)\to 0$ as $N\to\infty$. For N sufficiently large, we can ignore $c'(N)$ by increasing the estimate of the first summand:

$$a'(N)\le 2\max_{|t|<\delta}\Big|\frac{\varphi-\varphi(0)+t^2\alpha}{t^3\alpha}\Big|.$$

Let us pass to the second integral in (7.4):

$$\left|\int_{-\delta}^{\delta}[\psi(t)-\psi(0)]e^{N\varphi(t)}\,dt\right| \le c_1\int_{-\delta}^{\delta}|t|e^{N\varphi(0)}e^{N(-t^2\alpha+t^3\alpha\varphi_1(t))}\,dt \le$$

$$\le c_1\int_{-\delta}^{\delta}|t|e^{-\varkappa t^2N}\,dte^{N\varphi(0)} = c_1e^{N\varphi(0)}\frac{1-e^{-\varkappa N\delta^2}}{\varkappa N} \le \frac{c_1e^{N\varphi(0)}}{\varkappa N},$$

where

$$c_1 = \max_{|t|<\delta}\Big|\frac{\psi(t)-\psi(0)}{t}\Big|.$$

Finally, we see that, for N sufficiently large, we have

$$\int_{-\delta}^{\delta}\psi(t)e^{N\varphi(t)}\,dt = \sqrt{\frac{\pi}{N\alpha}}e^{N\varphi(0)}\Big(\Big(1+\frac{a'(N)}{\sqrt{N}}\Big)\psi(0)+\frac{b'(N)}{\sqrt{N}}\Big), \tag{7.9}$$

where

$$|a'(N)| \le 2\max_{|t|<\delta}(|\varphi_1(t)|+|\varphi_2(t)|), \quad |b'(N)| \le \max_{|t|<\delta}\Big|\frac{\psi(t)-\psi(0)}{t}\Big|.$$

Uniting (7.9) and (7.3) we complete the proof of the theorem. □

Chapter 2

REAL GASES

§ 8. Physical assumptions

8.1. Properties of interaction. We consider the gas as a collection of indistinguishable molecules which are massive points with pairwise interaction described by potential $u(x)$. The gas is confined in a large macroscopic vessel Ω [1)] and its volume will be denoted by $|\Omega|$. The Hamiltonian of the system consisting of M molecules is equal to

$$\mathcal{H} = \sum_{i=1}^{M} \frac{p_i^2}{2m} + \sum_{1 \le i < j \le M} v(q_i - q_j), \tag{8.1}$$

where $q_i = (q_i^{(1)}, q_i^{(2)}, q_i^{(3)}) \in \Omega$, $p_i = (p_i^{(1)}, p_i^{(2)}, p_i^{(3)})$. In order not to complicate the presentation by inessential details, we will always assume that $u(q)$ only depends on $|q| = \sqrt{{q_i^{(1)}}^2 + {q_i^{(2)}}^2 + {q_i^{(3)}}^2}$, and

$$v(q) \begin{cases} = +\infty & \text{for } |q| \le a, \\ \not\equiv \infty & \text{for } |q| > a, \\ = 0 & \text{for } |q| > b, \\ \not\equiv 0 & \text{in any interval } b_1 < |q| < b. \end{cases}$$

The assumption that $v(q) = \infty$ for $|q| \le a$ physically means that the molecules cannot be at distances smaller than a from each other; that is each of them is confined in the center of impenetrable spherical envelope of radius a. It is also possible to assume that every molecule is a hard ball of radius $\frac{a}{2}$ centered at q_i. The number $\frac{a}{2}$ is sometimes called *the radius of the hard core*.

The assumption that $v(q) = 0$ for $|q| > b$ means that the molecules do not interact if the distance between them is $> b$. The number b is called the *radius of interaction*. The numbers a and b are comparable with the actual sizes of molecules and are very small from the macroscopic point of view.

[1)] For example, assume that Ω is a room.

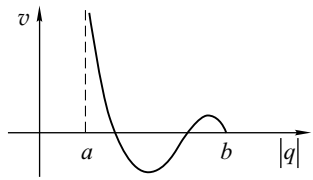

Figure 2.1. The typical graph of $v(q)$

The assumption on potential implies an important corollary: There exists a constant C independent of n such that

$$\sum_{i,j=1}^{n} v(x_i - x_j) \geq nC \quad \text{for any points } x_i.$$

8.2. The small and grand ensembles. In order to enter the realm of ideas of statistical physics we should subdivide the system into weakly interacting subsystems. Let us discuss how one can do it. Denote the system considered by C and its phase space by L.

Subdivide the volume Ω into a large number K of macroscopic non-interacting subvolumes Ω_α [2)]. Let us consider the volumes Ω_α separated from each other by imaginary partitions impenetrable for the particles but not preventing the interaction of the particles situated on different sides of the partition. Let each volume Ω_α contain the same number of particles N. The system thus obtained will be denoted by C' and its phase space by L_1. The part of the gas confined in Ω_α forms *the subsystem* needed; we denote it by C^1_α. We replace the initial system by the new system C^1 and enumerate the particles of gas again (there are $M = kN$ of them) and denote by N_α the set of numbers of the particles lying in Ω_α. The Hamiltonian of the system C^1 is of the form

$$\begin{aligned} &\mathcal{H} = \sum H_\alpha + V, \quad \text{where } H_\alpha = \sum_{i \in N_\alpha} \frac{p_i^2}{2m} + \sum_{\substack{i,j \in N_\alpha \\ i<j}} v(q_i - q_j), \\ &V = \sum_{\alpha<\beta} v_{\alpha,\beta}, \quad \text{and } v_{\alpha,\beta} = \sum_{\substack{i \in N_\alpha \\ j \in N_\beta}} v(q_i - q_j). \end{aligned} \tag{8.2}$$

The systems C^1_α are not quite identical: The coordinates $q_{i\alpha}$ run distinct sets Ω_α.

[2)] If Ω is a room then for Ω_α we can take a cube with volume 1 cm^3.

We may assume that the interaction between the subsystems C^1_α is small. Since, due to the fact that the potential $v(q)$ has a compact support, the energy of interaction of subsystems $\sum v_{\alpha,\beta}$ is of the same order of magnitude as the area of the surface that separates the volumes Ω_α, whereas the potential energy of the system is proportional to the volume of Ω_α and is therefore much larger.

Obviously, from the physical point of view, the replacement of the initial system C by an auxiliary system C^1 is unsatisfactory: the presence of impenetrable walls changes the properties of the gas confined in Ω: For example, it makes the large-scale (as compared with the size of Ω_α) movements of molecules (such as wind) impossible.

The situation can be corrected by changing the definition of the *subsystem*. Let us, as earlier, call a portion of the gas confined within Ω_α a *subsystem*; let also think that there are precisely N particles in each Ω_α but let us not assume that the particles contained in Ω_α are the same ones: The molecules can exit Ω_α and enter Ω_α from the other regions of Ω provided the number of exiting particles is always equal to the number of new arrivals.

The system obtained is said to be *a small canonical ensemble*. Let us denote it by C^2. We will denote its phase space by L_2. The Hamiltonian of the small canonical ensemble is obviously of the same form (8.1). Like L_1, the phase space L_2 is only a part of the total phase space of the initial system. Intuitively it is, however, clear that this part is *a main* one: The condition on the constant number of particles in Ω_α is satisfied with high accuracy and means, essentially, that the density of the gas in all chambers Ω_α is the same.

Let us study a relation between the phase space L_1 of the auxiliary system C^1 considered earlier and the space L_2. The phase space L_1 is determined by the condition

$$q_i \in \Omega_\alpha \quad \text{for} \quad i \in N_\alpha.$$

Let $g\colon i \to i_g$ be a permutation of the indices $1, \dots, M$. Denote by L_g a region similar to L_1:

$$q_{i_g} \in \Omega_\alpha \quad \text{for} \quad i \in N_\alpha.$$

Obviously, the phase space of the small canonical ensemble is $L_2 = \bigcup\limits_{g \in G} L_g$ where G is the group of all permutations of the indices $1, \dots, M$. Therefore L_2 is G-invariant and splits into $\dfrac{M!}{(N!)^K}$, where $M = NK$, domains congruent to L_1 and obtained from L_1 by the action of G. If $\mathcal{F}(P,Q) = \mathcal{F}(p_1, q_1, \dots, p_M, q_M)$ is a function symmetric with respect to

permutations of the pairs (p_i, q_i), then integrals of $\mathcal{F}$ over L_1 and L_2 only differ by a factor:

$$\int\limits_{L_2} \mathcal{F}\, dP\, dQ = \frac{M!}{(N!)^K} \int\limits_{L_1} \mathcal{F}\, dP\, dQ.$$

This implies that the microcanonical means of these functions coincide:

$$\frac{\int\limits_{L_2} \mathcal{F}\delta(\mathcal{H}-E)\, dP\, dQ}{\int\limits_{L_2} \delta(\mathcal{H}-E)\, dP\, dQ} = \frac{\int\limits_{L_1} \mathcal{F}\delta(\mathcal{H}-E)\, dP\, dQ}{\int\limits_{L_1} \delta(\mathcal{H}-E)\, dP\, dQ}. \tag{8.3}$$

Thus the statistical properties of the first auxiliary system and the small canonical ensemble coincide provided *the principle of indistinguishability of the particles* is applicable, i.e., if we only consider the means of symmetric functions.

The statistical physics of a real gas always assumes the indistinguishability of the particles. Only symmetric functions $\mathcal{F}(P, Q)$ exist for us.

Even a more liberal definition of a subsystem is possible. A portion of gas confined within Ω_α is said to be *a subsystem* without any assumption on the constant number of the particles in Ω_α; this assumption being replaced by a weaker assumption on the constant nature of the microcanonical mean number of particles in Ω_α. The collection of such subsystems is called *a grand canonical ensemble*. The phase space of the grand canonical ensemble L_3 obviously contains the space L_2 of the small canonical ensemble but is, obviously, contained within the phase space L of the initial system.

In conclusion, observe that the real gas is *an ensemble of macroscopic subsystems*. Unlike the systems studied in Chapter 1, for which the presence of one large number — the number of subsystems in a system — was a characteristic feature, the real gas is characterized by two large numbers: The number K $(K > 10^5)$ of subsystems in the system and the number N $(N > 10^{20})$ of particles in each subsystem.

Obviously, only the quantities obtained as a result of two consecutive passages to the limits (as $K \to \infty$ and $N \to \infty$) may possess a physical interpretation. Both limit processes are called *thermodynamical* ones and both processes assume that the density of the gas remains constant.

The first passage to the limit

$$K \to \infty, \quad |\Omega_\alpha| = \text{const}, \quad N = \text{const},$$

is analogous to the thermodynamical limit considered in Chapter 1. It turns the microcanonical distribution in the small canonical ensemble into the Gibbs distribution for the subsystem.

The second limiting process

$$N \to \infty, \quad \frac{N}{|\Omega_\alpha|} = \text{const},$$

is indigenous for the real gases and does not appear in the study of ensembles of microscopic subsystems.

§ 9. The Gibbs Distribution in the Small Canonical Ensemble

9.1. Step one. At the moment, no rigorous, in the modern sense of this word, deduction of the Gibbs distribution in this situation is known, and therefore we will confine ourselves to heuristic arguments.

First of all, assume that for the Hamiltonian (8.1) § 8 the ergodic hypothesis is applicable. This implies that the mean with respect to time of any physical quantity is equal to the mean over the surface of constant energy [3] (see. § 1).

$$\overline{\mathcal{F}} = \frac{\int \mathcal{F}\delta(\mathcal{H} - E)\, dP\, dQ}{\int \delta(\mathcal{H} - E)\, dP\, dQ}, \tag{9.1}$$

where $\mathcal{H}$ is the Hamiltonian (8.1), $P = (p_1, \dots, p_M)$, $Q = (q_1, \dots, q_M)$.

We assume that the principle of indistinguishibility of the particles is applicable, i.e., apply formula (8.1) only to the functions $\mathcal{F}$ symmetric with respect to permutations of the pairs (p_i, q_i).

Let N be the number of molecules in the cell Ω_α and K the number of cells in Ω and let $\chi_\alpha(q)$ be the characteristic function of the cell Ω_α. Observe that

$$1 = \sum_{\alpha=1}^{K} \chi_\alpha(q) = \prod_{i=1}^{M} \left(\sum_{\alpha=1}^{K} \chi_\alpha(q_i) \right) = \sum \chi_{\alpha_1}(q_1) \dots \chi_{\alpha_M}(q_M). \tag{9.2}$$

Using identity (9.2) and the symmetry of $\mathcal{F}$ we find that the numerator

[3] Unlike the ensemble of the microscopic subsystems, the theorem on ergodicity of the total system justifies now the passage from the mean with respect to time to the microcanonical mean (8.1). However, even now, the theorem on the ergodicity of the individual system (i.e., the system with a fixed function $\mathcal{H}$) seems to be not needed since we do not know the precise value of the potential of the intermolecular interaction anyway. The theorem on density of the set of ergodic dynamical systems with Hamiltonian (8.1), in the set of all systems of this type appears to be more natural. The arguments given in § 2 in a similar situation indicate that such a system would be sufficient, apparently, to justify the passage from the mean with respect to time to the microcanonical mean.

in (9.1) is equal to

$$\sum \frac{M!}{n_1!\dots n_K!}\int \mathcal{F}(P,Q)\chi_{\alpha_1}(q_1)\dots\chi_{\alpha_1}(q_{n_1})\chi_{\alpha_2}(q_{n_1+1})\dots\chi_{\alpha_2}(q_{n_1+n_2})\dots$$
$$\dots\chi_{\alpha_k}(q_{n_1+n_2+\dots+n_{k-1}+1})\dots\chi_{\alpha_k}(q_{n_1+n_2+n_k})\delta(\mathcal{H}-E)\,dP\,dQ. \quad (9.3)$$

It is natural to assume that the values of the individual integrals in (9.3) do not differ much from each other. Therefore the maximal summand in (9.3) is the one with the greatest factor. To find it, we proceed in the same way as in the deduction of the Gibbs distribution in § 3. Taking into account that between the numbers n_α there exists only one relation, namely $\sum n_\alpha = M$, we set

$$f = \ln\frac{M!}{n_1!\dots n_K!} + \mu\sum_i n_i = \ln M! - \sum_r n_r(\ln n_r - 1) + \mu\sum_r n_r.$$

This implies that

$$\frac{\partial f}{\partial n_i} = -\ln n_i + \mu. \quad (9.4)$$

Equating (9.4) to zero we obtain that $n_i = e^\mu$, i.e., the maximum is attained when all the n_i are equal: $n_i = N$ for all i. The denominator in (9.1) is obtained from the numerator after we set $\mathcal{F}\equiv 1$. Therefore it also admits a representation in the form of a sum similar to (9.3). Let us replace the numerator and the denominator by the maximal summands and denote their ratio by $\overline{\mathcal{F}}_1$. After simplification we get

$$\overline{\mathcal{F}}_1 = \frac{\int \mathcal{F}\chi_{\alpha_1}(q_1)\dots\chi_{\alpha_1}(q_N)\dots\chi_{\alpha_k}(q_{(k-1)N+1})\dots\chi_{\alpha_k}(q_{kN})\delta(\mathcal{H}-E)\,dP\,dQ}{\int \chi_{\alpha_1}(q_1)\dots\chi_{\alpha_1}(q_N)\dots\chi_{\alpha_k}(q_{(k-1)N+1})\dots\chi_{\alpha_k}(q_{kN})\delta(\mathcal{H}-E)\,dP\,dQ} =$$
$$= \frac{\int\limits_{L_1}\mathcal{F}\delta(\mathcal{H}-E)\,dP\,dQ}{\int\limits_{L_1}\delta(\mathcal{H}-E)\,dP\,dQ}, \quad (9.5)$$

where L_1 is the phase space of the auxiliary system C^1 described in § 8.

We should prove that in the thermodynamical limit that is as

$$|\Omega|\to\infty, \quad K\to\infty, \quad M\to\infty, \quad \text{provided } |\Omega_\alpha| = \text{const}, \quad \frac{|\Omega|}{M} = \text{const}, \quad (9.6)$$

we have

$$\lim\overline{\mathcal{F}} = \lim\overline{\mathcal{F}}_{1n}. \quad (9.7)$$

The equality (9.7) is a justification for the replacing of the initial system by the auxiliary system C^1 described in § 8 or, which is the same thanks

to identity (8.3), by a small canonical ensemble. This equality (9.7) is not however, rigorously proved at the moment so we will *accept it as a hypothesis*.

9.2. Step two. Let us transform the right-hand side of formula (9.5). First of all, we will apply it not to arbitrary functions $\mathcal{F}$ but to integrable functions of the form

$$\mathcal{F}(P,Q) = \left(\frac{M!}{n!(M-n)!}\right)^{-1}\left(f(p_1,q_1,\dots,p_n,q_n)\chi_0(q_1)\dots\chi_0(q_n)+\dots\right). \tag{9.8}$$

The dots stand for the summands obtained from the 1-st one under arbitrary permutations of the pairs (p_i,q_i). There are $\dfrac{M!}{n!(M-n)!}$ distinct summands altogether. Apart from the inequality $n \le N$, there is no relation between n and N. (In what follows we are interested in the limit as $N\to\infty$ whereas n remains constant.)

The numerator in the right-hand side of (9.5), after substituting the function $\mathcal{F}$ of the form (9.8) in it, takes the form

$$\int\limits_{L_1} f(p_1,q_1,\dots,p_n,q_n)\delta(H_1+\dots+H_K+V-E)\,dP\,dQ, \tag{9.9}$$

where H_α and V are of the form (8.2). Hereafter we assume, for convenience, that the set N_0 consists of the first N positive integers. We visualize the volumes Ω_α as small cubes centered at points a_α; let Ω_0 be a cube centered at the origin. Perform a coordinate change $\tilde{q}_i = q_i - a_\alpha$ for $i\in N_\alpha$. Observe that

$$H_\alpha(p,q) = \sum_{i\in N_\alpha}\frac{p_i^2}{2m} + \sum_{\substack{i,j\in N_\alpha\\ i<j}} v(q_i-q_j) = \sum_{i\in N_\alpha}\frac{p_i^2}{2m} + \sum_{\substack{i,j\in N_\alpha\\ i<j}} v(\tilde{q}_i-\tilde{q}_j).$$

As a result of the above change, the integral (9.9) turns into an integral over the cube Ω_0. Having denoted $\tilde{q}_i$ by q_i again, we see that the integral (9.9) is equal to

$$\int f(P_0,Q_0)\delta\Bigg(\sum_{\alpha=0}^{K} H(P_\alpha,Q_\alpha) + \sum_{0\le\alpha<\beta\le K} v_{\alpha\beta} - E\Bigg)\prod_\alpha dP_\alpha\,dQ_\alpha, \tag{9.10}$$

where $P_\alpha = \{p_i \mid i\in N_\alpha\}$, $Q_\alpha = \{q_i \mid i\in N_\alpha, q_i\in\Omega_0\}$ for all i and where

$$v_{\alpha\beta} = \sum_{\substack{i\in N_\alpha\\ j\in N_\beta}} v(q_i - q_j + a_\alpha - a_\beta). \tag{9.11}$$

The potential of interaction $v_{\alpha\beta}$ is nonzero only if a_α and a_β are the centers of neighboring cubes. Even in this case $v_{\alpha\beta}\ne 0$ only if the points $q_i + a_\alpha$

and $q_j + a_\beta$ are sufficiently close to each other. Therefore we may assume that interaction is "small". Ignoring it we replace the mean (9.5) by the new mean

$$\overline{\mathcal{F}}_2 = \frac{\int f(P_0, Q_0)\delta\Big(\sum\limits_{\alpha=0}^{K} H(P_\alpha, Q_\alpha) - E\Big) \prod dP_\alpha\, dQ_\alpha}{\int \delta\Big(\sum\limits_{\alpha=0}^{K} H(P_\alpha, Q_\alpha) - E\Big) \prod dP_\alpha\, dQ_\alpha}. \tag{9.12}$$

It is natural to assume that under the thermodynamical limit

$$|\Omega| \to \infty, \quad K \to \infty, \quad M \to \infty \quad \text{provided } |\Omega_\alpha| = \text{const}, \quad \frac{|\Omega|}{M} = \text{const}, \tag{9.13}$$

we have

$$\lim \overline{\mathcal{F}}_2 = \lim \overline{\mathcal{F}}_1. \tag{9.14}$$

Like equality (9.7), the equality (9.14) is not rigorously proved at the moment and this is our *next hypothesis*. Now observe that the equation (9.12) led us to the situation when the Gibbs distribution takes place. Taking into account (9.7) and (9.14) we obtain as a result of the 1-st thermodynamic passage to the limit that

$$\overline{\mathcal{F}} = \frac{\int f(p_1, q_1, \ldots, p_n, q_n) e^{-\beta H(p_1, q_1, \ldots, p_N, q_N)}\, d^N p\, d^N q}{\int e^{-\beta H(p_1, q_1, \ldots, p_N, q_N)}\, d^N p\, d^N q}, \tag{9.15}$$

where $\mathcal{F}$ is a function of the form (9.8) and

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{1 \le i < j \le N} v(q_i - q_j), \quad \text{where } q_i \in \Omega_0,$$

is the operator of the energy of the subsystem. The parameter β is determined, as usual, from the equation

$$\frac{\int H e^{-\beta H}\, d^N p\, d^N q}{\int e^{-\beta H}\, d^N p\, d^N q} = E. \tag{9.16}$$

This completes the deduction of the Gibbs distribution in the small canonical ensemble.

Remarks. 1) The fact that formula (9.15) yields the Gibbs distribution in the small canonical ensemble, i.e., that all subsystems determined by volumes Ω_α contain the same number of particles, follows directly from the deduction of this formula.

2) Formula (9.15) is true only asymptotically as $N \to \infty$ provided $\frac{N}{|\Omega_0|} = \gamma$; the right-hand side of (9.15) is equal to the microcanonical mean of $\mathcal{F}$ since the interaction between subsystems becomes small and we can ignore it with sufficient justification only as $|\Omega_\alpha| \to \infty$. This is precisely the reason why the number of arguments of the function f is taken to be equal to n — the number having nothing to do with the total number N of particles in the system: Otherwise we would have to change the number of arguments of f which is a bother.

§ 10. The correlation functions in the small canonical ensemble

10.1. Main definitions. Let a subsystem satisfying the Gibbs distribution be situated in a vessel Ω of volume $|\Omega|$. Observe that the density of the Gibbs distribution in the small canonical ensemble is a product

$$\rho(p_1, q_1, \dots, p_N, q_N) = \rho_p(p_1, \dots, p_N)\rho_q(q_1, \dots, q_N), \tag{10.1}$$

where ρ_p is the density of the distribution in the space of momenta which is a Gaussian one and does not depend on the potential of the interaction and where ρ_q is the density of the distribution in the space of positions which is equal to

$$\rho_q = \frac{e^{-\beta \sum\limits_{i<j} v(q_i - q_j)}}{z_N}, \quad \text{where } z_N = \int\limits_{q_i \in \Omega} e^{-\beta \sum\limits_{i<j} v(q_i - q_j)} d^N q. \tag{10.2}$$

Since the factor ρ_p is particularly simple, the function ρ_q, as well as the mean values of the functions that do not depend on p, are of greatest interest.

Consider the function

$$F(q) = f(q_1, \dots, q_n) + \dots, \tag{10.3}$$

where f is an integrable function, n a fixed number having no relation with N, and the sum in (10.3) is obtained from the first summand by permuting the q_i (altogether $\frac{N!}{n!(N-n)!}$ distinct summands).

Since f only depends on the coordinates of a finite number of particles, the mean of F over the Gibbs distribution should possess a physical interpretation, i.e., we may expect the existence of the thermodynamical limit of the mean values. Consider the mean value $\overline{F}$ in more detail. By (10.1),

(10.3) we have

$$\int F(q)\rho(p,q)\,d^Np\,d^Nq = \int F(q)\rho_q(q)\,d^Nq = \frac{N!}{n!(N-n)!}\int f(q)\rho_{n,N}(q)\,d^nq, \tag{10.4}$$

where

$$\rho_{n,N} = |\Omega|^n \frac{\int e^{-\beta \sum\limits_{1\le i<j\le N} v(q_i-q_j)}\,dq_{n+1}\dots dq_N}{z_N}. \tag{10.5}$$

The function $\rho_{n,N}(q_1,\dots,q_n)$ is called *n-particle correlation function*, (*pre-limit* one). Observe that

$$\frac{N!}{n!(N-n)!}|\Omega|^{-n} = \frac{N(N-1)\dots(N-n+1)}{n!}\Omega^{-n}$$

has a limit equal to $\dfrac{\gamma^n}{n!}$ as $N\to\infty$ provided $\dfrac{N}{|\Omega|} = \gamma = \text{const}$.

According to the above, we may expect the presence of thermodynamical limit in the left-hand side of (10.4), and hence in the right-hand side, and therefore the limit of the function $\rho_{n,\Omega}$. Assuming that such a limit exists, denote the limit function by ρ_n. Thus the thermodynamical limit of the mean values of F is equal to

$$\overline{F} = \frac{\gamma^n}{n!}\int f(q_1,\dots,q_n)\rho_n(q_1,\dots,q_n)\,d^nq. \tag{10.6}$$

Let h be an arbitrary vector whose length does not exceed the radius of interaction b. Observe that

$$\rho_{n,\Omega}(q_1+h,\dots,q_n+h) = \rho_{n,\Omega}(q_1,\dots,q_n) + \Delta_{n,\Omega},$$

where $\Delta_{n,\Omega}$ is obtained integrating the right-hand side of (10.5) over the domain in which at least one variable q_i is distant from the boundary of Ω not further than b. Therefore we expect that $\lim\limits_{|\Omega|\to\infty}\Delta_{n,\Omega} = 0$ and the limit correlation functions satisfy

$$\rho_n(q_1+h,\dots,q_n+h) = \rho_n(q_1,\dots,q_n). \tag{10.7}$$

The relation (10.7) being true for vectors h of small length remains obviously true for arbitrary vectors.

We often have to consider mean values of functions of the form (10.3) for which f is not, however, integrable but only satisfies (10.7), i.e., only depends on the mutual disposition of molecules but not of the location of the whole configuration, as total, in space.

The same arguments as above indicate that, in this case, it is natural to expect the existence of the thermodynamical limit of the function $\dfrac{F}{|\Omega|}$, which is equal to

$$\frac{\gamma^n}{n!}\int f(q_1,\dots,q_n)\rho_n(q_1,\dots,q_n)\,dq_1\dots dq_{n-1}.$$

In other words, the mean value $\overline{F}$ is asymptotically equal to

$$\overline{F}\approx|\Omega|\frac{\gamma^n}{n!}\int f(q_1,\dots,q_n)\rho_n(q_1,\dots,q_n)\,dq_1\dots dq_{n-1}. \tag{10.8}$$

as $|\Omega|\to\infty$, $N\to\infty$ provided $\dfrac{N}{|\Omega|}=\gamma$.

10.2. The asymptotics of the statistical integral. The thermodynamical potential. Leaving aside for a moment the question of existence of the limit correlation functions ρ_n let us discuss formulas (10.6)–(10.8). First of all, observe that

$$\begin{aligned}-\frac{\partial\ln z_N}{\partial\beta}&=\frac{1}{z_N}\int\sum v(q_i-q_j)e^{-\beta\sum\limits_{i<j}v(q_i-q_j)}\,d^Nq=\\&=\frac{N(N-1)}{2}|\Omega|^{-2}\int v(q_1-q_2)\rho_{2,N}(q_1,q_2)\,dq_1\,dq_2.\end{aligned}\tag{10.9}$$

If everything said above holds, then the asymptotics of the integral in the right-hand side of (10.9) is equal to

$$|\Omega|\int v(q)\rho(q)\,dq,$$

where, for brevity, we set $\rho(q)=\rho_2(q_1,q_2)$ and $q=q_1-q_2$. Therefore we expect that as $|\Omega|\to\infty$ (so that $\dfrac{N}{|\Omega|}=\gamma$) we should have

$$-\frac{1}{|\Omega|}\frac{\partial\ln z_N}{\partial\beta}=\gamma E(\beta,\gamma)+O(1),\quad E(\beta,\gamma)=\int v(q)\rho(q)\,dq, \tag{10.10}$$

where $E(\beta,\gamma)$ is the mean potential energy.

Observe that $z_N=|\Omega|^N$ at $\beta=0$. Therefore integrating (10.10) from 0 to β we find that

$$-\frac{1}{|\Omega|}(\ln z_N-N\ln|\Omega|)=\gamma\int\limits_0^\beta E(S,\gamma)\,dS+O(1). \tag{10.11}$$

Taking into account that $|\Omega| = \dfrac{N}{\gamma}$ we deduce from (10.11) that

$$\frac{1}{|\Omega|} \ln \frac{z_N}{\left(\frac{N}{\gamma}\right)^N} = -\gamma \int_0^\beta E(S,\gamma)\, dS + O(1).$$

Taking into account the Stirling formula $N! \sim \left(\dfrac{N}{e}\right)^N$ the latter formula finally get

$$\lim_{N\to\infty} \frac{1}{N} \ln \frac{z_N}{N!} = F(\beta,\gamma), \quad F(\beta,\gamma) = -\int_0^\beta E(S,\gamma)\, dS - \gamma^{-1} \ln \frac{\gamma}{e}. \quad (10.12)$$

Thus, assuming the existence of the second limit correlation function, we deduce the existence of the limit (10.12). The limit function $F(\beta,\gamma)$ is called *the thermodynamical potential of the small canonical ensemble.* At present no independent proofs of the existence theorems for the thermodynamical potential and the limit correlation functions are known. The existence of the thermodynamical potential is proved for all $\beta \geq 0$, $\gamma \geq 0$ and the existence of the correlation functions is proved only in a region [4)] of all possible values of β, γ.

In what follows, we will give the detailed proofs of analogous theorems for the grand canonical ensemble. Concerning the small canonical ensemble, due to much greater difficulty of the proofs, we will only sketch them and give heuristic arguments.

10.3. Pressure. Let us express the pressure in terms of 2-nd correlation function. We'll use the definition of the pressure given in § 5. According to this definition, the pressure of the gas confined in a finite volume is equal to

$$p_\Omega = \frac{1}{\beta} \frac{\partial \ln z_N}{\partial |\Omega|}. \quad (10.13)$$

In order to study the behaviour of p_Ω under the thermodynamic limit, suppose that Ω is a cube with side l and perform the change $q_i = lx_i$. In new variable, we have

$$z_N = |\Omega|^N \int_{x_i \in I} e^{-\beta \sum\limits_{i<j} v(lx_i - lx_j)}\, d^N x,$$

[4)] If the system is subject to phase transitions, the limit correlation functions may indeed be undefined for the values of β, γ at which the phase transition takes place. Observe, however, that the existence theorem is proved for the domain of values of β, γ much more narrow than the one for which such existence is natural to expect.

where I is the unit cube.

Observe that $|\Omega| = l^3$ and so

$$\frac{dl}{d|\Omega|} = \frac{1}{3}\frac{l}{|\Omega|}, \quad \frac{\partial \ln z_N}{\partial |\Omega|} = \frac{\partial \ln z_N}{\partial l}\frac{1}{3}\frac{l}{|\Omega|}.$$

Set

$$q_i = (q_i^1, q_i^2, q_i^3), \quad v'_\alpha(q) = \frac{\partial}{\partial q_\alpha} v(q).$$

Let us find $\dfrac{\partial}{\partial |\Omega|} z_N$:

$$\frac{\partial z_N}{\partial |\Omega|} = N|\Omega|^{N-1} \int\limits_{x_i \in I} e^{-\beta \sum\limits_{i<j} v(lx_i - lx_j)}\, d^N x +$$

$$+ |\Omega|^N \frac{1}{3}\frac{l}{|\Omega|}(-\beta) \int\limits_{x_i \in I} \sum_{i<j,\alpha} (x_i^\alpha - x_j^\alpha) v'_\alpha(lx_i - lx_j) e^{-\beta \sum\limits_{i<j} v(lx_i - lx_j)}\, d^N x =$$

$$= N|\Omega|^{N-1} \int\limits_{x_i \in I} e^{-\beta \sum\limits_{i<j} v(lx_i - lx_j)}\, d^N x -$$

$$- \beta \frac{N(N-1)}{2 \cdot 3} \cdot l|\Omega|^{N-1} \int\limits_{x_i \in I} \sum_\alpha (x_1^\alpha - x_2^\alpha) v'_\alpha(lx_1 - lx_2) e^{-\beta \sum\limits_{i<j} v(lx_i - lx_j)}\, d^N x =$$

$$= \frac{N}{|\Omega|} z_N - \beta \frac{N(N-1)}{6|\Omega|} \sum_{q_i \in \Omega} \sum_\alpha (q_1^\alpha - q_2^\alpha) v'_\alpha(q_1^\alpha - q_2^\alpha) e^{-\beta \sum\limits_{i<j} v(q_i - q_j)}\, d^N x.$$

We see that

$$p_\Omega = \frac{1}{\beta}\frac{\partial \ln z_N}{\partial |\Omega|} = \frac{1}{\beta} z_N^{-1} \frac{\partial z_N}{\partial |\Omega|} =$$

$$= \frac{N}{\beta |\Omega|} - \frac{N(N-1)}{6|\Omega||\Omega|^2} \int \sum_\alpha (q_1^\alpha - q_2^\alpha) v'_\alpha(q_1 - q_2) \rho_{2,N}(q_1, q_2)\, dq_1\, dq_2.$$

Therefore assuming that the second correlation function exists, we see that there exists a thermodynamical limit of p_Ω equal to

$$p = \frac{\gamma}{\beta} - \frac{\gamma^2}{6} \int \sum_\alpha q^\alpha \frac{\partial v}{\partial q_\alpha} \rho(q)\, dq. \tag{10.14}$$

The function $\sum\limits_\alpha q^\alpha \dfrac{\partial v}{\partial q_\alpha}$ is well-known in mechanics; it is called *the virial of force*. Thus, the pressure becomes closely connected with the mean of the virial of force of intermolecular interaction.

In conclusion, let us give an expression of the pressure in terms of the thermodynamic potential. Due to (10.12), for N and $|\Omega|$ large, we have

$$\frac{z_N}{N!} \approx e^{NF\left(\beta, \frac{N}{|\Omega|}\right)}.$$

Therefore

$$p_\Omega = \frac{1}{\beta}\frac{\partial \ln z_N}{\partial |\Omega|} \approx -\frac{\gamma^2}{\beta}\frac{\partial F}{\partial \gamma}.$$

The right-hand side of this formula gives a thermodynamic limit of p_Ω:

$$p = \lim_{|\Omega|\to\infty} p_\Omega = -\frac{\gamma^2}{\beta}\frac{\partial F}{\partial \gamma}. \tag{10.15}$$

§ 11. The Bogolyubov Equations

11.1. A deduction of the equations. The correlation functions of the small canonical ensemble are little adjusted to rigorous study. The correlation functions of the grand canonical ensemble are more appropriate.

In this section, we give a brief sketch of a heuristic study of correlation functions of the small canonical ensemble. The central role here is played by *the Bogolyubov equations.*

Set

$$u(x_1, \dots, x_n) = e^{-\beta \sum\limits_{1\le i<j\le n} v(x_i - x_j)}, \quad \text{where } x_i = (x_{i,1}, x_{i,2}, x_{i,3}). \tag{11.1}$$

Observe that

$$\frac{\partial u}{\partial x_{i,\varepsilon}} = -\beta \sum_{k=1}^{n} \frac{\partial v(x_i - x_k)}{\partial x_{i,\varepsilon}} u(x_1, \dots, x_n), \quad \text{for } \varepsilon = 1, 2, 3. \tag{11.2}$$

Let $i \le s$. Let us integrate (11.2) over $x_{s+1}, \dots, x_n$ and multiply by $\dfrac{|\Omega|^s}{z_n}$.

We get

$$\frac{\partial(x_1,\dots,x_s)}{\partial x_{i,\varepsilon}} = -\frac{\beta|\Omega|^s}{z_n}\int\sum_{k=1}^{n}\frac{\partial v(x_i-x_k)}{\partial x_{i,\varepsilon}}e^{-\beta\sum\limits_{1\le i<j\le n}v(x_i-x_j)}\,dx_{s+1}\dots dx_n =$$

$$= -\beta\sum_{p=1}^{s}\frac{\partial v(x_i-x_p)}{\partial x_{i,\varepsilon}}\rho_{s,n}(x_1,\dots,x_s) -$$

$$-\frac{\beta|\Omega|^s}{z_n}\sum_{k=s+1}^{n}\int\frac{\partial v(x_i-x_k)}{\partial x_{i,\varepsilon}}e^{-\beta v(x_i-x_j)}\,dx_{s+1}\dots dx_n =$$

$$= -\beta\sum_{p=1}^{s}\frac{\partial v(x_i-x_p)}{\partial x_{i,\varepsilon}}\rho_{s,n}(x_1,\dots,x_s) -$$

$$-\frac{\beta|\Omega|^s}{z_n}(n-s)\int\frac{\partial v(x_i-x_{s+1})}{\partial x_{i,\varepsilon}}e^{-\beta\sum\limits_{1\le i<j\le n}v(x_i-x_j)}\,dx_{s+1}\dots dx_n =$$

$$= -\beta\sum_{p=1}^{s}\frac{\partial v(x_i-x_p)}{\partial x_{i,\varepsilon}}\rho_{s,n}(x_1,\dots,x_s) -$$

$$-\frac{\beta(n-s)}{\Omega}\int\frac{\partial v(x_i-x_{s+1})}{\partial x_{i,\varepsilon}}\rho_{s+1,n}(x_1,\dots,x_{s+1})\,dx_{s+1}.$$

Therefore we have obtained a system of interrelated integro-differential equations for $\rho_{s,n}$ $(s=1,2,\dots,n)$ called *the chain of Bogolyubov equations*:

$$\frac{\partial\rho_{s,n}}{\partial x_{i,\varepsilon}} = -\beta\sum_{p=1}^{s}\frac{\partial v(x_i-x_p)}{\partial x_{i,\varepsilon}}\rho_{s,n} - \beta\frac{(n-s)}{\Omega}\int\frac{\partial v(x_i-x_{s+1})}{\partial x_{i,\varepsilon}}\rho_{s+1,n}\,dx_{s+1}. \tag{11.3}$$

Taking into account that $\dfrac{(n-s)}{\Omega}\to\gamma$ we can formally pass to the thermodynamic limit and obtain the equation for correlation functions in the limit case:

$$\frac{\partial\rho_s}{\partial x_{i,\varepsilon}} = -\beta\sum_{p=1}^{s}\frac{\partial v(x_i-x_p)}{\partial x_{i,\varepsilon}}\rho_s - \beta\gamma\int\frac{\partial v(x_i-x_{s+1})}{\partial x_{i,\varepsilon}}\rho_{s+1}\,dx_{s+1}. \tag{11.4}$$

The function

$$\tilde\rho_{s,n}(x_1,\dots,x_s) = e^{\beta\sum\limits_{i\le j\le s}v(x_i-x_j)}\rho_{s,n}(x_1,\dots,x_s) \tag{11.5}$$

is often more convenient. The limit function $\tilde\rho_s$ is similarly defined. For the functions $\tilde\rho_s$, we deduce from (11.4) the equations

$$\frac{\partial\tilde\rho_s}{\partial x_{i,\varepsilon}} = -\beta\gamma\int\frac{\partial v(x_i-x_{s+1})}{\partial x_{i,\varepsilon}}e^{-\beta\sum\limits_j v(x_j-x_{s+1})}\tilde\rho_{s+1}\,dx_{s+1}. \tag{11.6}$$

Similarly, from (11.3) we can derive the equations for $\tilde{\rho}_{s,n}$ but we will not give here their explicit form.

11.2. Extension with respect to degrees of density. Equations (11.4) or, which is the same (11.6)), are convenient for deducing formal expansions of the functions ρ_n in power series in γ. In order to obtain these expansions, we should complement the equations (11.4) (or (11.6)) by the boundary condition

$$\begin{aligned} &\lim \rho_n(x_1, \dots, x_n) = 1 \quad \text{as} \quad |x_i - x_j| \to \infty, \\ &\lim \tilde{\rho}_n(x_1, \dots, x_n) = 1 \quad \text{as} \quad |x_i - x_j| \to \infty. \end{aligned} \tag{11.7}$$

An (*heuristic*) deduction of conditions (11.7) will be given at the end of this section.

Let us find the 0-th and the first terms of the power series of expansion of $\tilde{\rho}_n$ in powers of γ:

$$\tilde{\rho}_n = \tilde{\rho}_n^{(0)} + \gamma \tilde{\rho}_n^{(1)} + O(\gamma^2), \quad \text{where } \tilde{\rho}_n^{(0)} = 1.$$

Indeed, eq. (11.6) implies $\dfrac{\partial}{\partial x_{i,\varepsilon}} \tilde{\rho}_n^{(0)} = 0$, and hence $\tilde{\rho}_n^{(0)} = \text{const}$. Let us use (11.7) and pass to the limit at each term of the expansion of $\tilde{\rho}_n$ in powers of γ. Since (11.7) holds identically with respect to γ, we have

$$\lim_{|x_i - x_j| \to \infty} \tilde{\rho}_n^{(0)} = 1, \qquad \lim_{|x_i - x_j| \to \infty} \tilde{\rho}_n^{(s)} = 0 \quad \text{for } s > 0. \tag{11.8}$$

Taking into account that $\tilde{\rho}_n^{(0)} = \text{const}$, the first relation of (11.8) yields the result desired: $\tilde{\rho}_n^{(0)} = 1$.

For $\tilde{\rho}_n^{(1)}$, we derive from (11.6) the equation

$$\frac{\partial \tilde{\rho}_n^{(1)}}{\partial x_{i,\varepsilon}} = -\beta \int \frac{\partial v(x_i - x_{n+1})}{\partial x_{i,\varepsilon}} e^{-\beta \sum\limits_j v(x_j - x_{n+1})} \, dx_{n+1} = \\ = \int \frac{\partial}{\partial x_{i,\varepsilon}} e^{-\beta \sum\limits_j v(x_j - x_{n+1})} \, dx_{n+1}.$$

Here the derivative cannot be interchanged with the integral sign since the function

$$e^{-\beta \sum\limits_j v(x_j - x_{n+1})}$$

is not integrable with respect to x_{n+1}. Set

$$e^{-\beta v(x)} = 1 + f(x). \tag{11.9}$$

Then

$$e^{-\beta\sum\limits_{j=1}^{n} v(x_j-x_{n+1})} = \prod_{j=1}^{n}(1+f(x_j-x_{n+1})) = 1+\sum_{j=1}^{n} f(x_j-x_{n+1}) + \\ + \sum_{j_1<j_2} f(x_{j_1}-x_{n+1})f(x_{j_2}-x_{n+1}) + \dots$$

$$\frac{\partial\tilde\rho_n^{(1)}}{\partial x_{i,\varepsilon}} = \int \frac{\partial}{\partial x_{i,\varepsilon}}\Big(1+\sum f(x_j-x_{n+1}) + \\ + \sum_{j_1<j_2} f(x_{j_1}-x_{n+1})f(x_{j_2}-x_{n+1}) + \dots\Big)\,dx_{n+1} = \\ = \int \frac{\partial}{\partial x_{i,\varepsilon}}\Big(\sum_{j_1<j_2} f(x_{j_1}-x_{n+1})f(x_{j_2}-x_{n+1}) + \dots\Big)\,dx_{n+1} = \\ = \frac{\partial}{\partial x_{i,\varepsilon}}\int\Big(\sum_{j_1<j_2} f(x_{j_1}-x_{n+1})f(x_{j_2}-x_{n+1}) + \dots\Big)\,dx_{n+1}.$$

Observe that the assumptions on $v(x)$ imply that $f(x)$ has a compact support. The integrand in the last integral is equal to

$$u(x_1,\dots,x_n \mid x_{n+1}) = \sum_{j_1<j_2} f(x_{j_1}-x_{n+1})f(x_{j_2}-x_{n+1}) + \dots = \\ = e^{-\beta\sum v(x_j-x_{n+1})} - 1 - \sum f(x_j-x_{n+1}), \quad (11.10)$$

it is integrable with respect to x_{n+1}, and therefore, in the last equality, we can interchange the partial derivative and the integral sign.

Thus,

$$\tilde\rho_n^{(1)} = \int u(x_1,\dots,x_n \mid x_{n+1})\,dx_{n+1} + C_n, \quad (11.11)$$

where u is defined from eq. (11.10).

In order to determine C_n, let us use eq. (11.8) at $s=1$. Integrating the first summand in (11.10) we see that

$$\int f(x_1-x_{n+1})f(x_2-x_{n+1})\,dx_{n+1} = \int f(y)f(x_2-x_1-y)\,dy. \quad (11.12)$$

Since $f(x)$ has a compact support, it follows that the integral (11.12) vanishes for sufficiently large $|x_1-x_2|$. The integrals of the remaining summands entering (11.10) are similarly studied. Therefore the first summand

in (11.11) vanishes for sufficiently large $|x_i - x_j|$. Hence, $C_n = 0$. Finally,

$$\tilde{\rho}_n^{(1)} = \int \Big(e^{-\beta \sum\limits_j v(x_j - x_{n+1})} - 1 - \sum_j f(x_j - x_{n+1}) \Big)\, dx_{n+1}. \qquad (11.13)$$

In principle, one can similarly find all the functions $\tilde{\rho}_n^{(s)}$ but the corresponding formulas are very cumbersome for $s > 1$.

Let us prove relations (11.7). To this end, let us find, starting from (11.6), the expansion of $\tilde{\rho}_n$ in power series in γ without appealing to (11.7). The functions obtained will be denoted by $\tilde{\tilde{\rho}}_n$ to distinguish them from the solutions of the system (11.6) that takes (11.7) into account. For $\tilde{\tilde{\rho}}_n^{(0)}$ and $\tilde{\tilde{\rho}}_n^{(1)}$ repeating the above arguments we find that

$$\tilde{\tilde{\rho}}_n^{(0)} = C_n^{(0)} = \text{const}, \quad \tilde{\tilde{\rho}}_n^{(1)} = C_{n+1}^{(0)} \tilde{\rho}_n^{(1)} + C_n^{(1)}.$$

One can easily establish by the induction that

$$\tilde{\tilde{\rho}}_n^{(s)} = C_{n+s}^{(0)} \tilde{\rho}_n^{(1)} + C_{n+s-1}^{(1)} \tilde{\rho}_n^{(s-1)} + \ldots + C_n^{(s)}. \qquad (11.14)$$

Eq. (11.14) implies that $\tilde{\tilde{\rho}}_n^{(s)}$ has a limit as $|x_i - x_j| \to \infty$ and this limit is equal to $C_n^{(s)}$. Therefore the function $\tilde{\tilde{\rho}}_n$ has a limit as $|x_i - x_j| \to \infty$ and this limit is equal to $\sum j^s C_n^{(s)} = a(\gamma)$. Let the correlation function be related to $\tilde{\tilde{\rho}}_n$ as follows

$$\rho_n = e^{-\beta \sum v(x_i - x_j)} \tilde{\tilde{\rho}}_n.$$

In this case

$$\lim \rho_n = \lim \tilde{\tilde{\rho}}_n = a(\gamma) \quad \text{as} \quad |x_i - x_j| \to \infty.$$

Therefore

$$\lim_{L \to \infty} \frac{1}{L^n} \int\limits_{|x_i| < L} \rho_n(x_1, \ldots, x_n)\, d^n x = a(\gamma).$$

Since $\rho_n = \lim\limits_{N \to \infty} \rho_{n,N}$, the relation

$$\lim_{L \to \infty} \frac{1}{L^n} \int\limits_{|x_i| < L} \rho_{n,N}(x_1, \ldots, x_n)\, d^n x = a(\gamma)$$

should also be satisfied. However, the expression under the limit sign is identically equal to 1. Therefore: $a(\gamma) \equiv 1$, relations (11.7) hold, $C_n^{(s)} = 0$ for $s > 0$, and $C_n^{(0)} = 1$.

§ 12. The Gibbs distribution in the grand canonical ensemble

12.1. Transforming the microcanonic mean. In the same way we did this in § 9, consider a system of M particles confined in the volume Ω partitioned into cells Ω_α, where $\alpha = 1, 2, \dots, K$. Let

$$\mathcal{F}(x_1, \dots, x_M) = \frac{\sum f(x_1, \dots, x_s)\chi_1(x_1)\dots\chi_1(x_s) + \dots}{\frac{M!}{s!(M-s)!}}, \tag{12.1}$$

where $\chi_1(x)$ is the characteristic function of Ω_1 and where dots denote, as usual, the sum of summands obtained from the first one by the permutation of the x_i.

As in § 8, the problem is to rearrange the microcanonic mean of $\mathcal{F}$ (with respect to the system considered). Let us subdivide the volume Ω into K_1 cells ω_σ, where $|\omega_\sigma| = |\omega|$, each of which consists, in turn, of K_2 subcells Ω_α so that $K = K_1 \cdot K_2$ and $|\omega| = K_2|\Omega_1|$. Consider the first thermodynamic limit as $K \to \infty$ и $|\Omega| \to \infty$ whereas Ω_α remains constant.

Let us perform the passage to the limit in two steps: First let $|\Omega|$ and K_1 tend to ∞ whereas the intermediate volumes ω_σ remain fixed, then tend ω_σ and K_2 to ∞. Denote by ω_1 the intermediate subvolume containing Ω_1.

As a result of the first step of the passage to the thermodynamic limit, we arrive at the situation considered in § 8: The microcanonic mean of the function $\mathcal{F}$ in the limit as $K_1 \to \infty$ and $|\Omega| \to \infty$ whereas $\dfrac{M}{|\Omega|} = \text{const}$ is equal to the canonical mean over the small canonical ensemble determined by the volume ω_1:

$$\overline{\mathcal{F}} = \frac{1}{z_n} \int\limits_{x_i \in \omega} f(x_1, \dots, x_s) e^{-\beta \sum\limits_{i<j<n} v(x_i - x_j)} \chi_1(x_1)\dots\chi_1(x_s)\, dx_1 \dots dx_n. \tag{12.2}$$

In formula (12.2), we have introduced, for brevity: $n = \dfrac{M}{K_1}$ is the number of particles in ω_σ, in particular in ω_1; $\omega = \omega_1$, and $\chi(x) = \chi_1(x)$ is the characteristic function of the subvolume $\Omega_1 \subset \omega$. Now, we have to investigate the integral (12.2) as $n \to \infty$ provided $\dfrac{n}{|\omega|} = \gamma$.

Let ω' be the complement to Ω_1 in ω. Further, at each point of Ω_1, we place the center of the ball of radius b, where b is the radius of intermolecular interaction. Let $\tilde{\Omega}_1$be the union of all these balls. Obviously, $\Omega_1 \subset \tilde{\Omega}_1$. Let $\tilde{\omega}'$ be the complement to ω in $\tilde{\Omega}_1$. The particles lying in $\tilde{\omega}'$ and Ω_1 do not interact since $|x - y| > b$ for $x \in \Omega_1$ and $y \in \tilde{\omega}'$, and therefore $v(x - y) = 0$.

One can consider the complement to Ω_1 in $\tilde{\Omega}_1$ as the partition whose thickness is equal to the radius of interaction. Let $\chi(x)$ be the characteristic function of Ω_1, and so $\chi'(x) = 1 - \chi(x)$ is the characteristic function of ω'. Using the identity

$$1 = \prod_{i=1}^{n}(\chi(x_i) + \chi'(x_i)) = \prod_{i=1}^{n}\chi'(x_i) + \sum_{j}(\prod\nolimits'_{j}\chi(x_i))\chi(x_j) + \\ + \sum_{j_1<j_2}(\prod\nolimits''_{j_1,j_2}\chi'(x_i))\chi(x_{j_1})\chi(x_{j_2}) + \ldots, \quad (12.3)$$

where $\prod^{(n)}_{j_1\ldots j_k}\chi'(x_i)$ denotes the product of the $\chi'(x_i)$ over all i except $i = j_1, \ldots, j_k$, we rewrite the expression for $z_n(\omega)$ as follows:

$$z_n(\omega) = \int\limits_{x_i\in\omega}\prod_{1}^{n}(\chi(x_i) + \chi'(x_i))e^{-\beta\sum v(x_i-x_j)}\,dx_1\ldots dx_n = \\ = z_n(\omega') + n\int\limits_{\substack{x_i\in\omega' \text{ as } i>1\\ x_1\in\Omega_1}} e^{-\beta\sum v(x_i-x_j)}\,dx_1\ldots dx_n + \\ + \frac{n(n-1)}{2!}\int\limits_{\substack{x_i\in\omega' \text{ as } i>2\\ x_1,x_2\in\Omega_1}} e^{-\beta\sum v(x_i-x_j)}\,dx_1\ldots dx_n + \ldots \quad (12.4)$$

Now, let us replace the exact equality (12.4) by an approximate one which differs from (12.4) in that ω' is replaced by $\tilde{\omega}'$. In view of the fact that $v(x-y) = 0$ for $x \in \Omega_1$ and $y \in \tilde{\omega}'$, we have

$$z_n(\omega) \approx z_n(\tilde{\omega}') + n|\Omega_1|z_{n-1}(\tilde{\omega}') + \frac{n(n-1)}{2!}z_2(\Omega_1)z_{n-2}(\tilde{\omega}') + \ldots \quad (12.5)$$

The approximate equality (12.5) is the more precise the greater the volumes ω, ω' and Ω_1.

Consider the ratio $\dfrac{z_{n-1}(\tilde{\omega}')}{z_n(\tilde{\omega}')}$ for n large. Setting

$$\lim_{n\to\infty}\frac{1}{n}\ln\frac{z_n}{n!} = F(\gamma,\beta), \quad \text{where } \gamma = \frac{n}{|\tilde{\omega}'|},$$

we see that

$$\frac{z_{n-1}(\tilde\omega')}{z_n(\tilde\omega')} \approx \frac{(n-1)!e^{(n-1)F\left(\frac{n-1}{|\tilde\omega'|},\beta\right)}}{n!e^{nF\left(\frac{n}{|\tilde\omega'|},\beta\right)}} \approx \frac{1}{n}e^{(n-1)F\left(\frac{n-1}{|\tilde\omega'|},\beta\right)-nF\left(\frac{n}{|\tilde\omega'|},\beta\right)} \approx$$
$$\approx \frac{1}{n}e^{(n-1)\left(-\frac{1}{|\tilde\omega'|}\frac{\partial F}{\partial\gamma}\left(\frac{n}{|\tilde\omega'|},\beta\right)\right)-F\left(\frac{n}{|\tilde\omega'|},\beta\right)} = \frac{1}{n}e^{-\left(F(\gamma,\beta)+\gamma\frac{\partial F}{\partial\gamma}(\gamma,\beta)\right)}.$$

Recall that $\gamma = \dfrac{n}{|\tilde\omega'|} \approx \dfrac{n-1}{|\tilde\omega'|}$.

Set

$$\beta\mu = -\Big(F(\gamma,\beta)+\gamma\frac{\partial F}{\partial\gamma}(\gamma,\beta)\Big), \quad \text{where } \zeta = e^{\beta\mu}. \tag{12.6}$$

The quantities μ and ζ are called *the chemical potential* and *activity*, respectively. We see that

$$\frac{z_{n-k}}{z_n} = \frac{z_{n-1}}{z_n}\cdot\frac{z_{n-2}}{z_{n-1}}\cdots\frac{z_{n-k}}{z_{n-k+1}} \approx \zeta^k\frac{1}{n(n-1)\dots(n-k+1)} = \zeta^k\frac{(n-k)!}{n!}. \tag{12.7}$$

We finally have

$$z_n(\omega) \approx z_n(\tilde\omega')\sum_0^\infty \frac{\zeta^k}{k!}z_k(\Omega_1) \quad (z_0=1,\ z_1=|\Omega_1|). \tag{12.8}$$

Let us pass to the integral in the numerator of (12.2) and transform it in the same way we have transformed z_n:

$$\int\limits_{x_i\in\omega} f(x_1,\dots,x_s)\chi(x_1)\dots\chi(x_s)\prod_{s=1}^n(\chi(x_i)+\chi'(x_i))e^{-\beta\sum v(x_i-x_j)}\,dx_1\dots dx_n =$$
$$= \int\limits_{\substack{x_i\in\Omega_1 \text{ for } i\le s\\ x_i\in\omega' \text{ for } i>s}} f(x_1,\dots,x_s)e^{-\beta\sum v(x_i-x_j)}\,dx_1\dots dx_n +$$
$$+(n-s)\int\limits_{\substack{x_i\in\Omega_1 \text{ for } i\le s+1\\ x_i\in\omega' \text{ for } i>s+1}} f(x_1,\dots,x_s)e^{-\beta\sum v(x_i-x_j)}\,dx_1\dots dx_n +$$
$$+\frac{(n-s)(n-s-1)}{2!}\int\limits_{\substack{x_i\in\Omega_1 \text{ for } i\le s+2\\ x_i\in\omega' \text{ for } i>s+2}} f(x_1,\dots,x_s)e^{-\beta\sum v(x_i-x_j)}\,dx_1\dots dx_n+\dots$$

Having replaced the integral over ω' by the integral over $\tilde{\omega}'$ we get an approximate equality

$$\int f(x_1,\dots,x_s)\chi(x_1)\dots\chi(x_s)e^{-\beta\sum\limits_{i<j\le n}v(x_i-x_j)}\,dx_1\dots dx_n \approx$$
$$\approx \int\limits_{x_i\in\Omega_1} f(x_1,\dots,x_s)e^{-\beta\sum\limits_{i<j\le n}v(x_i-x_j)}\,dx_1\dots dx_n z_{n-s}(\tilde{\omega}')+$$
$$+(n-s)\int\limits_{x_i\in\Omega_1} f(x_1,\dots,x_s)e^{-\beta\sum\limits_{i<j\le s+1}v(x_i-x_j)}\,dx_1\dots dx_{s+1}z_{n-s-1}(\tilde{\omega}')+\dots$$

Let us use relation (12.7):

$$\int\limits_{\omega} f(x_1,\dots,x_s)\chi(x_1)\dots\chi(x_s)e^{-\beta\sum v(x_i-x_j)}\,dx_1\dots dx_n \approx$$
$$\approx \frac{(n-s)!}{n!}z_(\tilde{\omega}')\int\limits_{\Omega_1} f(x_1,\dots,x_s)\times$$
$$\times\left(\sum_{k=0}^{\infty}\frac{\zeta^{s+k}}{k!}\int\limits_{\Omega_1} e^{-\beta\sum\limits_{i<j\le k+s}v(x_i-x_j)}\,dx_{s+1}\dots dx_{s+k}\right)dx_1\dots dx_s.$$

For the mean value (12.2), we get the following final approximate expression

$$\overline{F}=\frac{1}{s!}\int\limits_{\Omega_1} f(x_1,\dots,x_s)r_{s,\Omega_1}(x_1,\dots,x_s)\,d^sx, \tag{12.9}$$

where

$$r_{s,\Omega_1}(x_1,\dots,x_s)=\Xi^{-1}\sum\frac{\zeta^{s+k}}{k!}\int\limits_{\Omega_1} e^{-\beta\sum\limits_{i<j\le s+k}v(x_i-x_j)}\,dx_{s+1}\dots dx_{s+k}, \tag{12.10}$$

$$\Xi=\sum_{k=0}^{\infty}\frac{\zeta^k}{k!}z_k(\Omega_1). \tag{12.11}$$

It is natural to expect that the approximation (12.9) is such that the limit of the right-hand side of (12.9) as $|\Omega_1|\to\infty$ coincides with the limit of the left-hand side of (12.9) as $|\Omega_1|\to\infty$.

This is the reason why the left-hand side of (12.9 is sometimes called the *pre-limit mean*.

The functions (12.10) are called *the correlation functions of the grand canonical ensemble* and the function (12.11) is called *the statistical sum of the grand canonical ensemble* or just *the grand statistical sum*. This terminates the deduction of the Gibbs distribution in the grand canonical ensemble.

12.2. Remarks. 1) In what follows we will show that the statistical sum of the grand canonical ensemble is of the form

$$\Xi = e^{|\Omega|\Phi(\mu,\beta)(1+o(1))} \quad \text{as} \quad |\Omega| \to \infty. \tag{12.12}$$

The function

$$\Phi(\mu,\beta) = \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|} \ln \Xi$$

is called *the thermodynamic potential of the grand canonical ensemble*.

Let us find a relation between the thermodynamic potentials of the small and grand ensembles. To this end, in the sum (12.11), let us find the maximal summand and ignore the other summands assuming that their contribution to (12.11) in the thermodynamical limit is infinitesimal. Taking into account that $\frac{z_N}{N!} \approx e^{NF}$ we see that, for n and $|\Omega|$ sufficiently large, the generic term in (12.11) is of the form

$$e^{n\left(\mu\beta + F\left(\frac{n}{|\Omega|},\beta\right)\right)}. \tag{12.13}$$

Differentiating with respect to n and equating the derivative to zero we get

$$\mu\beta + F(\gamma,\beta)\gamma\frac{\partial F}{\partial\gamma}(\gamma,\beta) = 0. \tag{12.14}$$

Comparing (12.12) and (12.13) we see that if μ and γ are related by the equation (12.14), then

$$\gamma(\mu\beta + F(\gamma,\beta)) = \Phi(\mu,\beta). \tag{12.15}$$

Observe that (12.14) coincides with (12.6). This circumstance is an additional argument in favor of validity of relations (12.14) and (12.15). In what follows, we will give their rigorous proof and also justify the method used above.

2) Recall that the *grand canonical ensemble* is a set of subsystems whose microcanonic mean $\overline{N}$ of the number of particles N is fixed. Let us show that, for the subsystems confined in the cells Ω_α, this requirement is satisfied. For this, observe that the number of particles in Ω_α is a physical

quantity equal to

$$N_\alpha = \sum_{i=1}^{M} \chi_\alpha(x_i),$$

where $\chi_\alpha(x)$ is the characteristic function of Ω_α.

Obviously, the microcanonic mean N_α does not depend on α. Since $\sum N_\alpha = M$, we see that the microcanonic mean of N_α is equal to $\overline{N}_\alpha = \dfrac{M}{K_1 K_2}$ and $\dfrac{N_\alpha}{|\Omega_\alpha|} = \dfrac{M}{K_1 K_2 |\Omega_\alpha|} = \dfrac{M}{|\Omega|} = \gamma$. It is interesting to compute $\overline{N}_\alpha$ with the help of the canonical distribution. Instead of $\overline{N}_\alpha$ consider $\dfrac{\overline{N}_\alpha}{|\Omega_1|}$. Due to (12.9) we have

$$\frac{\overline{N}_\alpha}{|\Omega_1|} \approx \frac{1}{|\Omega_1|} \int\limits_{\Omega_1} r_{1,\Omega_1}(x)\, dx, \tag{12.16}$$

where $r_{1,\Omega_1}(x)$ is the first correlation function. The limit of the right-hand side of (12.16) should equal to γ as $|\Omega_1| \to \infty$. Observe that

$$\int\limits_{\Omega_1} r_{1,\Omega_1}(x)\, dx = \zeta \frac{\partial \ln \Xi(\Omega_1)}{\partial \zeta}. \tag{12.17}$$

Further, we have $r_{1,\Omega_1}(x) = \dfrac{\tilde{r}_{1,\Omega_1}(x)}{\Xi}$, where $\tilde{r}_{1,\Omega_1}(x)$ is the numerator in (12.10) Every integral entering $\tilde{r}_{1,\Omega_1}(x)$ as a summand ceases to depend on x as $|\Omega_1| \to \infty$ due to translational invariance. Therefore one should expect that the limit of $r_{1,\Omega_1}(x)$ does not depend on x as $\Omega_1 \to \infty$. Denote this limit by r_1. Comparing (12.16) and (12.17) we get

$$\lim_{|\Omega_1| \to \infty} \frac{\overline{N}_\alpha}{|\Omega_1|} = r_1 = \zeta \frac{\partial \Phi}{\partial \zeta} = \frac{1}{\beta} \frac{\partial \Phi(\mu, \beta)}{\partial \mu}.$$

Further, using (12.15) and (12.14) we get

$$\frac{1}{\beta} \frac{\partial \Phi}{\partial \mu} = \frac{1}{\beta} \Big(\frac{\partial \gamma}{\partial \mu} (\beta \mu + F(\gamma, \mu)) + \gamma \Big(\beta + \frac{\partial F}{\partial \gamma} \frac{\partial \gamma}{\partial \mu} \Big) \Big) =$$
$$= \frac{1}{\beta} \Big(\frac{\partial \gamma}{\partial \mu} \Big(-\gamma \frac{\partial F}{\partial \gamma} \Big) + \gamma \Big(\beta + \frac{\partial F}{\partial \gamma} \frac{\partial \gamma}{\partial \mu} \Big) \Big) = \gamma,$$

as expected.

3) Let $\overline{\overline{F}}$ denote the right-hand side of expression (12.9):

$$\overline{\overline{F}} = \frac{1}{s!} \int\limits_{x_i \in \Omega_1} f(x_1, \ldots, x_s) r_s(x_1, \ldots, x_s)\, d^s x = \frac{1}{\Xi} \sum_{n \geq 0} \frac{\zeta^n}{n!} z_n(\Omega_1) T_n,$$

where

$$T(n)=\begin{cases}(z_n(\Omega_1))^{-1}\int f(x_1,\dots,x_s)e^{-\beta\sum\limits_{i\le j\le n}(x_i-x_j)}\,d^nx & \text{for } n\ge s,\\ 0 & \text{for } n\le s.\end{cases} \tag{12.18}$$

Eq. (12.18) implies that $\overline{\overline{F}}$ has an important probabilistic interpretation: $\overline{\overline{F}}$ is the mathematical expectation of the quantity $T(n)$ that only depends on the number n of particles in the system under the assumption that the probability that the system contains exactly n particles is equal to

$$p_n(\Omega_1)=\frac{1}{\Xi(\Omega_1)}\frac{\zeta^n}{n!}z_n(\Omega_1).$$

4) As in the case of the small canonical ensemble, one should by no means expect that the microcanonical mean of the function (12.1) is equal to the canonical mean determined by formulas (12.9) and (12.10) for a finite $|\Omega_1|$. Such a coincidence can be only expected in the limit as $|\Omega_1|\to\infty$ and $\dfrac{|\Omega|}{|\Omega_1|}\to\infty$.

§ 13. The Kirkwood—Salzburg equations

The correlation functions in the grand canonical ensemble are a powerful tool for deriving rigorous results of statistical physics. In this section, we derive for them an existence theorem and also prove that the pre-limit correlation functions converge to the limit ones. The *Kirkwood—Salzburg equations* are the cornerstone of all the proofs.

13.1. The deduction of equations. Let $r_{\Omega,n}(x_1,\dots,x_n)$ be the n-th correlation function in the grand ensemble corresponding to the subsystem with volume Ω. By definition $r_{\Omega,n}=\Xi^{-1}\tilde{r}_{\Omega,n}$, where

$$\tilde{r}_{\Omega,n}(x_1,\dots,x_n)=\zeta^n e^{-\beta\sum\limits_{1\le i<j<n}v(x_i-x_j)}\Big(1+\frac{\zeta}{1!}\int e^{-\beta\sum\limits_1^n v(x_i-y_q)}\,dy_1+$$
$$+\frac{\zeta^2}{2!}\int e^{-\beta\left(\sum\limits_1^n v(x_i-y_1)+v(x_i-y_2)\right)+v(y_1-y_2)}\,dy_1\,dy_2+\dots\Big).$$

Let us break out $\zeta e^{-\beta\sum\limits_{i=1}^{n-1}v(x_i-x_n)}$ and set

$$e^{-\beta v(x_i-x_j)}=1+f(x_i-x_j).$$

As a result, we get

$$\tilde r_{\Omega,n}(x_1,\dots,x_n)=\zeta e^{-\beta\sum\limits_{i=1}^{n-1}v(x_i-x_n)}\Big(\tilde r_{\Omega,n-1}(x_1,\dots,x_{n-1})+ \\ +\frac{1}{1!}\int \tilde r_{\Omega,n}(x_1,\dots,x_{n-1},y)f(x_n-y)\,dy+ \\ +\frac{1}{2!}\int \tilde r_{\Omega,n+1}(x_1,\dots,x_{n-1},y_1,y_2)f(x_n-y_1)f(x_n-y_2)\,dy_1\,dy_2+\dots\Big). \tag{13.1}$$

Having divided both sides of (13.1) by Ξ we get *the Kirkwood—Salzburg equations* for the pre-limit correlation functions:

$$r_{\Omega,n}(x_1,\dots,x_n)=\zeta e^{-\beta\sum\limits_{i=1}^{n-1}v(x_i-x_n)}\Big(r_{\Omega,n-1}(x_1,\dots,x_{n-1})+ \\ +\sum_0^\infty\frac{1}{(k+1)!}\int\limits_{y_i\in\Omega} r_{\Omega,n+k}(x_1,\dots,x_{n-1},y_0,\dots,y_k)\times \\ \times f(x_n-y_0)\dots f(x_n-y_k)\,dy_0\dots dy_k\Big). \tag{13.2}$$

These equations hold for $n\ge 1$, and $r_{\Omega,0}=1$.

The equations for *the limit* correlation functions differ from (13.2) in that the integrals in the right-hand side are taken over the whole space.

One can use equations (13.2) in order to derive the formal expansions of r_n in powers of ζ similarly to the expansions of ρ_n in powers of γ were derived for the Bogolyubov equations. In this respect equations (13.2) are more convenient since they are not differential ones and therefore do not require any extra conditions. Besides equations (13.2) enable to justify this expansion.

13.2. The Bogolyubov—Khatset—Ruelle theorem. Consider the Banach space $B_\Omega(d)$ consisting of the infinite sequences of functions

$$\varphi=\begin{pmatrix}\varphi_1(x_1)\\ \varphi_2(x_1,x_2)\\ \varphi_3(x_1,x_2,x_3)\\ \vdots\end{pmatrix},\quad \text{where } x_i\in\Omega, \tag{13.3}$$

with the norm $\|\varphi\|=\sum\limits_n d^n\sup\limits_{x_i}|\varphi_n(x_1,\dots,x_n)|$. Let $B(d)$ be an analogous space consisting of the functions of the form (13.3), in which the condition

$x_i \in \Omega$ is replaced by the condition that x_i runs over the whole space, but still with the same norm.

Let R_Ω and R be the sequences of pre-limit and limit correlation functions:

$$R_\Omega = \begin{pmatrix} r_{1,\Omega}(x) \\ r_{2,\Omega}(x_1, x_2) \\ \vdots \end{pmatrix}, \quad R = \begin{pmatrix} r_1(x) \\ r_2(x_1, x_2) \\ \vdots \end{pmatrix}.$$

A formal solution of equations (13.2) in the form of the power series in ζ can be expressed as

$$R_\Omega = R_\Omega^{(0)} + \zeta R_\Omega^{(1)} + \ldots, \quad R = R^{(0)} + \zeta R^{(1)} + \ldots, \tag{13.4}$$

where

$$R_\Omega^{(0)} = R^{(0)} = \begin{pmatrix} \zeta \\ 0 \\ \vdots \end{pmatrix}.$$

The following theorem due to Bogolyubov, Khatset and Ruelle justifies the formal expressions (13.4):

13.2.1. Theorem. *Let*

1) the potential $v(x)$ be such that there exists a universal constant $c > -\infty$ such that, whatever the points $x_1, \ldots, x_n$, we have

$$\sum_{\substack{i \neq j \\ 1 \leq i,j \leq n}} v(x_i - x_j) \geq nc;$$

2) the inequality

$$|\zeta| < k^{-1} e^{-(\beta c + 1)},$$

holds, where

$$k = \int |e^{-\beta v(x)} - 1| \, dx. \tag{13.5}$$

Then the coefficients $R_\Omega^{(n)}$ and $R^{(n)}$ of the power series expansions of (13.4) *in powers of ζ belong to $B_\Omega(k)$ and $B(k)$, respectively (k is determined by formula (13.5)), and satisfy the estimates*

$$\|R_\Omega^{(n)}\| \leq |\zeta| k (k e^{\beta c + 1})^n, \quad \|R^{(n)}\| \leq |\zeta| k (k e^{\beta c + 1})^n.$$

The series (13.4) *converges in the norm of $B_\Omega(k)$ and $B(k)$, respectively*[5)].

[5)] Recall that the potential with a finite radius of interaction and hard core satisfies the conditions of the theorem, see § 8.

Proof is the same for the pre-limit and limit correlation functions, and therefore we will confine ourselves to the limit ones.

First of all, observe that the condition $\sum_{i\neq j} v(x_i - x_j) \geq nc$ implies that, among the points $x_1, \dots, x_n$, there exists at least one point (let its number be α) such that

$$\sum_{i\neq\alpha} v(x_\alpha - x_i) \geq c. \tag{13.6}$$

Which of the points x_i possesses this property depends, of course, on the mutual disposition of the points.

Now, observe that, in the Kirkwood—Salzburg equations, the variable x_n plays a particular role. Obviously, we can write similar equations with the role of x_n being played by any other variable x_i. Let us proceed as follows. For each set of variables $x_1, \dots, x_n$, let x_α play the distinguished role. Then *the Kirkwood—Salzburg equation* takes the form

$$\begin{aligned} r_n(x_1, \dots, x_n) = \zeta e^{-\beta \sum\limits_{x_i\neq x_\alpha} v(x_i - x_\alpha)} \Big(& r_{n-1}(x_1, \dots, \hat{x}_\alpha, \dots, x_n) + \\ & + \sum_0^\infty \frac{1}{(k+1)!} \int r_{n+k}(x_1, \dots, \hat{x}_\alpha, \dots, x_n, y_0, \dots, y_k) \times \\ & \times f(x_\alpha - y_0) \dots f(x_\alpha - y_k)\, dy_0 \dots dy_k \Big). \end{aligned} \tag{13.7}$$

(As usual, a $\hat{}$ over x_α means that this variable should be ignored.)

Consider the operator A in $B(d)$ determined by the right-hand side of (13.7):

$$\begin{aligned} (A\varphi)_n(x_1, \dots, x_n) = e^{-\beta \sum\limits_{i\neq\alpha} v(x_i - x_\alpha)} \Big(& \varphi_{n-1}(x_1, \dots, \hat{x}_\alpha, \dots, x_n) + \\ & + \sum_{k\geq 0} \frac{1}{(k+1)!} \int \varphi_{n+k}(x_1, \dots, \hat{x}_\alpha, \dots, x_n, y_0, \dots, y_k) \times \\ & \times f(x_\alpha - y_0) \dots f(x_\alpha - y_k)\, dy_0 \dots dy_k \Big), \end{aligned} \tag{13.8}$$

where $(A\varphi)_n$ denotes the n-th term of the sequence $A\varphi$. With the help of the operator A equations (13.7) can be expressed in the form

$$R = R^{(0)} + \zeta AR, \tag{13.8'}$$

where

$$R^{(0)} = \begin{pmatrix} \zeta \\ 0 \\ \vdots \end{pmatrix} \in B(d), \quad R = \begin{pmatrix} r_1(x) \\ r_2(x_1, x_2) \\ \vdots \end{pmatrix}. \qquad \square$$

Now theorem 13.2.1 follows from the next theorem.

13.2.2. Theorem. *Under conditions of theorem* 13.2.1 *the norm of* A *can be estimated as follows:*

$$\|A\| \le de^{\beta c+\frac{k}{d}}, \quad k = \int |e^{-\beta v(x)} - 1|\, dx. \tag{13.9}$$

Before we pass to the proof of this theorem let us deduce theorem 13.2.1 from it. First of all, observe that the function $\varphi(d) = de^{k/d}$ attains its minimum equal to $k \cdot e$ at $d = k$. Therefore $d = k$ is the best value for d. It follows from (13.9) that $\|A\| \le ke^{\beta c+1}$ at $d = k$. Therefore if $|\zeta| ke^{\beta c+1} < 1$, then the operator $1 + \zeta A$ is invertible in $B(k)$ and the inverse operator expands in the power series in ζ converging with respect to the operator norm. A solution of equation (13.8) can be expressed in the form

$$R = (1 + \zeta A)^{-1} R^{(0)} = \sum (-\zeta A)^n R^{(0)} = \sum \zeta^n R^{(n)},$$

where the norm of $R^{(n)} = (-A)^n R^{(0)}$ can be estimated as follows:

$$\|R^{(n)}\| \le \|A\|^n \|R^{(0)}\| \le (ke^{\beta c+1})^n k|\zeta| \qquad (\|R^{(0)}\| = k|\zeta|).$$

Proof of theorem 13.2.2. Starting from (13.8) and (13.6) we get

$$\sup |(A\varphi)_n| \le e^{\beta c}\left(\sup |\varphi_{n-1}| + \sum_{s=0}^{\infty} \sup |\varphi_{n+s}| \frac{k^{s+1}}{(s+1)!}\right), \tag{13.10}$$

where $\varphi_0 = 0$, $k = \int |f(x)|\, dx$. Multiplying both sides of (13.10) by d^n and adding them up we find an estimate of $\|A\varphi\|$:

$$\|A\varphi\| \le e^{\beta c} \sum_{n=1}^{\infty} d^n \sup |\varphi_{n-1}| + \sum_{s=0}^{\infty}\left(\sum_{n=1}^{\infty} d^{n+s} \sup |\varphi_{n+s}|\right) \frac{k^{s+1}}{(s+1)! d^s} \le$$

$$\le e^{\beta c}\left(d + \sum_{0}^{\infty} \frac{k^{s+1}}{(s+1)! d^s}\right) \|\varphi\| = de^{\beta c+\frac{k}{d}} \|\varphi\|.$$

Thus $\|A\| \le de^{\beta c+\frac{k}{d}}$.

Theorem 13.2.2 is proved together with Theorem 13.2.1. □

13.3. Convergence of pre-limit correlation functions to the limit ones.

13.3.1. Theorem. *Let $\Omega_0 \subset \Omega$ and let l be the distance from the boundary of Ω to the boundary of Ω_0; let the potential $v(x)$ have a compact support. Then, under conditions of theorem* 13.2.1*, we have*

$$\sup_{x_i \in \Omega_0} |r_n(x_1, \dots, x_n) - r_{n,\Omega}(x_1, \dots, x_n)| \le \frac{c_1 e^{-c_2 l}}{k^n},$$

where

$$c_1, c_2 > 0, \quad k = \int |e^{-\beta v(x)} - 1|\, dx.$$

Consider an element $\varphi = \begin{pmatrix} \varphi_1(x) \\ \varphi_2(x_1, x_2) \\ \vdots \end{pmatrix}$ of the space $B_\Omega(d)$ and extend all functions $\varphi_n = (x_1, \dots, x_n)$ by zero if x_i lies outside Ω. In this way we obtain an embedding of $B_\Omega(d)$ into $B(d)$. Denote by $P_\Omega \colon B(d) \to B_\Omega(d)$ the projection operator which acts as follows

$$(P_\Omega \varphi)_n(x_1, \dots, x_n) = \varphi_n(x_1, \dots, x_n)\chi_\Omega(x_1) \dots \chi_\Omega(x_n),$$

where $\chi_\Omega(x)$ is the characteristic function of Ω.

Observe that the equation for R_Ω can be expressed in terms of the operator A determined by formula (13.8) in the form

$$R_\Omega = P_\Omega R_\Omega^{(0)} + \zeta P_\Omega A P_\Omega R_\Omega. \tag{13.11}$$

Let $\delta_\Omega = R_\Omega - P_\Omega R \in B_\Omega(d) \subset B(d)$. Let us apply the operator P_Ω to both sides of equation (13.8′) and subtract the result from (13.11):

$$R_\Omega - P_\Omega R = \zeta P_\Omega A P_\Omega R_\Omega - \zeta P_\Omega A P_\Omega R - \zeta P_\Omega A (E - P_\Omega) R.$$

This yields an equation for δ_Ω:

$$\delta_\Omega = -\zeta \mathcal{E}_\Omega + \zeta P_\Omega A P_\Omega \delta_\Omega, \quad \text{where } \mathcal{E}_\Omega = P_\Omega A (E - P_\Omega) R. \tag{13.12}$$

Observe that

$$\begin{aligned}(\mathcal{E}_\Omega)_n(x_1, \dots, x_n) = \chi_\Omega(x_1) \dots \chi_\Omega(x_n) e^{-\beta \sum\limits_{i \ne \alpha} v(x_i - x_\alpha)} \times \\ \times \sum_{k=0}^{\infty} \frac{1}{(k+1)!} \int r_{n+k}(x_1, \dots, \hat{x}_\alpha, \dots, x_n, y_0, \dots, y_k) \times \\ \times (1 - \chi_\Omega(y_0) \dots \chi_\Omega(y_k)) f(x_\alpha - y_0) \dots f(x_\alpha - y_k)\, dy_0 \dots\, dy_k. \end{aligned} \tag{13.13}$$

The integrand in (13.13) is non-zero only if at least one of the variables y_i lies outside Ω. On the other hand, $f(x_\alpha - y_i) = 0$ if $|x_\alpha - y_i| > b$, where b is the radius of interaction. Therefore $\mathcal{E}_\Omega(x_1, x_n) = 0$ if all the x_i lie inside Ω at the distance $> b$ from the boundary of Ω.

Further,

$$(P_\Omega A P_\Omega \mathcal{E}_\Omega)_n =$$
$$= (P_\Omega A \mathcal{E}_\Omega)_n = \chi_\Omega(x_1) \dots \chi_\Omega(x_n) e^{-\beta \sum\limits_{i \neq \alpha} v(x_i - x_\alpha)} \Bigg(\int (\mathcal{E}_\Omega)_{n-1}(x_1, \dots, x_n) +$$
$$+ \sum_{k \geq 0} \frac{1}{(k+n)!} \int (\mathcal{E}_\Omega)_{n+k}(x_1, \dots, \hat{x}_\alpha, \dots, x_n, y_0, \dots, y_k) \times$$
$$\times f(x_\alpha - y_0) \dots f(x_\alpha - y_k)\, dy_0 \dots dy_k \Bigg). \quad (13.14)$$

It follows from (13.14) that $(P_\Omega A P_\Omega \mathcal{E}_\Omega)_n = 0$ if all the points x_i lie at a distance $> b$ from the boundary of Ω. Indeed, in this case $(\mathcal{E}_\Omega)_{n-1}(x_1, \dots, \hat{x}_\alpha, \dots, x_n) = 0$, whereas $(\mathcal{E}_\Omega)_{n+k}(x_1, \dots, \hat{x}_\alpha, \dots, x_n, y_0, \dots, y_k) \neq 0$ only if at least one y_i is at distance $< b$ from the boundary of Ω. But then $|y_i - x_\alpha| > b$ and $f(y_i - x_\alpha) = 0$.

We similarly see that $((P_\Omega A P_\Omega)\mathcal{E}_\Omega)_n(x_1, \dots, x_n) = 0$ if all the x_i lie at a distance $> sb$ from the boundary of Ω.

Let us express a solution of equation (13.12) in the form

$$\delta_\Omega = \sum_{p=0}^{\infty} (-\zeta)^{p+1} (P_\Omega A P_\Omega)^p \mathcal{E}_\Omega.$$

Therefore

$$(\delta_\Omega)_n = \sum_{p=0}^{\infty} (-\zeta)^{p+1} ((P_\Omega A P_\Omega)^p \mathcal{E}_\Omega)_n. \quad (13.15)$$

By the above remark if the distance of all points x_i to the boundary of Ω is $> sb$, then the first s summands in (13.15) vanish. Therefore, in this case, we get the following estimate:

$$|(\delta_\Omega)_n| \leq \sum_{p=s}^{\infty} |\zeta|^{p+1} |((P_\Omega A P_\Omega)^p \mathcal{E}_\Omega)_n| \leq \sum_{p=s}^{\infty} |\zeta|^{p+1} \sup_{x_i} |((P_\Omega A P_\Omega)^p \mathcal{E}_\Omega)_n| \leq$$
$$\leq \sum_{p=s}^{\infty} |\zeta|^{p+1} \|(P_\Omega A P_\Omega)^p)^p \mathcal{E}_\Omega\| \frac{1}{k^n} \leq \frac{|\zeta|}{k^n} \frac{\|\zeta A\|^s}{1 - \|\zeta A\|} \|\mathcal{E}_\Omega\|,$$

where k is defined by eq. (13.5) and serves a parameter that determines the norm in $B(k)$. By the assumption $\|\zeta A\| = \zeta < 1$. Therefore we can rewrite the estimate of $(\delta_\Omega)_n$ in the form

$$|(\delta_\Omega)_n| \leq \frac{c_1'}{k^n} e^{-c_2' s}. \tag{13.16}$$

If all the points x_i lie inside Ω_0 whose the distance from its boundary to the boundary of Ω is equal to l, then setting $s = \left[\frac{l}{b}\right]$ (here $[a]$ is the integer part of $a \in \mathbb{R}$), we finally deduce from (13.16) that

$$|(\delta_\Omega)_n| = |r_{\Omega,n}(x_1, \ldots, x_n) - r_n(x_1, \ldots, x_n)| \leq \frac{c_1 e^{-c_2 l}}{k^n}.$$

13.4. Translation invariance of the limit correlation functions.

13.4.1. Theorem. *Under the assumptions of theorem* 13.2.1. *the limit correlation functions of the grand ensemble are translation-invariant, i.e., for any vector h, we have*

$$r_n(x_1, \ldots, x_n) = r_n(x_1 + h, \ldots, x_n + h) = r_n(0, x_2 - x_1, \ldots, x_n - x_1). \tag{13.17}$$

Proof. In $B(d)$, consider the operator T_h given by the formula:

$$T_h \varphi = \begin{pmatrix} \varphi(x_1 + h) \\ \varphi(x_1 + h, x_2 + h) \\ \vdots \end{pmatrix}.$$

It is easy to see that A commutes with T_h and $R^{(0)}$ is invariant with respect to T_h. Hence

$$T_h R = T_h (E + \zeta A)^{-1} T_h^{-1} T_h R^{(0)} = (E + \zeta A)^{-1} R^{(0)} = R.$$

Thus, $T_h R = R$ which is equivalent to (13.17). □

Corollary. *The first limit correlation function is a constant:* $r_1(x) = r_1(0)$.

§ 14. A relation between correlation functionsin the grand and small canonical ensembles

Let $\tilde{\rho}_{n,N}$ denote the function

$$\tilde{\rho}_{n,N}(x_1, \ldots, x_n) = \int e^{-\beta \sum\limits_{1 \leq i \leq j \leq N} v(x_i - x_j)} \, dx_{n+1} \ldots dx_N. \tag{14.1}$$

In the right-hand side of (14.1), we single out the factor $e^{-\beta\sum\limits_i v(x_n-x_i)}$ and set

$$y_\alpha = x_{n+\alpha}, \quad \text{for } 1 \le \alpha \le N-n, \quad e^{-\beta v(x_n-y_\alpha)} = 1 + f(x_n - y_\alpha).$$

As a result, for the functions $\tilde\rho_{n,N}$, we get the recurrent relations

$$\begin{aligned}
\tilde\rho_{n,N}(x_1,\dots,x_n) &= e^{-\beta\sum\limits_{1<n} v(x_n-x_i)} \times \\
&\times \int e^{-\beta\Big(\sum\limits_{1\le i<j<n} v(x_i-x_j)+\sum\limits_{\substack{i<n\\ 1\le\alpha\le N-n}} v(x_i-y_\alpha)+\sum\limits_{1\le\alpha<\beta\le N-n} v(y_\alpha-y_\beta)\Big)} \times \\
&\qquad \times \prod_{\alpha=1}^{N-n} (1+f(x_n-y_\alpha))\,dy_1\dots dy_{N-n} = \\
&= e^{-\beta\sum\limits_{1<n} v(x_n-x_i)} \Big(\tilde\rho_{n-1,N-1}(x_1,\dots,x_{n-1}) + \\
&+ (N-n)\int \tilde\rho_{n,N-1}(x_1,\dots,x_{n-1},y_1) f(x_n-y_1)\,dy_1 + \\
&+ \frac{(N-n)(N-n-1)}{2!}\int \tilde\rho_{n+1,N-1}(x_1,\dots,x_{n-1},y_1,y_2)\times \\
&\qquad \times f(x_n-y_1)f(x_n-y_2)\,dy_1\,dy_2 + \dots\Big). \qquad (14.2)
\end{aligned}$$

Now, recall that the definition of the correlation functions implies that $\rho_{n,N} = \dfrac{|\Omega|^n}{z_N}\tilde\rho_{n,N}$. This in mind, we deduce from (14.2) a relation between the correlation functions

$$\begin{aligned}
\rho_{n,N}(x_1,\dots,x_n) &= e^{-\beta\sum\limits_{i=1}^{n-1} v(x_n-x_i)} \Big(|\Omega| \frac{z_{N-1}}{z_N} \rho_{n-1,N-1}(x_1,\dots,x_{n-1}) + \\
&+ \sum_{k=1}^{N-n} \frac{(N-n)\dots(N-n-k+1)}{k!} \frac{z_{N-1}}{z_N |\Omega|^{k-1}} \times \\
&\times \int \rho_{n+k-1,N-1}(x_1,\dots,x_{n-1},y_1,\dots,y_k) \prod_{\alpha=1}^{k} f(x_n-y_\alpha)\,dy_1\dots dy_k\Big). \qquad (14.3)
\end{aligned}$$

In (14.3), we can perform the passage to the limit as $N\to\infty$ and $|\Omega|\to\infty$ provided $\dfrac{N}{|\Omega|}\to\gamma$. Having in mind that under this passage $\lim \dfrac{|\Omega| z_{N-1}}{z_N} = \dfrac{\zeta}{\gamma}$

(see (12.7)), we get

$$\rho_n(x_1,\dots,x_n) = e^{-\beta\sum_i v(x_n-x_i)}\Big(\frac{\zeta}{\gamma}\rho_{n-1}(x_1,\dots,x_{n-1})+ \\ +\sum_{k=1}^{\infty}\gamma^{k-1}\zeta\int\rho_{n+k-1}(x_1,\dots,x_{n-1},y_1,\dots,y_k)\times \\ \times\prod_{\alpha=1}^{k}f(x_n-y_\alpha)\,dy_1\dots dy_k\Big). \quad (14.4)$$

Setting $\rho_n{=}\gamma^{-n}r_n$ we deduce from (14.4) the Kirkwood—Salzburg equations for the correlation functions of the grand canonical ensemble deduced in the preceding section. Therefore the limit correlation functions of the grand and small canonical ensembles are related as follows:

$$r_n(x_1,\dots,x_n) = \gamma^n\rho_n(x_1,\dots,x_n). \quad (14.5)$$

The deduction of relations (14.5) indicated in this section can be made quite rigorous if we apply the arguments developed in the preceding section. At the same time, we can obtain the existence theorem for the limit correlation functions in the small ensemble.

§ 15. The existence of the thermodynamical potential in the grand canonical ensemble

The results obtained in § 13 enable us to easily prove the existence of thermodynamical potential

$$\Phi = \lim_{|\Omega|\to\infty}\frac{1}{|\Omega|}\ln\Xi \quad \text{for small values of} \quad \zeta.$$

15.1. Theorem. *Under the assumptions of Theorem* 13.2.1*, there exists a limit*

$$\Phi(\zeta,\beta) = \lim_{|\Omega|\to\infty}\frac{1}{|\Omega|}\ln\Xi = \int_0^{\zeta} r_1(\xi,\beta)\xi^{-1}\,d\xi,$$

where $r_1(\xi,\beta)$ *is the first limit correlation function*[6)].

[6)] Recall that, in reality, $r_1(x) = r_1(\xi,\beta\,|\,x)$ does not depend on x, see Theorem 13.4.1.

Proof. First of all, let us prove the limit relation

$$r_1 = \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|} \int\limits_{x\in\Omega} r_{1,\Omega}(x)\,dx. \tag{15.1}$$

Let Ω be a cube with side l. Let Ω_1 be the cube concentric with Ω whose edges are parallel to the edges of Ω and whose length is equal to $l - \sqrt{l}$. By Theorem 13.3.1, for $x \in \Omega_1$, we have

$$|r_{1,\Omega}(x) - r_1| \le c_1 e^{-c_2\sqrt{l}}.$$

Hence

$$\left|\frac{1}{|\Omega_1|}\int\limits_{\Omega_1} r_{1,\Omega}(x)\,dx - r_1\right| = \frac{1}{|\Omega_1|}\left|\int\limits_{\Omega_1}(r_{1,\Omega}(x) - r_1)\,dx\right| \le$$

$$\le \frac{1}{|\Omega_1|}\int\limits_{\Omega_1} |r_{1,\Omega}(x) - r_1|\,dx \le c_1 e^{-c_2\sqrt{l}} \to 0, \quad \text{as } l\to\infty.$$

Therefore $\lim\limits_{l\to\infty} \frac{1}{|\Omega_1|}\int\limits_{\Omega_1} r_{1,\Omega}(x)\,dx = r_1$. Since

$$\lim_{l\to\infty}\frac{|\Omega|}{|\Omega_1|} = \lim_{l\to\infty}\frac{l^3}{(l+\sqrt{l})^3} = 1,$$

we have

$$\lim_{l\to\infty}\frac{1}{|\Omega|}\int\limits_{\Omega_1} r_{1,\Omega}(x)\,dx = r_1.$$

Finally, since the function $r_{1,\Omega}(x)$ is a first component of the column vector $R_\Omega \in B_\Omega^{(d)}$ (see § 13), it is bounded in Ω, and therefore

$$\left|\int\limits_{\Omega} r_{1,\Omega}(x)\,dx - \int\limits_{\Omega_1} r_{1,\Omega}(x)\,dx\right| \le$$

$$\le \int\limits_{\Omega-\Omega_1} |r_{1,\Omega}(x)|\,dx \le c(l^3 - (l-\sqrt{l})^3) = o(l^{2+\frac{1}{2}}). \tag{15.2}$$

Using equality (12.17) we deduce that $\zeta\dfrac{\partial \ln \Xi}{\partial \zeta} = \int\limits_{x\in\Omega} r_{1,\Omega}(x)\,dx$. Dividing both sides of (15.2) by l^3 and passing to the limit as $l\to\infty$ we derive the

existence of the limit of $\frac{1}{|\Omega|}\zeta\frac{\partial \ln \Xi}{\partial \zeta}$ and the equality

$$\zeta \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|}\frac{\partial \ln \Xi}{\partial \zeta} = r_1. \tag{15.3}$$

Therefore

$$\frac{1}{|\Omega|}\frac{\partial \ln \Xi}{\partial \zeta} = r_1\zeta^{-1} + o(1). \tag{15.4}$$

Since $\Xi = 1$ at $\zeta = 0$, it follows that $\ln \Xi = 0$ at $\zeta = 0$. Therefore integrating (15.4) from 0 to ζ we get

$$\frac{1}{|\Omega|}\ln \Xi(\zeta, \beta) = \int_0^\zeta \xi^{-1} r_1(\xi, \beta)\, d\xi + o(1). \tag{15.5}$$

The integral in the right-hand side of (15.5) exists, since, under the assumptions of Theorem 13.2.1, the function $\xi^{-1}r_1(\xi, \beta)$ analytically depends on ξ. Passing in (15.5) to the limit as $|\Omega| \to \infty$ we get the statement desired. □

15.1.1. Corollary. *Under the assumptions of theorem 13.2.1,* $\Phi(\zeta, \beta)$ *is an analytic function of* ζ.

Indeed, under these assumptions $r_1(\xi, \beta)\xi^{-1}$ is an analytic function expandable into a converging series in powers of ζ. Therefore so is $\int_0^\zeta r_1(\xi, \beta)\, d\xi$.

§ 16. Existence of the thermodynamic potential in the grand canonical ensemble (continued).

16.1. Formulation of the theorem. In the preceding section we proved the existence of *thermodynamic potential* in the grand canonical ensemble under the following conditions:

1) There exists a constant C independent of n such that

$$\sum_{\substack{i\neq j \\ 1\le i,j\le n}} v(x_i - x_j) \ge nC.$$

2) $|\zeta| < k^{-1}e^{-\beta C - 1}$, where $k = \int |e^{-\beta v(x)} - 1|\, dx$.

The first condition imposes a restriction on the potential $v(x)$, which is certainly satisfied if the potential possesses a hard core and a finite radius of interaction. This assumption looks rather natural.

The second condition means that $|\zeta|$ is very small for a fixed β. For positive values of ζ, this condition is not needed [7]. This section is devoted to the proof of this fact.

The proof is based on the ideas quite distinct from those used in § 14 and is much more complicated. If we assume that the potential $v(x)$ possesses a hard core and a finite radius of interaction, it becomes simpler. And so we prove it under these assumptions.

Before we formulate the theorem, observe that, for real values $\zeta > 0$, the domain of existence of correlation functions established in § 13 is significantly more narrow than the domain of existence of thermodynamic potential since it requires ζ to be small whereas the thermodynamic potential exists for all $\zeta > 0$ and β.

Question. *Is it possible to prove the existence of the correlation functions for all $\zeta > 0$ and β?*

It turns out that, for certain potentials and certain values of $\zeta > 0$ and β, the limit correlation functions may not exist. The corresponding values of ζ and β are called *the points of phase transition*. Thus, a precise description of the existence domain of correlation functions is closely related with a description of phase transitions — one of the main problems of statistical physics.

Let us pass to the main topic of this section.

16.1.1. Theorem. *Let the potential $v(x)$ possess a hard core of radius $a > 0$ and let its radius of interaction be equal to $b < \infty$. Let Ω be a sequence of cubes such that $|\Omega| \to \infty$.*

Then, for any real β and μ, there exists a limit

$$\Phi(\beta, \mu) = \lim_{|\Omega| \to \infty} \frac{1}{|\Omega|} \ln \Xi(\Omega), \tag{16.1}$$

that does not depend on the choice of the sequence Ω.

Proof. (The idea.) It turns out that the statistical sum $\Xi(\Omega)$ is almost multiplicative as the function of volume Ω: If $\Omega = \Omega_1 \cup \Omega_2$ and $\Omega_1 \cap \Omega_2 = 0$, then

$$\Xi(\Omega) \simeq \Xi(\Omega_1)\Xi(\Omega_2), \tag{16.2}$$

[7] Recall that, in the heuristic deduction of the Gibbs distribution in the grand canonical ensemble, (see (12.6)) we have found that

$$\zeta = e^{\beta\mu}, \quad \mu\beta = -F(\gamma, \beta) - \gamma \frac{\partial F(\gamma, \beta)}{\partial \gamma},$$

where F is the thermodynamic potential of the small canonical ensemble. Therefore only positive values of ζ make sense.

Would the equality (16.2) be not approximate but an exact one, and moreover, were Ξ depending only on $|\Omega|$, then we would have had $\Xi = e^{|\Omega|\Phi}$, where Φ does not depend on Ω for a finite volume $|\Omega|$. Since the equality (16.2) is an approximate one, in reality, $\Xi \neq e^{|\Omega|\Phi}$ for any finite volume $|\Omega|$. The approximate nature of (16.2) is, however, such that it ensures the fulfillment of the limit relation (16.1).

Let $\Omega = \Omega_1 \cup \Omega_2$, where Ω_2 is a cube and $\Omega_1 \cap \Omega_2$ coincides with one of the faces of Ω_2. Consider a partition of unity in Ω:

$$1 = \prod_{i=1}^{n} (\chi_1(x_i) + \chi_2(x_i)) = \\ = \prod_{i=1}^{n} \chi_1(x_i) + \sum_{k=1}^{\infty} \Big(\prod\nolimits_{j_1 \dots j_k}^{(k)} \chi_1(x_i) \Big) \chi_2(x_{j_1}) \dots \chi_2(x_{j_k}), \quad (16.3)$$

where $\chi_\alpha(x)$ is the characteristic function of Ω_α for $\alpha = 1, 2$ and $\prod_{j_1 \dots j_k}^{(k)} \chi_1(x_i)$ denotes the product of all $\chi_1(x_i)$ except for $x_i = x_{j_1}, \dots, x_{j_k}$. Using (16.3) let us rewrite $z_n(\Omega)$ as follows:

$$z_n(\Omega) = z_n(\Omega_1 \cup \Omega_2) = z_n(\Omega_1) + \sum_{k=1}^{n} \frac{n!}{k!(n-k)!} Q_{n,k}, \quad (16.4)$$

where

$$Q_{n,k} = \int\limits_{\substack{x_i \in \Omega_1 \\ y_j \in \Omega_2}} e^{-\beta \sum\limits_{1 \le i < j < n-k} v(x_i - x_j) + \sum\limits_{1 \le i < j \le k} v(y_i - y_j) + \sum\limits_{\substack{1 \le i \le n-k \\ 1 \le j \le k}} v(x_i - y_j)} d^{n-x}x \, d^k y.$$

Denote the integral in (16.4) by $Q_{n,k}$ and estimate it. We set

$$e^{-\beta \sum\limits_{1 \le i < \le n-k} v(x_i - y)} = 1 + f(x_1, \dots, x_{n-k} \mid y). \quad (16.5)$$

Since there exists a hard core, the integrand in $Q_{n,k}$ does not vanish only if $|x_i - x_j| > a$. Under these conditions and since the potential has a compact support, the exponential in (16.5) contains only a finite number of summands A that do not depend on n and k. Thus. we get the following estimate of f:

$$-1 \le f \le e^{\beta A v_0} - 1, \quad \text{where } v_0 = -\min v(x).$$

This implies that

$$|f| \le \delta, \quad \delta = \max(1, e^{\beta A v_0} - 1). \quad (16.6)$$

Using functions f we express $Q_{n,k}$ as follows:

$$Q_{n,k} = \int\limits_{\substack{x_i\in\Omega_1\\ y_j\in\Omega_2}} e^{-\beta\sum\limits_{1\le i\le j\le n-k} v(x_i-x_j)-\beta\sum\limits_{1\le i\le j\le k} v(y_i-y_j)}\times$$

$$\times\prod_{i=1}^{k}(1+f(x_1,\dots,x_{n-k}\mid y_i)\,d^{n-k}x\,d^k y=$$

$$= z_{n-k}(\Omega_1)z_k(\Omega_2) + k\int\limits_{\substack{x_i\in\Omega_1\\ y_j\in\Omega_2}} e^{-\beta(\sum v(x_i-x_j)+\sum v(y_i-y_j))}\times$$

$$\times f(x_1,\dots,x_{n-k}\mid y_1)\,d^{n-k}x\,d^k y+$$

$$+\frac{k(k-1)}{2!}\int\limits_{\substack{x_i\in\Omega_1\\ y_j\in\Omega_2}} e^{-\beta\left(\sum\limits_{1\le i\le j\le n-k} v(x_i-x_j)+\sum\limits_{1\le i\le j\le k} v(y_i-y_j)\right)}\times$$

$$\times f(x_1,\dots,x_{n-k}\mid y_1)f(x_1,\dots,x_{n-k}\mid y_2)\,d^{n-k}x\,d^k y+\dots=$$

$$= z_{n-k}(\Omega_1)z_k(\Omega_2)+R_{n,k}. \quad (16.7)$$

Denote by $\Delta\subset\Omega_2$ the portion of Ω_2 separated from the boundary between Ω_1 and Ω_2 by a plane parallel to the boundary and situated at distance b from it, where b is the radius of interaction. Obviously, $f(x_1,\dots,x_{n-k}\mid y)\neq 0$ for $x_i\in\Omega_1$ and $y\in\Omega_2$ only if $y\in\Delta$. Therefore we get the following estimate of $R_{n,k}$:

$$|R_{n,k}|\le z_{n-k}(\Omega_1)\Bigg(k\delta\int\limits_{\substack{y_i\in\Delta\\ y_j\in\Omega_2,\,i>1}} e^{-\beta(\sum v(y_i-y_j)}\,d^k y+$$

$$+\frac{k(k-1)}{2!}\delta^2\int\limits_{\substack{y_1,y_2\in\Delta\\ y_i\in\Omega_2,\,i>2}} e^{-\beta(\sum v(y_i-y_j)}\,d^k y+\dots\Bigg).$$

Let us estimate the integral

$$J_{p,k}=\int\limits_{\substack{y_i\in\Delta,\,1\le i\le p\\ y_j\in\Omega_2,\,p<i\le k}} e^{-\beta\sum\limits_{1\le i\le j\le k}(\sum v(y_i-y_j)}\,d^k y. \quad (16.8)$$

Let us again use the fact that the integrand in (16.8) is non-zero only if $|y_i-y_j|>a$. Thanks to this and also since the potential has a compact

support, each of the sums

$$\sum_{i=p+1}^{k} v(y_\alpha - y_i), \quad \text{where } \alpha = 1, 2, \dots, p,$$

in the exponent of (16.8) contains not more than A summands, where A is an absolute constant. Therefore

$$\sum_{i=p+1}^{k} v(y_\alpha - y_i) \geq -Av_0, \quad v_0 = -\min v(x),$$

$$e^{-\beta \sum\limits_{\substack{1\leq\alpha\leq p \\ p+1\leq i\leq k}} v(y_\alpha - y_i)} \leq e^{pAv_0}.$$

We get the following estimate of $I_{p,k}$ [8]:

$$I_{p,k} \leq z_{k-p}(\Omega_2 \setminus \Delta)\Delta^p e^{pAv_0} \leq z_{k-p}(\Omega_2)(|\Delta|e^{Av_0})^p. \tag{16.9}$$

Thus,

$$R_{n,k} \leq z_{n-k}(\Omega_1) \sum_{p=1}^{k} \frac{k!}{p!(k-p)!} z_{k-p}(\Omega_2)(|\Delta|e^{Av_0})^p.$$

In what follows, we will need inequality that follows from theorem proved in § 20:

$$\frac{z_{n-k}(\Omega)}{z_n(\Omega)} \leq \frac{c}{|\Omega|}. \tag{16.10}$$

Inequality (16.10) implies that $\dfrac{z_{k-p}(\Omega_2)}{z_k(\Omega_2)} \leq \left(\dfrac{c}{|\Omega_2|}\right)^p$. From this inequality we deduce that

$$|R_{n,k}| \leq z_{n-k}(\Omega_1) z_k(\Omega_2) \left(\left(1 + \varepsilon \frac{|\Delta|}{|\Omega_2|}\right)^k - 1 \right), \quad \text{where } \varepsilon = c\delta e^{Av_0}. \tag{16.11}$$

Next, observe that $z_k(\Omega_2) = 0$ if $|\Omega_2| < k\gamma_0$, where γ_0 is the maximal density of the packing of balls of radius a. Therefore in (16.11) we may set $|\Omega_2| > k\gamma_0$, which implies

$$\left(1 + \frac{\varepsilon|\Delta|}{|\Omega_2|}\right)^k \leq \left(1 + \frac{\varepsilon\gamma_0|\Delta|}{k}\right)^k \leq e^{\varepsilon\gamma_0|\Delta|}.$$

Finally,

$$|R_{n,k}| \leq z_{n-k}(\Omega_1) z_k(\Omega_2) \left(e^{\varepsilon\gamma_0|\Delta|} - 1 \right).$$

[8] We use the fact that $z_n(\Omega_1) \leq z(\Omega_2)$ for $\Omega_1 \subset \Omega_2$.

Returning to $Q_{n,k}$ we get

$$Q_{n,k} = z_{n-k}(\Omega_1)z_k(\Omega_2) + R_{n,k} \le \\ \le z_{n-k}(\Omega_1)z_k(\Omega_2) + |R_{n,k}| \le z_{n-k}(\Omega_1)z_k(\Omega_2)e^{\varepsilon\gamma_0|\Delta|}. \quad (16.12)$$

Let us estimate the grand statistical sum:

$$\Xi(\Omega_1 \cup \Omega_2) = \sum_n \frac{\zeta^n}{n!} z_n(\Omega_1 \cup \Omega_2) = \sum_n \frac{\zeta^n}{n!} \left(z_n(\Omega_1) + \sum_{k=1}^{n} \frac{n!}{k!(n-k)!} Q_{n,k} \right) \le \\ \le \sum_n \frac{\zeta^n}{n!} \left(z_n(\Omega_1)e^{\varepsilon\gamma_0|\Delta|} + \sum_{k=1}^{n} \frac{n!}{k!(n-k)!} z_{n-k}(\Omega_1)z_k(\Omega_2)e^{\varepsilon\gamma_0|\Delta|} \right) = \\ = \sum_n \frac{\zeta^n}{n!} \sum_{p+q=n} \frac{n!}{p!q!} z_p(\Omega_1)z_q(\Omega_2)e^{\varepsilon\gamma_0|\Delta|} = \Xi(\Omega_1)\Xi(\Omega_2)e^{\varepsilon\gamma_0|\Delta|}. \quad (16.13)$$

The relation (16.13) is the *"almost multiplicativity"*. we need.

Fix a cube Ω with edge of length l and consider the sequence of cubes Ω_n concentric with Ω and with edges parallel to the edges of Ω. Let the length of the edge of Ω_n be equal to $l_n = nl$. Therefore each cube Ω_n naturally splits in the union of n^3 cubes congruent to Ω. Since $\Xi(\widetilde{\Omega}) = \Xi(\widetilde{\widetilde{\Omega}})$ if the volumes of $\widetilde{\Omega}$ and $\widetilde{\widetilde{\Omega}}$ are congruent, by iterating the relation (16.13) we get

$$\Xi(\Omega_n) \le (\Xi(\Omega))^{n^3} e^{n^3\varepsilon\gamma_0|\Delta|}. \quad (16.14)$$

Taking logarithm of (16.14) and dividing both its sides by $|\Omega_n| = n^3|\Omega|$ we get

$$\frac{1}{|\Omega_n|} \ln \Xi(\Omega_n) \le \frac{1}{|\Omega|} \ln \Xi(\Omega) + \varepsilon\gamma_0 \frac{|\Delta|}{|\Omega|}. \quad (16.15)$$

Tending n to ∞ and passing to the upper limit we get

$$\overline{\lim_{n\to\infty}} \frac{1}{|\Omega_n|} \ln \Xi(\Omega_n) \le \frac{1}{|\Omega|} \ln \Xi(\Omega) + \varepsilon\gamma_0 \frac{|\Delta|}{|\Omega|}. \quad (16.16)$$

Let us show that (16.16) holds not only for the described particular sequence Ω_n but for any increasing sequence of cubes. Let Ω'_n be an arbitrary increasing sequence of cubes such that $|\Omega'_n| \to \infty$. Since, for congruent cubes, the statistical sums coincide, we may assume, without loss of generality, that the cubes Ω_n have the common center with Ω and their edges are parallel to the edges of Ω. Let

$$\Omega_{n(p)} \subset \Omega'_p \subset \Omega_{n(p)+1}.$$

In this case [9)]

$$\begin{aligned} &\Xi(\Omega'_p) < \Xi(\Omega_{n(p)+1}), \\ &\frac{1}{|\Omega'_p|}\ln\Xi(\Omega'_p) \le \frac{1}{|\Omega'_p|}\ln\Xi(\Omega_{n(p)+1}). \end{aligned} \tag{16.17}$$

Observe that $|\Omega_{n(p)}| = n^3(p)|\Omega|$ and $|\Omega_{n(p)+1}| = (n(p)+1)^3|\Omega|$, and therefore $\lim\limits_{p\to\infty}\dfrac{|\Omega_{n(p)}|}{|\Omega_{n(p)+1}|} = 1$. Since $|\Omega_{n(p)}| \le |\Omega'_p| \le |\Omega_{n(p)+1}|$, we also have

$$\lim_{p\to\infty}\frac{|\Omega_{n(p)}|}{|\Omega'_p|} = \lim_{p\to\infty}\frac{|\Omega_{n(p)+1}|}{|\Omega'_p|} = 1.$$

Taking this into account passing to the upper limit as $p\to\infty$ we deduce from (16.17):

$$\overline{\lim_{n\to\infty}}\frac{1}{|\Omega'_p|}\ln\Xi(\Omega'_p) \le \overline{\lim_{n\to\infty}}\frac{1}{|\Omega_{n(p)+1}|}\ln\Xi(\Omega_{n(p)+1}) \le \overline{\lim_{n\to\infty}}\frac{1}{|\Omega_n|}\ln\Xi(\Omega_n).$$

Therefore relation (16.16) holds for any sequence of cubes Ω_n for which $|\Omega_n|\to\infty$.

Now, observe that the right-hand side of (16.16) depends on a parameter Ω. Let Ω run over the sequence of cubes $\widetilde{\Omega}_n$ such that $|\widetilde{\Omega}_n|\to\infty$. Observe that $\Delta = l^2 b$, where l is the length of the edge of Ω and b is the radius of interaction. Therefore the second summand in (16.16) is $\varepsilon\gamma_0\dfrac{b}{l}$ and $\varepsilon\gamma_0\dfrac{b}{l}\to 0$ as $l = |\widetilde{\Omega}_n|^{1/3}\to\infty$. Passing in the right-hand side of (16.16) to the lower limit over the sequence $\widetilde{\Omega}_n$ we deduce that

$$\overline{\lim_{n\to\infty}}\frac{1}{|\Omega_n|}\Xi(\Omega_n) \le \lim_{n\to\infty}\frac{1}{|\widetilde{\Omega}_n|}\Xi(\widetilde{\Omega}_n), \tag{16.18}$$

whatever the sequences of cubes Ω_n and $\widetilde{\Omega}_n$ provided $|\widetilde{\Omega}_n|\to\infty$. Inequality (16.18) obviously implies the existence of the limit $\lim\limits_{|\Omega|\to\infty}\dfrac{1}{|\Omega|}\ln\Xi(\Omega)$ over any sequence of cubes Ω such that $|\Omega|\to\infty$ and independence of this limit on this sequence. □

§ 17. Properties of the grand and small statistical Sums

[9)] Since $\Xi(\Omega) = \sum\dfrac{\zeta^n}{n!}z_n(\beta\,|\,\Omega)$ for $\zeta > 0$ and $z_n(\Omega_1) \le z_n(\Omega_2)$ for $\Omega_1 \subset \Omega_2$.

17.1. The probability distribution of the number of particles. Let us discuss certain properties of the statistical sums. Let us begin with the grand statistical sum

$$\Xi(\beta,\mu\,|\,\Omega)=\sum_{n=0}^{\infty}\frac{\zeta^n}{n!}z_n(\beta\,|\,\Omega),\quad \zeta=e^{\beta\mu}. \tag{17.1}$$

Let us interpret the number

$$p_n=\frac{\dfrac{\zeta^n}{n!}z_n}{\Xi} \tag{17.2}$$

as the probability of the system to have exactly n particle. Let us find the mean number of particles:

$$\overline{n}=\sum_n np_n=\Xi^{-1}\sum_n n\frac{\zeta^n}{n!}z_n=\zeta\frac{\partial\ln\Xi}{\partial\zeta}=\frac{1}{\beta}\frac{\partial\ln\Xi}{\partial\mu}, \tag{17.3}$$

and their dispersion:

$$\begin{aligned}D&=\sum_n(n-\overline{n})^2p_n=\sum_n(n^2-2n\overline{n}+\overline{n}^2)p_n=\\&=\sum_n(n^2-\overline{n}^2)p_n=\sum_n n^2p_n-\overline{n}^2=\Xi^{-1}\Big(\Big(\zeta\frac{d}{d\zeta}\Big)^2\Xi\Big)-\Xi^{-2}\Big(\zeta\frac{d}{d\zeta}\Xi\Big)^2=\\&=\Big(\zeta\frac{d}{d\zeta}\Big)^2\ln\Xi=\frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\ln\Xi.\end{aligned} \tag{17.4}$$

Let $\Phi_\Omega(\beta,\mu)$ denote the pre-limit value of the thermodynamic potential

$$\Phi_\Omega(\beta,\mu)=\frac{1}{|\Omega|}\ln\Xi.$$

Observe that the left-hand sides of formulas (17.3) and (17.4) are positive, and therefore so are their right-hand sides; hence

$$\frac{\partial\Phi_\Omega}{\partial\mu}>0,\quad \frac{\partial^2\Phi_\Omega}{\partial\mu^2}>0. \tag{17.5}$$

the inequalities (17.5) imply that Φ_Ω as a function of μ grows monotonically and is convex. Therefore the thermodynamic potential $\Phi=\lim\limits_{|\Omega|\to\infty}\Phi_\Omega$ as a function of μ is monotonically non-decreasing and convex. The convexity of Φ implies that Φ is twice differentiable almost everywhere. The first

derivative does not exist only at the *points of sharp bend*, still, left and right derivatives exist at these points. The points on the plane (β, μ) at which $\dfrac{\partial \Phi}{\partial \mu}$ does not exist are called *the points of phase transition of the first type*. The points where $\dfrac{\partial \Phi}{\partial \mu}$ exists but $\dfrac{\partial^2 \Phi}{\partial \mu^2}$ does not exist are called *the points of phase transition of the second type*.

Let us return to the probability distribution (17.2). From (17.3) and (17.4) we find that

$$\overline{n} = |\Omega| \frac{1}{\beta} \frac{\partial}{\partial \mu} \Phi_\Omega,$$
$$D = |\Omega| \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \Phi_\Omega.$$

Suppose that at the points where $\dfrac{\partial}{\partial \mu}$ and $\dfrac{\partial^2}{\partial \mu^2}$ exist we have [10)]

$$\frac{\partial \Phi}{\partial \mu} = \lim_{|\Omega| \to \infty} \frac{\partial \Phi_\Omega}{\partial \mu}, \quad \frac{\partial^2 \Phi}{\partial \mu^2} = \lim_{|\Omega| \to \infty} \frac{\partial^2 \Phi_\Omega}{\partial \mu^2}. \tag{17.6}$$

Let $\dfrac{\partial^2 \Phi}{\partial \mu^2}$ exist. With the help of Chebyshev trick let us estimate the probability of the number of particle n deviate from $\overline{n}$ more than by α:

$$p(|n - \overline{n}| > \alpha) = \sum_{|n-\overline{n}|>\alpha} p_n \leq \sum_{|n-\overline{n}|>\alpha} \frac{(n-\overline{n})^2}{\alpha^2} p_n \leq$$
$$\frac{1}{\alpha^2} \sum_{|n-\overline{n}|>\alpha} (n-\overline{n})^2 p_n = \frac{D}{\alpha^2}.$$

Set $\alpha = c|\Omega|^{(1/2)+\varepsilon}$. Then

$$p(|n - \overline{n}| > c|\Omega|^{(1/2)+\varepsilon}) \leq |\Omega|^{-2\varepsilon} \frac{1}{c^2 \beta^2} \frac{\partial^2 \Phi_\Omega}{\partial \mu^2}. \tag{17.7}$$

Since the limit $\lim\limits_{|\Omega| \to \infty} \dfrac{\partial^2 \Phi_\Omega}{\partial \mu^2}$ exists, and therefore $\left| \dfrac{\partial^2 \Phi}{\partial \mu^2} \right| < \text{const}$, it follows

[10)] The first of relations (17.6) follows easily from the general properties of monotonous and convex functions. The second relation is connected with the specifics of the functions considered. For the values of β, μ for which in § 13 the existence of correlation functions is proved, it follows immediately from the relation between the correlation functions and the thermodynamic potential. For the remaining values of β, μ it is not proved at the moment.

that the inequality (17.7) implies that

$$\lim_{|\Omega|\to\infty} p(|n-\overline{n}| > c|\Omega|^{(1/2)+\varepsilon}) = 0, \tag{17.8}$$

that is deviations of the number of particles from the mean value greater than by $c|\Omega|^{(1/2)+\varepsilon}$ are practically impossible. The following useful relation is another form of statement (17.8):

$$\lim_{|\Omega|\to\infty} p(|n-\overline{n}| \le c|\Omega|^{(1/2)+\varepsilon}) = \lim_{|\Omega|\to\infty} \frac{\sum\limits_{\overline{n}-c|\Omega|^{1/2-\varepsilon}}^{\overline{n}+c|\Omega|^{(1/2)+\varepsilon}} \frac{\zeta^n}{n!} z^n}{\Xi} = 1. \tag{17.9}$$

Relation (17.9) shows that in the sum (17.1) that determines Ξ, the only essential part of summands for $|\Omega|$ large, is the part determined by the condition $|n-\overline{n}| < c|\Omega|^{(1/2)+\varepsilon}$. Observe that since the ratio $\dfrac{\overline{n}}{|\Omega|} = \dfrac{1}{\beta}\dfrac{\partial\Phi_\Omega}{\partial\mu} \to \gamma$ is bounded from above and below and since the constant c in formulas (17.7)–(17.9) is arbitrary, it follows that $|\Omega|$ can be replaced by $\overline{n}$.

Note that formulas (17.8) and (17.9) are only proved under the condition that $\dfrac{\partial^2\Phi_\Omega}{\partial\mu^2}$ is bounded. In the case of phase transition of the first type, $\dfrac{\partial\Phi}{\partial\mu}$ becomes discontinuous, and therefore $\dfrac{\partial^2\Phi}{\partial\mu^2} = \infty$.

Therefore, in this case, we should expect that $\dfrac{\partial^2\Phi_\Omega}{\partial\mu^2} \to \infty$ and so relations (17.8) and (17.9 might be not true.

17.2. A relation between the thermodynamic potentials of the grand and small canonical ensembles. Consider the small ensemble. In § 12 from heuristic considerations we obtained a relation between the thermodynamic potentials in the grand and small canonical ensembles

$$\begin{aligned} &\Phi(\mu,\beta) = \gamma(\beta\mu + F(\gamma,\beta)), \\ &\beta\mu + F(\gamma,\beta) + \gamma\frac{\partial F}{\partial\gamma}(\gamma,\beta) = 0. \end{aligned} \tag{17.10}$$

We have also deduced from (17.10) that

$$\gamma = \frac{1}{\beta}\frac{\partial\Phi}{\partial\mu}. \tag{17.11}$$

Set

$$\mu\beta = \nu, \quad \gamma F = -F, \quad \Phi(\beta,\mu) = \Phi_1(\nu,\beta).$$

Equations (17.10) and (17.11) show that F_1 and Φ_1, as functions of ν and γ, are related by *Legendre transform*:

$$\begin{cases} \Phi_1 = \gamma\nu - F_1, \\ \nu = \dfrac{\partial}{\partial\gamma} F_1 \end{cases} \qquad \begin{cases} F_1 = -\Phi_1 + \gamma\nu, \\ \gamma = \dfrac{\partial\Phi_1}{\partial\nu}. \end{cases} \tag{17.12}$$

It follows from (17.12) that F_1 is either monotonically non-decreasing or non-increasing depending on the sign of F_1. Further, the function F_1 is convex like Φ_1. For the twice differentiable functions F_1 and Φ_1 this can be verified by direct differentiating

$$\frac{\partial^2 F_1}{\partial\gamma} = \frac{\partial\nu}{\partial\gamma} = \left(\frac{\partial\gamma}{\partial\nu}\right)^{-1} = \left(\frac{\partial^2\Phi}{\partial\nu^2}\right)^{-1} > 0.$$

In the general case, this follows from the properties of the Legendre transform.

Finally, let us find out how the points of phase transition of the first type affect F_1. Let ν_0 be such a point. According to (17.12) γ, as a function of ν, is discontinuous at ν_0. The inverse function $\nu(\gamma)$ is a constant between γ_1 and γ_2. Therefore, F_1 is linear on this interval (see 2.2).

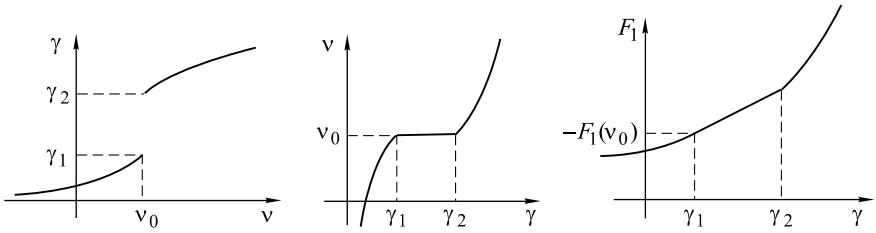

Figure 2.2

The complete proof of the existence of the thermodynamic potential in the small canonical ensemble is essentially more difficult than the proof of such existence for the grand canonical ensemble. However, in the absence of phase transitions, this proof, as well as justification of formulas (17.12), can be derived from the already obtained results.

In conclusion, observe that (17.10) implies that

$$\Phi(\mu,\beta) = \Phi_1(\nu,\beta) = -\gamma^2\frac{\partial F}{\partial\gamma},$$

i.e., $\beta\Phi$ can be interpreted as pressure, see (10.15). Thus, at the points of phase transition, the pressure, as the function of density, is constant since so is $\nu(\gamma)$.

§ 18. The existence of the thermodynamic potential in the small ensemble.

In this section, we establish the existence theorem for the thermodynamic potential in the small canonical ensemble in the absence of phase transitions of the first and second type and justify formula (17.10) that relates thermodynamical potentials in the grand and small canonical ensembles.

18.1. Theorem. *Let*

1) $v(x)$ *possess a hard core of radius* $a > 0$ *and let the radius of interaction* b *be* $< \infty$*;*

2) Ω *run a sequence of cubes such that* $|\Omega| \to \infty$*;*

3) μ *and* β *be such that* $\dfrac{\partial^k \Phi}{\partial \mu^k}(\beta, \mu)$ *for* $k = 1, 2$ *exist, where* Φ *is the thermodynamic potential of the grand canonical ensemble*;

4) $\dfrac{\partial^k \Phi}{\partial \mu^k}(\beta, \mu) = \lim\limits_{|\Omega| \to \infty} \dfrac{\partial^k \Phi_\Omega}{\partial \beta^k}$, *where* $k = 1, 2$, $\Phi_\Omega = \dfrac{1}{|\Omega|} \ln \Xi$*;*

5) $\gamma = \dfrac{1}{\beta} \dfrac{\partial \Phi}{\partial \mu}$.

Then

1) *The thermodynamic potential of the small ensemble exists:*

$$F(\gamma, \beta) = \lim_{|\Omega| \to \infty} \frac{1}{|\Omega|} \ln \frac{z_n(\Omega)}{n!}, \quad \text{as} \quad \frac{n}{|\Omega|} \to \gamma.$$

2) *The relation between the thermodynamic potentials of the grand and small canonical ensembles is of the form*

$$\Phi(\mu, \beta) = \gamma(\beta\mu + F(\gamma, \beta)).$$

Proof. Denote, for brevity, by S the following part of the statistical sum:

$$S = \sum_{\overline{n} - c\overline{n}^{\varkappa}}^{\overline{n} + c\overline{n}^{\varkappa}} \frac{\zeta^n}{n!} z_n, \quad \text{where } \varkappa = \frac{1}{2} + \varepsilon.$$

By formula (17.9) and under the assumptions of the theorem we have

$$S = \Xi(1 + o(1)). \tag{18.1}$$

Taking the logarithm of (18.1), dividing both sides of the equality obtained by $|\Omega|$ and passing to the limit as $|\Omega| \to \infty$ we get

$$\Phi(\beta, \mu) = \lim_{|\Omega| \to \infty} \frac{1}{|\Omega|} \ln S. \tag{18.2}$$

In what follows, we will need the estimates proved in § 20:

$$c_1|\Omega| \le \frac{z_n}{z_{n-1}} \le c_2|\Omega|. \tag{18.3}$$

Using (18.3) we rearrange and estimate S:

$$S = \frac{\zeta^{\overline{n}}}{\overline{n}!}\left(1 + \sum_1^{\overline{n}^\varkappa} \zeta^p \frac{\overline{n}!}{(\overline{n}+p)!}\frac{z_{\overline{n}+p}}{z_{\overline{n}}} + \sum_1^{\overline{n}^\varkappa} \zeta^{-p}\frac{\overline{n}!}{(\overline{n}-p)!}\frac{z_{\overline{n}-p}}{z_{\overline{n}}}\right).$$

Further,

$$\frac{z_{\overline{n}+p}}{z_{\overline{n}}} \le c_2^p|\Omega|^p, \quad \frac{z_{\overline{n}-p}}{z_{\overline{n}}} \le \frac{1}{c_1^p|\Omega|^p}.$$

Therefore

$$S \le \frac{\zeta^{\overline{n}}}{\overline{n}!}z_{\overline{n}}\left(\sum_0^{\overline{n}^\varkappa}\frac{\overline{n}!}{(\overline{n}+p)!}(\zeta c_2)^p|\Omega|^p + \sum_1^{\overline{n}^\varkappa}\frac{1}{(\zeta c_1)^p|\Omega|^p}\frac{\overline{n}!}{(\overline{n}-p)!}\right). \tag{18.4}$$

Let us consider inequality (18.4) in more detail:

$$\frac{\overline{n}!}{(\overline{n}+p)!} = \frac{1}{(\overline{n}+1)\dots(\overline{n}+p)} \le \frac{1}{\overline{n}^p}.$$

Hence, for $\overline{n}$ large, we have

$$\sum_0^{\overline{n}^\varkappa}\frac{\overline{n}!}{(\overline{n}+p)!}(\zeta c_2)^p|\Omega|^p \le \sum_0^{\overline{n}^\varkappa}(\zeta c_2)^p\left(\frac{\Omega}{\overline{n}}\right)^p \le$$

$$\le \sum_0^{\overline{n}^\varkappa}\left(\frac{\zeta c_2}{\gamma_1}\right)^p = \frac{1-\left(\frac{\zeta c_2}{\gamma_1}\right)^{\overline{n}^\varkappa+1}}{1-\frac{\zeta c_2}{\gamma_1}} \le A^{\overline{n}^\varkappa}, \tag{18.5}$$

where $0 < \gamma_1 < \gamma$ and $A > 0$ is a constant.

Similarly,

$$\frac{\overline{n}!}{(\overline{n}-p)!} = \overline{n}(\overline{n}-1)\dots(\overline{n}-p+1) \le \overline{n}^p;$$

$$\sum_1^{\overline{n}^\varkappa}\frac{\overline{n}!}{(\overline{n}-p)!}\frac{1}{(\zeta c_1)^p|\Omega|^p} \le \sum_0^{\overline{n}^\varkappa}\frac{\overline{n}^p}{(\zeta c_1)^p|\Omega|^p} = \sum_0^{\overline{n}^\varkappa}\left(\frac{\gamma_2}{\zeta c_1}\right)^p = \frac{1-\left(\frac{\gamma_2}{\zeta c_1}\right)^{\overline{n}^\varkappa+1}}{1-\frac{\gamma_2}{\zeta c_1}} \le$$

$$B^{\overline{n}^\varkappa},$$

where $\gamma < \gamma_2 < \infty$ and B is a constant. Thus, for $\overline{n}$ sufficiently large, we have

$$S \le \frac{\zeta^{\overline{n}}}{\overline{n}!} z_{\overline{n}} c^{\overline{n}^{\varkappa}}, \quad \text{where}|;\ c = \max(A, B) + 1. \tag{18.6}$$

Taking the logarithm of (18.6), dividing both sides by $|\Omega|$, and passing to the limit as $|\Omega| \to \infty$, we get

$$\Phi(\beta, \mu) = \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|} \ln S \le \lim_{|\Omega|\to\infty} \Big(\frac{1}{|\Omega|} \ln \frac{\zeta^{\overline{n}}}{\overline{n}!} z_{\overline{n}} + \overline{n}^{\varkappa} \ln c \Big) =$$

$$= \beta\mu\gamma + \gamma \lim_{|\Omega|\to\infty} \frac{1}{\overline{n}} \ln \frac{z_{\overline{n}}}{\overline{n}!}. \tag{18.7}$$

On the other hand,

$$\Xi > \zeta^{\overline{n}} \frac{z_{\overline{n}}}{\overline{n}!},$$

since Ξ is the sum of positive summands, one of which is $\dfrac{\zeta^{\overline{n}}}{\overline{n}!} z_{\overline{n}}$. Therefore we similarly deduce that

$$\Phi(\beta, \mu) \ge \overline{\lim_{|\Omega|\to\infty}} \frac{1}{|\Omega|} \ln \frac{\zeta^{\overline{n}} z_{\overline{n}}}{\overline{n}!} = \beta\mu\gamma + \gamma \overline{\lim_{|\Omega|\to\infty}} \frac{1}{\overline{n}} \ln \frac{z_{\overline{n}}}{\overline{n}!}. \tag{18.8}$$

The inequalities (18.7) and (18.8) imply

$$\overline{\lim_{|\Omega|\to\infty}} \frac{1}{n} \ln \frac{z_n}{n!} \le \gamma^{-1}\Phi(\mu, \beta) - \beta\mu \le \lim_{|\Omega|\to\infty} \frac{1}{n} \ln \frac{z_n}{n!}. \tag{18.9}$$

Inequality (18.9) means that the limit desired exists and

$$F(\beta, \gamma) = \lim_{n\to\infty} \frac{1}{n} \ln \frac{z_n}{n!} = \gamma^{-1}\Phi(\beta, \mu) - \beta\mu.$$

The theorem is proved. □

§ 19. The Mean over the distribution of the number of particles

Since the distribution of the number of particles in the grand ensemble is concentrated around their mean number, we can deduce a general formula that relates the thermodynamic limit of a given function $f(n, \Omega)$ with the mean of this function over the number of particles.

The formula obtained is useful for heuristic deductions.

Let $f(n,\Omega)$ be a function depending on the number of particles in the system, n, and on Ω. Assuming that the probability of the system to have precisely n particles is equal to

$$p_n(\Omega)=\frac{\dfrac{\zeta^n z_n(\Omega)}{n!}}{\Xi(\Omega)},$$

let us find the mathematical expectation of f for a fixed Ω:

$$M_\Omega(f)=\Xi^{-1}(\Omega)\sum\frac{\zeta^n z_n(\Omega)}{n!}f(n,\Omega). \tag{19.1}$$

19.1. Theorem. *Let*

1) *the potential $v(x)$ be such that the thermodynamic potential of the grand canonical ensemble $\Phi(\beta,\mu)$ exists;*

2) *the limits*

$$\frac{\partial\Phi}{\partial\mu}=\lim_{|\Omega|\to\infty}\frac{\partial\Phi_\Omega}{\partial\mu}\quad u\quad \frac{\partial^2\Phi}{\partial\mu^2}=\lim_{|\Omega|\to\infty}\frac{\partial^2\Phi_\Omega}{\partial\mu^2};$$

exist at $\beta=\beta_0$, $\mu=\mu_0$;

3) *the function $f(n,\Omega)$ be bounded uniformly with respect to n and Ω;*

4) *for $|p|<n^{1/2+\varepsilon}$ and any c, we have*

$$\sup_p|f(n+p,\Omega)-f(n,\Omega)|=o(1)\quad as\quad n\to\infty,\ \frac{|\Omega|}{n}\to c;$$

5) *there exist a limit of $M_\Omega(f)$ as $|\Omega|\to\infty$ at $\beta=\beta_0$, $\mu=\mu_0$.*

Then there exists a limit of $f([\overline{n}],\Omega)$, where $[\overline{n}]$ is the integer part of $\overline{n}=\sum\limits_n np_n(\Omega)$, and

$$\lim_{|\Omega|\to\infty}M_\Omega(f)=\lim_{|\Omega|\to\infty}f([\overline{n}],\Omega). \tag{19.2}$$

Proof. Set $\varkappa=\dfrac{1}{2}+\varepsilon$. Denote by $\tilde{M}_\Omega(f)$ the partial sum of the series (19.1):

$$\tilde{M}_\Omega(f)=\Xi^{-1}(\Omega)\sum_{|n-\overline{n}|<\overline{n}^\varkappa}\frac{\zeta^n z_n(\Omega)}{n!}f(n,\Omega), \tag{19.3}$$

where, as usual, $\overline{n}=\sum\limits_n np_n$ is the mean number of particles in the system.

Let us prove, first of all, that the limit $\lim\limits_{|\Omega|\to\infty}\tilde{M}_\Omega(f)$ exists and this limit is equal to the left-hand side of (19.2). Indeed,

$$M_\Omega(f)=\tilde{M}_\Omega(f)+\tilde{M}'_\Omega(f), \tag{19.4}$$

where

$$\tilde{M}'_\Omega(f) = \Xi^{-1}(\Omega) \sum_{|n-\overline{n}|\geq \overline{n}^{\varkappa}} \frac{\zeta^n z_n(\Omega)}{n!} f(n,\Omega).$$

Relations (17.8) and the fact that f is bounded imply that

$$|\tilde{M}'_\Omega(f)| \leq (\sup|f|)\Xi^{-1}(\Omega) \sum_{|n-\overline{n}|>\overline{n}^{\varkappa}} \frac{\zeta^n z_n(\Omega)}{n!} \to 0 \quad \text{as } |\Omega| \to \infty.$$

We deduce from (19.4) that the limit $\lim\limits_{|\Omega|\to\infty} \tilde{M}_\Omega(f)$ exists and

$$\lim_{|\Omega|\to\infty} M_\Omega(f) = \lim_{|\Omega|\to\infty} \tilde{M}_\Omega(f). \tag{19.5}$$

Set

$$\alpha(\Omega) = f([\overline{n}],\Omega),$$

where, as usual, $\overline{n} = \sum np_n(\Omega)$ is the mean number of particles in the system.

Since α does not depend on n, we see that

$$\tilde{M}_\Omega(f) = \alpha(\Omega) \sum_{|n-\overline{n}|<\overline{n}^{\varkappa}} p_n(\Omega) + \tilde{M}_\Omega(f-\alpha). \tag{19.6}$$

Let us estimate $\tilde{M}_\Omega(f-\alpha)$. We have:

$$|\tilde{M}_\Omega(f-\alpha)| = \Big| \sum_{|n-\overline{n}|<\overline{n}^{\varkappa}} p_n(\Omega)(f(n,\Omega)-\alpha) \Big| \leq \sup_{|n-\overline{n}|<\overline{n}^{\varkappa}} |f(n,\Omega)-\alpha|.$$

By the hypothesis of theorem 19.1

$$\sup_{|n-\overline{n}|<\overline{n}^{\varkappa}} |f(n,\Omega) - f([\overline{n}],\Omega)| = o(1),$$

since $\lim\limits_{|\Omega|\to\infty} \dfrac{|\Omega|}{[\overline{n}]} = \gamma^{-1}$. Therefore $\lim\limits_{|\Omega|\to\infty} \tilde{M}_\Omega(f-\alpha) = 0$. Passing to the limit as $|\Omega| \to \infty$ in (19.6) and applying once again relation (17.8) we see that the limit of $\alpha(\Omega) = f([\overline{n}],\Omega)$ as $|\Omega| \to \infty$ exists and

$$\lim_{|\Omega|\to\infty} f([\overline{n}],\Omega) = \lim_{|\Omega|\to\infty} \tilde{M}_\Omega(f) = \lim_{|\Omega|\to\infty} M_\Omega(f).$$

Let us illustrate the result obtained.

19.2. Examples. 1) Set

$$f(n,\Omega)=\frac{z_{n+1}(\Omega)}{z_n(\Omega)}.$$

Applying the theorem we find

$$\lim_{|\Omega|\to\infty} f([\overline{n}],\Omega)=\lim_{|\Omega|\to\infty} M_\Omega(f)=\lim_{|\Omega|\to\infty}\sum_n \Xi^{-1}\frac{\zeta^n z_n(\Omega)}{n!}\frac{z_{n+1}(\Omega)}{z_n(\Omega)}=$$

$$=\lim_{|\Omega|\to\infty}\frac{1}{|\Omega|}\frac{\partial}{\partial\zeta}\ln\Xi=\zeta^{-1}\frac{1}{\beta}\frac{\partial\Phi}{\partial\mu}=\frac{\gamma}{\zeta}.$$

Therefore

$$\lim_{|\Omega|\to\infty}\frac{z_{[\overline{n}]+1}(\Omega)}{|\Omega| z_{[\overline{n}]}(\Omega)}=\frac{\gamma}{\zeta},$$

and we get the formula we already know.

Let us pass to the correlation functions.

By definition

$$r_{n,\Omega}(x_1,\dots,x_n)=\Xi^{-1}\sum_{p=0}^{\infty}\frac{\zeta^{n+p}}{p!}\int e^{-\beta\sum\limits_{1\le i\le j\le n+p} v(x_i-x_j)}\,dx_{n+1}\dots dx_{n+p}=$$

$$=\zeta^n\Xi^{-1}\sum_{p=0}^{\infty}\frac{\zeta^p}{p!}z_p\frac{z_{p+n}}{z_p|\Omega|^n}\frac{|\Omega|^n}{z_{p+n}}\int e^{-\beta\sum\limits_{1\le i\le j\le n+p} v(x_i-x_j)}\,dx_{n+1}\dots dx_{n+p}=$$

$$=\zeta^n\Xi^{-1}\sum_{p=0}^{\infty}\frac{\zeta^p}{p!}z_p\frac{z_{p+n}}{z_p|\Omega|^n}\rho_{n,n+p}(x_1,\dots,x_n),$$

where

$$\rho_{n,n+p}=\frac{|\Omega|^n}{z_{p+n}}\int e^{-\beta\sum\limits_{1\le i\le j\le n+p} v(x_i-x_j)}\,dx^{n+1}\dots dx^{n+p}$$

is the pre-limit correlation function of the small canonical ensemble. Fix $x_1,\dots,x_n$ and set

$$f(p,\Omega)=\frac{z_{p+n}(\Omega)}{z_p(\Omega)|\Omega|^n}\rho_{n,n+p}.$$

Applying Theorem 19.1 we see that

$$r_n(x_1,\dots,x_n)=\lim_{|\Omega|\to\infty} r_{n,\Omega}(x_1,\dots,x_n)=\zeta^n\lim_{\substack{p\to\infty\\ \frac{[p]}{|\Omega|}\to\gamma}}\frac{z_{p+n}}{z_p|\Omega|^n}\rho_{n,n+p}(x_1,\dots,x_n),$$

wherefrom

$$r_n(x_1,\dots,x_n)=\gamma^n\rho_n(x_1,\dots,x_n).$$

In both cases, to make the deduction rigorous is not easy since it is very difficult to verify condition (4) of Theorem 19.1. □

§ 20. Estimates of the small statistical sum

In this section we prove the estimates that we already used earlier.

20.1. Theorem. *Let the potential $v(x)$ possess a hard core of radius a and the radius of interaction equal to b. Then there exist constants c_1 and c_2 such that*

$$c_2|\Omega| \le \frac{z_{n+1}(\Omega)}{z_n(\Omega)} \le c_1|\Omega|. \tag{20.1}$$

for $|\Omega|$ sufficiently large.

Proof. Let $x = (x_1, \dots, x_n)$ be a point of the $3n$-dimensional space. Observe that, in the statistical integral $z_n(\Omega)$, we may assume that the variable of integration x runs not over the whole set $\underbrace{\Omega \times \dots \times \Omega}_{n \text{ times}}$ but over its part singled out by the condition

$$|x_i - x_j| > a \tag{20.2}$$

Indeed, if condition (20.2) does not hold, then the integrand in z_n vanishes thanks to the existence of a hard core. This in mind, let us transform the expression for z_{n+1}

$$z_{n+1}(\Omega) = \int\limits_{\underbrace{\Omega\times\dots\times\Omega}_{n \text{ times}}} \left(e^{-\beta \sum\limits_{1\le i\le j\le n} v(x_i - x_j)} \int\limits_{\substack{x_{n+1}\in\Omega \\ |x_{n+1}-x_i|>a}} e^{-\beta \sum\limits_{i=1}^{n} v(x_i - x_{n+1})}\, dx_{n+1} \right) d^n x. \tag{20.3}$$

Since $|x_i - x_j| > a$ and the potential $v(x)$ has a compact support, it follows that, for every fixed x_{n+1}, the sum $\sum\limits_{i=1}^{n} v(x_i - x_{n+1})$ contains not more than A non-zero summands, where A is an absolute constant. Therefore

$$e^{-\beta \sum\limits_{i=1}^{n} v(x_i - x_{n+1})} \le e^{\beta A v_0} = c_1, \tag{20.4}$$

where $v_0 = \min v(x)$. From (20.4) we derive

$$z_{n+1}(\Omega) \le |\Omega| e^{\beta A v_0} z_{n-1}. \tag{20.5}$$

Now, let us estimate the inner integral in (20.3) from below. Fix points $x_1, \dots, x_n$. As we have already mentioned, under these conditions, the sum $\sum\limits_{i=1}^{n} v(x_i - x_{n+1})$ contains not more than A non-zero summands. Let, for

definiteness sake, $v(x_i - x_{n+1}) = 0$ for $i > A$. Then

$$\int\limits_{\substack{x_{n+1}\in\Omega \\ |x_i - x_{n+1}|>a}} e^{-\beta\sum\limits_i v(x_i - x_{n+1})}\, dx_{n+1} \geq \int\limits_{\substack{x_{n+1}\in\Omega \\ |x_{n+1} - x_i|>2a}} e^{-\beta\sum\limits_{i=1}^{A} v(x_i - x_{n+1})}\, dx_{n+1} \geq$$

$$\geq (e^{-\beta v_1})^A (|\Omega| - hA) \geq c e^{-\beta A v_1} |\Omega|, \tag{20.6}$$

where h is the volume of the ball of radius $2a$, $v_1 = \max\limits_{|x|>2a} v(x)$, $|\Omega| - hA > c|\Omega|$ and $c < 1$ is a constant. Inequality (20.6) holds for $|\Omega| > \dfrac{hA}{1-c}$. □

20.2. Theorem. *Let*

1) $v(x)$ *be the same as in Theorem* 20.1,

2) $\Omega \subset \Omega_1$ *be sequences of concentric cubes with parallel edges such that* $|\Omega| \to \infty$,

3) $\lim\limits_{|\Omega|\to\infty} \dfrac{n}{|\Omega|} = \gamma$.

Then, for n *sufficiently large, we have*

$$1 < \frac{z_n(\Omega_1)}{z_n(\Omega)} < e^{c|\Delta|},$$

where $|\Delta|$ *is the volume of the domain* $\Delta = \Omega_1 \setminus \Omega$.

Proof. Let $\chi_1(x)$ be the characteristic function of Ω and $\chi_2(x)$ the characteristic function of Δ. Using a partition of unity in Ω_1:

$$1 = \prod_{i=1}^{n} (\chi_1(x_i) + \chi_2(x_i)) = \prod_{i=1}^{n} \chi_1(x_i) + \sum_j \Big(\prod_j^{(1)} \chi_1(x_i)\Big)\chi_2(x_j) + \dots$$

$$\dots + \sum_{j_1<\dots<j_k} \Big(\prod_{j_1,\dots,j_k}^{(k)} \chi_1(x_i)\Big)\chi_2(x_{j_1})\dots\chi_2(x_{j_k}), \tag{20.7}$$

where $\prod\limits_{j_1,\dots,j_k}^{(k)} \chi_1(x_i)$ is the product of the $\chi_1(x_i)$ over all the x_i except for

$i = j_1, \dots, j_k$, let us represent $z_n(\Omega_1)$ in the form

$$z_n(\Omega_1) = z_n(\Omega) + n \int\limits_{x_i \in \Omega} \left(e^{-\beta \sum\limits_{1 \le i \le j \le n-1} v(x_i - x_j)} \int\limits_{x_n \in \Delta} e^{-\beta \sum\limits_i v(x_i - x_n)} \, dx_n \right) d^{n-1}x +$$

$$+ \frac{n(n-1)}{2!} \int\limits_{x_i \in \Omega} \left(e^{-\beta \sum\limits_{1 \le i \le j \le n-2} v(x_i - x_j)} \times \right.$$

$$\left. \times \int\limits_{x_n, x_{n-1} \in \Delta} e^{-\beta(v(x_{n-1} - x_n) + \sum\limits_i v(x_i - x_{n-1}) + \sum\limits_i v(x_i - x_n))} \, dx_{n-1} \, dx_n \right) dx_1 \dots dx_{n-2} +$$

$$+ \dots$$

Apply the estimate (20.4) to $\exp\left(-\beta \sum\limits_{i=1}^{n-k} v(x_i - x_\alpha)\right)$. As a result, we get an estimate for $z_n(\Omega_1)$:

$$z_n(\Omega_1) \le z_n(\Omega) + n z_{n-1}(\Omega) c_1 |\Delta| + \frac{n(n-1)}{2!} z_{n-2}(\Omega) z_2(\Delta) c_1^2 + \dots$$

Further, since

$$e^{-\beta \sum\limits_{1 \le i \le j \le p} v(x_i - x_j)} \, e^{-\beta \frac{1}{2} \sum\limits_j \sum\limits_{i \ne j} v(x_i - x_j)} \le c_1^{p/2}$$

for the x considered, we get an estimate of $z_p(\Delta)$:

$$z_p(\Delta) \le |\Delta|^p c_1^{p/2}.$$

Therefore

$$z_n(\Omega_1) \le z_n(\Omega) + n z_{n-1}(\Omega) c_1 |\Delta| + \frac{n(n-1)}{2!} z_{n-2}(\Omega) c_1^{2+1} |\Delta|^2 + \dots$$

$$\dots + \frac{n!}{k!(n-k)!} z_{n-k}(\Omega) c_1^{k+k/2} |\Delta|^k + \dots$$

This and (20.1) implies that, for n sufficiently large, we have

$$\frac{z_n(\Omega_1)}{z_n(\Omega)} \le 1 + \frac{n c' |\Delta|}{|\Omega|} + \frac{n(n-1)}{2!} \left(\frac{c' |\Delta|}{|\Omega|} \right)^2 + \dots \le$$

$$\le \sum_{k=0}^{\infty} \frac{1}{k!} \frac{n^k}{|\Omega|^k} (c' |\Delta|)^k \le \sum_{k=0}^{\infty} \frac{(\gamma' c' |\Delta|)^k}{k!} = E^{c|\Delta|},$$

where $\gamma' > \gamma = \lim\limits_{|\Omega| \to \infty} \dfrac{n}{|\Omega|}$ and $c = \gamma' c'$. The inequality $\dfrac{z_n(\Omega_1)}{z_n(\Omega)} > 1$ obviously follows from the fact that $\Omega \subset \Omega_1$. Theorem is proved. □

Part II

THE QUANTUM STATISTICAL PHYSICS

§ 21. Background from Quantum Mechanics

In this section, we give initial background from quantum mechanics necessary to understand the next two sections.

More detailed information needed for statistical physics (the method of second quantization) are postponed to § 25. For the goals of statistical physics it is sufficient, as a rule, to consider physical quantities with discrete spectrum. Therefore for the initial understanding of the quantum statistical physics it suffices to consider the operators in the infinite dimensional Hilbert space as matrices whose properties do not differ from the properties of matrices of finite size.

For completeness, in the second part of this section we will briefly present general features of the spectral theory of self-adjoint operators in a form convenient for us. We advise the reader completely ignorant of this theory to begin by first skimming through the second part of this section and then pass to the first part.

21.1. The main notions of quantum mechanics. Every *state* of the quantum mechanical system is described by the unit vector f of the complex Hilbert space $\mathcal{H}$. To each physical quantity there corresponds a self-adjoint operator in $\mathcal{H}$ and speaking about *physical quantities* we will always have in mind the corresponding operators.

To the *energy* of the system the *energy operator* H corresponds sometimes called the *Hamiltonian*. The state of a given quantum mechanical system is developed in time in accordance with *the Schrödinger equation*

$$i\hbar\frac{\partial f}{\partial t} = Hf. \tag{21.1}$$

The solution of equation (21.1) is expressed in the form

$$f = e^{i\frac{t}{\hbar}H} f_0.$$

The number $\hbar = \dfrac{h}{2\pi}$, where h is a constant with a dimension, is called *Planck's constant*. In the system of units adjusted for macroscopic quantities it is exceedingly small ($h = 6{,}54 \cdot 10^{-27}\text{erg} \cdot \text{sec}$).

In the atomic system of units, $\hbar = 1$. Except for § 30, where we investigate the relation between the quantum and classical statistical physics, we adopt the system of units in which $\hbar = 1$.

In each state of the system, every physical quantity possesses a probability distribution. In the simplest case, where the spectrum of operator A is discrete [11)]. It is constructed as follows. Let a_1 be the eigenvalues and let e_i be the corresponding unit eigenvectors; let $f = \sum c_i e_i$ and let $\|e_i\| = 1$ be a state of the system. The probability p_k of the quantity A in the state f to attain value a_k is equal to $|c_k|^2$, so

$$\sum p_k = \sum |c_k|^2 = (f, f) = 1.$$

For the mathematical expectation and distortion of A in the state f, we have the following expressions:

$$M_f(A) = (Af, f), \tag{21.2}$$

$$D_f(A) = (A^2 f, f) - (Af, f)^2. \tag{21.3}$$

Indeed,

$$\begin{aligned} M_f(A) &= \sum a_k p_k = \sum a_k |c_k|^2 = (Af, f), \\ D_f(A) &= \sum (a_k - M_f(A))^2 |c_k|^2 = \\ &= \sum a_k^2 |c_k|^2 - 2M_f(A) \sum a_k |c_k|^2 + M_f^2(A) = \\ &= \sum a_k^2 |c_k|^2 - M_f^2(A) = (A^2 f, f) - (Af, f)^2. \end{aligned}$$

In the general case, the probability distribution of A in the state f is given by the formula $P(\lambda) = (E_\lambda f, f)$, where E_λ is the spectral projector of the operator A and the expressions (21.2) and (21.3) still hold. If A is unbounded, the mathematical expectation and dispersion exist not for every vector f. In order for $M_f(A)$ and $D_f(A)$ to exist, it is necessary and sufficient for f to belong to the domain of definition of A. In what follows when we consider $M_f(A)$ or $D_f(A)$ we always assume that f belongs to the domain of definition of A.

Let the evolution of the system be determined by the Hamiltonian H. A physical quantity A is said to be *preserved* or *an integral of motion* if its

[11)] The spectrum is said *to be discrete* if it is the closure of the set of eigenvalues such that each eigenvalue possesses a finite multiplicity and is an inner point of an interval that has no other eigenvalues.

mean value at every state is time-independent, that is $M_{f_t}(A) = M_{f_0}(A)$ or, in more details,

$$(Ae^{itH}f, e^{itH}f) = (Af, f). \tag{21.4}$$

Set $f = g + \varepsilon h$, where ε is an arbitrary complex number. The left- and right-hand sides of(21.4) are second degree polynomials in ε and $\overline{\varepsilon}$. Equating the coefficients of ε we see that

$$(e^{-itH}Ae^{itH}, g) = (Ae^{itH}h, e^{itH}g) = (Ah, g).$$

Therefore

$$e^{-itH}Ae^{itH} = A \tag{21.5}$$

for any t, i.e., the operators A and H commute: $AH = HA$. The converse is obviously also true: If (21.5) holds, then $M_{f_t}(A) = M_{f_0}(A)$. Thus A is an integral of motion if and only if $AH = HA$. In the infinite dimensional spaces, where the operators A and H are unbounded, the equality $AH = HA$ can be interpreted in several ways. The strongest of them is that the spectral projectors of A and H commute. From the general spectral theorem we easily deduce that the equality $A = e^{itH}Ae^{-itH}$ for all t guarantees that $AH = HA$ in this strongest sense. Therefore if A is an integral of motion, then so are spectral projectors E_λ, and therefore not only $M_{f_t}(A)$ does not depend on t but the probability distribution of A in the state f_t does not depend on t.

21.2. Non-interacting subsystems. Let the quantum mechanical system L consist of non-interacting subsystems L_i, where $i = 1, \ldots, n$. Each subsystem L_i is described by the Hilbert space $\mathcal{H}_i$ and a Hamiltonian H_i acting in $\mathcal{H}_i$. The Hilbert space $\mathcal{H}$ of the states of the system L is the tensor product of the spaces $\mathcal{H}_i$. The Hamiltonian of the system L is the direct sum $H = \oplus H_i$ of the Hamiltonians H_i.

If the subsystems are identical, the spaces $\mathcal{H}_i$ coincide, $\mathcal{H}_i = \mathcal{H}_1$, and the space $\mathcal{H}$ is the n-th tensor power of $\mathcal{H}_1$.

Let us recall the definition of the tensor product of Hilbert spaces the tensor sum and the tensor product of operators.

The space $\mathcal{H}$ is said to be *the tensor product* of spaces $\mathcal{H}_i$ and is denoted by $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \ldots \otimes \mathcal{H}_n$ if, for any set of vectors $f_1, \ldots, f_n$, where $f_i \in \mathcal{H}_i$, the map $F(f_1, \ldots, f_n)$ of this set into $\mathcal{H}$ is defined such that

(1) If $f_i = \alpha f_i' + \beta f_i''$, then

$$F(f_1, \ldots, f_n) = \alpha F(f_1, \ldots, f_i', \ldots, f_n) + \beta F(f_1, \ldots, f_i'', \ldots, f_n).$$

(2) If $e_\alpha^{(i)}$ is an orthonormal basis in $\mathcal{H}_i$, then the vectors

$$e_{\alpha_1 \dots \alpha_n} = F(e_{\alpha_1}^{(1)}, \dots, e_{\alpha_n}^{(n)}$$

constitute an orthonormal basis in $\mathcal{H}$.

If the spaces $\mathcal{H}_i$ coincide, i.e., if $\mathcal{H}_i = \mathcal{H}_1$ for all i, then the function F is a multilinear function depending on n elements of $\mathcal{H}_1$:

$$F = F(f_1, \dots, f_n), \quad \text{where} \quad f_i \in \mathcal{H}_1 \quad \text{for} \quad i = 1, \dots, n.$$

In what follows, we will use a shorthand notation expressing $F(f_1, \dots, f_n)$ as a product $F(f_1, \dots, f_n) = f_1 \dots f_n$.

Let A_i be some operators in $\mathcal{H}$ defined on a dense domains D_{A_i}. In $\mathcal{H}$, we first define a linear operator A on the products:

$$Af_1 \dots f_n = (A_1 f_1) f_2 \dots f_n + f_1 (A_2 f_2) \dots f_n + \dots + f_1 \dots f_{n-1} (A_n f_n), \tag{21.6}$$

where $f_i \in D_{A_i}$. Next, we extend the operator obtained by linearity on the set of finite linear combinations of the products $f_1, \dots, f_n$, where $f_i \in D_{A_i}$; this set is dense in $\mathcal{H}$ thanks to property (2).

Finally, we consider the closure of this set (if possible).

If the operators A_i are self-adjoint, the operator A thus obtained is also self-adjoint. The operator A is called *the tensor sum* of the operators A_i. We will express A as a usual sum [12)]:

$$A = A_1 + \dots + A_n.$$

Define the tensor product A of bounded operators A_i acting in $\mathcal{H}$.

Step one: Set

$$Af_1 \dots f_n = (A_1 f_1)(A_2 f_2) \dots (A_n f_n).$$

Step two: Continue onto the finite linear combinations of products via linearity and close. The tensor product of operators is denoted by

$$A = A_1 \otimes A_2 \otimes \dots \otimes A_n.$$

It is easy to verify that if each A_i is a self-adjoint operator and $A = A_1 + \dots + A_n$ is their tensor sum, then

$$e^{itA} = e^{itA_1} \otimes e^{itA_2} \otimes \dots \otimes e^{itA_n}.$$

[12)] Such an expression is widespread in physical literature and never leads to misunderstanding. In the mathematical literature a more cumbersome notation is used.

If the spaces $\mathcal{H}_i$ are realized as $L_2(M_i)$, where M_i is a set with measure, then $\mathcal{H} = \mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_n$ is naturally realized as $L_2(M_i)$, where $M = M_1 \times \ldots \times M_n$ with measure equal to the product of measures on M_i. The map $(f_1, \ldots, f_n) \mapsto f_1 \ldots f_n$ that determines the tensor product turns into the product of functions

$$f1(x_1) \ldots f_n(x_n), \quad \text{where } x_i \in M_i, \quad \text{and } f_i(x_i) \in L_2(M_i).$$

The operator A_i entering as a summand the tensor sum or as a factor the tensor product acts on $f(x_1, \ldots, x_n) \in L_2(M_1 \times \ldots \times M_n)$ as on a function in x_i with the other variables considered as parameters.

21.3. The spectral theorem for self-adjoint operators in Hilbert space.

21.3.1. Theorem (The spectral theorem for self-adjoint operators). *Let $\mathcal{H}$ be a Hilbert space and A a self-adjoint operator in $\mathcal{H}$. There exists a set M with measure and isomorphism $U\colon \mathcal{H} \to L_2(M)$ such that the operator $\widetilde{A} = UAU^{-1}$ in $L_2(M)$ — the image of A under the isomorphism U — is the multiplication operator by a measurable real-valued function*

$$(\widetilde{A}f)(x) = \lambda(x)f(x).$$

The domain of definition $D_{\widetilde{A}}$ of $\widetilde{A}$ consists of the functions $f \in L_2(M)$ for which $\int |f(x)|^2\lambda^2(x)\,dx < \infty$. The domain of definition D_A of the initial operator A is the pre-image of $D_{\widetilde{A}}$ with respect to U, i.e., $D_A = U^{-1}D_{\widetilde{A}}$.

If $\mathcal{H}$ is of finite dimension, then the number of points in M is equal to the dimension of $\mathcal{H}$ and the spectral theorem turns into the theorem on the reduction of a given Hermitian matrix to the diagonal form.

The *spectral projector of an operator* $\widetilde{A}$ is the operator $\widetilde{E}_\lambda$ of multiplication by the characteristic function of the set $\{x \mid \lambda(x) < \lambda\}$:

$$(\widetilde{E}_\lambda f)(x) = \theta(\lambda - \lambda(x))f(x), \quad \text{where } \theta(\lambda) = \begin{cases} 1, & \lambda > 0, \\ 0, & \lambda \le 0. \end{cases} \tag{21.7}$$

The operator $E_\lambda = U^{-1}\widetilde{E}_\lambda U$ is said to be *the spectral projector of the operator A.*

Neither the set M nor the homomorphism U are invariantly related with the operator A since there exist distinct realizations of the space $\mathcal{H}$ in the form $L_2(M)$ that realize A as the operator of multiplication by function. It is remarkable that, although the construction of E_λ involves both M and U, it does not depend on either M or U but only on the operator A itself. One

can recover A if the operators E_λ are known with the help of the operator Riemann—Stieltjes integral:

$$A = \int \lambda \, dE_\lambda = \lim_{\substack{a \to -\infty \\ b \to \infty}} \int_a^b \lambda \, dE_\lambda, \tag{21.8}$$

$$\int_a^b \lambda \, dE_\lambda = \lim_{\max_k (\lambda_{k+1} - \lambda_k) \to 0} \sum \lambda_k (E_{\lambda_{k+1}} - E_{\lambda_k}). \tag{21.9}$$

Both limits (21.8) and (21.9) are understood in the strong sense. Eq. (21.8) follows easily from the spectral theorem.

In what follows, the notion of *the function of an operator* is important. If A and $\widetilde{A}$ are the same type of operators as in the spectral theorem and $\varphi(x)$ a piecewise continuous function of real variable, then by definition

$$\varphi(A) = U^{-1} \varphi(\widetilde{A}) U,$$

where $\varphi(\widetilde{A})$ acts on $L_2(M)$ by the formula

$$(\varphi(\widetilde{A}) f)(x) = \varphi(\lambda(x)) f(x).$$

The spectral theorem implies a representation of $\varphi(\widetilde{A})$ in terms of E_λ:

$$\varphi(A) = \int \varphi(\lambda) dE_\lambda. \tag{21.10}$$

The meaning of the integral (21.10) is the same as the meaning of (21.8).

Eq. (21.10) implies that the operator $\varphi(A)$ does not depend on the choice of the set M and the map U but only on the operator A and the function φ.

One can define the operator $\varphi(A)$ not only for the piecewise continuous functions φ, and the set of the functions for which it is possible and natural to define $\varphi(A)$ depends on the operator A itself.

It is possible to generalize the spectral theorem to the case of a family of commuting self-adjoint operators.

21.3.2. Theorem. *Let A_i, where $i = 1, 2, \ldots$, be a family commuting with each other in the strongest sense*[13)] *self-adjoint operators in the Hilbert space $\mathcal{H}$. Then there exists a set M with measure and an isomorphism $U \colon \mathcal{H} \to L_2(M)$ such that the operators $\widetilde{A}_i = U A_i U^{-1}$ are operators of multiplication by real measurable functions: $(\widetilde{A}_i f)(x) = \lambda_i(x) f(x)$.*

[13)] That is their spectral projectors commute.

Let $A_1, \dots, A_n$ be commuting in the strongest sense self-adjoint operators and $\varphi(x_1, \dots, x_n)$ a piecewise continuous function of n real variables. Set

$$\varphi(A_1, \dots, A_n) = U^{-1}\varphi(\widetilde{A}_1, \dots, \widetilde{A}_n)U,$$

where U and $\widetilde{A}_i$ are the same as in Theorem 21.3.2 and $\varphi(\widetilde{A}_1, \dots, \widetilde{A}_n)$ is the operator of multiplication by the function $\varphi(\lambda_1(x), \dots, \lambda_n(x))$.

The operator $\varphi(A_1, \dots, A_n)$ admits an integral representation similar to (21.10) which shows that it only depends on $A_1, \dots, A_n$ and φ, but not on M and U:

$$\varphi(A_1, \dots, A_n) = \int \varphi(\lambda_1, \dots, \lambda_n)\, dE_{\lambda_1} \dots\, dE_{\lambda_n}. \tag{21.11}$$

The set of functions φ for which $\varphi(A_1, \dots, A_n)$ can be defined depends on the operators A_i.

The meaning of the integral (21.11) is similar to the meaning of (21.8).

In the finite-dimensional case the operator A is said to be *an operator with simple spectrum* if its eigenvalues corresponding to distinct eigenvectors are distinct. In general, the operator A is said to be *an operator with simple spectrum* if, being realized as the operator of multiplication by a function $\lambda(x)$, we have $\lambda(x) \neq \lambda(y)$ for almost all [14] pairs x, y.

The definition of the simple spectrum of the system of commuting in the strongest sense operators $A_1, A_2, \dots$ is similar: The sequence of numbers $(\lambda_1(y), \lambda_2(y), \dots)$ should be distinct from the sequence $(\lambda_1(x), \lambda_2(x), \dots)$ for almost all pairs x, y.

21.3.3. Theorem. *In order for a system of commuting in the strongest sense self-adjoint operators $A_1, \dots, A_n$ have a simple spectrum it is necessary and sufficient that each operator B commuting with all the A_i in the strongest sense were a function of them, i.e., $B = \varphi(A_1, \dots, A_n)$.*

Theorem 21.3.3 is obvious in the important for the statistical physics case where the operators A_i possess a discrete spectrum and is rather delicate in the general case. In the general case, the function φ might be not piecewise continuous.

[14] In the sense of the natural measure on $M \times M$.

Chapter 3

ENSEMBLE OF MICROSCOPIC SUBSYSTEMS

§ 22. The mean with respect to time. The ergodic hypothesis.

22.1. The mean of measurable quantities. Let the energy operator of the system, H, possess a discrete spectrum. A physical quantity A is said *to be measurable with respect to* H if the eigen vectors of H belong to the domain of definition of A.

The mean with respect to time of A is

$$\overline{A} = \lim_{T\to\infty} \frac{1}{T} \int_0^T e^{-itH} A e^{itH}\, dt. \tag{22.1}$$

Remark. The reason for considering the means with respect to time in quantum statistical physics are the same as those in the classical statistical physics. The result of the measurement of the mean of A in state ψ during the time interval T is given by the formula

$$\frac{1}{T} \int_0^T (Ae^{itH}\psi_1, e^{itH}\psi)\, dt. \tag{22.2}$$

The measurement time T is exceedingly long from the point of view of the system under the study and therefore (22.2) can be replaced by its limit as $T \to \infty$. As a result we see that the measured value of A is equal to $(\overline{A}\psi, \psi)$, where $\overline{A}$ is given by the expression (22.1).

Consider the matrix element of the operator $\overline{A}$ in the eigenbasis of H

$$\overline{a}_{ke} = \lim_{T\to\infty} \frac{1}{T} \int_0^T e^{it(\lambda_e - \lambda_k)}\, dt = a_{ke} \lim_{T\to\infty} \frac{e^{iT(\lambda_e-\lambda_k)}}{iT(\lambda_e - \lambda_k)} = a_{kl}\delta_{\lambda_e\lambda_k},$$

where λ_e are the eigenvalues of H and $\delta_{\lambda\mu}$ is the Kronecker symbol. Suppose that the eigenvectors corresponding to one eigenvalue are numbered

consecutively. In this case the matrix of the operator $\overline{A}$ is block-diagonal:

$$\overline{A} = \operatorname{diag}(A_1, A_2, \dots) := \begin{pmatrix} A_1 & & 0 \\ & A_2 & \\ 0 & & \ddots \end{pmatrix}.$$

Observe that in the same basis the operator P_i of projecting onto the eigenspace of H with eigenvalue λ_i is of a similar form

$$P_i = \operatorname{diag}(0, \dots, 0, 1_i, 0, \dots, 0),$$

where 1_i is the unit matrix occupying the slot of the block A_i. We see that

$$\overline{A} = \sum P_i A P_i,$$

in particular, $\overline{A}$ commutes with H.

22.2. The ergodic hypothesis. The quantum system determined by the Hamiltonian H and possessing commuting with each other integrals of motion $K_1, \dots, K_n$ is said to be *ergodic* if each preserved quantity is a function of H and $K_1, \dots, K_n$; in other words (see the end of § 21), if the mutual spectrum of the operators H and $K_1, \dots, K_n$ is simple.

In particular, when there are no first integrals and the spectrum of H is discrete, the system is ergodic if all the eigenvalues of H are distinct.

For simplicity of the exposition we will almost always confine ourselves to the case where the additional first integrals are absent. All the arguments considered can be automatically generalized to the general case. In what follows, we assume that the spectra of the operators H and the H_n are discrete.

Let the system determined by the Hamiltonian H be non-ergodic but is a limit of ergodic ones $H = \lim\limits_{n\to\infty} H_n$, where the spectrum of H_n is simple and discrete. Consider an arbitrary (measurable with respect to H_n and H) operator A and set

$$\overline{A}_n = \lim_{T\to\infty} \frac{1}{T} \int_0^T e^{-itH_n} A e^{itH_n}\, dt. \tag{22.3}$$

Due to ergodicity $\overline{A}_n = f_n(H_n)$. Let the sequence H_n and the operator A be such that the limit $f(x) = \lim\limits_{n\to\infty} f_n(x)$ as $n \to \infty$ exists. Set

$$\overline{A}_\infty = \lim_{n\to\infty} \overline{A}_n = f(H).$$

Like the operator (22.1), the operator $\overline{A}_\infty$ commutes with H but, moreover, it is a multiple of the unit operator on each eigenspace of H.

Let Ψ_E be an eigenvector of H with eigenvalue E. Let us transform $(\overline{A}_\infty \Psi_E, \Psi_E)$ to a form more convenient in what follows:

$$(\overline{A}_\infty \Psi_E, \Psi_E) = \lim_{n\to\infty} (\overline{A}_n \Psi_E, \Psi_E) = (f(H)\Psi_E, \Psi_E) = f(E) = \frac{\operatorname{sp}(\overline{A}_\infty P_E)}{\operatorname{sp} P_E}, \tag{22.4}$$

where P_E is the projection operator onto the eigenspace of H with eigenvalue E.

Now, observe that

$$\operatorname{sp}(\overline{A}_\infty P_E) = \operatorname{sp}(AP_E). \tag{22.5}$$

Let us multiply the equality (22.3) by P_E from the left and take the trace. We get

$$\operatorname{sp}(P_E \overline{A}_n) = \lim_{T\to\infty} \frac{1}{T} \int_0^T \operatorname{sp}(P_E e^{-itH_n} A e^{itH_n})\, dt =$$

$$= \lim_{T\to\infty} \frac{1}{T} \int_0^T \operatorname{sp}(e^{itH_n} P_E e^{-itH_n} A)\, dt.$$

Since $\lim\limits_{n\to\infty} H_n = H$, it follows that $\lim\limits_{n\to\infty} e^{itH_n} P_E e^{-itH_n} = P_E$. Therefore passing to the limit as $n \to \infty$ we get (22.5). This and (22.4) implies that

$$(\overline{A}_\infty \Psi_E, \Psi_E) = \frac{\operatorname{sp}(AP_E)}{\operatorname{sp} P_E}. \tag{22.6}$$

If there are extra first integrals, let $\Psi_{E,k_1,\dots,k_n}$ be the common eigenfunction of H and the H_i whose eigenvalues are E and k_i, respectively. Then

$$(\overline{A}_\infty \Psi_{E,k_1,\dots,k_n}, \Psi_{E,k_1,\dots,k_n}) = \frac{\operatorname{sp}(AP_{E,k_1,\dots,k_n})}{\operatorname{sp} P_{E,k_1,\dots,k_n}}, \tag{22.7}$$

where $P_{E,k_1,\dots,k_n}$ is the projection operator onto the common eigenspace of the operators H and H_i with eigenvalues E and k_i.

The right-hand sides of formulas (22.6) and (22.7) are called the *quantum microcanonic mean*. The meaning of these formulas is that if an ergodic system is close to a non-ergodic one, then the mean with respect to time on the mean of any physical quantity over the eigenstate of the Hamiltonian of the non-ergodic system is close to the microcanonic mean.

§ 23. The Gibbs distribution

23.1. The ensemble of microscopic subsystems. Consider a system $L^N(\varepsilon)$ consisting of N weakly interacting similar subsystems L_i which are copies of the system L. Denote the space of states of the system L by $\mathcal{H}$ and let H be its Hamiltonian. The space $\mathcal{H}^N = \mathcal{H} \otimes \mathcal{H} \otimes \ldots \otimes \mathcal{H}$ of states of $L^N(\varepsilon)$ is the N-th tensor power of $\mathcal{H}$. The Hamiltonian of $L^N(\varepsilon)$ is of the form

$$H^{(N)}(\varepsilon) = \sum_{i=1}^{N} H_i + V_\varepsilon, \tag{23.1}$$

where H_i is the Hamiltonian of L_i and the sum is the tensor one and V_ε describes the interaction.

Let $L^N(\varepsilon)$ be ergodic. The interaction V_ε is small if we consider not the isolated system $L^N(\varepsilon)$ but a sequence of such systems depending on a parameter so that the limit as $\varepsilon \to 0$ system L^N consists of non-interacting subsystems and therefore is not ergodic. Let $H^{(N)}$ denote the Hamiltonian of L^N. This Hamiltonian is obtained from (23.1) if $V_\varepsilon = 0$.

An individual subsystem is microscopic if it does not depend on N.

Let A be a physical quantity describing the system L measurable with respect to H and A_i — a copy of A describing the system L_i. Consider the corresponding physical quantity describing the whole system $L^N(\varepsilon)$:

$$A^{(N)} = \frac{1}{N} \sum_{i=1}^{N} A_i. \tag{23.2}$$

The quantities of the form (23.2) are said to be *summatory*.

We are interested in the mean with respect to time of the mean of $H^{(N)}$ over the eigenvectors of $A^{(N)}$ for N large. For N and ε fixed, this mean is equal to

$$\overline{A^{(N)}}(\varepsilon) = \lim_{T\to\infty} \frac{1}{T} \int_0^T \left(e^{-itH^{(N)}(\varepsilon)} A^{(N)} e^{itH^{(N)}(\varepsilon)} f_E, f_E \right) dt. \tag{23.3}$$

Since the system $L^N(\varepsilon)$ is close to a non-ergodic system $L^{(N)}$, it follows that $\overline{A}^{(N)}(\varepsilon)$ is with good accuracy equal to its limit $\overline{A}^{(N)} = \lim\limits_{\varepsilon\to 0} \overline{A}^{(N)}(\varepsilon)$ as $\varepsilon \to 0$. By § 22 $\overline{A}(N)$ coincides, in its turn, with the microcanonic mean of

$$\overline{A}^{(N)} = \frac{\operatorname{sp}(A^{(N)} P_E^{(N)})}{\operatorname{sp} P_E^{(N)}}, \tag{23.4}$$

where $P_E^{(N)}$ is the projection onto the eigenspace of the operator $H^{(N)}$ corresponding to the eigenvalue E. Thus, the study of the mean with respect to time (23.3) as $\varepsilon \to 0$ and N large reduces to the study of (23.4) as $N \to \infty$. We will see that this expression possesses a limit as $N \to \infty$ provided $\dfrac{E}{N} = \text{const}$ is interpreted as *the mean energy* of the subsystem.

Let e_i be the eigenvector of H and ε_i the corresponding eigenvalue. Consider the eigenvector of the operator $H^{(N)}$ with eigenvalue E which is of the form

$$f_{i_1,\dots,i_N} = e_{i_1} \dots e_{i_N}. \tag{23.5}$$

To the vector $f_{i_1,\dots,i_N}$ assign a sequence of non-negative integers $\{n\} = (n_1, n_2, \dots)$, where the number n_α, called *the occupation number* of the state e_α, indicates how many numbers among the indices $i_1, \dots, i_N$ are equal to α. Obviously, the eigenvalue E is expressed in terms of the occupation numbers as follows:

$$\varepsilon_1 n_1 + \varepsilon_2 n_2 + \dots = E. \tag{23.6}$$

Besides, the occupation numbers satisfy the relation

$$n_1 + n_2 + \dots = N. \tag{23.7}$$

A sequence $\{n\}$ of non-negative integers is said to be *admissible* if it satisfies relations (23.6) and (23.7). Let $R_{N,E}$ denote the set of admissible sequences. Elementary combinatorial arguments show that the number of linearly independent vectors $f_{i_1,\dots,i_N}$ whose occupation numbers are equal to a given admissible sequence $(n_1, n_2, \dots)$ is equal to

$$\frac{N!}{n_1! n_2! \dots}.$$

Since $\operatorname{sp} P_E$ is equal to the number of linearly independent eigenvectors of $H^{(N)}$ with eigen value E we see that

$$\operatorname{sp} P_E = \sum_{\{n\} \in R_{N,E}} \frac{N!}{n_1! n_2! \dots}. \tag{23.8}$$

Now, let us express the numerator in (23.4) in terms of the occupation numbers. Observe that

$$\operatorname{sp}(A^{(N)} P_E^{(N)}) = \sum_{i_1 \dots i_k} (A^{(N)} f_{i_1,\dots,i_k}, f_{i_1,\dots,i_k}) =$$

$$\frac{1}{N} \sum_{p=1}^{N} \sum_{i_1 \dots i_k} (A_p f_{i_1,\dots,i_N}, f_{i_1,\dots,i_N}),$$

where $f_{i_1,\dots,i_k}$ are the eigenvectors (with eigenvalue E) of the form (23.5). Further on,

$$(A_p f_{i_1,\dots,i_k}, f_{i_1,\dots,i_k}) = (Ae_{i_p}, e_{i_p}).$$

For brevity, set $\alpha_i = (Ae_i, e_i)$.

Then

$$\operatorname{sp}(A^{(N)} P_E^{(N)}) = \frac{1}{N} \sum_{p=1}^{N} \sum_{i_1 \dots i_N} \alpha_{i_p} = \frac{1}{N} \sum_{i_1 \dots i_N} \sum_{p=1}^{N} \alpha_{i_p}. \tag{23.9}$$

Fix the indices $i_1, \dots, i_N$. Let $n_1, n_2, \dots$ be a sequence of occupation numbers corresponding to these indices. The inner sum in (23.9) is equal to $\sum n_s \alpha_s$. Since the number of distinct sets of indices $i_1, \dots, i_N$ with the same occupation numbers is equal to $\dfrac{N!}{n_1! n_2! \dots}$, we finally get

$$\operatorname{sp}(A^{(N)} P_E^{(N)}) = \sum_{\{n\} \in R_{N,E}} \frac{N!}{n_1! n_2! \dots} \sum_s \frac{n_s}{N} \alpha_s. \tag{23.10}$$

Comparing (23.8) and (23.10) we obtain for the microcanonical mean (23.4) expressions identically coinciding with the expression (3.6) for the classical microcanonical mean. Therefore our further study copies the contents of § 3. We interpret the microcanonical mean as the mean of $\varphi = \sum \dfrac{n_s}{N} \alpha_s$ over all admissible sequences assuming that the probability of a fixed sequence is equal to

$$P(\{n\}) = \frac{\dfrac{N!}{n_1! n_2! \dots}}{\displaystyle\sum_{\{m\} \in R_{N,E}} \frac{N!}{m_1! m_2! \dots}}.$$

Then we find a sequence for which $P(\{n\})$ attains its maximum. For the most probable sequence, it turns out that asymptotically we have

$$n_s = N a e^{-\beta \varepsilon_s} \quad \text{as} \quad N \to \infty, \tag{23.11}$$

where β and a are determined from the relations

$$\frac{\sum \varepsilon_s e^{-\beta \varepsilon_s}}{\sum e^{-\beta \varepsilon_s}} = \varepsilon = \frac{N}{E}, \quad a \sum e^{-\beta \varepsilon_s} = 1. \tag{23.12}$$

Therefore

$$\lim_{N \to \infty} \frac{\operatorname{sp}(A^{(N)} P_E^{(N)})}{\operatorname{sp} P_E^{(N)}} = \sum a e^{-\beta \varepsilon_s} \alpha_s. \tag{23.13}$$

The right-hand side of (23.13) looks as the mean of the quantity α_s over the probability distribution $p_s = ae^{-\beta\varepsilon_s}$. This probability distribution is called *the Gibbs distribution* for the quantum statistical physics.

Recall that $\alpha_s = (Ae_s, e_s)$, where e_s is the eigen vector of H with eigen value ε_s. Therefore the expression (23.13) can be presented in the form

$$\lim_{N\to\infty} \frac{\operatorname{sp}(A^{(N)}P_E^{(N)})}{\operatorname{sp} P_E^{(N)}} = \frac{\operatorname{sp} Ae^{-\beta H}}{\operatorname{sp} e^{-\beta H}}. \tag{23.14}$$

If in addition to Hamiltonian the system L possesses commuting first integrals $H_1, \dots, H_n$ then the formula (23.14) is replaced by

$$\lim_{N\to\infty} \frac{\operatorname{sp}(A^{(N)}P^{(N)}_{E,k_1,\dots,k_n})}{\operatorname{sp} P^{(N)}_{E,k_1,\dots,k_n}} = \frac{\operatorname{sp} Ae^{-\beta(H+\mu_1H_1+\dots+\mu_nH_n)}}{\operatorname{sp} e^{-\beta(H+\mu_1H_1+\dots+\mu_nH_n)}}, \tag{23.15}$$

where $P^{(N)}_{E,k_1,\dots,k_n}$ is the projection onto the subspace $\mathcal{H}^{(N)}$ eigen with respect to $H, H_1, \dots, H_n$ with eigen values $E = N\varepsilon$ and $k_i = N\varkappa_i$ accordingly and where ε, $\varkappa_i$ do not depend on N.

The operator

$$T = \frac{e^{-\beta(H+\mu_1H_1+\dots+\mu_nH_n)}}{\operatorname{sp} e^{-\beta(H+\mu_1H_1+\dots+\mu_nH_n)}}$$

is called the Gibbs density matrix and $\operatorname{sp} e^{-\beta(H+\mu_1H_1+\dots+\mu_nH_n)}$ the statistical sum.

The numbers β and μ are related with ε and $\varkappa_i$ by the relations

$$\operatorname{sp}(HT) = \varepsilon, \quad \operatorname{sp}(H_iT) = \varkappa_i. \tag{23.16}$$

The equations (23.16) might be solvable not for arbitrary ε and $\varkappa_i$. If they are however solvable then the solution is unique. This fact is proved in the next section under the assumption that the operators entering (23.16) act in a finite-dimensional space.

23.2. Remarks. 1) Formula (23.14) can be rigorously proved. For this it suffices to additionally assume that $\varepsilon_k \geq 0$ and the multiplicity of ε_k does not exceed $c^n\varepsilon_k^n$, where c, n are some constants. Now we may use the Laplace transform in the same way we did it in § 4. Under the same conditions it is easy to prove that equation (23.12) for β has a unique positive solution for any $\varepsilon > 0$. For the proof of a similar statement see § 4.

2) The reduction of the mean with respect to time to the microcanonical mean is based on the same arguments as in the classical statistical physics. In its foundation lies our belief that the ergodic systems form a tense in

some sense subset in the set of all quantum systems whereas non-ergodic systems are exceptions. Since the quantities under our study in particular the mean with respect to time should be stable with respect to small changes of the Hamiltonian we inevitably have to compute the mean with respect to time formed not with the help of the Hamiltonian H of the initial system consisting of non-interacting subsystems but with the help of some close Hamiltonian $H + V$ which is necessarily ergodic due to the said assumption. Since V is small the mean with respect to time computed with the help of the Hamiltonian $H + V$ is close to the microcanonical mean obtained with the help of the initial Hamiltonian H. Thus it does not depend on the nature of the additional operator V which is interpreted as the energy operator of the interaction between subsystems. The assumption that in quantum mechanics the ergodic systems constitute a dense set is to an extent justified by the following theorem which can be easily proved by means of the elementary perturbation theory [1)].

23.3. Theorem. *1) Let H be a self-adjoint operator with discrete spectrum. There exists a bounded self-adjoint operator V such that $H + \varepsilon V$ has a simple spectrum for any ε however small in absolute value.*

2) Let H be a self-adjoint operator with simple spectrum whose eigen values satisfy $|\lambda_i - \lambda_j| > \alpha$. Then if V is self-adjoint and $\|V\| < \alpha$ then $H + V$ also has a simple spectrum.

This theorem is not sufficient to justify the passage from the mean with respect to time to microcanonical mean mainly because it is unclear how the passage to the limit of the integral (23.3) as $T \to \infty$ is slowed down as the system $L^{(N)}(\varepsilon)$ approaches the non-ergodic system $L^{(N)}$.

3) The consideration of the ensemble of microscopic subsystems in the quantum case is basically an ideal pastime. As we will see the interesting from the physical point of view systems are macroscopic, i.e., depend on the number N of subsystems in the whole system. This applies even to the ideal quantum gases unlike the classical ideal gases which can be considered both as ensemble of microscopic subsystems and as ensembles of macroscopic subsystems. In a due place we will see that the physical justifications for the application of the Gibbs distribution for the ensemble of macroscopic subsystems in the quantum case are the same as in the classical case.

§ 24. A Relation with thermodynamics. Entropy

[1)] The background from the perturbation theory necessary for the proof of this theorem can be found in the textbook of Riesz and Nagy [RN].

1. A relation with thermodynamics in the quantum statistical physics is given by the same formulas as in the classical one. The parameter β is related with the absolute temperature by means of the expression $\beta = \frac{1}{kT}$, where k is the Boltzmann constant. If the Hamiltonian H of the subsystem depends on the parameters $\lambda_1, \dots, \lambda_s$ then

$$p_s = -N \frac{\operatorname{sp}\left(\frac{\partial H}{\partial \lambda_s} e^{-\beta H}\right)}{\operatorname{sp} e^{-\beta H}} = \frac{N}{\beta} \frac{\partial}{\partial \lambda_s} \ln \operatorname{sp} e^{-\beta H}$$

is called *the generalized pressure*. In particular, if $\lambda = |\Omega|$, where the Ω is the volume occupied by the system then

$$p = -\frac{N}{\beta} \frac{\partial}{\partial \lambda} \ln \operatorname{sp} e^{-\beta H}$$

is *the usual pressure*. The reasons for identification of the quantities p_s with the generalized pressure are the same as in the classical physics [2)].

Every classical system can be considered as a quantum one if one takes into account the microscopic structure of the objects that constitute it. The thermodynamic notions for the classical systems have been introduced earlier and a question arises if they might be contradicting to the corresponding quantum notions.

From purely mathematical point of view this question is equivalent to the following one: Will the quantum thermodynamical characteristic of the system have the corresponding classical values in the limit as $h \to 0$, where h is the Planck constant?

In § 30 we will show that the quantum statistical sum $z_{n\ \mathrm{quant}}$ of the small canonical ensemble has the asymptotics

$$z_{n\ \mathrm{quant}} \approx \frac{1}{(2\pi h)^{3n}} z_{n\ \mathrm{class}}, \quad \text{as } h \to 0,$$

where

$$z_{n\ \mathrm{class}} = \int e^{-\beta H_n}\, dp\, dq, \quad H_n = \sum_1^n p^2 + \sum_{1 \le i < j \le n} v(q_i - q_j).$$

Since all thermodynamic quantities are expressed in terms of the derivatives of $\ln z_n$ with respect to β or λ, we deduce from here the desired correspondence of the quantum and classical thermodynamic quantities.

[2)] Obviously, the generalized pressure is a characteristic of macroscopic subsystem, not a microscopic one. Accordingly, under a more pedantic presentation, it should be introduced later.

Observe specifically that the temperature $T = \dfrac{1}{k\beta}$ in the quantum case possesses the same characteristic property as in the classical one: Two systems in equilibrium with temperatures T_1 and T_2 being intermixed form a system with an equilibrium if and only if $T_1 = T_2$. Formula (5.14) for the temperature of the mixture also holds. The proof of these statements is based essentially on the same arguments as in § 5.

24.1. The properties of the entropy. The entropy of an arbitrary discrete probability distribution p_k is equal to $s = -\sum p_k \ln p_k$. In particular, the entropy of the canonical Gibbs distribution is equal to

$$s = -\sum a e^{-\beta\varepsilon_k} \ln(a e^{-\beta\varepsilon_k}) = -\operatorname{sp}(A(\beta)\ln A(\beta)), \tag{24.1}$$

where $A(\beta)$ is the density matrix

$$A(\beta) = \frac{e^{-\beta(H+\mu_1 H_1+\ldots+\mu_n H_n)}}{\operatorname{sp} e^{-\beta(H+\mu_1 H_1+\ldots+\mu_n H_n)}}.$$

24.2. Theorem (Nernst). *Let the eigenvalues ε_k of the operator*

$$H + \mu_1 H_1 + \ldots + \mu_n H_n$$

be such that $\varepsilon_k \geq \varepsilon$, the multiplicity of n_k be such that $n_k \leq (c\varepsilon_k)^m$, where c and m are constants. Then the entropy $s(\beta)$ has a limit as $\beta \to \infty$ ($T \to 0$) equal to $-\ln n_0$. In particular,[3] *if $n_0 = 1$, then $\lim\limits_{\beta\to\infty} s = 0$.*

Proof. Let us transform expression (24.1) to the form

$$s = -\ln a + \beta\varepsilon, \quad a = \Big(\sum e^{-\beta\varepsilon_k}\Big)^{-1}, \quad \varepsilon = a\sum \varepsilon_k e^{-\beta\varepsilon_k}. \tag{24.2}$$

Let us find the asymptotics of each summand in (24.2):

$$-\ln a = \ln\Big(\sum e^{-\beta\varepsilon_k}\Big) = \ln\left(n_0 e^{-\beta\varepsilon_0}\left(1 + \sum_{\varepsilon_k>\varepsilon_0} \frac{n_k}{n_0} e^{-\beta(\varepsilon_k-\varepsilon_0)}\right)\right) = \tag{24.3}$$

$$= -\beta\varepsilon_0 + \ln n_0 + \ln\Big(1 + \sum_{\varepsilon_k>\varepsilon_0} \frac{n_k}{n_0} e^{-\beta(\varepsilon_k-\varepsilon_0)}\Big). \tag{24.4}$$

[3] In actual systems this case is most often realized.

Then

$$\beta\varepsilon = \beta\frac{n_0\varepsilon_0 e^{-\beta\varepsilon_0}\Big(1+\sum\limits_{\varepsilon_k>\varepsilon_0}\dfrac{\varepsilon_k n_k}{n_0\varepsilon_0}e^{-\beta(\varepsilon_k-\varepsilon_0)}\Big)}{n_0 e^{-\beta\varepsilon_0}\Big(1+\sum\limits_{\varepsilon_k>\varepsilon_0}\dfrac{n_k}{n_0}e^{-\beta(\varepsilon_k-\varepsilon_0)}\Big)} =$$

$$= \beta\varepsilon_0 + \frac{\beta\sum\limits_{\varepsilon_k>\varepsilon_0}\dfrac{n_k}{n_0}\Big(\dfrac{\varepsilon_k}{\varepsilon_0}-\varepsilon_0\Big)e^{-\beta(\varepsilon_k-\varepsilon_0)}}{1+\sum\limits_{\varepsilon_k>\varepsilon_0}\dfrac{n_k}{n_0}e^{-\beta(\varepsilon_k-\varepsilon_0)}}. \quad (24.5)$$

Simple estimates indicate that under the above assumptions the expression under the logarithm sign in (24.4) tends to 1 as $\beta\to\infty$ same as the denominator of (24.5) whereas the numerator in (24.5) tends to zero. Hence

$$\lim_{\beta\to\infty} s(\beta) = -\beta\varepsilon_0 + \ln n_0 + \beta\varepsilon_0 = \ln n_0. \quad \square$$

24.3 The maximum principle. In the general case an arbitrary positive Hermitian operator with the trace equal to 1 is said to be *the density matrix.*

24.3.1. Theorem. *Let $H, H_1, \ldots, H_n$ be commuting with each other self adjoint operators. Denote by $M_{E,k_1,\ldots,k_n}$ the set of density matrices such that*

$$\operatorname{sp}(AH) = E, \quad \operatorname{sp}(AH_i) = k_i. \quad (24.6)$$

Let the numbers E and k_i be such that $M_{E,k_1,\ldots,k_n} \neq$. On $M_{E,k_1,\ldots,k_n}$ define the functional

$$S(A) = -\operatorname{sp}\, A\ln A.$$

This functional attains its only maximum at $A = A_G$, where

$$A_G = A_G(\beta,\mu_1,\ldots,\mu_n) = \frac{e^{-\beta(H+\mu_1H_1+\ldots+\mu_nH_n)}}{\operatorname{sp}\, e^{-\beta(H+\mu_1H_1+\ldots+\mu_nH_n)}}$$

is the Gibbs density matrix.

In particular, the system of equations for β and μ_i

$$\operatorname{sp}(A_GH) = E, \quad \operatorname{sp}(A_GH_i) = k_i \quad (24.7)$$

has a unique solution.

In order not to overburden the proof by inessential details we assume that $n=1$, $H_1 = H$, $k_1 = k$ and the operators considered act in a finite-dimensional space.

Let us preface the proof of the theorem with the following lemma.

Lemma. *Let C be an Hermitian operator, $\sigma_k = (Cf_k, f_k)$ its diagonal elements in an orthonormal basis $\{f_n\}$ and c_k its eigen values. Let further $\varphi(x)$ be a convex function. Then*

$$\sum_k \varphi(\sigma_k) \le \sum_k \varphi(c_k). \tag{24.8}$$

If $\varphi(x)$ is a strictly convex function then inequality (24.8) turns into equality if and only if $\{f_k\}$ is an eigen basis of C.

Proof. Let $\{e_k\}$ be an eigen basis of C, i.e., $Ce_k = c_k e_k$, $u = \|u_{ik}\|$ — the unitary matrix sending the basis $\{e_k\}$ into the basis $\{f_k\}$:

$$f_k = \sum_k u_{ki} e_i.$$

Then

$$\sigma_k = (Cf_k, f_k) = \Big(C \sum_k u_{ki} e_i, \sum_{i'} u_{ki'} e_{i'}\Big) =$$

$$= \Big(\sum_k u_{ki} c_i e_i, \sum_{i'} u_{ki'} e_{i'}\Big) = \sum_i |u_{ki}|^2 c_i.$$

Since φ is convex, it follows that $\varphi\Big(\sum p_i x_i\Big) \le \sum p_i \varphi(x_i)$ if $p_i \ge 0$ and $\sum p_i = 1$ where the inequality for a strictly convex function φ turns into equality if and only if $x_i = \sum p_k x_k$. Set $p_i = |u_{ki}|^2$ [4]. Then

$$\varphi(\sigma_k) = \varphi\Big(\sum_i |u_{ki}|^2 c_i\Big) \le \sum_i |u_{ki}|^2 \varphi(c_i). \tag{24.9}$$

Summing over k and applying once again the unitarity of u we get (24.8). The inequality (24.8) turns into an equality if and only if all the inequalities (24.9) turn into equalities. For a strictly convex function φ inequality (24.9) turns into equality only if $\sigma_k = c_\alpha$. The equality $c_\alpha = \sum\limits_i |u_{ki}|^2 c_i$ in its turn is only possible if $u_{ki} = 0$ for $c_i \ne c_\alpha$, i.e., if f_k is a linear combination of the vectors e_i with the same eigenvalue. In this case the vector f_k itself is eigenvector for C. □

Proof of theorem. Set $\varphi(x) = x \ln x$, where $x > 0$. Let f_k be a common orthonormal eigenbasis of the operators H and K and $\alpha_k = (Af_k, f_k)$. Since the function $\varphi(x)$ is strictly convex our lemma implies

$$\sum \alpha_k \ln \alpha_k \le \operatorname{sp}(A \ln A), \quad S(A) = -\operatorname{sp}(A \ln A) \le -\sum \alpha_k \ln \alpha_k, \tag{24.10}$$

[4] $\sum p_i = 1$ due to unitarity of u.

and inequality (24.10) turns into equality if and only if $\{f_k\}$ is an eigenbasis for A. Therefore it suffices to consider matrices having an eigenbasis common with H and K. Let A be such a matrix, α_p, ε_p, $\varkappa_p$ — the eigenvalues of A, H and K, respectively corresponding to the vector f_p. We have to find the maximum of the function $S(\alpha_1, \dots, \alpha_n) = -\sum \alpha_p \ln \alpha_p$ provided $(\alpha_1, \dots, \alpha_n) \in M_{E,k}$, where $M_{E,k}$ is the set singled out by the relations

$$1)\ \alpha_p \geq 0,\ \sum \alpha_p = 1, \quad 2)\ \sum \alpha_p \varepsilon_p = E, \quad 3)\ \sum \alpha_p \varkappa_p = k.$$

Observe first of all that the function $S(\alpha_1, \dots, \alpha_n)$ is strictly concave [5)] and bounded and therefore it attains its maximum on $M_{E,k}$. Let us show that the maximum is attained inside $M_{E,k}$ and not on the boundary. Let M be a simplex singled out by the conditions $\alpha_p \geq 0$, $\sum \alpha_p = 1$. The set $M_{E,k}$ is the intersection of M with the hyperplanes L_E: $\sum \varepsilon_p \alpha_p = E$ and L_k: $\sum \alpha_p \varkappa_p = k$.

In the space of variables $\alpha_1, \dots, \alpha_n$ introduce the inner product $(\alpha, \beta) = \sum \alpha_p \beta_p$ and let P be the operator of orthogonal projection onto the subspace $\sum \varepsilon_p \alpha_p = 0$, $\sum \varkappa_p \alpha_p = 0$. The function $S = -\alpha_p \ln \alpha_p$ is naturally defined on M. Denote temporarily the restriction of S to $M_{E,k}$ by $S_{E,k}$.

In order to see that the maximum of $S_{E,k}$ is attained inside $M_{E,K}$ it suffices to verify that the gradient of $S_{E,k}$ at any point of the boundary of $M_{E,k}$ is directed inside $M_{E,k}$.

Observe that $\operatorname{grad} S_{E,k} = P \operatorname{grad} S$. Consider $\operatorname{grad} S$ at a point close to a boundary $\alpha_1 = 0$:

$$\operatorname{grad} S = -\ln \alpha_1 \Big(1 + \frac{1}{\ln \alpha_1}, \frac{\ln \alpha_2 + 1}{\ln \alpha_1}, \dots, \frac{\ln \alpha_n + 1}{\ln \alpha_1}\Big). \tag{24.11}$$

Expression (24.11) implies that $\dfrac{\operatorname{grad} S}{-\ln \alpha_1} \to (1, 0, \dots, 0)$ as $\alpha_1 \to 0$ and $\alpha_p > 0$ for $p > 1$. Since $-\ln \alpha_1 > 0$ we see that $\lim\limits_{\alpha_1 \to 0} \dfrac{\operatorname{grad} S}{-\ln \alpha_1}$ is orthogonal to the boundary $\alpha_1 = 0$ and directed inside the simplex M. Hence the vector

$$\lim \alpha_1 \to 0 \frac{P \operatorname{grad} S}{-\ln \alpha_1} = \lim \alpha_1 \to 0 \frac{\operatorname{grad} S_{E,k}}{-\ln \alpha_1}$$

[5)] Strict concavity of this function follows from the fact that the matrix of second partial derivatives is negatively definite

$$\frac{\partial^2 S}{\partial \alpha_i \partial \alpha_p} = -\frac{1}{\alpha_i} \delta_{ip}.$$

is also directed inside M and therefore inside of $M_{E,k}$. Therefore $S_{E,k}$ cannot attain the maximum on the boundary of $M_{E,k}$. Further, the strict concavity implies that the maximum of $S_{E,k}$ is the only extremum of $S_{E,k}$ inside $M_{E,k}$. To find it we use the method of Lagrange multipliers. Set

$$F = S - \beta \sum \alpha_p \varepsilon_p - \gamma \alpha_p \varkappa_p - \delta \sum \alpha_p,$$

then

$$\frac{\partial F}{\partial \alpha_p} = -\ln \alpha_p - \beta \varepsilon_p - \gamma \varkappa_p - \delta - 1.$$

The equation $\dfrac{\partial F}{\partial \alpha_p} =$ yields $\alpha_p = Ce^{-\beta\varepsilon_p - \gamma\varkappa_p}$, $C = e^{-\delta-1}$. Excluding C from the relation $\sum \alpha_k = 1$ and setting $\beta\mu = \gamma$ we see that $A = A_G = \dfrac{e^{-\beta(H+\mu K)}}{\operatorname{sp} e^{-\beta(H+\mu K)}}$. We find β and μ from equation (24.7). The uniqueness of solution of these equations follows from the fact that S possesses an only extremum inside M_{EkK}. □

Chapter 4

QUANTUM GASES

§ 25. The Method of Second Quantization

25.1. Creation and annihilation operators. Let $\mathcal{L}$ and $\mathcal{H}$ be Hilbert spaces and $\mathcal{L}$ possess an *involution*, i.e., a map $f \to f^*$ for any $f \in \mathcal{L}$ with the following properties 1) $(f^*)^* = f$, 2) $(f_1 + f_2)^* = f_1^* + f_2^*$, 3) $(\lambda f)^* = \overline{\lambda} f^*$, 4) $(f_1^*, f_2^*) = (f_2, f_1)$. *The creation* and *annihilation* operators are linear functions on $\mathcal{L}$ whose values are the operators $a^*(f)$ and $a(f)$ in $\mathcal{H}$. We assume that

1) there exists a dense in $\mathcal{H}$ set D, on which the operators $a(f)$ and $a^*(f)$ are defined for all $f \in \mathcal{L}$ and which is invariant with respect to these operators,

2) the operator $a^*(f^*)$ is the Hermitian conjugate of $a(f)$ on D i.e.,

$$(a(f)\Phi, \Psi) = (\Phi, a^*(f^*)\Psi) \quad \text{for any } \Phi, \Psi \in D,$$

3) the closure of the operator $n(f) = a^*(f^*)a(f)$ defined on D is self-adjoint for any $f \in D$,

4) The operators $a(f), a^*(f)$ satisfy one of the following two systems of relations: either

$$\begin{cases} [a(f), a(g)] = [a^*(f), a^*(g)] = 0, \\ [a(f), a^*(g)] = (f, g^*) \end{cases} \tag{25.1 b}$$

or

$$\begin{cases} \{a(f), a(g)\} = \{a^*(f), a^*(g)\} = 0, \\ \{a(f), a^*(g)\} = (f, g^*), \end{cases} \tag{25.1 f}$$

where $[A, B] = AB - BA$ is *the commutator* and $\{A, B\} = AB + BA$ is the *anti-commutator*.

The operator $a^*(f)$ is said to be *the creation operator* and $a(f)$ *the annihilation operator*. The relation (1 b) corresponds to Bose particles and (1 f) to Fermi particles. This construction is called *the second quantization* [1)].

[1)] On the origin of the term see Sec. 4 in what follows.

The system of operators $a(f)$ and $a^*(f)$ with the properties 1) – 3) (25.1) and satisfying relations (1b) or (1f) is called *the representation* of Bose or respectively Fermi *commutation relations*.

Remark. In the Fermi case the operators $a(f)$ and $a^*(f)$ are bounded. Indeed, let $\|f\| = 1$. Then (1f) implies that

$$(n(f))^2 = a^*(f^*)a(f)a^*(f^*)a(f) = \\ = a^*(f^*)((f,f) - a^*(f^*)a(f))a(f) = a^*(f^*)a(f) = n(f).$$

We used the fact that (1f) implies in particular that $[a(f)]^2 = 0$. Since the closure of $n(f)$ is self-adjoint the equation $n^2(f) = n(f)$ implies that $n(f)$ is a projection operator and therefore $\|n(f)\| = 1$ and hence $\|a(f)\| = 1$. Therefore in the Fermi case for the set D we can take the whole space $\mathcal{H}$. We do not do this only in order to proceed uniformly in the Bose and Fermi cases as long as possible. In the Bose case the operators $a(f)$ are not bounded and therefore D is much more narrow than the whole space $\mathcal{H}$.

If $\mathcal{L}$ is realized as the space of square integrable functions on a set M with measure $\mathcal{L} = L^2(M)$ then it is natural to express $a(f)$ and $a^*(f)$ in the form

$$a(f) = \int f(\xi)a(\xi)\,d\xi,$$
$$a^*(f) = \int f(\xi)a^*(\xi)\,d\xi.$$

The symbols $a(\xi)$ and $a^*(\xi)$ determined by these formulas are said to be *operator generalized functions*. If the measure is discrete then for a fixed ξ_0, the functions $a(\xi_0)$, $a^*(\xi_0)$ are annihilation and creation operators respectively corresponding to the function

$$\delta_{\xi_0}(\xi) = \begin{cases} \dfrac{1}{\mu(\xi_0)} & \text{as} \quad \xi = \xi_0, \\ 0 & \text{as} \quad \xi \neq \xi_0. \end{cases}$$

In the general case $a(\xi_0)$ and $a^*(\xi_0)$ cannot be interpreted as operators. Relation (1) for $a(\xi)$, $a^*(\xi)$ imply that

$$\begin{cases} [a(\xi), a(\eta)] = [a^*(\xi), a^*(\eta)] = 0, \\ [a(\xi), a^*(\eta)] = \delta(\xi, \eta). \end{cases} \tag{25.2 b}$$

Similarly in the Fermi case we have

$$\begin{cases} \{a(\xi), a(\eta)\} = \{a^*(\xi), a^*(\eta)\} = 0, \\ \{a(\xi), a^*(\eta)\} = \delta(\xi, \eta), \end{cases} \tag{25.2 f}$$

where $\delta(\xi, \eta)$ is the δ-function on M that is

$$\int f(\xi)\delta(\xi, \eta)\, d\xi = f(\eta).$$

The dimension of the space $\mathcal{L}$ or which is the same number of points in the set M is called *the number of degrees of freedom* of the system.

If the number of degrees of freedom is finite there exists a unique up to unitary equivalence irreducible [2)] representation of Bose and Fermi commutation relations. If the number of degrees of freedom is infinite this is not so. In physics the most important is one the so-called *Fock representation.*

For the completeness sake let us give the definition of *a unitary equivalence of representations* of the commutation relations. Two representations $\{\mathcal{L}_1, \mathcal{H}_1, a_1(f), a_1^*(f)\}$ and $\{\mathcal{L}_2, \mathcal{H}_2, a_2(f), a_2^*(f)\}$ are said to *be equivalent*, if there exist unitary isomorphisms $u\colon \mathcal{L}_1 \to \mathcal{L}_2$ and $v\colon \mathcal{H}_1 \to \mathcal{H}_2$ such that

$$a_2(uf) = va_1(f)v^{-1}, \quad a_2^*(u, f) = va_1^*(f)v^{-1}.$$

25.2. The Fock representation. This is the name of the representation of commutation relations possessing a vector Φ_0 entering the domain D and such that

$$a(f)\Phi_0 = 0 \quad \text{for all} \quad f \in \mathcal{L}. \tag{25.3}$$

If $a(f) = \int a(\xi)f(\xi)\, d\xi$, where $a(\xi)$ is an operator generalized function it is possible to consider relation (25.3) a corollary of the relation

$$a(\xi)\Phi_0 = 0. \tag{25.3′}$$

The vector Φ_0 is said to be *a vacuum one.* In what follows we assume that $\|\Phi_0\| = 1$.

Let us sketch the proof of existence and uniqueness (up to unitary equivalence) of the Fock representation. Consider vectors of the form

$$\Psi = \begin{cases} a^*(f_1) \dots a^*(f_k)\Phi_0, & \text{as } k > 0, \\ \Phi_0, & \text{as } k = 0. \end{cases} \tag{25.4}$$

[2)] That is, such that it has no subspace distinct from 0 and $\mathcal{H}$ and the whole space and invariant with respect to operators $a(f)$ and $a^*(f)$ in which these operators possess properties 1)—4) (25.1).

where $\Psi = \Phi_0$ for $k = 0$. The commutation relations (1b) or (1f) and (25.3) imply that the set of finite linear combinations of the vectors of the form (25.4) is invariant both with respect to $a^*(f)$ (this is obvious) and with respect to $a(f)$ [3)].

Let us temporarily denote this set by D' and its closure by $\overline{D}'$. The system of operators $a(f)$ and $a^*(f)$ possesses properties 1) and 2) (25.1). In order to check that it constitutes the representation of commutation relations it remains to check that the closure $\overline{n}(f)$ of the operator $n(f) = a^*(f)a(f)$ is self-adjoint. From the general operator theory it follows (since $n(f)$ is non-negative) that $\overline{n}(f)$ is self-adjoint if and only if the operator $1 + n(f)$ sends D' into a dense subset of $\overline{D}'$. Making use of relations (1b) or (1f) it is not difficult to check that

$$(1 + n(f))D' = D'.$$

We leave the verification of this relation as an exercise. It is a bit more difficult to establish that the representation of commutation relations in D' is irreducible. We will omit this proof as well. Thus the Fock representation exists and $\overline{D}' = \mathcal{H}$.

Denote by $\mathcal{H}_n$ the subspace of $\mathcal{H}$ generated by linear combinations of the vectors of the form (25.4) for a fixed $n \geq 0$, where $\mathcal{H}_0 = \{C\Phi_0\|$.

Let us realize the space $\mathcal{L}$ as $L_2(M)$ in such a way that the involution becomes the complex conjugation. Any finite linear combination of vectors (25.4) for a fixed n is of the form

$$\Psi = \int K(\xi_1, \ldots, \xi_n) a^*(\xi_1) \ldots a^*(\xi_n)\, d^n\xi \Phi_0, \tag{25.5}$$

[3)] In the Bose case we have

$$\begin{aligned} a(f)\Psi &= ([a(f), a^*(f_1)] + a^*(f_1)a(f))a^*(f_2)\ldots a^*(f_k)\Phi_0 = \\ &= ([a(f), a^*(f_1)]a^*(f_2)\ldots a^*(f_k) + a^*(f_1)[a(f), a(f_2)]a^*(f_3)\ldots a^*(f_k) + \ldots \\ &\quad \ldots + a^*(f_1)\ldots a^*(f_{k-1})[a(f), a^*(f_k)] + a^*(f_1)\ldots a^*(f_k)a(f))\Phi_0 = \\ &= ((f, f_1^*)a^*(f_2)\ldots a^*(f_k) + \ldots + (f, f_k^*)a^*(f_1)\ldots a^*(f_{k-1}))\Phi_0. \end{aligned}$$

In the Fermi case we similarly have

$$\begin{aligned} a(f)\Psi &= a(f)a^*(f_1)\ldots a^*(f_k)\Phi_0 = (\{a(f), a^*(f_1)\| - a^*(f_1)a(f))a^*(f_2)\ldots a^*(f_k)\Phi_0 = \\ &= (\{a(f), a^*(f_1)\}a^*(f_2)\ldots a^*(f_k) - a^*(f_1)\{a(f), a^*(f_2)\}a^*(f_3)\ldots a^*(f_k) + \ldots \\ &\quad \ldots + (-1)^{k-1}a^*(f_1)\ldots a^*(f_{k-1})\{a(f), a^*(f_k)\} + (-1)^k a^*(f_1)\ldots a^*(f_k)a(1))\Phi_0 = \\ &= ((f, f_1^*)a^*(f_2)\ldots a^*(f_k) - \ldots + (-1)^{k-1}(f, f_k^*)a^*(f_1)\ldots a^*(f_{k-1}))\Phi_0. \end{aligned}$$

where $K(\xi_1, \dots, \xi_n)$ is a finite linear combination of functions of the form $f_1(\xi_1) \dots f_n(\xi_n)$. Since for distinct ξ_i the operators $a^*(\xi_i)$ commute in the Bose case and anticommute in the Fermi case the function $K(\xi_1, \dots, \xi_n)$ can be symmetrized in the Bose case and anti-symmetrized in the Fermi case without changing Ψ. Hereafter we will always assume the function $K(\xi_1, \dots, \xi_n)$ in expressions of type (25.5) symmetric with respect to all arguments in the Bose case and skew-symmetric in the Fermi case.

The commutation relations show that [4)]

$$\|\Psi\|^2 = n! \int |K(\xi_1, \dots, \xi_n)|^2 \, d^n\xi \tag{25.6}$$

and for distinct n the vectors of the form (25.5) are orthogonal to each

[4)] Consider, for definiteness sake, the Bose case. Let Ψ_n and $\Psi_{n'}$ be vectors of the form (25.5) and $n > n'$. Then

$$(\Psi_n, \Psi_{n'}) =$$
$$= \Big(\int K_n(\xi_1, \dots, \xi_n) a^*(\xi_1) \dots a^*(\xi_n) \, d^n\xi \Phi_0, \int K'_{n'}(\eta_1, \dots, \eta_{n'}) a^*(\eta_1) \dots a^*(\eta_{n'}) \, d^{n'}\eta \Phi_0 \Big) =$$
$$= \int K_n(\xi_1, \dots, \xi_n) \overline{K}'_{n'}(\eta_1, \dots, \eta_{n'}) (\Phi_0, a(\xi_n) \dots a(\xi_1) a^*(\eta_1) \dots a^*(\eta_{n'}) \Phi_0) \, d^n\xi \, d^{n'}\eta.$$

We use the identity

$$a(\xi_1) a^*(\eta_1) \dots a^*(\eta_{n'}) = ([a(\xi_1), a^*(\eta_1)] + a^*(\eta_1) a(\xi_1)) a^*(\eta_2) \dots a^*(\eta_{n'}) =$$
$$= [a(\xi_1), a^*(\eta_1)] a^*(\eta_2) \dots a^*(\eta_{n'}) + a^*(\eta_1) [a(\xi_1), a^*(\eta_2)] a^*(\eta_3) \dots a^*(\eta_{n'}) + \dots$$
$$\dots + a^*(\eta_1) \dots a^*(\eta_{n'-1}) [a(\xi_1), a^*(\eta_{n'})] + a^*(\eta_1) \dots a^*(\eta_{n'}) a(\xi_1).$$

The latter summand annihilates Φ_0. In the remaining summands we use the relations $[a(\xi_1), a^*(\eta_i)] = \delta(\xi_1, \eta_i)$. From symmetry of $K'_{n'}$ we deduce that

$$(\Psi_n, \Psi'_{n'}) = n' \int K_n(\xi_1, \xi_2, \dots, \xi_n) \overline{K}'(\xi_1, \eta_2, \dots, \eta_{n'}) \, d\xi \times$$
$$\times (\Phi_0, a(\xi_n) \dots a(\xi_2) a^*(\eta_2) \dots a^*(\eta_{n'}) \Phi_0) \, d^n\xi \, d^{n'-1}\eta.$$

Continue this process further, we get

$$(\Psi_n, \Psi'_{n'}) = n'! \int K_n(\xi_1, \dots, \xi_{n'}, \xi_{n'+1}, \dots, \xi_n) K'_{n'}(\xi_1, \dots, \xi_{n'}) \, d^n\xi' \times$$
$$\times (\Phi_0, a(\xi_n) \dots a(\xi_{n'+1}) \Phi_0) \, d^{n-n'}\xi = 0.$$

If $n = n'$, then

$$(\Psi_n, \Psi'_n) = n! \int K_n(\xi_1, \dots, \xi_n) \overline{K}'_n(\xi_1, \dots, \xi_n) \, d^n\xi (\Phi_0, \Phi_0) =$$
$$= n! \int K_n(\xi_1, \dots, \xi_n) \overline{K}'_n(\xi_1, \dots, \xi_n) \, d^n\xi.$$

The Fermi case is similar.

other. Therefore the space $\mathcal{H}_n$ is naturally isomorphic to the space of square integrable functions of n variables symmetric in the Bose case and antisymmetric in the Fermi case.

We retain the expression (25.5) for an arbitrary element of $\mathcal{H}_n$. Since by the above the union of the spaces $\mathcal{H}_n$ is dense in $\mathcal{H}$ it follows that $\mathcal{H}$ is the direct sum of the spaces $\bigoplus_{n=0}^{\infty} \mathcal{H}_n$. An arbitrary element $\mathcal{H}$ can be represented as

$$\Phi = \sum \frac{1}{\sqrt{n!}} \int K_n(\xi_1, \ldots, \xi_n) a^*(\xi_1) \ldots a^*(\xi_n)\, d^n\xi \Phi_0. \qquad (25.6')$$

where

$$(\Phi, \Phi) = \sum \int |K(\xi_1, \ldots, \xi_n)|^2\, d^n\xi.$$

This construction immediately implies the uniqueness of the Fock representation in the following sense: if the spaces $\mathcal{L}_1$ and $\mathcal{L}_2$ are isomorphic then the corresponding Fock representations (both Fermi and Bose ones) are equivalent. In particular, for an infinite number of degrees of freedom the Fock representation is unique.

Proof is left to the reader as an exercise.

In conclusion of this section we introduce an important definition.

A vector Φ is called *finite* if the sum (25.6′) consists of a finite number of summands.

25.3. A physical interpretation of the Fock representation. The space $\mathcal{L}$ and the naturally isomorphic to it space $\mathcal{H}_1$ are the space of states of one particle. The set M is said to be the *set of quantum numbers of the particle*. The space $\mathcal{H}_n$ is the space of the states of the system in which the system has precisely n particles. In particular, $\mathcal{H}_0$ corresponds to the case when the system has no particles. All the particles are always considered to be indistinguishable. An arbitrary vector $\mathcal{H}$ describes the state of the system in which the number of particles is not fixed.

The distinction between the Bose and Fermi commutation relations corresponds to the difference between the types of particles: all the particles that quantum mechanics deals with are either Bose particles [5)] or Fermi particles [6)]. The system of identical Bose particles is described by the Bose scenario of second quantization and the system of identical Fermi particles by the Fermi version.

[5)] Examples: photon, π-meson.

[6)] Examples: electron, proton, neutron.

The operator $a^*(f)$ sends $\mathcal{H}_n$ to $\mathcal{H}_{n+1}$ it is the creation operator of the particle in state f. Similarly, the operator $a(f)$ is the annihilation operator of a particle in state f and it sends $\mathcal{H}_n$ to $\mathcal{H}_{n-1}$. The identity $(a^*(f))^2 = 0$ in the Fermi case is one of mathematically equivalent versions of formulation of the *Pauli principle*: in one state there cannot occur more than one fermion[7].

25.4. Operators. Together with the space $\mathcal{H}$ consider a wider space $\widetilde{\mathcal{H}}$ consisting of formal series of the form (6′). If $\Phi \in \widetilde{\mathcal{H}}$, then the coefficient functions in (25.6′) can be *generalized* ones, see [GSh].

We will not need to make this notion more precise. Let now interpret the operator generalized functions $a(\xi)$ and $a^*(\xi)$ as operators sending $\mathcal{H}$ to $\widetilde{\mathcal{H}}$:

$$a(\xi)\Phi = \sum \frac{1}{\sqrt{n!}} \int (\varepsilon_1 K_n(\xi, \xi_1, \dots, \xi_{n-1}) + \varepsilon_2 K_n(\xi_1, \xi, \xi_2, \dots, \xi_{n-1}) + \dots \\ \dots + \varepsilon_n K_n(\xi_1, \dots, \xi_{n-1}, \xi)) a^*(\xi_1) \dots a^*(\xi_{n-1})\, d^{n-1}\Phi_0, \quad (25.7)$$

$$a^*(\xi)\Phi = a^*(\xi) \sum \frac{1}{\sqrt{n!}} \int K_n(\xi_1, \dots, \xi_n) a^*(\xi_1) \dots a^*(\xi_n)\, d^n\xi\Phi_0 = \\ = \sum \frac{1}{\sqrt{n!}} \frac{1}{n} \int (\varepsilon_1 K_n(\xi_2, \dots, \xi_{n+1})\delta(\xi_1, \xi) + \varepsilon_2 K_n(\xi_1, \xi_3, \dots, \xi_{n+1})\delta(\xi_2, \xi) + \dots \\ \dots + \varepsilon_n K_n(\xi_1, \dots, \xi_{n-2},)\delta(\xi_{n+1}, \xi)) a^*(\xi_1) \dots a^*(\xi_{n+1})\, d^{n+1}\xi\Phi_0, \quad (25.7')$$

Expressions (25.7) and (25.7′) are obtained by formally applying (25.2 b) or (25.2 f) respectively. In the deduction of (25.7) we use the fact that

[7] An equivalent formulation: The functions K_n in (25.6) are skew-symmetric.

$a(\xi)\Phi = 0$ [8] where

$$\varepsilon_k = \begin{cases} 1 & \text{in the Bose case,} \\ (-1)^{k-1} & \text{in the Fermi case.} \end{cases}$$

Consider a function $A_{mn}(\xi_1, \dots, \xi_m \mid \eta_1, \dots, \eta_n)$ perhaps a generalized one, which we consider as the kernel of a densely determined operator sending a dense subset $D \subset \mathcal{H}_n$ to $\mathcal{H}_m$ by the formula

$$f(\xi_1, \dots, \xi_n) \mapsto \int A_{mn}(\xi_1, \dots, \xi_m \mid \eta_1, \dots, \eta_n) f(\eta_1, \dots, \eta_n) d n\eta.$$

We assume that A_{mn} is symmetric with respect to each group of variables in the Bose case and skew-symmetric in the Fermi case. To the function $A_{mn}(\xi_1, \dots, \xi_m \mid \eta_1, \dots, \eta_n)$ we assign the operator A_{mn} sending $\mathcal{H}$ to $\widetilde{\mathcal{H}}$ by the formula

$$A_{mn} = \int A_{mn}(\xi_1, \dots, \xi_m \mid \eta_1, \dots, \eta_n) \times \\ \times a^*(\xi_1) \dots a^*(\xi_m) a^*(\eta_1) \dots a^*(\eta_n)\, d^m\xi\, d^n\eta, \quad (25.8)$$

where $a(\xi)$ and $a^*(\xi)$ are defined by formulas (25.7) and (25.7′). The set of the elements of $\mathcal{H}$ that A_{mn} does not send outside $\mathcal{H}$ will be referred to as *the domain of definition* $D_{A_{mn}}$ of A_{mn}. The assumptions on the nature of the function $A_{mn}(\xi_1, \dots, \xi_m \mid \eta_1, \dots, \eta_n)$ imply that $D_{A_{mn}}$ is dense in $\mathcal{H}$.

Now consider an operator of a more general form $A = \sum A_{mn}$ that is

$$A = \sum \int A_{mn}(\xi_1, \dots, \xi_m \mid \eta_1, \dots, \eta_n) \times \\ \times a^*(\xi_1) \dots a^*(\xi_m) a^*(\eta_1) \dots a^*(\eta_n)\, d^m\xi\, d^n\eta. \quad (25.9)$$

[8] Only (25.7) needs to be elucidated. We use the identities

$$a(\xi)a^*(\xi_1)\dots a^*(\xi_n) = ([a(\xi), a^*(\xi_1)] + a^*(\xi_1)a(\xi))a^*(\xi_2)\dots a^*(\xi_n) = \\ = [a(\xi), a^*(\xi_1)]a^*(\xi_2)\dots a^*(\xi_n) + a^*(\xi_1)[a(\xi), a^*(\xi_2)]a^*(\xi_3)\dots a^*(\xi_n) + \dots \\ \dots + a^*(\xi_1)\dots a^*(\xi_{n-1})[a(\xi), a^*(\xi_n)] + a^*(\xi_1)\dots a^*(\xi_n)a(\xi)$$

in the Bose case and

$$a(\xi)a^*(\xi_1)\dots a^*(\xi_n) = (\{a(\xi), a^*(\xi_1)\} - a^*(\xi_1)a(\xi))a^*(\xi_2)\dots a^*(\xi_n) = \\ = \{a(\xi), a^*(\xi_1)\}a^*(\xi_2)\dots a^*(\xi_n) - a^*(\xi_1)\{a(\xi), a^*(\xi_2)\}a^*(\xi_3)\dots a^*(\xi_n) + \dots \\ \dots + (-1)^{n-1}a^*(\xi_1)\dots a^*(\xi_{n-1})\{a(\xi), a^*(\xi_n)\} + (-1)^n a^*(\xi_1)\dots a^*(\xi_n)a(\xi)$$

in the Fermi case. The last summand of these identities annihilates Φ_0 and we get (25.7) from these identities after renaming the variables of integration.

It's domain of definition as an operator in $\mathcal{H}$ will be denoted by D_A. It consists of the elements of $\bigcap\limits_{m,n} D_{A_{mn}}$ on which the series (25.9) weakly converges.

The expression of the operator in the form (25.9) is called *the weak normal form*.

25.5. Examples. 1) Let $A_{01}(1\eta) = f(\eta)$ and $A_{10}(\xi 1) = g(\xi)$ the corresponding operators $A_{01} = \int f(\eta)a(\eta)\,d\eta$ and $A_{10} = \int g(\xi)a^*(\xi)\,d\xi$ considered in $\mathcal{H}$ serve as closures of the earlier considered operators $a(f)$ and $a^*(g)$.

2) Set

$$N = \int a^*(\xi_1)a(\xi)\,d\xi. \tag{25.10}$$

The definition of N immediately implies that the spaces $\mathcal{H}_n$ are eigen spaces of N with eigen value n. Therefore the operator N is said to be *the operator of the number of particles*. Or the occupation number operator. Its role in the statistical physics is distinguished.

3) Let $K(\xi \mid \eta)$ be the kernel of the operator $\widetilde{K}$ in $L_2(M)$, i.e.,

$$(\widetilde{K}f)(\xi) = \int K(\xi \mid \eta)f(\eta)\,d\eta.$$

Let us assign to it the operator in $\mathcal{H}$ given by the formula

$$K = \int K(\xi \mid \eta)a^*(\xi_1)a(\eta)\,d\xi\,d\eta. \tag{25.11}$$

It is not difficult to show that if the operator $\widetilde{K}$ is *densely defined* in $L_2(M)$ then K is densely defined in $\mathcal{H}$. The operator N is a particular case of (25.11) when $\widetilde{K}$ is the unit operator and $K(\xi \mid \eta) = \delta(\xi, \eta)$. Observe that the operator (25.11) resembles the quadratic form of the operator $\widetilde{K}$:

$$(\widetilde{K}f, f) = \int K(\xi \mid \eta)f(\xi_1)\overline{f}(\eta)\,d\xi\,d\eta. \tag{25.12}$$

The similarity of formulas (25.11) and (25.12) occasioned the creation of the term "*second quantization*": the operator $\widetilde{K}$ in $L_2(M)$ is obtained from the classically observable quantity $\varphi(p, q)$ by means of "quantization" consisting in the replacement of the commuting variables p, q (momenta and position) by the non-commuting operators of the momenta and position. In reality this operation has no precise meaning.

The operator K is similarly obtained from $\widetilde{K}$ by replacing in the quadratic form (25.12) the usual functions f, $\overline{f}$ by non-commuting operator generalized functions $a(\xi)$, $a^*(\eta)$.

4) Let $K_n(\xi_1, \dots, \xi_n)$ be a collection of square integrable functions such that $\sum \int |K_n|^2 \, d^n\xi < \infty$. Then on the set of finite vectors the following operator is defined:

$$A = \sum \frac{1}{\sqrt{n!}} \int K_n(\xi_1, \dots, \xi_n) a^*(\xi_1) \dots a^*(\xi_n) \, d^n\xi. \tag{25.13}$$

Applying operator (25.13) to the vacuum vector we obtain an arbitrary vector of $\mathcal{H}$. Thus the expression of an arbitrary vector in the form (25.6) acquires a non-formal interpretation.

5) An arbitrary bounded operator in $\mathcal{H}$ is representable in the form (25.9), where for D we can consider the set of finite vectors.

The proof of the latter statement is essentially more difficult than the proof of the preceding statements.

25.6. Splitting of the space $\mathcal{L}$ into a direct sum. Let $\mathcal{L} = \mathcal{L}_1 \oplus \mathcal{L}_2$. Let $\mathcal{H}$, $\mathcal{H}_1$ and $\mathcal{H}_2$ be the Fock spaces constructed with the help of $\mathcal{L}$, $\mathcal{L}_1$ and $\mathcal{L}_2$ respectively. The construction of the spaces $\mathcal{H}$, $\mathcal{H}_i$ implies that $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$ is the tensor product. Let the spaces $\mathcal{L}_i$ be realized as $L_2(M_i)$. Denote by K_i the operators of type (25.12), where $\xi, \eta \in M$. In this case the operator $K = K_1 + K_2$ is their tensor sum.

Observe that the creation and annihilation operators in $\mathcal{H}$ are of the form

$$a^*(f) = a^*(f_1) + a^*(f_2), \quad a(f) = a(f_1) + a(f_2), \tag{25.14}$$

where $f = f_1 + f_2$ and $f_i \in \mathcal{L}_i$. In the Bose case both sums in (25.14) are tensor ones whereas in the Fermi case this is not so as is clear from the fact that in the Fermi case the operators $a(f_1)$ and $a(f_2)$ do not commute.

§ 26. Macroscopic Subsystems

26.1. x-representation. The Gibbs distribution and the correlation functions. In the 3-dimensional space $\mathbb{R}^3$ consider the cube Ω centered at the origin with edges parallel to the axis and of length l. In Ω introduce the usual (Lebesgue) measure and with the help of $L_2(\Omega)$ construct the Fock representation of commutation relations. Let $\mathcal{H}(\Omega)$ be the space of states. Further consider the Laplace operator with some self-adjoint boundary conditions in $L_2(\Omega)$. Most often one considers the zero or period boundary conditions. In the latter case the variables x, y considered below run over

the solid torus obtained from Ω by gluing the opposite faces. Set

$$H_\Omega = -\int\limits_\Omega a^*(x)\Delta a(x)\,d^3x + \frac{1}{2}\int\limits_\Omega\int\limits_\Omega v(x-y)a^*(x)a^*(y)a(y)a(x)\,d^3x\,d^3xy. \tag{26.1}$$

Observe that H_Ω commutes with the operator

$$H_\Omega = \int a^*(x)a(x)\,d^3.$$

The subspaces $\mathcal{H}_k$ with the fixed number of particles are invariant with respect to operator (26.1). The restriction of the operator (26.1) onto $\mathcal{H}_k$ is of the form

$$H_{k,\Omega}f = -(\Delta_1 + \ldots + \Delta_k)f + \sum_{i<j} v(x_i - y_j)f, \tag{26.2}$$

where $f = f(x_1, \ldots, x_k) \in \mathcal{H}_k$. And f is symmetric with respect to its arguments in the Bose case and skew-symmetric in the Fermi case.

The system with Hamiltonian (26.1) is a quantum analogue of the real gas. This system (or systems close to it) are the main object of the study of the quantum statistical physics. The first summand in (26.1) can be interpreted as the kinetic energy of the system and the second one as the potential energy. The function $v(x-y)$ is the potential energy of the particles situated at points x and y. The function $v(x)$ is supposed to decay fast or have a compact support. The system obtained from (26.1) for $v(x) \equiv 0$ is called *the ideal gas* (Bose or Fermi one).

Let us subdivide the cube Ω by the planes parallel to its faces into n identical cubes Ω_ν. Let $\mathcal{H}(\Omega_\nu)$ be the Fock space constructed with the help of Ω_ν in the same way as $\mathcal{H}(\Omega)$ is constructed with the help of Ω. In this case $\mathcal{H}(\Omega) = \mathcal{H}(\Omega_1) \otimes \ldots \otimes \mathcal{H}(\Omega_n)$, see the end of § 25.

The operator $\mathcal{H}_\Omega$ is not the tensor sum of the operators $\mathcal{H}_{\Omega_\nu}$ for the following two reasons: first since the Laplace operator in Ω is not the direct sum of similar operators in the small cubes Ω_ν because the boundary conditions prevent this and second because of the potential of interaction. Since the potential of interaction has a finite support or rapidly decays both obstructions are occasioned only by effects that occur in the vicinity of the boundary of the cubes Ω_ν. Therefore we should expect that if Ω runs over a sequence of ever enlarging concentric cubes so that $|\Omega_\nu| \to \infty$ then

$$\mathcal{H}_\Omega \approx \overline{\mathcal{H}}_\Omega = \sum H_{\Omega_\nu} \tag{26.3}$$

and this approximate equality is the more accurate the greater $|\Omega_\nu|$. The operator of the number of particles N_Ω is precisely equal to the tensor sum of the operators N_{Ω_ν}. Let Ω_0 be the cube Ω_ν, whose center coincides with the origin. Consider an isomorphism T_ν of $L(\Omega_\nu)$ and $L(\Omega_0)$ given by the formula

$$(T_\nu f)(x) = f(x - \xi_\nu), \tag{26.4}$$

where $f(x) \in L_{\Omega_0}$ and ξ_ν is the center of the cube Ω_ν and $x \in \Omega_\nu$. The isomorphism (26.4) can be naturally extended to an isomorphism U_ν of $\mathcal{H}(\Omega_\nu)$ and $\mathcal{H}(\Omega_0)$ and this isomorphism sends the operator H_{Ω_0} to H_{Ω_ν}

$$U_\nu a(x) U_\nu^{-1} = a(x - \xi_\nu), \quad U_\nu a^*(x) U_\nu^{-1} = a^*(x - \xi_\nu).$$

Thus the systems determined by the Hamiltonian H_Ω in the space H_{Ω_ν} are copies of each other. In A_ν consider the operator $\mathcal{H}(\Omega_\nu)$ given by the formula

$$A_\nu = \int\limits_{x_i, y_i \in \Omega_\nu} A(x_1 - \xi_\nu, \dots, x_n - \xi_\nu \mid y_1 - \xi_\nu, \dots, y_n - \xi_\nu) \times \\ \times a^*(x_1) \dots a^*(x_n) a^*(y_1) \dots a^*(y_n)\, d^n x\, d^n y, \tag{26.5}$$

where the function $A(x_1, \dots, x_n \mid y_1, \dots, y_n)$ has a compact support with respect to each variable [9]. Obviously A_ν and therefore

$$A_n = \frac{1}{n} \sum A_\nu \tag{26.6}$$

is a summatory quantity. Suppose that the system with Hamiltonian (26.1) is ergodic in the sense that it has no other first integrals except the number of particles. In this case the mean with respect to time of the mean of A over the common eigen vectors f_Ω of operators H_Ω and N_Ω is equal thanks to § 22 to $(Af_\Omega, f_\Omega) = \overline{A}_{\Omega,n}$. Since as Ω_ν goes the approximate equality 26.3 becomes more and more precise for the reasons presented in § 22 we expect that

$$\overline{A}_{\Omega,n} = (Af_\Omega, f_\Omega) \approx \frac{\operatorname{sp} A\widetilde{P}}{\operatorname{sp} \widetilde{P}}, \tag{26.7}$$

where $\widetilde{P}$ is the projection operator onto the common eigen space of H_Ω and N_Ω. Now suppose that not only $|\Omega_\nu| \to \infty$ but also $n \to \infty$. In this case

[9] We only consider the operators of the form (26.5) with the same number of creations and annihilations since due to the fact that the operator H_Ω preserves the number of particles the mean (26.8) considered in what follows vanishes, obviously, for the operators of a more general type.

the microcanonic mean (26.7) of the operator (26.5) should approach to the canonic one. Thus we should expect that

$$\overline{A} = \lim_{\substack{|\Omega|\to\infty \\ n\to\infty}} \overline{A}_{\Omega,n} = \lim_{|\Omega_0|\to\infty} \frac{\operatorname{sp} A_0 e^{-\beta(H_{\Omega_0}+\mu N_{\Omega_0})}}{\operatorname{sp} e^{-\beta(H_{\Omega_0}+\mu N_{\Omega_0})}}. \tag{26.8}$$

The right-hand side of (26.8) is called *the Gibbs mean* of A_0. It is the main object of the study in statistical physics. Hereafter we omit the index 0 of the quantities entering (26.8). Observe that the mean (26.8) can be expressed as

$$\overline{A} = \int A(x_1,\dots,x_n \mid y_1,\dots,y_n)\rho_n(x_1,\dots,x_n \mid y_1,\dots,y_n)\, d^n x\, d^n y, \tag{26.9}$$

where $\rho_n = \lim\limits_{|\Omega|\to\infty} \rho_{n,\Omega}$, and

$$\rho_{n,\Omega} = \frac{\operatorname{sp}\left(a^*(x_1)\dots a^*(x_n)a(y_1)\dots a(y_n)e^{-\beta(H_\Omega+\mu N_\Omega)}\right)}{\operatorname{sp} e^{-\beta(H_\Omega+\mu N_\Omega)}}. \tag{26.10}$$

The functions ρ_n and $\rho_{n,\Omega}$ are called *the limit* and *prelimit correlation function* respectively. As in the classical statistical physics the limit correlation functions are translational invariant:

$$\rho_n(x_1+h,\dots,x_n+h \mid y_1+h,\dots,y_n+h) = \rho_n(x_1,\dots,x_n \mid y_1,\dots,y_n),$$

where $h \in \mathbb{R}^3$ is any vector from $\mathbb{R}^3$. Observe that the existence of prelimit correlation functions to say nothing about the limit ones is highly non-trivial fact. For its heuristic proof see Appendix 2. Ginibre found its rigorous proof (see Appendix 3).

Finally make a remark concerning the statistical sum

$$\Xi_\Omega = \operatorname{sp} e^{-\beta(H_\Omega+\mu N_\Omega)}.$$

An approximate equality (26.3) implies a similar equality for the statistical sums

$$\Xi_\Omega \approx \prod_i^n \Xi_{\Omega_\nu} = \left(\Xi_{\Omega_0}\right)^n.$$

This equality in turn enable us to assume that Ξ_Ω as an asymptotics as $|\Omega| \to \infty$ analogous to the classical statistical sum

$$\Xi_\Omega \approx e^{|\Omega|\Phi(\beta,\mu)}. \tag{26.11}$$

The function $\Phi(\beta, \mu)$ is called *the thermodynamic potential*. It follows from (26.10) that the mean number of the particles in the system is equal to

$$\overline{n}_\Omega = \int \rho_{1,\Omega}(x \mid x)\, dx.$$

Thanks to the translational invariance the limit function does not depend on x. Therefore the asymptotics of $\overline{n}_\Omega$ is of the form

$$\overline{n}_\Omega \approx |\Omega|\gamma,$$

where $\gamma = \lim\limits_{|\Omega|\to\infty} \dfrac{\overline{n}_\Omega}{|\Omega|}$ is the density of the particles. We easily derive from (26.10) an expression for γ in terms of the potential Φ:

$$\gamma = -\frac{1}{\beta}\frac{\partial}{\partial\mu} \ln \Phi(\beta, \mu). \tag{26.12}$$

Similar arguments show that the asymptotics of the mean energy of the system

$$E_\Omega = \frac{\operatorname{sp} H_\Omega e^{-\beta(H_\Omega + \mu N_\Omega)}}{\operatorname{sp} e^{-\beta(H_\Omega + \mu N_\Omega)}}$$

is

$$E_\Omega \approx |\Omega|\varepsilon,$$

where ε — the mean energy of one particle — is related with the potential Φ by the formula

$$\varepsilon + \mu\gamma = -\frac{\partial}{\partial\mu} \ln \Phi(\beta, \mu). \tag{26.13}$$

Formulas (26.12) and (26.13) coincide with analogous formulas for the grand canonical ensemble. In Appendix 2 we give a heuristic proof of formula (26.11) for periodic boundary conditions. A rigorous proof was first obtained by Ruelle fir the zero boundary conditions and later I. Novikov generalized this result to a wide class of boundary conditions period included and proved the independence of thermodynamical potential of these conditions.

The ensemble considered is analogous to the grand canonical ensemble. Together with it, the researchers sometimes consider a small quantum ensemble similar to the small classical ensemble. The number of particles is being fixed and the Hamiltonian of the system is given by formula (26.2). The thermodynamic limit means that $n \to \infty$ and $|\Omega| \to \infty$, so that $\dfrac{n}{|\Omega|} \to \gamma$,

where γ is the density of the particles in the system. The statistical sum of this ensemble is equal to $z_n = \operatorname{sp} e^{-\beta H_{\Omega,n}}$ and its asymptotics is

$$z_n \approx e^{nF(\rho,\beta)} \quad \text{as} \quad \frac{n}{|\Omega|} \to \gamma.$$

The thermodynamic potentials Φ and F are related in the same way as the analogous functions are related in the classical statistical physics (see § 17).

26.2. *p*-representation. In $L_2(\Omega)$ consider an orthonormal basis consisting of the functions

$$e_p(x) = \frac{1}{\sqrt{|\Omega|}} e^{\frac{2\pi i}{l}(k_1x_1+k_2x_2+k_3x_3)}, \quad \text{where } p = \frac{2\pi}{l}(k_1,k_2,k_3), \tag{26.14}$$

where $k_i \in \mathbb{Z}$. Let p be the lattice over which runs the vector Γ_Ω. We pass from the operator generalized functions $a(x)$ and $a^*(x)$ to their Fourier transforms

$$\begin{aligned} b(p) &= a(e_p) = \frac{1}{\sqrt{|\Omega|}} \int\limits_{|\Omega|} a(x) e^{i(p,x)}\, d^3x, \\ (p,x) &= p_1x_1 + p_2x_2 + p_3x_3, \\ b^*(p) &= a^*(\overline{e}_p) = \frac{1}{\sqrt{|\Omega|}} \int\limits_{|\Omega|} a^*(x) e^{-i(p,x)}\, d^3x. \end{aligned} \tag{26.15}$$

Formulas (26.15) can be generalized:

$$a(x) = \frac{1}{\sqrt{|\Omega|}} \sum_{\Gamma_\Omega} b(p) e^{-i(p,x)}, \quad a^*(x) = \frac{1}{\sqrt{|\Omega|}} \sum_{\Gamma_\Omega} b^*(p) e^{i(p,x)}. \tag{26.16}$$

We will consider the operator (26.1) with periodic boundary conditions. In this case let x, y run over the solid torus obtained from Ω by gluing the opposite faces, $e^{i(p,x)}$ the eigen function of Δ with eigen value $-p^2 = -(p_1^2 + p_2^2 + p_3^2)$. Therefore

$$\Delta a(x) = \frac{1}{\sqrt{|\Omega|}} \sum_{\Gamma_\Omega} p^2 b(p) e^{-i(p,x)}.$$

Using orthogonality of the functions (26.14) we find that

$$-\int\limits_{\Omega} a^*(x) \Delta a(x)\, d^3x = \sum_{\Gamma_\Omega} p^2 b^*(p) b(p). \tag{26.17}$$

Substituting (26.16) in the right-hand side of (26.1) we get

$$\int v(x-y)a^*(x)a^*(y)a(x)a(y)\,dx\,dy = \\ = \frac{1}{|\Omega|^2}\sum W_\Omega(p_1,p_2\mid q_1,q_2)b^*(p_1)b^*(p_2)b(q_1)b(q_2), \quad (26.18)$$

where

$$W_\Omega(p_1,p_2\mid q_1,q_2) = \widetilde{V}_\Omega(p_1-q_1)\delta_\Omega(p_1+p_2-q_1-q_2),$$
$$\widetilde{V}_\Omega(p) = \int\limits_\Omega V(x)e^{i(x,p)}\,d^3x, \quad \delta_\Omega(p) = \begin{cases} |\Omega| & \text{as} \quad p=0, \\ 0 & \text{as} \quad p\neq 0. \end{cases} \quad (26.19)$$

Thus in p-representation the operator (26.1) with periodic boundary conditions is of the form

$$H_\Omega = \sum_{p\in\Gamma_\Omega} p^2 b^*(p)b(p) + \\ + \frac{1}{|\Omega|^2}\sum_{p_i,q_i\in\Gamma_\Omega} W_\Omega(p_1,p_2\mid q_1,q_2)b^*(p_1)b^*(p_2)b(q_1)b(q_2). \quad (26.20)$$

26.3. Generalizations. There exist interesting for physics systems whose Hamiltonians H_Ω are of the form distinct from (26.1). In particular, the operator of kinetic energy can be given not with the help of the Laplace operator but somehow differently and the number of particles might vary. The main requirements that the Hamiltonians H_Ω should satisfy are:

1) The transformation (26.4) should generate unitary equivalence of the spaces H_{Ω_ν} in the same way as this were for the operators (26.1) and (26.2);

2) The coefficient functions in the normal series for H_Ω in the x-representation should rapidly decay. Under all these conditions the arguments leading to the Gibbs distribution developed in Sec. 1 still hold. The individual summand in the normal series of H_Ω is of the form

$$\int\limits_{x_i,y_i\in\Omega} v_{m,n}(x_1,\dots,x_m\mid y_1,\dots,y_n)\times \\ \times a^*(x_1)\dots a^*(x_m)a(y_1)\dots a(y_n)\,d^mx\,d^ny. \quad (26.21)$$

The requirements formulated above essentially mean that $v_{m,n}$ rapidly decays with respect to all arguments and

$$v_{m,n}(x_1+h,\dots,x_m+h\mid y_1+h,\dots,y_n+h) = \\ = v_{m,n}(x_1,\dots,x_m\mid y_1,\dots,y_n) \ \text{ for any } \ h\in\mathbb{R}^3. \quad (26.22)$$

In p-representation, the Hamiltonian H_Ω is of the form

$$H_\Omega = \sum \omega(p) b^*(p) b(p) + \\ + \sum_{m,n} \frac{1}{|\Omega|^{\frac{m+n}{2}}} \sum_{p,q \in \Gamma_\Omega} W_{m,n,\Omega}(p_1, \dots, p_m \mid q_1, \dots, q_n) \times \\ \times b^*(p_1) \dots b^*(p_m) b(q_1) \dots b(q_n), \quad (26.23)$$

where

$$W_{m,n,\Omega} = v_{m,n}(p_1, \dots, p_m \mid q_1, \dots, q_n) \delta_\Omega(p_1 + \dots + p_m - q_1 - \dots - q_n),$$

and $\widetilde{V}_{m,n}$ is a smooth function and $\delta_\Omega(p)$ is the same function as in (26.19). The factor δ_Ω is a specific feature of the function $W_{m,n,\Omega}$, which is occasioned by the translational invariance (26.22) of the functions $v_{m,n}$.

Euristic arguments developed in Appendix 2 enable us to establish for the Hamiltonians of the type (26.23) the existence of the correlation functions and thermodynamical potential.

There are no rigorous theorems here in any case where the operator (26.23) differs from (26.20) even if the second summand in (26.23) coincides with the second summand in (26.20) and $\omega(p)$ differs from p^2 however small.

26.4. Statistical physics on a lattice. Let x run an integer lattice Γ in the s-dimensional space. In the Fermi case we consider the Hamiltonian analogous to (26.1) but without the first summand

$$H_\Omega = \sum_{x,y \in \Gamma} v(x-y) a^*(x) a^*(y) a(x) a(y). \quad (26.24)$$

We shall additionally assume that $v(0) = 0$. In this case the statistical sum $\Xi_\Omega = \operatorname{sp} e^{-\beta(H_\Omega + \mu N_\Omega)}$ can easily transformed to the form

$$\Xi_\Omega = \sum_{n=0}^{\infty} \frac{\zeta^n}{n!} \sum_{x_i \in \Gamma \cap \Omega} e^{-\beta \sum\limits_{i<j} v(x_i - x_j)}, \quad \zeta = e^{-\beta\mu}. \quad (26.25)$$

The difference of the expression (26.25) from the corresponding classical one is in the replacement of the integral over $x_1, \dots, x_n$ by the sum over $x_i \in \Gamma \cap \Omega$. In case where $v(x) = 0$ for $|x| > 1$ that is only if the nearest neighbors interact the ensemble of the systems with Hamiltonians (26.24) is called *the Ising model*, see. [Ba].

The lattice systems are studied relatively well. In particular, for them the existence of phase transitions for the selected value μ_0 of the chemical potential is proved. For the flat Ising model ($s = 2$) for the same value of the chemical potential the thermodynamical potential is explicitly computed by Onzager (see Appendix 2)

§ 27. The ideal Bose gas

27.1. The statistical sum. In the p-representation, the Hamiltonian of the ideal Bose gas is of the form

$$H_\Omega = \sum_{p\in\Gamma_\Omega} \omega(p) b^*(p) b(p). \tag{27.1}$$

The Focks base $\mathcal{H}$ is naturally represented as the tensor product of the spaces $\mathcal{H}_p$ describing a Bose system with one degree of freedom (system of particles with a fixed value of momenta p).

The expression (27.1) shows that H_Ω is the tensor sum of the operators $H_{\Omega,p} = \omega(p) b^*(p) b(p)$ acting in $\mathcal{H}_p$. The operator of the number of particles is obtained from (27.1) for $\omega(p) \equiv 1$. It is the tensor sum of the operators $n(p) = b^*(p) b(p)$ is interpreted as the operator of the number of particles with momentum p. Therefore the operator $e^{-\beta(H_\Omega + \mu N_\Omega)}$ is the tensor product of the operators $e^{-\beta(H_{\Omega,p} + \mu n(p))}$ and the statistical sum is the product of the traces of these operators

$$\Xi_\Omega = \operatorname{sp} e^{-\beta(H_\Omega + \mu N_\Omega)} = \prod_{p\in\Gamma_\Omega} \operatorname{sp} e^{-\beta(H_{\Omega,p} + \mu n(p))}. \tag{27.2}$$

The vectors $\frac{1}{\sqrt{n!}}(b^*(p))^n \Phi_0$ constitute an orthonormal basis in $\mathcal{H}_p$. These vectors are eigen vectors for $H_{\Omega,p}$ and $n(p)$ with eigen values $n\omega(p)$ and n respectively. Therefore

$$\operatorname{sp} e^{-\beta(H_{\Omega,p} + \mu n(p))} = \sum e^{-n(\beta\omega(p) + \mu)} = \frac{1}{1 - e^{-\beta(\omega(p)+\mu)}}, \tag{27.3}$$

$$\Xi_\Omega = \prod_{p\in\Gamma_\Omega} \frac{1}{1 - e^{-\beta(\omega(p)+\mu)}}.$$

Suppose $\omega(p) \geq 0$ and let $\omega(p)$ go sufficiently fast so that the infinite product in (27.3) converges.

The mean number of particles with momentum p is equal to

$$\begin{aligned} \overline{n}(p) &= \frac{\operatorname{sp} n(p) e^{-\beta(H_\Omega + \mu N_\Omega)}}{\operatorname{sp} e^{-\beta(H_\Omega + \mu N_\Omega)}} = \frac{\operatorname{sp} n(p) e^{-\beta(H_{\Omega,p} + \mu n(p))}}{\operatorname{sp} e^{-\beta(H_{\Omega,p} + \mu n(p))}} = \\ &= -\frac{1}{\beta}\frac{\partial}{\partial\mu} \ln \frac{1}{1 - e^{-\beta(\omega(p)+\mu)}} = \frac{e^{-\beta(\omega(p)+\mu)}}{1 - e^{-\beta(\omega(p)+\mu)}} = \frac{1}{e^{\beta(\omega(p)+\mu)} - 1}. \end{aligned} \tag{27.4}$$

We determine β and μ from the equations

$$\sum \omega(p)\overline{n}(p) = N\varepsilon, \quad \sum \overline{n}(p) = N, \tag{27.5}$$

where $N = \gamma|\Omega|$ is the number of particles in the system.

It is natural to rewrite equations (27.5) in the form

$$\frac{1}{|\Omega|}\sum \frac{\omega(p)}{e^{\beta(\omega(p)+\mu)}-1} = \varepsilon\gamma, \tag{27.6}$$

$$\frac{1}{|\Omega|}\sum \frac{1}{e^{\beta(\omega(p)+\mu)}-1} = \gamma. \tag{27.7}$$

Observe that only non-zero values of the chemical potential have a physical meaning: it follows from (27.4) that for $\mu < 0$ there exist γ and β such that $\overline{n}(p) < 0$ which contradicts to the physical meaning of the number $\overline{n}(p)$.

Let $\omega(0) = 0$. In this case equation (27.7) is solvable for μ for any β and γ. The left-hand side of (27.7) monotonically decays with respect to μ and its limit as $\mu \to \infty$ is equal to 0 and to ∞ as $\mu \to 0$ since it contains the summand $\dfrac{1}{e^{\beta\mu}-1}$ (for $p = 0$) [10].

The volume of the unit parallelepiped in the lattice L_Ω is equal to $\dfrac{(2\pi)^3}{|\Omega|}$. Therefore the left-hand sides of equations (27.6) and (27.7) are integral sides. In the limit as $|\Omega| \to \infty$ these equations take the form

$$\frac{1}{(2\pi)^3}\int \frac{\omega(p)}{e^{\beta(\omega(p)+\mu)}-1}\,d^3p = \varepsilon\gamma, \tag{27.8}$$

$$\frac{1}{(2\pi)^3}\int \frac{d^3p}{e^{\beta(\omega(p)+\mu)}-1} = \gamma. \tag{27.9}$$

It can happen that equation (27.9) for fixed β and γ has no solution for positive μ. For example if $\omega(p) = p^2$ then the left-hand side of (27.8) attains the maximal value γ_0 for $\mu = 0$:

$$\gamma_0 = \gamma_0(\beta) = \frac{1}{(2\pi)^3}\int \frac{d^3p}{e^{\beta p^2}-1}. \tag{27.10}$$

The right-hand side of (27.10) is obviously finite and therefore for $\gamma > \gamma_0$ and $\omega(p) = p^2$ equation (27.9) is impossible to resolve for μ. The difference

[10] It is not difficult to prove that if $\omega(0) = 0$ and $\omega(p) \to \infty$ as $|p| \to \infty$ sufficiently rapidly (for example, for $\omega(p) = p^2$), then both equations (27.6) and (27.7) are solvable for any positive right-hand sides). We will not however, dwell on this. For the proof, one should apply the arguments developed in § 24 in the proof of the maximum principle for the entropy.

in the properties of equations (27.7) and (27.9) is related with the fact that for $\gamma > \gamma_0(\beta)$ the solution of equation (27.7) is of the form $\mu = \mu(\Omega)$, where $\mu(\Omega) \to 0$ as $|\Omega| \to \infty$. Therefore for $\gamma > \gamma_0$ the passage from the sum to the integral is not automatic.

For $\gamma > \gamma_0(\beta)$ the phase transition arises called the *Bose—Einstein condensation.*

27.2. Bose—Einstein condensation. Denote the left-hand side of (27.7) by $s(\Omega, \mu)$. Fix $\varepsilon > 0$ and present $s(\Omega, \mu)$ as the sum of two summands

$$s(\Omega, \mu) = s'_\varepsilon(\Omega, \mu) + s''_\varepsilon(\Omega, \mu),$$

where

$$s'_\varepsilon(\Omega, \mu) = \frac{1}{|\Omega|} \sum_{|p|<\varepsilon} \frac{1}{e^{\beta(p^2+\mu)} - 1},$$
$$s''_\varepsilon(\Omega, \mu) = \frac{1}{|\Omega|} \sum_{|p|>\varepsilon} \frac{1}{e^{\beta(p^2+\mu)} - 1}.$$

Let $\mu(\Omega)$ denote the solution of equation (27.7) for fixed γ and β. Let $\gamma \geq \gamma_0(\beta)$. In this case we inevitably have $\mu(\Omega) \to 0$ as $|\Omega| \to \infty$ [11)].

Let us show that the limit

$$\lim_{|\Omega|\to\infty} s''_\varepsilon(\Omega, \mu(\Omega)) = \frac{1}{(2\pi)^3} \int\limits_{|p|>\varepsilon} \frac{d^3p}{e^{\beta p^2} - 1}. \tag{27.11}$$

exists. Indeed,

$$0 \leq \frac{1}{e^{\beta p^2} - 1} - \frac{1}{e^{\beta(p^2+\mu(\Omega))} - 1} \leq (e^{\beta\mu(\Omega)} - 1) \frac{e^{\beta p^2}}{(e^{\beta p^2} - 1)^2}. \tag{27.12}$$

Dividing by $|\Omega|$ and taking the sum of these inequalities and using the convergence of the integral sums to the respective integrals we deduce that

$$-\delta(\Omega) \leq \frac{1}{(2\pi)^3} \int \frac{d^3p}{e^{\beta p^2} - 1} - s''_\varepsilon(\Omega, \mu(\Omega)) \leq (e^{\beta\mu(\Omega)} - 1)c,$$

[11)] Otherwise there would have existed a sequence Ω_n for which $\mu_n = \mu(\Omega_n) \geq \mu_0$. But then $\gamma = s(\Omega_n, \mu_n) \leq s(\Omega_n, \mu_0)$. Passing to the limit we deduce that

$$\gamma \leq \frac{1}{(2\pi)^3} \int \frac{d^3p}{e^{\beta(p^2+\mu_0)} - 1} < \frac{1}{(2\pi)^3} \int \frac{d^3p}{e^{\beta p^2} - 1} = \gamma_0(\beta),$$

which contradicts to the condition $\gamma \geq \gamma_0(\beta)$.

and moreover,

$$\lim_{|\Omega|\to\infty}\delta(\Omega)=0,\quad \text{where } \delta(\Omega)=\left|\frac{1}{(2\pi)^3}\int\frac{d^3p}{e^{\beta p^2}-1}-\sum_{p\in\Gamma_\Omega}\frac{1}{|\Omega|}\frac{1}{e^{\beta p^2}-1}\right|.$$

Tending $\mu(\Omega)$ to zero we get (27.11). The sum $s'_E(\Omega,\mu)$ contains a summand corresponding to $p=0$ and hence we can estimate $s'_E(\Omega,\mu)$ as follows: $s'_E(\Omega,\mu)\ge\dfrac{1}{|\Omega|(e^{\beta\mu}-1)}$. For $p\ne 0$ we use the inequality (27.12). Thus

$$\frac{1}{|\Omega|(e^{\beta\mu}-1)}\le s'_E(\Omega,\mu)\le\frac{1}{|\Omega|(e^{\beta\mu}-1)}+\frac{1}{|\Omega|}\sum_{0<|p|<\varepsilon}\frac{1}{e^{\beta p^2}-1},\qquad(27.13)$$

and the limit of the second summand in the right-hand side of (27.13) as $|\Omega|\to\infty$ is equal to

$$\frac{1}{(2\pi)^3}\int\limits_{|p|<\varepsilon}\frac{d^3p}{e^{\beta p^2}-1}.$$

It is most easy to see this passing to the polar coordinates. As a result, we obtain the integral sum for the integral of a bounded function.

It follows from (27.11) and (27.13) that

$$\gamma=s(\Omega,\mu(\Omega))=\lim_{|\Omega|\to\infty}s(\Omega,\mu(\Omega))\le\varliminf_{|\Omega|\to\infty}\frac{1}{|\Omega|(e^{\beta\mu(\Omega)}-1)}+\frac{1}{(2\pi)^3}\int\limits_{|p|<\varepsilon}\frac{d^3p}{e^{\beta p^2}-1},$$

for $\mu=\mu(\Omega)$, and from the other hand

$$\gamma=s(\Omega,\mu(\Omega))=\lim_{|\Omega|\to\infty}s(\Omega,\mu(\Omega))\ge\varlimsup_{|\Omega|\to\infty}\frac{1}{|\Omega|(e^{\beta\mu(\Omega)}-1)}+\frac{1}{(2\pi)^3}\int\limits_{|p|>\varepsilon}\frac{d^3p}{e^{\beta p^2}-1}.$$

In the second inequality we can perform an auxiliary passage to the limit as $\varepsilon\to 0$. As a result we see that

$$\varliminf_{|\Omega|\to\infty}\frac{1}{|\Omega|(e^{\beta\mu(\Omega)}-1)}=\varlimsup_{|\Omega|\to\infty}\frac{1}{|\Omega|(e^{\beta\mu(\Omega)}-1)}=$$
$$=\lim_{|\Omega|\to\infty}\frac{1}{|\Omega|(e^{\beta\mu(\Omega)}-1)}=\gamma-\gamma_0(\beta).\qquad(27.14)$$

as $|\Omega|\to\infty$. It follows from (27.14) that

$$\mu(\Omega)=\nu\frac{1}{|\Omega|}+o\Big(\frac{1}{|\Omega|}\Big),\quad \frac{1}{\beta\nu}=\gamma-\gamma_0(\beta).\qquad(27.15)$$

Now let us find the limit of the mean number of particles at point p. Let $\overline{n}(p) = \dfrac{1}{e^{\beta(p^2+\mu)} - 1}$. For Ω fixed the function $\overline{n}(p)$ is only defined in the nodes of the lattice Γ_Ω. Let us shift the lattice Γ_Ω parallel to itself in such a way so that the centers of the cells in the new lattice coincide with the nodes of Γ_Ω. Let Γ'_Ω be the shifted lattice. Let Λ_{p_0} be an elementary cube of the lattice Γ'_Ω and $p_0 \in \Lambda_{p_0} \cap \Gamma_\Omega$ the center of Λ_{p_0}. Let us define the function $\overline{n}(p)$ on the whole space by setting $\overline{n}(p_0) = \overline{n}_\Omega(p)$ for $p \in \Lambda_{p_0}$.

The result obtained can be interpreted as follows: there exists a limit of the integrals $\int \overline{n}_\Omega(p, \mu(\Omega))\, d^3p$ as $|\Omega| \to \infty$ equal to

$$\lim_{|\Omega|\to\infty} \frac{1}{(2\pi)^3} \int \overline{n}_\Omega(p, \mu(\Omega))\, d^3p = \frac{1}{\beta\nu} + \frac{1}{(2\pi)^3} \int \frac{d^3p}{e^{\beta p^2} - 1}.$$

Moreover, $\overline{n}_\Omega(p, \mu(\Omega))$ uniformly converges to $\dfrac{1}{e^{\beta p^2} - 1}$ outside any ball centered at the origin. Therefore the sequence $\overline{n}_\Omega(p, \mu(\Omega))$ has a limit in the sense of generalized functions:

$$\lim_{|\Omega|\to\infty} \overline{n}_\Omega(p, \mu(\Omega)) = \frac{(2\pi)^3}{\beta\nu}\delta(p) + \frac{1}{e^{\beta p^2} - 1}. \tag{27.16}$$

Formula (27.16) shows that for the density greater than a critical one, γ_0 the momentum of a portion of particles is identically equal to zero. The set of such particles constitutes a phase which is called *the Bose condensate*. Formula (27.10) implies that the critical density grows monotonically together with temperature (i.e., as β the case).

Finally let us find the thermodynamic potential. The statistical sum is given by expression (27.3). Taking its logarithm dividing by $|\Omega|$ and passing to the limit we get

$$\Phi(\beta, \mu) = \frac{1}{(2\pi)^3} \int \ln(1 - e^{-\beta(\omega(p)+\mu)})\, d^3p. \tag{27.17}$$

the passage from the integral sum to the integral (27.17) is obviously lawful here for $\gamma < \gamma_0(\beta)$ and $\mu > 0$. For $\gamma \geq \gamma_0(\beta)$ this passage to the limit is also possible and thanks to the relation (see (27.18))

$$\mu(\Omega) = \nu\frac{1}{|\Omega|} + o\Big(\frac{1}{|\Omega|}\Big), \quad \frac{1}{\beta\nu} = \gamma - \gamma_0(\beta). \tag{27.18}$$

we get as a result $\Phi(\beta, 0)$. Recall that

$$\Phi(\beta, \mu) = \lim_{|\Omega|\to\infty} \frac{\partial}{\partial|\Omega|} \ln \Xi_\Omega$$

is interpreted as pressure. Thus we see that for $\gamma \geq \gamma_0(\beta)$ the pressure does not depend on the density — the situation typical for a phase transition.

In conclusion observe that formula (27.10) implies the decrease of the critical density $\gamma_0(\beta)$ as the temperature diminishes. In particular, for the zero temperature we have $\gamma_0 = \lim\limits_{\beta\to\infty} \gamma_0(\beta) = 0$, i.e., all particles belong to the condensate.

§ 28. The Ideal Fermi Gas

28.1. The non-zero temperature. In the p-representation the space $\mathcal{H}$ is as in the Bose case the tensor product of the spaces $\mathcal{H}_p$ describing a system of particles with fixed momentum p. The form of the energy operator and the operator of the number of particles is the same as in the Bose case:

$$H_\Omega = \sum \omega(p) b^*(p) b(p), \quad N_\Omega = \sum b^*(p) b(p). \tag{28.1}$$

It is clear from (28.1) that these operators are tensor sums of the operators $H_{\Omega,p} = \omega(p) b^*(p) b(p)$ and $n(p) = b^*(p) b(p)$, where $H_{\Omega,p}$ act in $\mathcal{H}_p$. In $\mathcal{H}_p$ there exists a common for $H_{\Omega,p}$ and $n(p)$ orthonormal basis consisting of the vectors $(b^*(p))^n \Phi_0$, where $n = 0, 1$. Recall that $(b^*(p))^2 = 0$, and therefore the space $\mathcal{H}_p$ is two-dimensional in the Fermi case [12]. The eigenvalues of the operators $H_{\Omega,p}$ and $n(p)$ on the vector $(b^*(p))^n \Phi_0$ are equal to $n\omega(p)$ and n respectively. Thus,

$$\begin{aligned} &\operatorname{sp} e^{-\beta(H_{\Omega,p} - \mu n(p))} = 1 + e^{-\beta(\omega(p)-\mu)}, \\ &\Xi_\Omega = \operatorname{sp} e^{-\beta(H_\Omega - \mu N_\Omega)} = \prod_{p\in\Gamma_\Omega} \operatorname{sp} e^{-\beta(H_{\Omega,p} - \mu n(p))} = \prod_{p\in\Gamma_\Omega} (1 + e^{-\beta(\omega(p)-\mu)}). \end{aligned} \tag{28.2}$$

The infinite product (28.2) converges if $\omega(p)$ sufficiently fast as $|p| \to \infty$, for example for $\omega(p) = p^2$. The mean number of particles with momentum p is equal to

$$\overline{n}(p) = \frac{\operatorname{sp}(n(p) e^{-\beta(H_\Omega - \mu N_\Omega)})}{\operatorname{sp} e^{-\beta(H_\Omega - \mu N_\Omega)}} = \frac{e^{-\beta(\omega(p)-\mu)}}{1 + e^{-\beta(\omega(p)-\mu)}} = \frac{1}{e^{\beta(\omega(p)-\mu)} + 1}.$$

The equation

$$\frac{1}{|\Omega|} \sum \overline{n}(p) = \gamma, \quad \frac{1}{|\Omega|} \sum \omega(p) \overline{n}(p) = \gamma\varepsilon, \tag{28.3}$$

[12] Actually, 1|1-dimensional.

that relate the temperature and the chemical potential with the density and mean energy of the particle can obviously survive the passage to the limit as $|\Omega| \to \infty$:

$$\frac{1}{(2\pi)^3}\int \frac{d^3p}{e^{\beta(\omega(p)-\mu)}+1} = \gamma, \quad \frac{1}{(2\pi)^3}\int \frac{\omega(p)d^3p}{e^{\beta(\omega(p)-\mu)}+1} = \gamma\varepsilon. \tag{28.4}$$

We similarly obtain an expression for the thermodynamical potential:

$$\Phi = \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|}\ln \Xi_\Omega = \frac{1}{(2\pi)^3}\int \ln(1+e^{-\beta(\omega(p)-\mu)})\, d^3p. \tag{28.5}$$

there are no complications during the passage from the integral sums to the integrals since the functions encountered have no singularities with respect to p for any β and μ.

If the function $\omega(p)$ grows sufficiently fast as $|p| \to \infty$ the equations (28.4) are uniquely solvable for β and μ for any positive right-hand sides [13)].

28.2. The Fermi gas at zero temperature. Let $\omega(p)$ be a continuous function, $\omega(p) \geq 0$ and $\omega(p) \to \infty$ sufficiently fast as $|p| \to \infty$. We fix the density of particles $\gamma > 0$ and start cooling. Let $\mu(\beta)$ be the solution of the first of equations (28.4) for μ. We see from (28.4) that $\mu(\beta)$ for a sufficiently large β otherwise the limit of the left-hand side of (28.4) would be 0. Let us show that for any sequence $\beta_n \to \infty$ we have $\mu(\beta_n) \leq c < \infty$ starting with a number n_0. Let $\mu(\beta_n) \geq \mu_0$ for a sequence $\beta_n \to \infty$. Then for $\beta = \beta_n$ we have

$$\gamma = \frac{1}{(2\pi)^3}\int \frac{d^3p}{e^{\beta(\omega(p)-\mu(\beta))}+1} \geq \frac{1}{(2\pi)^3}\int \frac{d^3p}{e^{\beta(\omega(p)-\mu_0)}+1}. \tag{28.6}$$

The limit of the function $\dfrac{1}{e^{\beta(\omega(p)-\mu_0)}+1}$ as $\beta \to \infty$ is the characteristic function of the set $\omega(p) < \mu_0$. Therefore passing in (28.6) to the limit as $\beta_n \to \infty$ we get

$$\gamma \geq \frac{1}{(2\pi)^3}\int\limits_{\omega(p)\leq\mu_0} d^3p. \tag{28.7}$$

The integral in the right-hand side of (28.7) tends to ∞ as $\mu_0 \to \infty$. The right-hand side of (28.7) is a monotonically increasing function μ_0 and thanks to the assumed continuity of $\omega(p)$ it is even strictly monotonous.

[13)] See footnote on page 146.

Therefore inequality (28.7) implies that $\mu_0 \le \omega_F$, where ω_F is the solution of the equation

$$\gamma = \frac{1}{(2\pi)^3} \int\limits_{\omega(p)\le\omega_F} d^3p. \tag{28.8}$$

Thus whatever the sequence $\beta_n \to \infty$ we have $\mu(\beta_n) \le \omega_F$ starting from a certain number. Therefore $\mu(\beta_n)$ has a limit as $\beta_n \to \infty$. Let μ_0 be this limit. Obviously this limit satisfies the equation obtained from (28.8) by replacing ω_F by μ_0. Due to strict monotonicity of the right-hand side of (28.8) with respect to ω_F we have $\mu_0 = \omega_F$. Therefore we proved the existence of the limit of $\mu(\beta)$ as $\beta \to \infty$ and

$$\lim_{\beta\to\infty} \mu(\beta) = \omega_F, \tag{28.9}$$

where ω_F is the solution of equation (28.8).

The number ω_F is called *the Fermi energy*, and the surface $\omega(p) = \omega_F$ — *the Fermi surface*. For $\omega(p) = p^2$ this surface is a sphere.

These arguments are also applicable to finite volumes. They indicate that the mean number of particles $n(p)$ has a limit as $\beta \to \infty$ equal to the characteristic function of the set $\{p \,|\, \omega(p) < \omega_{F,\Omega}\}$ [14], where $n(p) = \frac{1}{2}$ for $\omega(p) = \omega_{F,\Omega}$, where $\omega_{F,\Omega}$ — the Fermi energy for a finite volume Ω — has a limit equal to ω_F as $|\Omega| \to \infty$.

Thus for the zero temperature the Fermi gas turns into a state for which the momenta of the particles fill out the interior of the Fermi surface. This state denoted by $\Phi_{F,\Omega}$ is an element of the Fock space $\mathcal{H}$ equal to

$$\Phi_{F,\Omega} = c \prod_{\omega(p)<\omega_{F,\Omega}} b^*(p)\Phi_0,$$

where Φ_0 is the vacuum vector. The vector $\Phi_{F,\Omega}$ admits an important interpretation. Let $\widetilde{H}_{\Omega,\beta} = H_\Omega - \mu N_\Omega$, where H_Ω and N_Ω are given by expressions (28.1) and $\mu = \mu_\Omega(\beta)$ be determined from the first of equations (28.3) for a fixed γ. Since $\mu_\Omega(\beta) \to \omega_{F,\Omega}$ as $\beta \to \infty$ the limit of $\widetilde{H}_{\Omega,\beta}$ as $\beta \to \infty$ is equal to $\widetilde{H}_\Omega = H_\Omega - \omega_{F,\Omega}N_\Omega$ [15]. It turns out that if the Fermi surface does not pass through the nodes of the lattice Γ_Ω then the operator $\widetilde{H}_\Omega$ possesses a non-degenerate minimal eigen value E_0 and $\Phi_{F,\Omega}$ is the corresponding eigenvectors.

[14] Everywhere except the points of the Fermi surface.

[15] In the strong sense on finite vectors entering the domain of definition of H_Ω.

It is most easy to establish this as follows. Set

$$\begin{aligned} c(p) &= \theta(\omega(p) - \omega_{F,\Omega})b(p) + \theta(\omega_{F,\Omega} - \omega(p))b^*(p), \\ c^*(p) &= \theta(\omega_{F,\Omega} - \omega(p))b(p) + \theta(\omega(p) - \omega_{F,\Omega})b^*(p), \end{aligned} \tag{28.10}$$

where

$$\theta(t) = \begin{cases} 1 & \text{as} \quad t > 0, \\ 0 & \text{as} \quad t \leq 0. \end{cases}$$

It follows from (28.10) that $c(p)$ and $c^*(p)$ is the system of operators satisfying the same relations as $b(p)$ and $b^*(p)$. The relation (28.10) that relates two systems of operators b, b^* and c, c^* is an example of what is called *the linear canonic transformation*. One can show that there exists a unitary operator $\mathcal{H}$ in U such that [16)]

$$c(p) = Ub(p)U^{-1}; \quad c^*(p) = Ub^*(p)U^{-1}. \tag{28.11}$$

Let us find the operator $\widetilde{H}'_\Omega = U\widetilde{H}_\Omega U^{-1}$. Using (28.10), (28.11), and commutation relations between $c(p)$, $c^*(p)$ we see that

$$\widetilde{H}'_\Omega = \sum |\omega(p) - \omega_{F,\Omega}| b^*(p)b(p) - \sum_{\omega(p)<\omega_{F,\Omega}} (\omega_{F,\Omega} - \omega_(p)). \tag{28.12}$$

The first summand in (28.12) is a non-negative operator and the second one is proportional to the unit operator. Therefore the minimal eigenvalue of $\widetilde{H}'_\Omega$ and hence H'_Ω is equal to

$$E_0 = -\sum_{\omega(p)<\omega_{F,\Omega}} (\omega_{F,\Omega} - \omega_(p)) \sim -|\Omega|(2\pi)^3 \int\limits_{\omega(p)<\omega_F} (\omega_F - \omega_(p))\, d^3p. \tag{28.13}$$

The vacuum vector $\widetilde{H}'_\Omega$ is an eigenvector of Φ_0 corresponding to the eigenvalue (28.13). If the Fermi surface $\omega(p) = \omega_{F,\Omega}$ does not pass through the

[16)] This statement is a corollary of the general fact discussed in more detail in the next section. For the transformation (28.10), the existence of an operator U that generates it is easy to prove directly. Consider a vector $\Phi_{F,\Omega} = \prod\limits_{\omega(p)<\omega_{F,\Omega}} b^*(p)\Phi_0$. Then (28.10) implies $c(p)\Phi_{F,\Omega} = 0$. Therefore, in the subspace $\widetilde{\mathcal{H}} \subset \mathcal{H}$ generated by the action of $c(p)$ and $c^*(p)$ on $\Phi_{F,\Omega}$, a Fock representation for the system $c(p)$, $c^*(p)$ arises. Further, the operators $b(p)$, $b^*(p)$ are expressed in terms of $c(p)$, $c^*(p)$ by the formulas similar to (28.10). Therefore the subspace $\widetilde{\mathcal{H}}$ is invariant with respect to $b(p)$ and $b^*(p)$, and therefore $\widetilde{\mathcal{H}} = \mathcal{H}$ since $\mathcal{H}$ is irreducible. Thus in $\mathcal{H}$, there act two Fock representations. The uniqueness, up to a unitary equivalence, of the Fock representation implies the existence of an operator U with the property (28.11).

points of the lattice Γ_Ω there are no other eigenvectors with this eigenvalue. Let us find the pre-image $\Psi = U^{-1}\Phi_0$ of Φ_0 with respect to U. Observe that

$$Uc(p)U^{-1} = U^2 b(p)U^{-2} = b(p).$$

Therefore $U^{-1}b(p)U = c(p)$. The vector Φ_0 is the only up to a factor solution of the equation $b(p)\Phi_0 = 0$. Therefore the vector $\Psi = U^{-1}\Phi_0$ is the only up to a factor solution of the system of equations

$$c(p)\Psi = 0. \tag{28.14}$$

It is easy to see that the vector

$$\Psi = \prod_{\omega(p)<\omega_{F,\Omega}} b^*(p)\Phi_0, \tag{28.15}$$

coinciding with the earlier introduced vector $\Phi_{F,\Omega}$ up to a multiple is a solution of equation (28.14).

In conclusion observe that the above investigation is based on the fact that in the Fermi case the operator $\widetilde{H}_{\Omega,\beta}$ has a limit equal to $\widetilde{H}_\Omega = H_\Omega - \omega_{F,\Omega}N_\Omega$ as $\beta \to \infty$. Such simplicity of the behavior of $\widetilde{H}_{\Omega,\beta}$ as $\beta \to \infty$ is indigenous precisely for the Fermi systems. In the Bose case as is clear from formula (27.18) § 27 the analogous operator $\widetilde{H}_{\Omega,\beta}$ has an asymptotic

$$\widetilde{H}_{\Omega,\beta} \approx H_\Omega + \frac{1}{\beta\nu|\Omega|}N_\Omega$$

as $\beta \to \infty$.

§ 29. The Bardeen—Cooper—Schrieffer model of superconductivity

29.1. Setting of the problem. At temperatures close to the absolute zero the electric resistance of the metals disappears. This phenomenon is called *superconductivity*. It is explained by the peculiarities of the interaction of the electrons in the metal with the frequencies of its crystal lattice. The complete Hamiltonian describing this interaction (*the Frölich Hamiltonian*) is rather complicated and is hard to study mathematically. Bardeen, Cooper and Schrieffer made a decisive progress in the theory of superconductivity: from physical considerations they approximately studied oscillations of the lattice and suggested a Hamiltonian for a system of interacting electrons assuming that the nature of this interaction is as follows: moving over the

crystal lattice the electron excites its oscillations and these oscillations in their turn act on other electrons.

Without going into the details of physical justifications we will realistically study the Hamiltonian suggested by Bardeen, Cooper and Schrieffer (with the help of the principle of maximum of entropy we find the lower part of the spectrum and the statistical sum). The results obtained can be rigorously justified but this justification considerably exceeds the level of difficulty adopted at these lectures and therefore we'll skip it [17]. The Bardeen—Cooper—Schrieffer Hamiltonian is of the form

$$H = \sum \omega(p)(a_1^*(p)a_1(p) + a_2^*(p)a_2(p)) - \\ - \frac{1}{|\Omega|}\sum B(p_1,p_2)a_1^*(p_1)a_2^*(-p_1)a_2(-p_2)a_1(p_2), \quad (29.1)$$

where $\omega(p) = \tilde{\omega}(|p|)$ that is $\omega(p)$ only depends on $|p| = \sqrt{p_1^2+p_2^2+p_3^2}$, where as usual p runs over the cubic lattice Γ_Ω with the volume of the unit cube equal to $\frac{(2\pi)^3}{|\Omega|}$, $a_i^*(p)$ and $a_i(p)$ are Fermi operators of creation and annihilation. The complementary to $a_i(p)$ variable i used as an index is related with electron's spin $\frac{1}{2}$. This variable assumes two values 1 or 2 corresponding to two possible directions of the spin. The function $B(p_1,p_2)$ describing the interaction is supposed to be non-vanishing with respect to each variable only in a small vicinity of the Fermi surface of the free Hamiltonian, i.e., obtained from (29.1) at $B=0$.

29.2. The maximum principle. Denote by $M'_{\varepsilon,\gamma}$ the set of non-negative operators ζ with converging trace and such that

$$\frac{\operatorname{sp} H\zeta}{\operatorname{sp}\zeta} = \varepsilon|\Omega|, \quad \frac{\operatorname{sp} N\zeta}{\operatorname{sp}\zeta} = \gamma|\Omega|, \quad (29.2)$$

where H, N are the operators of energy and the number of particles, ε and γ is the mean energy and the density of the particles. On the set $M'_{\varepsilon,\gamma}$ consider the functional

$$S'(\zeta) = -\frac{\operatorname{sp}\zeta\ln\zeta}{\operatorname{sp}\zeta} + \ln\operatorname{sp}\,\zeta. \quad (29.3)$$

Observe that the functional $S'(\zeta)$ is constant on the rays: $S'(\lambda\zeta) = S'(\zeta)$ for any real $\lambda > 0$. The left-hand sides of (29.2) possess the same property.

Denote by $M_{\varepsilon,\gamma}$ the subset of $M'_{\varepsilon,\gamma}$ consisting of the operators with the additional property $\operatorname{sp}\zeta = 1$ (i.e., of the density matrices). On $M_{\varepsilon,\gamma}$, the

[17] For details, see [B], [M], [BM].

functional $S'(\zeta)$ coincides with the entropy $S(\zeta) = -\operatorname{sp}(\zeta \ln \zeta)$, and therefore according to § 24 in an inner point of $M_{\varepsilon,\gamma}$ the functional $S'(\zeta)$ possesses the only extremum which is the global maximum in $M_{\varepsilon,\gamma}$ attained at

$$\zeta = (\operatorname{sp} e^{-\beta(H-\mu N)})^{-1} e^{-\beta(H-\mu N)}.$$

Returning to $S'(\zeta)$ we see that in $M'_{\varepsilon,\gamma}$ the extrema are only attained on the ray $\lambda e^{-\beta(H-\mu N)}$.

In what follows we will often consider the expressions of the form $\dfrac{\operatorname{sp} A\zeta}{\operatorname{sp}\zeta}$, where A is a given operator. Let us introduce a shorthand notation

$$\langle A \rangle_\zeta := \frac{\operatorname{sp} A\zeta}{\operatorname{sp}\zeta}.$$

Let $\Phi(\zeta)$ denote the functional

$$\Phi(\zeta) = -\langle \ln \zeta \rangle_\xi - \beta \langle H - \mu N \rangle_\xi + \ln \operatorname{sp} \zeta. \tag{29.4}$$

According to the above (one can easily verify this directly) the maximum of $\Phi(\zeta)$ is attained at

$$\zeta = \zeta_0 = \lambda e^{-\beta(H-\mu N)}. \tag{29.5}$$

For us the following formula easy to verify directly is essential:

$$\Xi = \operatorname{sp} e^{-\beta(H-\mu N)} = e^{\Phi(\zeta_0)}. \tag{29.6}$$

The scheme of the further study is as follows. We first find ζ in the form

$$\zeta = U e^{-\beta A} U^{-1}, \tag{29.7}$$

where A is a quadratic operator

$$A = \sum E(p)(a_1^*(p)a_1(p) + a_2^*(p)a_2(p)), \quad \text{and } E(p) = \widetilde{E}(|p|) \geq 0, \tag{29.8}$$

and U is a unit operator sailed out by the properties

$$\begin{aligned} &U a_1(p) U^{-1} = b_1(p) = \varphi(p) a_1(p) + \psi(p) a_2^*(-p), \\ &\varphi(p) = \varphi(-p), \quad \psi(p) = -\psi(-p), \\ &U a_2(p) U^{-1} = b_2(p) = \varphi(p) a_2(p) + \psi(-p) a_1^*(-p). \end{aligned} \tag{29.9}$$

(the expressions for the adjoint operators are automatically obtained and therefore can be omitted).

Substituting ζ of the form (29.7) into (29.4) we obtain the functional $\Phi(\zeta) = \Phi(A, U)$. Variation of A, i.e., $E(p)$ and U yields a maximum of Φ and we further establish that it is the only one attained at a point A_0, U_0.

Further using expression (29.6) we find the statistical sum and its asymptotics as $\beta \to \infty$ gives the lower end of the spectrum of $H - \mu N$. A characteristic feature of the spectrum is the presence of a gap Δ which is an explanation of the superconductivity.

A remarkable feature of the model is the fact that although the statistical sum and the gap are found approximately the limits of $\frac{1}{|\Omega|} \ln \Xi$ and Δ as $|\Omega| \to \infty$ coincide with the precise value of thermodynamic potential and the precise value of the gap, respectively.

The proof of these statements is omitted because it is too complicated [18)]. Before we pass to the calculations let us make a remark concerning the operator U. The expression of the form

$$b_n = \sum_m (\varphi_{nm} a_m + \psi_{nm} a_m^*),$$
$$b_n^* = \sum_m (\overline{\psi}_{nm} a_m + \overline{\varphi}_{nm} a_m^*) \tag{29.10}$$

is called a *linear canonic transformation* if the operators b_n, b_n^* satisfy the same commutation relations as a_n, a_n^* and the relations (29.10) considered as equations for a_n^*, a_n can be resolved.

The canonical transformation (29.10) is said to be *the inner* one if there exists a unitary operator U in $\mathcal{H}$ such that $b_n = U a_n U^{-1}$ (and therefore $b_n^* = U a_n^* U^{-1}$). Since the family of operators a_n, a_n^* acts irreducibly in the Focks space. It follows that if such an operator U exists it is the only one up to a scalar factor. The inequality is a necessary and sufficient condition of the operator U [19)]

$$\sum_{m,n} |\psi_{m,n}|^2 < \infty. \tag{29.11}$$

Since (29.9) is a canonical transformation it follows that

$$|\varphi(p)|^2 + |\psi(p)|^2 = 1. \tag{29.12}$$

In our case the condition (29.11) means that

$$\sum_{p \in \Gamma_\Omega} |\psi(p)|^2 < \infty. \tag{29.13}$$

[18)] See footnote on page 155.
[19)] For the proof, see [B8].

In what follows we assume that the functions $\varphi(p)$ and $\psi(p)$ are real valued ones and $\varphi(p) \geq 0$ and so $\varphi(p)$ can be expressed in terms of $\psi(p)$ from the equation (29.12).

It turns out that the factor up to which the operator U is defined by formulas (29.9) is inessential and so varying U reduces to varying ψ taking (29.13) into account.

29.3. Calculations. Let us find $\operatorname{sp}\zeta$:

$$\operatorname{sp}\zeta = \operatorname{sp} Ue^{-\beta A}U = \operatorname{sp} Ue^{-\beta A} =$$
$$= \prod_{p\in\Gamma_\Omega} \operatorname{sp} e^{-\beta E(p)a_1^*(p)a_1(p)} \operatorname{sp} e^{-\beta E(p)a_2^*(p)a_2(p)} = \prod_{p\in\Gamma_\Omega} (1+e^{-\beta E(p)})^2.$$

Compute $\langle \ln\zeta\rangle_\zeta$:

$$\langle \ln\zeta\rangle_\zeta = \frac{-\operatorname{sp}(e^{-\beta A}\sum\limits_{p,s}\beta E(p)a_s^*(p)a_s(p))}{\operatorname{sp} e^{-\beta A}} =$$
$$= -\sum_{p,s\ (s=1,2)} \frac{\beta \operatorname{sp}(e^{-\beta A}E(p)a_s^*(p)a_s(p))}{\operatorname{sp} e^{-\beta A}} =$$
$$= -\sum_{p,s\ (s=1,2)} \frac{\beta \operatorname{sp}(e^{-\beta E(p)a_s^*(p)a_s(p)}E(p)a_s^*(p)a_s(p))}{\operatorname{sp} e^{-\beta E(p)a_s^*(p)a_s(p)}} = -2\sum_p \frac{\beta E(p)e^{-\beta E(p)}}{1+e^{-\beta E(p)}}.$$

Thus

$$S'(\zeta) = -\langle \ln\zeta\rangle_\zeta + \ln\operatorname{sp}\zeta = 2\sum_p \Big(\frac{\beta E(p)e^{-\beta E(p)}}{1+e^{-\beta E(p)}} + \ln(1+e^{-\beta E(p)})\Big).$$

Set $\sigma(p) = \dfrac{1}{1+e^{\beta E(p)}}$. It is easy to express $S'(\zeta)$ in terms of σ:

$$S'(\zeta) = -2\sum_p \Big(\sigma(p)\ln\sigma(p) + (1-\sigma(p))\ln(1-\sigma(p))];$$
$$E(p) = \frac{1}{\beta}\ln\frac{1-\sigma(p)}{\sigma(p)}.$$

Let us find $\langle H\rangle_\zeta$:

$$\langle H\rangle_\zeta = \frac{\operatorname{sp}\zeta H}{\operatorname{sp}\zeta} = \frac{\operatorname{sp}(Ue^{-\beta A}U^{-1}H)}{\operatorname{sp}(Ue^{-\beta A}U^{-1})} = \frac{\operatorname{sp}(e^{-\beta A}U^{-1}HU)}{\operatorname{sp} e^{-\beta A}} = \langle U^{-1}HUe^{-\beta A}\rangle_{e^{-\beta A}}.$$

The Hamiltonian H is a sum (29.1) and we will compute the trace of each summand separately. Use formulas (29.9):

$$U^{-1}a_1^*(p)a_1(p)U = U^{-1}a_1^*(p)UU^{-1}a_1(p)U = b_1^*(p)b_1(p) = \\ = (\varphi(p)a_1^*(p) + \psi(p)a_2(-p))(\varphi(p)a_1(p) + \psi(p)a_2^*(-p)).$$

Recall that we assume that φ and ψ are real valued. For $U^{-1}a_2^*(p)a_2(p)U$ a similar expression holds. Further on

$$\langle a_1^*(p)a_2^*(-p)\rangle_{e^{-\beta A}} = \\ = \frac{\operatorname{sp}\left(e^{-\beta\sum E(p)a_1^*(p)a_1(p)}a_1^*(p)e^{-\beta\sum E(p)a_2^*(p)a_2(p)}a_2^*(-p)\right)}{\operatorname{sp} e^{-\beta\sum E(p)[a_1^*(p)a_1(p)+a_2^*(p)a_2(p)}} = \\ = \frac{\operatorname{sp}(e^{-\beta E(p)a_1^*(p)a_1(p)}a_1^*(p))\operatorname{sp}(e^{-\beta E(-p)a_2^*(-p)a_2(-p)}a_2^*(-p))}{\operatorname{sp} e^{-\beta E(p)a_1^*(p)a_1(p)}\operatorname{sp} e^{-\beta E(p)a_1^*(-p)a_1(-p)}}.$$

Here we used of the fact that the trace of the tensor product of the operators is equal to the product of the traces in the two-dimensional spaces

$$\operatorname{sp}(e^{-\beta E(p)a_1^*(p)a_1(p)}a_1^*(p)) = \\ = \operatorname{sp}(a_1^*(p)(1 - \beta E(p)a_1^*(p)a_1(p) + \ldots)) = \operatorname{sp} a_1^*(p) = 0.$$

Thus $\langle a_1^*(p)a_2^*(-p)\rangle_{e^{-\beta A}} = 0$ and we similarly prove that

$$\langle a_2(-p)a_1(p)\rangle_{e^{-\beta A}} = 0,$$
$$\langle a_1^*(p)a_1(p)\rangle_{e^{-\beta A}} = \frac{\operatorname{sp}(e^{-\beta E(p)a_1^*(p)a_1(p)}a_1^*(p)a_1(p))}{\operatorname{sp} e^{-\beta E(p)a_1^*(p)a_1(p)}} = \frac{e^{-\beta E(p)}}{1 + e^{-\beta E(p)}}.$$

In precisely the same way we prove that

$$\langle a_2^*(-p)a_2(-p)\rangle_{e^{-\beta A}} = \frac{e^{-\beta E(-p)}}{1 + e^{-\beta E(-p)}} = \frac{e^{-\beta E(p)}}{1 + e^{-\beta E(p)}}.$$

Further we have

$$\langle a_2(-p)a_2^*(-p)\rangle_{e^{-\beta A}} = \langle 1 - a_2^*(-p)a_2(-p)\rangle_{e^{-\beta A}} = \frac{1}{1 + e^{-\beta E(-p)}} = \frac{1}{1 + e^{-\beta E(p)}}.$$

From the above calculations we deduce that

$$\langle a_1^*(p)a_1(p)\rangle_\zeta = \varphi^2(p)\frac{1}{e^{\beta E(p)} + 1} + \psi^2(p)\frac{e^{\beta E(p)}}{1 + e^{\beta E(p)}} = \\ = (1 - \rho(p)\sigma(p) + \rho(p)(1 - \sigma(p)) = \sigma(p) + \rho(p) - 2\rho(p)\sigma(p),$$

where

$$\rho(p) = \psi^2(p), \quad \sigma(p) = \frac{1}{1 + e^{\beta E(p)}}.$$

We similarly calculate the mean values of the terms of the Hamiltonian corresponding to the interaction. Observe only that

$$\langle b_1^*(p) b_2^*(-p) b_2(-q) b_1(q) \rangle_{e^{-\beta A}} = \langle b_1^*(p) b_2^*(-p) \rangle_{e^{-\beta A}} \langle b_2(-q) b_1(q) \rangle_{e^{-\beta A}}.$$

Let us express the final result for $\langle H \rangle_\zeta$ as

$$\langle H \rangle_\zeta = 2 \sum_p \omega(p)(\sigma(p) + \rho(p) - 2\rho(p)\sigma(p)) -$$
$$- \frac{1}{|\Omega|} \sum_{p,q} B(p,q)(1 - 2\sigma(p))(1 - 2\sigma(q)) \sqrt{\rho(p)(1 - \rho(p))} \sqrt{\rho(q)(1 - \rho(q))}.$$

The value of $\langle N \rangle_\zeta$ is analogously computed to be

$$\langle N \rangle_\zeta = 2 \sum (\sigma(p) + \rho(p) - 2\rho(p)\sigma(p)).$$

Now compute the extremum of the functional $\Phi(\zeta)$ determined by (29.4). The results obtained imply that $\Phi(\zeta)$ is of the form

$$\Phi(\zeta) = \Phi(\sigma, \rho) = -2 \sum \big(\sigma(p) \ln \sigma(p) + (1 - \sigma(p)) \ln(1 - \sigma(p))\big) -$$
$$- \beta \Big\{ 2 \sum (\omega(p) - \mu)(\sigma(p) + \rho(p) - 2\rho(p)\sigma(p)) -$$
$$- \frac{1}{|\Omega|} \sum B(p,q)(1 - 2\sigma(p))(1 - 2\sigma(q)) \sqrt{\rho(p)(1 - \sigma(p))\rho(q)(1 - \rho(q))} \Big\}.$$

In what follows we will be mainly interested in low temperatures i.e., the large values of β. As we know for three fermions $\mu(\beta) \to \omega_{F,\Omega}$ as $\beta \to \infty$ in our case the interaction is weak and therefore $\mu(\beta)$ as $\beta \to \infty$ is situated near the boundary energy $\omega_{F,\Omega}$ determined by the free Hamiltonian. In its turn, $\omega_{F,\Omega}$ is close to $\omega_F = \lim\limits_{|\Omega| \to \infty} \omega_{F,\Omega}$. And therefore to compute the asymptotics as $\beta \to \infty$ we may assume that $\mu = \omega_F$ does not depend on β. Hereafter we will always keep this circumstance into account. Equating the derivatives with respect to $\sigma(p)$ and $\rho(p)$ to zero we get

$$\ln \frac{\sigma(p)}{1 - \sigma(p)} + \beta(\omega(p) - \mu)(1 - 2\rho(p)) + 2\beta \sqrt{\rho(p)(1 - \rho(p))} \varepsilon(p) = 0, \tag{29.14}$$

$$(\omega(p) - \mu)(1 - 2\sigma(p)) - \frac{1}{2} \frac{(1 - 2\sigma(p))(1 - 2\rho(p))}{\sqrt{\rho(p)(1 - \rho(p))}} \varepsilon(p) = 0, \tag{29.15}$$

where for brevity we have set

$$\varepsilon(p) = \frac{1}{|\Omega|}\sum_q B(p,q)(1-2\sigma(q))\sqrt{\rho(q)(1-\rho(q))}. \tag{29.16}$$

and therefore (29.15) can be divided by $1-2\sigma(p)$ which turns into a quadratic equation for $\rho(p)$. The solution of the quadratic equation is

$$\rho(p) = \frac{1}{2}\Big(1 \pm \frac{\omega(p)-\mu}{\sqrt{(\omega(p)-\mu)^2+\varepsilon^2(p)}}\Big).$$

Only the sign "$-$" makes sense since for the "$+$" sign for infinitely many points (at all points outside the Fermi sphere, i.e., $\omega(p) > \mu = \omega_F$ we have

$$\rho(p) > \frac{1}{2} \quad \text{and} \quad \sum \rho(p) = \sum |\psi(p)|^2 = \infty,$$

which contradicts (29.13), i.e., which implies that the canonical transformation is not inner. Observe by the way that in the absence of the interaction $\varepsilon(p) = 0$ and selecting the sign "$-$" the transformation (29.9) turns into the canonical transformation (28.10). Thus

$$\rho(p) = \frac{1}{2}\Big(1 - \frac{\omega(p)-\mu}{\sqrt{(\omega(p)-\mu)^2+\varepsilon^2(p)}}\Big). \tag{29.17}$$

Substituting

$$\sqrt{\rho(p)(1-\rho(p))} = \frac{\varepsilon(p)}{2\sqrt{(\omega(p)-\mu)^2+\varepsilon^2(p)}}$$

and

$$1-2\rho(p) = \frac{\omega(p)-\mu}{\sqrt{(\omega(p)-\mu)^2+\varepsilon^2}}$$

into (29.14) we get

$$\ln\frac{\sigma(p)}{1-\sigma(p)} + \beta\sqrt{(\omega(p)-\mu)^2+\varepsilon^2(p)} = 0,$$

implying

$$\sigma(p) = -\frac{1}{2}\mathrm{th}\Big(\frac{\beta}{2}\sqrt{(\omega(p)-\mu)^2+\varepsilon^2(p)}\Big) + \frac{1}{2}. \tag{29.18}$$

We have expressed σ and p in terms of ε. Now substitute the expressions obtained in the definition (29.16) of ε:

$$\varepsilon(p) = \frac{1}{2|\Omega|}\sum_q B(p,q)\frac{\varepsilon(q)}{\sqrt{(\omega(q)-\mu)^2+\varepsilon^2(q)}}\mathrm{th}\frac{\beta}{2}\sqrt{(\omega(q)-\mu)^2+\varepsilon^2(q)}.$$

The right-hand side of the equality is an integral sum and tending $|\Omega|$ to ∞, we get an integral equation for $\varepsilon(p)$:

$$\varepsilon(p) = \frac{1}{2(2\pi)^3} \int B(p,q) \frac{\varepsilon(q)}{\sqrt{(\omega(q)-\mu)^2 + \varepsilon^2(q)}} \operatorname{th} \frac{\beta}{2} \sqrt{(\omega(q)-\mu)^2 + \varepsilon^2(q)}\, dq. \tag{29.19}$$

Now recall that $B(p,q) \neq 0$ only in a vicinity of the Fermi sphere. Let $D = \{p \mid |\omega(p) - \mu| < \alpha\}$. For simplicity, set

$$B(p,q) = \begin{cases} q & \text{if } (p,q) \in D \times D, \\ 0 & \text{if } (p,q) \notin D \times D. \end{cases}$$

For the potential in this form the equation (29.19) becomes

$$\varepsilon(p) = \frac{g}{2(2\pi)^3} \int\limits_D \frac{\varepsilon(q)\, d^3q}{\sqrt{(\omega(q)-\mu)^2 + \varepsilon^2(q)}} \operatorname{th}\Big(\frac{\beta}{2} \sqrt{(\omega(q)-\mu)^2 + \varepsilon^2(q)}\Big). \tag{29.20}$$

Here the integral does not depend on p and therefore $\varepsilon(p) = \varepsilon = \text{const}$ (although ε does not depend on p it depends on β. Assuming that $\varepsilon \neq 0$ we can divide (29.20) by $\varepsilon = \varepsilon(p)$ as a result we get

$$1 = \frac{g}{2(2\pi)^3} \int\limits_D \frac{d^3q}{\sqrt{(\omega(q)-\mu)^2 + \varepsilon^2}} \operatorname{th}\Big(\frac{\beta}{2} \sqrt{(\omega(q)-\mu)^2 + \varepsilon^2}\Big). \tag{29.21}$$

Assume that $\varepsilon \to \varepsilon_0 \neq 0$ as $\beta \to \infty$, i.e., when the temperature tends to zero. Let us find ε_0. For these observe that

$$\operatorname{th}\Big(\frac{\beta}{2} \sqrt{(\omega(q)-\mu)^2 + \varepsilon^2(q)}\Big) \to 1 \quad \text{as } \beta \to \infty.$$

Passing to the spherical coordinates in the integral (29.20) we find an equation from which to define ε_0

$$1 = 4\pi \frac{g}{2(2\pi)^3} \int\limits_{|q^2-\mu|<\alpha} \frac{q^2 dq}{\sqrt{(\omega(q)-\mu)^2 + \varepsilon_0^2}}. \tag{29.22}$$

In order to further investigate the integral (29.22) set $\omega(q) = q^2$ and introduce a new variable $t = q^2 - \omega_F = q^2 - \mu$. On the interval $|\omega(q) - \omega_F| \leq \alpha$ the derivative $\dfrac{d|q|}{dt} = \gamma(t)$ does not vary much. Therefore we set

$\dfrac{d|q|}{dt} = \gamma = \text{const}$. Now we can compute the integral (29.22) exactly

$$1 = \frac{2\pi g}{(2\pi)^3} \int\limits_{|q^2-\mu|<\alpha} \frac{q^2 dq}{\sqrt{(q^2-\mu)^2+\varepsilon^2}} \approx \frac{2\pi g\gamma}{(2\pi)^3} \int\limits_{|t|<\alpha} \frac{(t+\mu)\,dt}{\sqrt{t^2+\varepsilon^2}} =$$

$$= \frac{2\pi g\gamma}{(2\pi)^3} \int\limits_{|t|<\alpha} \frac{\mu\,dt}{\sqrt{t^2+\varepsilon^2}} = 2\pi g\gamma\mu(2\pi)^{-3} \ln(t+\sqrt{t^2+\varepsilon^2})\Big|_{-\alpha}^{+\alpha},$$

implying

$$\sqrt{\alpha^2+\varepsilon^2} = \alpha \frac{e^{\frac{1}{gc}}+1}{e^{\frac{1}{gc}}-1}, \quad \text{where } \ c = 2\pi\gamma\mu(2\pi)^{-3}.$$

If $g \to 0$, then $\varepsilon \to 0$ and the singularity at $g = 0$ is not analytic.

29.3.1. Remark. At $g = 0$ the BCS Hamiltonian turns into a free Hamiltonian. Therefore it seems natural to obtain the spectrum statistical sum and other parameters of the BCS Hamiltonian applying the perturbation theory. The non-analytic nature of dependence of $\varepsilon(p)$ on the constant g indicates however, that the perturbation theory is inapplicable here.

When $\beta = 0$ equation (29.20) has no non-zero solutions. Indeed if $\varepsilon \neq 0$ then (29.20) is equivalent to (29.21) but the right-hand side of (29.21) is equal to 0 at $\beta = 0$. In what follows it is easy to verify that the integrand in (29.21) decays as ε grows. Therefore if for some β we have

$$\frac{g}{2(2\pi)^3} \int\limits_{|\omega(q)-\mu|<\alpha} |\omega(q)-\mu|^{-1} \mathrm{th}\Big(\frac{\beta}{2}\sqrt{(\omega(q)-\mu)^2}\Big) d^3q < 1,$$

then the equality (29.21) is impossible for any ε. Solving the equation

$$\frac{g}{2(2\pi)^3} \int |\omega(q)-\mu|^{-1} \mathrm{th}\Big(\frac{\beta}{2}|\omega(q)-\mu|\Big) d^3q = 1$$

for β we can find the threshold value β_0 for $\beta > \beta_0$ there exists a non-zero ε and for $\beta < \beta_0$ there are no such ε.

Now let us study the asymptotics of the statistical sum $\Xi = \mathrm{sp}\, e^{-\beta(H-\mu N)}$ for β large. According to (29.6) we have

$$\Xi = e^{\Phi} = e^{\varphi}\, \mathrm{sp}\, \zeta, \quad \text{where } \ \varphi = -\langle \ln \zeta \rangle_\zeta - \beta\langle H - \mu N \rangle.$$

Taking into account $\zeta = Ue^{-\beta A}U^{-1}$ we use the earlier obtained expressions for $\langle \ln \zeta \rangle_\zeta$ and $\langle H - \mu N \rangle_\zeta$ and as a result we get

$$\varphi = -\beta \sum_p \Big(\omega(p) - \mu - E(p) + \frac{\varepsilon^2(p)}{2E(p)} \operatorname{th} \frac{\beta E(p)}{2} \Big). \tag{29.23}$$

The asymptotics of Ξ for β large is easy to find. Indeed, $\beta \to \infty$ as $\varepsilon \to \infty$, and

$$E(p) \to E_0(p) = \sqrt{(\omega(p) - \mu)^2 + \varepsilon_0^2}, \quad \operatorname{th} \frac{\beta}{2} E(p) \to 1,$$

and therefore

$$\ln \Xi \approx \sum \ln \operatorname{sp} \zeta + \varphi \approx 2 \sum \ln(1 + e^{-\beta E_0(p)}) - \\ - 2\beta \sum \Big(\frac{\omega(p) - \mu - E_0(p)}{2} + \frac{\varepsilon_0^2(p)}{4E_0(p)} \Big).$$

Denote $c = -\lim\limits_{\beta \to \infty} \dfrac{1}{\beta} \varphi$. Then asymptotically we have

$$\Xi \cong e^{-\beta c} \prod (1 + e^{-\beta E_0(p)})^2 = e^{-\beta c} (1 + \sum e^{-\beta E_0(p)} + \ldots). \tag{29.24}$$

Observe that all the numbers $E_0(p)$ are separated from zero:

$$E_0(p) = \sqrt{(\omega(p) - \mu)^2 + \varepsilon_0^2} \geq \varepsilon_0 > 0.$$

This fact enables us to conclude that the least eigen value of the operator $H - \mu N$ is equal to c only once and is separated from the other eigen values by a gap of width ε_0.

Indeed, let $H \geq 0$ and its eigen values are $\lambda_k \geq \lambda_0 \geq 0$ and r_k are the respective multiplicities. Then $\operatorname{sp} e^{-\beta H}$ admits the following asymptotic expansion as $\beta \to \infty$

$$\operatorname{sp} e^{-\beta H} = \sum r_k e^{-\beta \lambda_k} e^{-\beta \lambda_0} (r_0 + \sum r_i e^{-\beta(\lambda_i - \lambda_0)} + \ldots). \tag{29.25}$$

The coincidence of the first terms of the asymptotics (29.24) and (29.25) indicates that $r_0 = 1$, $\lambda_0 = c$, and the coincidence of the second terms implies that $\lambda_i - \lambda_0 \geq \varepsilon_0$.

§ 30. A Relation between the quantum and classical statistical physics

Consider a Bose or Fermi system in a finite volume Ω with Hamiltonian

$$H = -\int (\Delta a^*(x))a(x)\,dx + \frac{1}{2}\int v(x-y)a^*(x)a^*(y)a(x)a(y)\,dx\,dy,$$

where $x \in \mathbb{R}^3$ and the zero boundary conditions are assumed.

Denote by $\widehat{H}_n$ the restriction of H onto the n-particle subspace. In this section we will show that under the passage from the quantum system to the classical one there exists a limit of $(2\pi h)^{3n} \operatorname{sp} e^{-\beta \widehat{H}_n}$ equal to

$$\lim_{h\to 0}(2\pi h)^{3n} \operatorname{sp} e^{-\beta \widehat{H}_n} = \frac{1}{n!}\int\limits_{q_i\in\Omega} e^{-\beta H_n(p,q)}\,d^{3n}p\,d^{3n}q, \tag{30.1}$$

where $H_n(p,q) = \sum\limits_{k=1}^{n} p_k^2 + \sum\limits_{1\le i<j\le n} v(q_i - q_j)$ is the Hamiltonian function of the corresponding classical system and h is the Planck constant.

The operator $\widehat{H}_n$ is the restriction onto the subspace of symmetric (in the Bose case) or skew symmetric (in the Fermi case) functions of the operator

$$\widetilde{H}_n = -h^2 \sum_{i=1}^{n} \Delta_i + \sum_{1\le i<j\le n} v(x_i - x_j), \tag{30.2}$$

considered in $L_2(\Omega^n)$.

To prove (30.1) we will need the following digression.

30.1. The Weyl symbols. Let $\hat{p}_1, \dots, \hat{p}_N, \hat{q}_1, \dots, \hat{q}_N$ be self-adjoint operators with the canonical commutation relations

$$[\hat{p}_k, \hat{q}_j] = \frac{1}{i} h\delta_{kj}.$$

Let f be a function in $2N$ real variables, $p = (p_1, \dots, p_N)$ and $q = (q_1, \dots, q_N)$ represented as a Fourier transform

$$f(p,q) = \int e^{i\sum(\alpha_k p_k + \beta_k q_k)} \varphi(\alpha,\beta)\,d^N\alpha\,d^N\beta.$$

Following H.Weyl we assign to f the operator

$$\hat{f} = \int e^{i\sum(\alpha_k \hat{p}_k + \beta_k \hat{q}_k)} \psi(\alpha,\beta)\,d^N\alpha\,d^N\beta.$$

The function $f(p,q)$ is called *the Weyl symbol* of the operator $\hat{f}$. Assuming that the operators $\hat{p}_k$ and $\hat{q}_k$ are realized in a usual way in $L_2(\mathbb{R}^N)$ as

$$(\hat{p}_k g)(x) = \frac{h}{i}\frac{\partial g}{\partial x_k}, \quad (\hat{q}_k g)(x) = x_k g(x).$$

We find as the operator $g \in L_2(\mathbb{R}^N)$ acts on $\hat{f}$. We first consider $e^{i\sum(\alpha_k\hat{p}_k+\beta_k\hat{q}_k)}$. Let

$$g(t,x) = (e^{it\sum(\alpha_k\hat{p}_k+\beta_k\hat{q}_k)}g)(x).$$

Then

$$\frac{1}{i}\frac{\partial}{\partial t}g(t,x) = \sum(\alpha_k\hat{p}_k + \beta_k\hat{q}_k)g(t,x) = \sum(\alpha_k\frac{h}{i}\frac{\partial}{\partial x_k} + \beta_k x_k)g(t,x).$$

Solving this equation with the initial condition $g(0,x) = g(x)$, we find that $g(t,x)$:

$$g(t,x) = g(x+\alpha ht)e^{\sum\frac{i\beta_k t}{2}(2x_k+\alpha_k ht)},$$

thus

$$(\hat{f}g)(x) = \int \varphi(\alpha,\beta)e^{\sum\frac{i\beta_k}{2}(2x_k+\alpha_k h)}g(x+\alpha h)\,d\alpha\,d\beta = \\ = \frac{1}{h^N}\int \varphi\Big(\frac{y-x}{h},\beta\Big)e^{\sum\frac{i\beta}{2}(x_k+y_k)}g(y)\,dy\,d\beta.$$

In setting here

$$\varphi = \frac{1}{(2\pi)^{2N}}\int f(p,q)e^{-i\sum(\alpha_k p_k+\beta_k q_k)}\,dp\,dq$$

we finally find:

$$(\hat{f}g)(x) = \int K(x,y)g(y)\,dy,$$

where

$$K(x,y) = \frac{1}{(2\pi h)^N}\int f\Big(p,\frac{x+y}{2}\Big)e^{\frac{1}{ih}\sum p_k(y_k-x_k)}\,d^N p. \tag{30.3}$$

It is easy to invert expression (30.3):

$$f(p,q) = \int K\Big(q-\frac{\xi}{2},q+\frac{\xi}{2}\Big)e^{\frac{1}{ih}\sum p_k\xi_k}\,d^N\xi. \tag{30.4}$$

If $\hat{f} = \hat{p}_k^n$, then

$$K(x,y) = \left(\frac{h}{i}\right)^n \delta^{(n)}(x_k - y_k) \prod_{j \neq k} \delta(x_j - y_j).$$

It follows from (30.4) that the one symbol of $\hat{p}_k^n$ is equal to p_k^n and similarly if f is the operator of a multiplication by a function $v(x)$, then $K(x,y) = v(x)\delta(x-y)$ and it follows from (30.4) that in this case $f(p,q) = v(q)$. Therefore the Weyl symbol operator (30.2) considered in the whole space $L^2(R^{3n})$ is equal to

$$H_n(p,q) = \sum p_k^2 + \sum_{i<j} v(q_i - q_j), \tag{30.5}$$

i.e., coincides with the Hamiltonian function of the corresponding classical system. Expressions (30.3) and (30.4) imply that if $\hat{f} = \hat{f}_1 \cdot \hat{f}_2$ then for the corresponding Weyl symbols we have

$$f(p,q) = \frac{1}{(\pi h)^{2N}} \int f_1(p_1,q_1) f_2(p_2,q_2) e^{-\frac{2}{ih}\sum \begin{vmatrix} 1 & 1 & 1 \\ q_{1k} & q_{2k} & q_k \\ p_{1k} & p_{2k} & p_k \end{vmatrix}} \times \\ \times \prod dp_{1k}\, dp_{2k}\, dq_{1k}\, dq_{2k}. \tag{30.6}$$

For the trace of the operator $\hat{f}$ we have an expression in terms of its Weyl symbol [20]:

$$\operatorname{sp} \hat{f} = \frac{1}{(2\pi h)^N} \int f(p,q)\, d^N p\, d^N q. \tag{30.7}$$

From (30.6) and (30.7) we deduce that

$$\operatorname{sp} \hat{f}_1 \hat{f}_2 = \frac{1}{(2\pi h)^N} \int f_1(p,q) f_2(p,q)\, dp\, dq. \tag{30.8}$$

It follows from (30.6) that if at least one of the functions f_1 or f_2 is sufficiently smooth then

$$f(p,q) = f_1(p,q) f_2(p,q) + O(h). \tag{30.9}$$

[20] Formulas (30.6) and (30.7) are obtained from (30.3) and (30.4) together with

$$K(x,y) = \int K_1(x,y') K_2(y',y)\, dy', \quad \operatorname{sp} \hat{f} = \int K(x,x)\, dx,$$

where K_1, K_2, K are the kernels of the operators $\hat{f}_1$, $\hat{f}_2$, $\hat{f} = \hat{f}_1 \hat{f}_2$, respectively.

It is most easy to deduce (30.9) by means of Fourier transformation. Let φ, φ_1, φ_2 be the Fourier transforms of f, f_1, f_2 respectively. Then (30.6) implies that

$$\varphi(\alpha,\beta)=\int \varphi_1(\alpha-\alpha',\beta-\beta')\varphi_2(\alpha',\beta')e^{ih\left|\begin{smallmatrix}\alpha & \beta\\ \alpha' & \beta'\end{smallmatrix}\right|}\,d^N\alpha'\,d^N\beta'. \qquad (30.10)$$

If f_2 is sufficiently smooth then φ_2 rapidly decays. Therefore (30.10) implies that

$$\varphi(\alpha,\beta)=\int \varphi_1(\alpha-\alpha',\beta-\beta')\varphi_2(\alpha',\beta')\,d^N\alpha\,d^N\beta+O(h),$$

and passing from φ, φ_1, φ_2 to f, f_1, f_2 we get (30.9).

From expression (30.10) we can derive the complete asymptotic expansion of φ and therefore f with respect to powers of h and with a detailed description of the rest term. For our purposes however, this is not needed.

30.2. The asymptotics of the tracesp $e^{-\beta H_n}$. Let us extend the operator $e^{-\beta\overline{H}_n}$ from $L_2(\Omega^n)$ onto the whole space $L_2(\mathbb{R}^{3n})$ by zero in the orthogonal complement and denote by $\widehat{G}(\beta)$ the operator thus obtained. Denote by $G_h(\beta\,|\,p,q)$ the Weyl symbol of $\widehat{G}(\beta)$. Denote by T the operator of projecting from $L_2(\mathbb{R}^{3n})$ onto the subspace $L_2^s(\mathbb{R}^{3n})$ of symmetric (or skew symmetric) functions and let $T_h(p,q,)$ be the Weyl symbol of this operator. It follows from (30.8) that

$$\operatorname{sp} e^{-\beta\widehat{H}_n}=\operatorname{sp}\widehat{G}\widehat{T}=\frac{1}{(2\pi h)^{3n}}\int G_h(\beta\,|\,p,q)T_h(p,q)\,d^{3n}p\,d^{3n}q. \qquad (30.11)$$

Our nearest goal is to find the limit of the integral in (30.11) as $h\to 0$. As we will see the function $G_h(\beta\,|\,p,q)$ has a limit as $h\to 0$ and $T_h(p,q)$ has no limit. However, for any smooth with respect to p function $\alpha(p,q)$ the limit exists:

$$\lim_{h\to 0}\int \alpha(p,q)T_h(p,q)\,d^{3n}p\,d^{3n}q=\frac{1}{n!}\int \alpha(p,q)\,d^{3n}p\,d^{3n}q.$$

Let us find $G_0(\beta\,|\,p,q)$. For this denote by $\hat{p}$ the projection operator from $L_2(\mathbb{R}^{3n})$ onto $L_2(\Omega^n)$, where we consider $L_2(\Omega^n)$ embedded into $L_2(\mathbb{R}^{3n})$ in a "natural" way the functions from $L_2(\Omega^n)$ are extended onto the whole space $\mathbb{R}^{3n}$ by zero. The operator $\hat{p}$ is obviously the operator by multiplication by $\chi_\Omega(x_1)\cdot\ldots\cdot\chi_\Omega(x_n)$, where $\chi_\Omega(x)$ is the characteristic function of Ω. Therefore the Weyl symbol of $\hat{p}$ is equal to

$$p_\Omega(q_1,\ldots,q_n)=\chi_\Omega(q_1)\ldots\chi_\Omega(q_n).$$

Now we use the expression

$$\widehat{G}(\beta) = \lim_{n\to\infty} \left(\hat{p}e^{-\frac{\beta}{n}\widetilde{\widetilde{H}}_n}\hat{p}\right)^n, \tag{30.12}$$

where $\widetilde{\widetilde{H}}_n$ is the operator determined on the whole space $L_2(\mathbb{R}^{3n})$ by formula (30.2) [21].

Formula (30.9) implies that the symbol of the operator $e^{-\beta\widetilde{\widetilde{H}}_n}$ in the zero-th approximation with respect to h is equal to

$$e^{-\beta\left(\sum p_k^2 + \sum\limits_{i<j} v(q_i-q_j)\right)}.$$

Applying formula (30.9) once again we see using (30.12) that

$$G_0(\beta \mid p,q) = e^{-\beta\left(\sum p_k^2 + \sum\limits_{i<j} v(q_i-q_j)\right)} p_\Omega(q_1,\dots,q_n). \tag{30.13}$$

Let us pass to $T_h(p,q)$. Observe that

$$\widehat{T} = \frac{1}{n!}\sum \varepsilon(g)\widehat{T}(g),$$

where $g = \begin{pmatrix} 1 & \dots & n \\ 1' & \dots & n' \end{pmatrix}$ is a permutation and

$$(\widehat{T}(g)f)(x_1,\dots,x_n) = f(x_{1'},\dots,x_{n'}),$$

where

$$\varepsilon(g) = \begin{cases} 1 & \text{in the Bose case,} \\ \operatorname{sgn}(g) & \text{in the Fermi case.} \end{cases}$$

Let us find the symbol $T_h(g \mid p,q)$ of the operator T_g. Assuming that g is not the identical permutation represent e as a product of independent cycles. Let for definiteness sake $g = g_1 g_2 \dots$, where $g_1 = (1,\dots,n_1)$,

[21] Roughly speaking, expression (30.12) is due to the fact that $\widetilde{H}_n = \hat{p}\widetilde{\widetilde{H}}_n\hat{p}$. Therefore

$$\hat{p}e^{-\frac{\beta}{n}\widetilde{\widetilde{H}}_n}\hat{p} = \hat{p}\Big(I - \frac{\beta}{n}\hat{p}\widetilde{\widetilde{H}}_n\hat{p} + o\Big(\frac{1}{n^2}\Big)\Big) = \hat{p}\Big(I - \frac{\beta}{n}\widetilde{H}_n + o\Big(\frac{1}{n^2}\Big)\Big),$$

and in $L_2(\Omega^n)$, we have

$$\lim_{n\to\infty}(\hat{p}e^{-\frac{\beta}{n}\widetilde{\widetilde{H}}_n}\hat{p})^n = e^{-\beta\hat{p}\widetilde{\widetilde{H}}_n\hat{p}} = e^{-\beta\widetilde{H}_n}.$$

The rigorous proof (see [B3]) consists in an exposition of this argument. It is essential here that the operator H (together with $\widetilde{H}_n$ has zero boundary values).

$g_2 = (n_1+1, \dots, n_1+n_2), \dots$ The kernel of $\widehat{T}(g_1)$ is equal to

$$Kg_1 = \delta(x_1 - y_2)\dots\delta(x_{n_1-1} - y_{n_1})\delta(x_{n_1} - y_1)\delta(x_{n_1+1} - y_{n_1+1})\dots\delta(x_n - y_n).$$

Things to (30.4) the symbol $T_h(g_1 \mid p,q)$ of the corresponding operator is equal to

$$T_h(g_1 \mid p,q) = \int \delta\Big(q_1 - q_2 - \frac{\xi_1+\xi_2}{2}\Big)\delta\Big(q_2 - q_3 - \frac{\xi_2+\xi_3}{2}\Big)\dots$$
$$\dots\delta\Big(q_{n_1} - q_1 - \frac{\xi_{n_1}+\xi_1}{2}\Big)e^{\frac{1}{ih}\sum(p_k,\xi_k)}\,d^3\xi_1\dots d^3\xi_{n_1}. \quad (30.14)$$

Obviously $T_h(g \mid p,q)$ is equal to the product of symbols corresponding to the independent cycles:

$$T_h(g \mid p,q) = T_h(g_1 \mid p,q)T_h(g_2 \mid p,q)\dots$$

The symbols (30.14) behave somewhat differently depending on the parity of n_1. In order to simplify our presentation we consider the cases $n_1 = 2$ and $n_1 = 3$. For $n_1 = 2$ we have

$$T_h(g \mid p,q) = \int \delta\Big(q_1 - q_2 - \frac{\xi_1+\xi_2}{2}\Big)\delta\Big(q_2 - q_1 - \frac{\xi_1+\xi_2}{2}\Big)\times$$
$$\times\, e^{\frac{1}{ih}((p_1,\xi_1)+(p_2,\xi_2))}\,d^3\xi_1\,d^3\xi_2 = (2\pi h)^3\delta(p_1-p_2)\delta(q_1-q_2),$$

and for $n_1 = 3$ we have

$$T_h(g \mid p,q) = \int \delta\Big(q_1 - q_2 - \frac{\xi_1+\xi_2}{2}\Big)\delta\Big(q_2 - q_3 - \frac{\xi_2+\xi_3}{2}\Big)\times$$
$$\times\,\delta\Big(q_3 - q_1 - \frac{\xi_3+\xi_2}{2}\Big)e^{\frac{1}{ih}((p_1,\xi_1)+(p_2,\xi_2)+(p_3,\xi_3))}\,d^3\xi_1\,d^3\xi_2\,d^3\xi_3 =$$
$$= e^{\frac{2i}{h}[p_1(q_3-q_2)+p_2(q_1-q_3)+p_3(q_2-q_1)]}. \quad (30.15)$$

The function (30.15) oscillates very fast as $h \to 0$ and the integral of the product of it by any smooth with respect to p function tends to zero [22]. Therefore if $g \neq e$, then $\int G_0(\beta \mid p,q)T_h(g \mid p,q)\,d^{3n}p\,d^{3n}q \to 0$.

[22] We will have to integrate the product of the function (30.15) by $G_0 = e^{-\beta\sum p_i^2}\psi(q)$. Integrating first with respect to p_i we find

$$I = \int G_0(\beta \mid p,q)T_h(g \mid p,q)\,d^{3n}p\,d^{3n}q = h^2\frac{1}{h^2}\int e^{-\frac{\beta}{h}[(q_3-q_2)^2+(q_1-q_3)^2+(q_2-q_1)^2]}\psi(q)\,d^3q$$

and since $\lim\limits_{h\to 0}\dfrac{1}{h^2}e^{-\frac{\beta}{h}[(q_3-q_2)^2+(q_1-q_3)^2+(q_2-q_1)^2]} = c\delta(q_3-q_2)\delta(q_1-q_3)$, we have $I = O(h^2)$.

Since $T_h(e \mid p, q) = 1$ we finally get

$$\int G_0(\beta \mid p, q) T_h(p, q)\, d^{3n}p\, d^{3n}q = \frac{1}{n!} \int G_0(\beta \mid p, q)\, d^{3n}p\, d^{3n}q + o(1),$$

and therefore

$$\operatorname{sp} e^{-\beta H_n} = \frac{1}{(2\pi h)^{3n}} \frac{1}{n!} \int\limits_{g_i \in \Omega} e^{-\beta H_n(p,q)}\, d^{3n}p\, d^{3n}(1 + o(1)),$$

where $H_n(p, q) = \sum\limits_{i=1}^{n} p_k^2 + \sum\limits_{1 \le i < j \le n} v(q_i - q_j)$ is the Hamiltonian function of the classical system into which turns the considered quantum one as $h \to 0$.

APPENDIX 1. **Semi-Invariants in the classical statistical physics**

Notations in this appendix differ from those in the main text: The correlation functions of the grand canonical ensemble are denoted by ρ_n, the activity by z and ζ denotes an auxiliary variable not interpreted in thermodynamical terms.

The only way to compute correlation functions known at the moment is to consider their power series expansion in powers of $z = e^{-\beta\mu}$. The Bogolyubov—Khatset—Ruelle theorem ([BoH], [R]) guarantees the convergence of the series for $|z|$ small. However, the common term of this series is rather difficult to express explicitly. It turns out that closely related with correlation functions are It turns out that closely related to correlation functions are the so-called semi-invariants for which such a expansion is contrariwise quite elegant.

A1.1. Definition of semi-invariants. Consider the functional $K(\zeta, z \mid \alpha)$

$$K(\zeta, z \mid \alpha) = 1 + \sum_1^\infty \frac{\zeta^n}{n!} \int \rho_n(x_1, \dots, x_n \mid z)\alpha(x_1) \dots \alpha(x_n)\, d^{3n}x, \quad \text{(AA1.1)}$$

where ρ_n is the n-th correlation function of the grand canonical ensemble and $\alpha(x)$ an integrable function. Expand $\ln K(\zeta, z \mid \alpha)$ into the power series in ζ:

$$\ln K(\zeta, z \mid \alpha) = \sum_1^\infty \frac{\zeta^n}{n!} \int \sigma_n(x_1, \dots, x_n \mid z)\alpha(x_1) \dots \alpha(x_n)\, d^{3n}x. \quad \text{(AA1.2)}$$

We may assume the functions $\sigma_n(x_1, \dots, x_n \mid z)$ symmetric with respect to $x_1, \dots, x_n$. Under this extra symmetry condition they are uniquely defined by the functional $\ln K(\zeta, z \mid \alpha)$ and said to be semi-invariants.

The first three semi-invariants are expressed in terms of correlation functions as follows:

$$\begin{aligned}
&\sigma_1(x) = \rho_1(x),\\
&\sigma_2(x_1, x_2) = \rho_2(x_1, x_2) - \rho_1(x_1)\rho_1(x_2),\\
&\sigma_3(x_1, x_2, x_3) = \rho_3(x_1, x_2, x_3) - \rho_1(x_3)\rho_2(x_1, x_2) - \rho_1(x_2)\rho_2(x_1, x_3) -\\
&\qquad\qquad \rho_1(x_1)\rho_2(x_2, x_3) + 2\rho_1(x_1)\rho_1(x_2)\rho_1(x_3). \qquad \text{(AA1.3)}
\end{aligned}$$

In what follows we will need the differential equations with respect to activity for σ_n. Preliminarily let us find analogous equations for ρ_n.

A1.2. Differential equations with respect to activity for correlation functions and semi-invariants. Consider the n-th correlation function

$$\rho_n(x_1,\dots,x_n)=\Xi^{-1}\sum_{p=0}^{\infty}\frac{z^{n+p}}{p!}\int e^{-\beta u_{n+p}(x_1,\dots,x_{n+p})}\,d^3x_{n+1}\dots\,d^3x_{n+p}. \tag{AA1.4}$$

Everywhere unless specified to the contrary we assume that x_i runs a domain Ω of finite volume. In what follows we will be only interested in the pairwise interactions where $u_k(x_1,\dots,x_k)=\sum\limits_{1\le i<j\le k}u(x_i-x_j)$. The deduction of differential equations for ρ_n in what follows is however true for any functions $u_k(x_1,\dots,x_k)$ not only for the case of the pairwise interaction.

Differentiating (AA1.4) with respect to z we get

$$\frac{\partial\rho_n}{\partial z}=-\Xi^{-2}\frac{\partial\Xi}{\partial z}\sum_{p=0}^{\infty}\frac{z^{n+p}}{p!}\int e^{-\beta u_{n+p}}\,d^3x_{n+1}\dots\,d^3x_{n+p}+$$

$$n\Xi^{-1}\sum_{p=0}^{\infty}\frac{z^{n+p-1}}{p!}\int e^{-\beta u_{n+p}}\,d^3x_{n+1}+\Xi^{-1}\sum_{p=0}^{\infty}\frac{z^{n+p-1}}{(p-1)!}\int e^{-\beta u_{n+p}}\,d^3x_{n+1}. \tag{AA1.5}$$

Observe that

$$\Xi^{-1}\frac{d\Xi}{dz}=z^{-1}\int\rho_1(x)\,dx.$$

Comparing the second and third summands in the right-hand side of (AA1.5) with the definition of correlation function (AA1.4) we see that they are equal to $nz^{-1}\rho_n$ and $z^{-1}\int\rho_{n+1}\,d^3x_{n+1}$ respectively. Thus for the correlation function (AA1.4) we get an equation

$$z\frac{\partial\rho_n}{\partial z}=n\rho_n+\int[\rho_{n+1}(x_1,\dots,x_{n+1})-\rho_n(x_1,\dots,x_n)\rho_1(x_{n+1})]\,d^3x_{n+1}. \tag{AA1.6}$$

In the works of Bogolyubov-Hatzet and Ruelle (see section 13) it is proved that if the potentials u_n satisfy $\sum\limits_{y_i}u_n(x,y_1,\dots,y_{n-1})>-B$, where B does not depend on n, $0<B<\infty$ and $|z|<\varkappa$, where $\varkappa=,\varkappa(B,\beta)>0$, then the correlation functions ρ_n exist are analytic with respect to z and have a limit as $|\Omega|\to\infty$.

In what follows this result is referred to as *the BHR theorem* (see. § 13). From the BHR theorem the existence of the limit in the left-hand side of (AA1.6) as $|\Omega|\to\infty$ follows. Therefore the integral in the right-hand side

of (AA1.6) has a similar limit. The existence of this integral in the limit of the infinite volume is one of the forms of *the principle of weakening of correlations*. Let us pass to the deduction of differential equations for semi-invariants. Differentiating (AA1.1) with respect to z and taking (AA1.6) into account we see that

$$z\frac{\partial K}{\partial z} = \sum \frac{\zeta^n}{n!} \int z\frac{\partial}{\partial z}\rho_n \alpha(x)\dots\alpha(x_n)\, d^{3n}x =$$
$$= \sum \frac{\zeta^n}{n!} \int \left(n\rho_n + \int (\rho_{n+1} - \rho_n\rho_1)\, d^3x_{n+1} \right) \alpha(x_1)\dots\alpha(x_n)\, d^{3n}x =$$
$$= \zeta\frac{\partial K}{\partial z} + \int \Big(\frac{1}{\zeta}\frac{\delta_K}{\delta\alpha(x)} - K\rho_1(x) \Big) d^3x.$$

Multiplying both parts by K^{-1} we get

$$z\frac{\partial}{\partial z}\ln K = \zeta\frac{\partial}{\partial\zeta}\ln K + \int \Big(\frac{1}{\zeta}\frac{\delta \ln K}{\delta\alpha(x)} - \rho_1(x) \Big) d^3x.$$

Using the expression (AA1.2) for $\ln K$ we finally obtain

$$z\frac{\partial}{\partial z}\sigma_n(x_1,\dots,x_n) = n\sigma_n(x_1,\dots,x_n) + \int \sigma_{n+1}(x_1,\dots,x_{n+1})\, d^2x_{n+1}. \tag{AA1.7}$$

The initial conditions for this equation are obtained as follows: Observe first of all that (AA1.4) implies $\lim\limits_{z\to 0} z^{-n}\rho_n = e^{-\beta u_n}$. This implies that

$$\lim_{z\to 0} z^{-n}\sigma_n(x_1,\dots,x_n) = \varphi_n(x_1,\dots,x_n), \tag{AA1.8}$$

where φ_n is the function related with $e^{-\beta u_n}$ by the same formulas as the function σ_n is related to ρ_n:

$$\varphi_1 = 1,$$
$$\varphi_2(x_1,x_2) = e^{-\beta u_2(x_1,x_2)} - 1,$$
$$\varphi_3(x_1,x_2,x_3) = e^{-\beta u_3(x_1,x_2,x_3)} - e^{-\beta u_2(x_1,x_2)} - e^{-\beta u_2(x_1,x_3)} - e^{-\beta u_2(x_2,x_3)} + 2,$$

And so on. The relations (AA1.8) serve as the initial conditions for (AA1.7).

A1.3. Solving equations for semi-invariants. Set

$$\sigma_n = z^n\tilde{\sigma}_n.$$

From (AA1.7) we deduce differential equations for $\tilde{\sigma}_n$:

$$\frac{\partial}{\partial z}\tilde{\sigma}_n(x_1,\dots,x_n \mid z) = \int \tilde{\sigma}_{n+1}(x_1,\dots,x_{n+1} \mid z)\, d^3x_{n+1}. \tag{AA1.9}$$

The initial conditions for (AA1.9) follow from (AA1.8):

$$\tilde{\sigma}_n(x_1, \dots, x_n \mid 0) = \varphi_n(x_1, \dots, x_n). \tag{AA1.10}$$

Equations (AA1.9) and (AA1.10) imply

$$\frac{\partial^k}{\partial z^k}\tilde{\sigma}_n(x_1, \dots, x_n \mid z)_{z=0} = \int \varphi_{n+k}(x_1, \dots, x_{n+k})\, d^3x_{n+1} \dots\ d^3x_{n+k}.$$

Therefore

$$\tilde{\sigma}_n = \varphi_n + \sum_1 \frac{z^k}{k!} \int \varphi_{n+k}\, d^3x_{n+1} \dots\ d^3x_{n+k} \tag{AA1.11}$$

and finally

$$\sigma_n(x_1, \dots, x_n \mid z) = z^n \varphi_n(x_1, \dots, x_n \mid z) + \\ + \sum_1 \frac{z^{n+k}}{k!} \int \varphi_{n+k}(x_1, \dots, x_{n+k} \mid z)\, d^3x_{n+1} \dots\ d^3x_{n+k}. \tag{AA1.12}$$

It is easy to deduce from (AA1.12) the expression of the thermodynamical potential in the power series. Indeed, $\sigma_1 = \rho_1$, and on the other hand, $\rho_1 = z\dfrac{\partial \Phi}{\partial z}$, where Φ is the thermodynamic potential. Taking into account that $\Phi = 0$ for $z = 0$ we get

$$\Phi = \sum_1^\infty \frac{z^n}{n!} \int \varphi_n(x_1, \dots, x_n)\, d^3x_1 \dots\ d^3x_{n-1}.$$

In the case of pairwise potential we can deduce from (AA1.12) similar relations between the correlation functions expressing the highest correlation functions in terms of the first two ones. These relations are power series expansion in powers of ρ_1 that is they only make sense for small densities, [B].

Let us give the explicit expressions for the first terms of the expansion for the third correlation function. Set

$$r_3(x_1, x_2, x_3) = \frac{\rho_3(x_1, x_2, x_3)}{\rho_1(x_1)\rho_1(x_2)\rho_1(x_3)}, \quad S(x_1, x_2) = \frac{\rho_2(x_1, x_2)}{\rho_1(x_1)\rho_1(x_2)} - 1,$$

In the limit of infinite volume we get

$$\rho_1(x) = \rho, \quad S(x_1, x_2) = S(x_1 - x_2),$$

and

$$r_3(x_1,x_2,x_3) = S(x_1-x_2)S(x_1-x_3)S(x_2-x_3)+ \\ + \rho(S(x_1-x_2)S(x_1-x_3)S(x_2-x_3) + S(x_1-x_2)S(x_1-x_3)+ \\ + S(x_1-x_2)S(x_2-x_3) + S(x_1-x_3)S(x_2-x_3) + S(x_1-x_2)+ \\ + S(x_1-x_3) + S(x_2-x_3) + 1) \int S(x_1-y)S(x_2-y)S(x_3-y)\,dy.$$

At $\rho = 0$ we obtain the expression which was first used by Kirkwood who called it *the superpositional approximation*. Using this approximation together with equations for correlation functions we can obtain a non-linear integral equation to determine $S(x_1 - x_2)$ which should be valid for small values of densities. For more details see the textbook by Landau and Lifshits [LL].

APPENDIX 2. **Continual Integrals and the Green Function**

The Green functions are a powerful tool for an heuristic study of quantum statistical ensembles. In this appendix we give the definition deduce the main equations and prove (in an heuristic sense) with their help the theorem on existence of thermodynamic potential and correlation functions.

A2.1. The Wick symbols. The Bose case. Let the operator A in the Fock space be represented as a normal series

$$\widehat{A} = \sum_{m,n} |\Omega|^{-\frac{m+n}{2}} \sum_{p_i,q_j} A_{m,n}(p_1,\dots,p_m \mid q_1,\dots,q_n)\times \\ \times a^*(p_1)\dots a^*(p_m)a(q_1)\dots a(q_n), \quad \text{(AA2.1)}$$

where $[a(p), a^*(q)] = \delta_{p,q}$ and p_i, q_j runs over a lattice with the volume of the unit parallelepiped equal to $|\Omega|^{-1}$. We assume that the functions $A_{m,n}$ are symmetric separately with respect to the first and second group of arguments.

To $\widehat{A}$ assign the functional $A(\overline{z}, z)$ referred to *the Wick symbol* of $\widehat{A}$:

$$A(\overline{z},z) = \sum_{m,n} |\Omega|^{-\frac{m+n}{2}} \sum_{p_i,q_j} A_{m,n}(p_1,\dots,p_m \mid q_1,\dots,q_n)\times \\ \times \overline{z}(p_1)\dots\overline{z}(p_m)z(q_1)\dots z(q_n), \quad \text{(AA2.2)}$$

where $z(p)$ is a square integrable function and $\sum |z(p)|^2 < \infty$. Obviously one can recover from $A(\overline{z}, z)$ the coefficient functions $A_{m,n}$ and therefore the operator $\widehat{A}$ itself.

For us the expressions that relate the symbol of the product of the operators with the symbols of the initial operators and the formula are essential as well as the expression for the trace of the operator. These expressions are: If $\widehat{A} = \widehat{B}\widehat{C}$, then

$$A(\overline{z}, z) = \int B(\overline{z}, v)C(\overline{v}, z)e^{-\sum(\overline{z}(p)-\overline{v}(p))(z(p)-v(p))} \prod d\overline{v}\, dv. \qquad \text{(AA2.3)}$$

In particular, if $\widehat{B} = a^*(p)$ or $\widehat{C} = a(p)$ then

$$A(\overline{z}, z) = \overline{z}(p)C(\overline{z}, z) \text{ or respectively } A(\overline{z}, z) = B(\overline{z}, z)z(p), \qquad \text{(AA2.3}')$$

$$\operatorname{sp} \widehat{A} = \int A(\overline{z}, z) \prod dz\, d\overline{z}. \qquad \text{(AA2.4)}$$

The integrals in the right-hand sides of (AA2.5) and (AA2.4) are iterated ones with the infinite number of iterations. They should be understood as the limits of those with finitely many iterations

$$\prod dv\, d\overline{v} = \prod_p \frac{dv_1(p)\, dv_2(p)}{\pi}, \quad \text{where} \quad v_1(p) = \operatorname{Re} v(p), v_2(p) = \operatorname{Im} v(p).$$

The deduction of expressions (AA2.2) and (AA2.3) is not difficult, for this deduction see [B8].

A2.2. The Wick symbol. The Fermi case. Denote by G the Grassmann algebra whose generators are $z(p)$ and $\overline{z}(p)$, where p runs over the nodes of the lattice with the volume of the unit parallelepiped equal to $|\Omega|$. The elements of G can be expressed as

$$f(\overline{z}, z) = \sum_{m,n} \sum_{p_i, q_j} f_{m,n}(p_1, \dots, p_m \mid q_1, \dots, q_n)\overline{z}(p_1) \dots \overline{z}(p_m)z(q_1) \dots z(q_n).$$

The sum of such elements is obviously defined whereas the product is determined with the help of the commutation relations between the generators:

$$\overline{z}(p)z(q) + z(q)\overline{z}(p) = \overline{z}(p)\overline{z}(q) + \overline{z}(q)\overline{z}(p) = z(p)z(q) + z(q)z(p) = 0.$$

Without affecting the element f we can skew symmetrize the functions $f_{m,n}$ separately with respect to the first and second groups of arguments. In what follows they will always be assumed to be skew symmetric. Obviously under this condition they are uniquely defined by f.

On the Grassmann algebra, there are defined the derivatives and the integral. They are linear operators in G and therefore it suffices to define them on the generators. Let $\xi(p) = z(p)$ or $\overline{z}(p)$. We set

$$\frac{\partial}{\partial \xi(q)} \xi(p_1) \dots \xi(p_n) = \delta_{p_1 - q} \xi(p_2) \dots \xi(p_n) - \delta_{p_2 - q} \xi(p_1)\xi(p_3) \dots \xi(p_n) + \dots$$

We define the integral by setting

$$\int \xi(p)\,\mathrm{vol}(p) = 1, \quad \int \mathrm{vol}(p) = 0.$$

The iterated integral is understood as the repeated one [23)]. The integral with infinitely many iterations that will be encountered in what follows is by definition the limit of those with finitely many iterations. The following formula of integration by parts holds:

$$\int f(\xi)\Big(\frac{\partial}{\partial\xi(p)}g(\xi)\Big)\prod \mathrm{vol}(p) = (-1)^{p(f)}\int \Big(\frac{\partial}{\partial\xi(p)f(\xi)}f(\xi)\Big)g(\xi)\prod d\xi(p), \tag{AA2.5}$$

where $p(f)$ — the parity of f — is equal to the number of indeterminates in the monomial f. In the Fermi case to every operator that can be expressed as the normal series (AA2.1) we assign its symbol (AA2.2) which is an element of the Grassmann algebra G. Unlike the Bose case the coefficients $A_{m,n}$ are now skew symmetric with respect to the first and the second groups of arguments. The formula which expresses the symbol A of the operator $\widehat{A} = \widehat{B}\widehat{C}$ in terms of the symbols B, C of the operators $\widehat{B}$, $\widehat{C}$ has the same form as (AA2.3) and ($AA2.3'$) whereas the formula for the trace differs from (AA2.4):

$$\mathrm{sp}\,\widehat{A} = \int A(\overline{z}, z)e^{2\sum \overline{z}(p)z(p)}\prod dz(p)\,d\overline{z}(p). \tag{AA2.6}$$

For details see [B8].

A2.3. The expression for the statistical sum in the form of the continual integral. In this section we give an exposition for the Bose and Fermi cases simultaneously. Let H be the operator of the energy of the system. For simplicity assume it to be equal to

$$H = \sum(\omega(p) - \mu)a^*(p)a(p) + \\ + \frac{1}{2}\frac{g}{|\Omega|^2}\sum v(p_1, p_2 \mid q_1, q_2)a^*(p_1)a^*(p_2)a(q_1)a(q_2), \tag{AA2.7}$$

[23)] It is not difficult to see that the *Berezin integral* AA2.5 of a given function f is equal to the coefficient of the highest term of f in the fixed "coordinates". (The reader knows, of course, that one never integrates functions, but only densities; but when a density or a volume element is fixed, we say, by abuse of language that we "integrate functions.) When, together with odd indeterminates, one encounters even indeterminates, the integral ceases to be a differential operator and the corresponding theory (developed, mainly, by V. Shander) is rather complicated, see [SoS]. — *Ed.*.

where

$$v(p_1,p_2\mid q_1,q_2)=W(p_1,p_2\mid q_1,q_2)\delta_\Omega(p_1+p_2-q_1-q_2),$$
$$\delta_\Omega(p)=\begin{cases}|\Omega| & \text{as} \quad p=0,\\ 0 & \text{as} \quad p\neq 0.\end{cases}$$

As we will see that specific form of H is irrelevant and the constructions given in what follows obviously apply to the case of an arbitrary operator H admitting a representation in the normal form. For the existence of the thermodynamic potential (see § 5), it is essential that H is translationally invariant. A manifestation of this circumstance is the presence of the δ_Ω-function as a factor of $v(p_1,p_2\mid q_1,q_2)$.

Denote by $G(\beta\mid\overline{z},z)$ the symbol of the operator $e^{-\beta H}$ and find $G(\beta\mid\overline{z},z)$ with accuracy up to $O(\beta^2)$. Observe that $e^{-\beta H}=1-\beta H+\beta^2R_1$ and therefore

$$G=1-\beta H(\overline{z},z)+\beta^2r_1(\beta\mid\overline{z},z)=e^{-\beta H(\overline{z},z)}+\beta^2r(\beta\mid\overline{z},z), \qquad \text{(AA2.8)}$$

where r_1 is the symbol of the operator R_1 and

$$r=r_1+\frac{1}{\beta^2}(1-\beta H(\overline{z},z)-e^{-\beta H(\overline{z},z)}).$$

Accordingly

$$e^{-\beta H}=u(\beta)+\beta^2R(\beta), \qquad \text{(AA2.9)}$$

where $u(\beta)$ and $R(\beta)$ are the operators whose symbols are $e^{-\beta H(\overline{z},z)}$ and $r(\beta\mid\overline{z},z)$ respectively.

Using (AA2.9) we get

$$e^{-\beta H}=\left(e^{-\frac{\beta}{N}H}\right)^N=\left(u\Big(\frac{\beta}{N}\Big)+\frac{\beta^2}{N^2}R\Big(\frac{\beta}{N}\Big)\right)^N.$$

The summand $N\to\infty$ does not contribute in the limit as $\frac{\beta^2}{N^2}R\Big(\frac{\beta}{N}\Big)$ and therefore we finally get

$$e^{-\beta H}=\lim_{N\to\infty}\left(u\Big(\frac{\beta}{N}\Big)\right)^N.$$

Denote by $G_N(\beta\mid\overline{z},z)$ the symbol of the operator $\left(u\Big(\frac{\beta}{N}\Big)\right)^N$ and let $\Xi_{N,\Omega}=\mathrm{sp}\left(u\Big(\frac{\beta}{N}\Big)\right)^N$. Applying repeatedly formulas (AA2.3) and either

(AA2.4) or (AA2.6) we obtain the following expressions for G_N and $\Xi_{N,\Omega}$

$$G_N(\beta \mid \overline{z}, z) = \int e^{-\frac{\beta}{N}\sum_0^{N-1} H(\overline{z}_k, z_{k+1}) + \sum_0^{N-1} (\overline{z}_k - \overline{z}_{k+1}) z_{k+1}} \prod_1^{N-1} d\overline{z}_k \, dz_k,$$

where $\overline{z}_0 = \overline{z}_N = \overline{z}, \quad z_0 = z_N = z, \quad z_k = z_k(p), \quad \overline{z}_k = \overline{z}_k(p);$

$$\Xi_{N,\Omega} = \int e^{-\frac{\beta}{N}\sum_0^{N-1} H(\overline{z}_k, z_{k+1}) + \sum_0^{N-1} (\overline{z}_k - \overline{z}_{k+1}) z_{k+1}} \prod_1^{N} d\overline{z}_k \, dz_k,$$

where $z_0 = \pm z_N, \quad \overline{z}_0 = \pm \overline{z}_N.$

(AA2.10)

Here the upper sign corresponds to the Bose case and the lower sign of the Fermi case. In formulas (AA2.7), (AA2.8) we always assume that $z_k = z_k(p)$ and $\overline{z}_k = \overline{z}_k(p)$. Expression (AA2.10) is the desired one. It holds for any operator H.

A2.4. The Green functions. Consider the function

$$\rho_{m,n}^{(N,\Omega)}(k_1, p_1; \ldots; k_m, p_m \mid l_1, q_1; \ldots; l_n, q_n) =$$
$$= |\Omega|^{\frac{m+n}{2}} \Xi_{N,\Omega}^{-1} \int \overline{z}_{k_1}(p_1) \ldots \overline{z}_{k_m}(p_m) z_{l_1}(q_1) \ldots z_{l_n}(q_n) \times$$
$$\times e^{-\frac{\beta}{N}\sum_{k=0}^{N-1} H(\overline{z}_k, z_{k+1}) + \sum_0^{N-1} (\overline{z}_k - \overline{z}_{k+1}) z_{k+1}} \prod_{k=1}^{N} d\overline{z}_k \, dz_k. \quad \text{(AA2.11)}$$

The Green function (*pre-limit temperature*) (is the function

$$\rho_{m,n}^{(\Omega)}(t_1, p_1; \ldots; t_m, p_m \mid s_1, q_1; \ldots; s_n, q_n) =$$
$$= \lim_{N\to\infty} \rho_{m,n}^{(N,\Omega)}(k_1, p_1; \ldots; k_m, p_m \mid l_1, q_1; \ldots; l_n, q_n),$$

where $t_i = \lim\limits_{N\to\infty} \beta \dfrac{k_i}{N}$, $s_i = \lim\limits_{N\to\infty} \beta \dfrac{l_i}{N}$. If $s_i \neq t_j$ the functions $\rho_{m,n}(\Omega)$ can be defined without using integral representation. Let $\tau_i = s_i$ or t_i, where $\tau_1 \leq \tau_2 \leq \ldots \leq \tau_{m+n}$ and $\alpha_i = \begin{cases} a^*(p_i), & \text{if } \tau_i = t_i, \\ a(q_i), & \text{if } \tau_i = s_i. \end{cases}$ Then

$$\rho_{m,n}^{(\Omega)}(t_1, p_1; \ldots; t_m, p_m \mid s_1, q_1; \ldots; s_n, q_n) =$$
$$= \Xi^{-1} \operatorname{sp}(e^{-\beta\tau_1 H} \alpha_1 e^{-\beta(\tau_2 - \tau_1)H} \alpha_2 \ldots e^{-\beta(\tau_{m+n} - \tau_{m+n-1})H} \alpha_{m+n} e^{-(\beta - \tau_{m+n})H}).$$

(AA2.11′)

In particular,

$$\rho^{(\Omega)}_{m,n}(0,p_1;\dots;0,p_m\mid\beta,q_1;\dots;\beta,q_n)= \\ =\Xi^{-1}\operatorname{sp}(a^*(p_1)\dots a^*(p_m)e^{-\beta H}a(q_1)\dots a(q_n)).$$

It is easy to deduce from formulas (AA2.3), (AA2.3′) for the product of operators that (AA2.11′) coincides with the above definition. Now observe that the translational invariance of H implies that

$$\rho^{(N,\Omega)}_{m,n}(k_1,p_1;\dots;k_m,p_m\mid l_1,q_1;\dots;l_n,q_n)= \\ =\delta_\Omega(p_1+\dots+p_m-q_1-\dots-q_n)\sigma^{(N,\Omega)}_{m,n}(k_1,p_1;\dots\mid\dots;l_n,q_n). \tag{AA2.12}$$

To prove this let us perform the change of variables in the integral (AA2.11):

$$z_k(p)\mapsto e^{i(p,\xi)}z_k(p),\quad \overline{z}_k(p)\mapsto e^{-i(p,\xi)}\overline{z}_k(p),$$

where ξ is an arbitrary vector. Since H is translation-invariant i.e., $V(p_1,p_2\mid q_1,q_2)=\delta_\Omega(p_1+p_2-q_1-q_2)W(p_1,p_2\mid q_1,q_2)$ the exponent does not vary under this change. Since the Jacobian of this change of variables is equal to 1 we get the identity

$$\rho^{(N,\Omega)}_{m,n}(k_1,p_1;\dots\mid\dots;l_n,q_n)= \\ =e^{-i(p_1+\dots+p_m-q_1-\dots-q_n,\xi)}\rho^{(N,\Omega)}_{m,n}(k_1,p_1;\dots\mid\dots;l_n,q_n).$$

Obviously this identity is only possible if $\rho^{(N,\Omega)}_{m,n}$ is of the form (AA2.12).

If H preserves the number of particles in particular if it is of the form (AA2.7) it is easy to verify [24] that $\rho^{(N,\Omega)}_{m,n}=0$ for $m\neq n$. In this case we will briefly denote the function $\rho^{(N,\Omega)}_{n,n}$ by $\rho^{(N,\Omega)}_n$.

Let us deduce equations for the Green functions. For definiteness sake consider the Bose case. Observe that

$$z_{l_n}(q_n)e^{-\sum\overline{z}_{k+1}(p)z_{k+1}(p)}=-\frac{\partial}{\partial\overline{z}_{l_n}(q_n)}e^{-\sum\overline{z}_{k+1}(p)z_{k+1}(p)}.$$

[24] Indeed, let us make the change of variables $z_k(p)\mapsto e^{i\theta}z_k(p)$, $\overline{z}_k(p)\mapsto e^{-i\theta}\overline{z}_k(p)$. This does not affect the exponent and the product whereas the pre-exponential factor and therefore the whole integral will acquire the factor $e^{i(n-m)\theta}$. Since the integral cannot vary under the change of variables it follows that $\rho^{(N,\Omega)}_{m,n}=0$ for $m\neq n$.

Integrating this by parts and taking into account that H is of the form (AA2.7) we get

$$|\Omega|^{-n}\rho_n^{(N,\Omega)}(k_1,p_1;\dots;k_n,p_n\mid l_1,q_1;\dots;l_n,q_n)=$$
$$=\Xi_{N,\Omega}^{-1}\int\frac{\partial}{\partial\overline{z}_{l_n}(q_n)}\Big(\overline{z}_{k_1}(p_1)\dots\overline{z}_{k_n}(p_n)\overline{z}_{l_1}(q_1)\dots\overline{z}_{l_{n-1}}(q_{n-1})\times$$
$$\times e^{-\frac{\beta}{N}\sum H(\overline{z}_k,z_{k+1})+\sum\overline{z}_kz_{k+1}}\Big)e^{-\sum\overline{z}_{k+1}z_{k+1}}\prod d\overline{z}\,dz=$$
$$=|\Omega|^{-n}\rho_n^{(N,\Omega)}(k_1,p_1;\dots;k_n,p_n\mid l_1,q_1;\dots;l_{n-1},q_{n-1};l_n+1,q_n)-$$
$$-|\Omega|^{-n}\frac{\beta}{N}(\omega(q_n)-\mu)\rho_n^{(N,\Omega)}(k_1,p_1;\dots;k_n,p_n\mid l_1,q_1;\dots;l_n+1,q_n)-$$
$$-\frac{|\Omega|^{-(n+1)}}{|\Omega|^2}g\sum_{p',q_1',q_2'}v(p_1',q_n\mid q_1',q_2')\times$$
$$\times\rho_{n+1}^{(N,\Omega)}(k_1,p_1;\dots;k_n,p_n;l_n,p_1'\mid l_1,q_1;\dots;l_{n-1},q_n;l_n+1,q_1';l_n+1,q_2')+$$
$$+|\Omega|^{-(n-1)}\rho_{n-1}^{(N,\Omega)}(k_1,p_1;\dots;k_{n-1},p_n\mid l_1,q_1;\dots;l_{n-1},q_{n-1})\times$$
$$\times\delta_{l_n,k_n}\delta_{p_n,q_n}+(k,p),$$

where (k,p) as well as a similar expression in what follows denotes the sum of the summands obtained from those written before them by permutations of k_i and p_i.

Let us transplant the first two summands from the right-hand side into the left-hand side and divide both sides by $\frac{\beta}{N}|\Omega|^{-n}$. As a result, we get an expression in which the passage to the limit as $N\to\infty$ and $|\Omega|\to\infty$ is possible.

Passing to the limit as $N\to\infty$ we find the equation for the prelimit Green functions

$$\Big(\frac{\partial}{\partial s_n}-(\omega(q_n)-\mu)\Big)\rho_n^{(\Omega)}(t_1,p_1;\dots\mid\dots;s_n,q_n)=$$
$$=\frac{1}{|\Omega|^3}g\sum_{p_1',q_1',q_2'}v(p_1',q_n\mid q_1',q_2')\times$$
$$\times\rho_{n+1}^{(\Omega)}(t_1,p_1;\dots;t_n,p_n;s_n,p_n'\mid s_1,q_1;\dots;s_n,q_1';\dots;s_n,q_2')-$$
$$-\rho_n^{(\Omega)}(t_1,p_1;\dots;t_{n-1},p_{n-1}\mid s_1,q_1;\dots;s_{n-1},q_{n-1})\times$$
$$\times\delta(t_n-s_n)\delta_\Omega(p_n-q_n)-(t,p).\quad\text{(AA2.13)}$$

where (t,p) in (AA2.13) denotes the sum of the terms obtained of the written

ones by all permutations of (t_i, p_i), and where

$$\delta_\Omega(p) = \begin{cases} |\Omega| & \text{for} \quad p = 0, \\ 0 & \text{for} \quad p \neq 0. \end{cases}$$

It is possible to pass to the limit as $|\Omega| \to \infty$ in (AA2.13). The sum in the right-hand side turns into the integral and $\delta_\Omega(p)$ into the Dirac's delta function $\delta(p)$. As a result, we obtain equations for the prelimit Green functions

$$\Big(\frac{\partial}{\partial s_n} - (\omega(q_n) - \mu)\Big)\rho_n(t_1, p_1; \ldots \mid \ldots; s_n, q_n) = g \int v(p', q_n \mid q_1', q_2') \times$$
$$\times\, \rho_{n+1}(t_1, p_1; \ldots; t_n, p_n; s_n, p' \mid s_1, q_1; \ldots; s_n, q_1'; s_n, q_2')\, dp'\, dq_1'\, dq_2' -$$
$$- \rho_{n-1}(t_1, p_1; \ldots; t_{n-1}, p_{n-1} \mid s_1, q_1; \ldots; s_{n-1}, q_{n-1}) \times$$
$$\times\, \delta(t_n - s_n)\delta(p_n - q_n) - (t, p), \quad \text{(AA2.14)}$$

where

$$v(p_1, p_2 \mid q_1, q_2) = W(p_1, p_2 \mid q_1, q_2)\delta(p_1 + p_2 - q_1 - q_2).$$

Returning to $\rho_n^{(N,\Omega)}(k_1, p_1; \ldots \mid \ldots; l_n, q_n)$ we find, starting from (AA2.11) that this function is periodic with respect to integer arguments k_i, l_i with period N. This property is inherited by the limit function $\rho_n(t_1, p_1; \ldots \mid \ldots; s_n, q_n)$ which is periodic with respect to each variable t_i, s_i with period β.

Further the deduction of equation (AA2.14) implies that the expression $\rho_{n+1}(t_1, p_1; \ldots; s_n, p' \mid s_1, q_1; \ldots; s_n, q_1'; s_n, q_2')$ in the right-hand side should be understood as the limit

$$\rho_{n+1}(t_1, p_1; \ldots; t_{n-1}, p_{n-1}; s_n, p' \mid s_1, q_1; \ldots; s_n, q_{n-1}; s_n, q_1'; s_n, q_2') =$$
$$= \lim_{\varepsilon \to +0} \rho_{n+1}(t_1, p_1; \ldots; t_{n-1}, p_{n-1}; s_n, p' \mid s_1, q_1; \ldots$$
$$\ldots; s_{n-1}, q_{n-1}; s_n + \varepsilon, q_1'; s_n + \varepsilon, q_2').$$

One should always have in mind a similar relation when one encounters the Green functions with coinciding arguments $t_i = s_j$. Equation (AA2.11) implies that $\rho_0 \equiv 1$.

Equation (AA2.14) can be expressed in an equivalent integral form. For this let us find the Green functions $\rho_n^{(0)}$ of free particles. It follows from (AA2.14) an equation for $\rho_1^{(0)}$:

$$\Big(\frac{\partial}{\partial s} - (\omega(q) - \mu)\Big)\rho_1^{(0)} = -\delta(t - s)\delta(p - q). \quad \text{(AA2.15)}$$

Equation (AA2.15) possesses a unique solution periodic with respect to t and s:

$$\rho_1^{(0)} = \delta(p-q)\sigma(t-s \mid p),$$
$$\text{where } \sigma(t-s \mid p) = \frac{\theta(t-s)e^{-(t-s)(\omega(p)-\mu)} + \theta(s-t)e^{-(\beta+t-s)(\omega(p)-\mu)}}{1-e^{-\beta(\omega(p)-\mu)}}, \tag{AA2.16}$$
$$\text{and } \theta(t) = \begin{cases} 1 & \text{as} \quad t > 0, \\ 0 & \text{as} \quad t \le 0. \end{cases}$$

Observe that the function $\sigma(t \mid p)$ satisfies an equation similar to (AA2.15):

$$\Big(\frac{\partial}{\partial t} + (\omega(q)-\mu)\Big)\sigma = \delta(t-s). \tag{AA2.17}$$

Let now $f(t_1, \dots, t_m \mid s_1, \dots, s_n)$ be an arbitrary function periodic with respect to t_i, s_j with period β. Observe that

$$\int (\Big(\frac{\partial}{\partial s_n} - (\omega(q_n)-\mu)\Big) f(t_1, \dots, t_m \mid s_1, \dots, s_n)\sigma(s_n - \tilde{s} \mid q_n) s_n = \\ = -f(t_1, \dots, t_m \mid s_1, \dots, s_{n-1}, \tilde{s}).$$

Let us multiply both sides of (AA2.14) by $\sigma(s_n - \tilde{s} \mid q_n)$ and integrate over s_n. Now let us make a change of variables $s_n \mapsto s'$, $\tilde{s} \to s_n$. As a result we get

$$\rho_n(t_1, p_1; \dots; t_n, p_n \mid s_1, q_1; \dots; s_n, q_n) = -g \int v(p', q_n \mid q_1', q_2') \times \\ \times \sigma(s' - s_n \mid q_n)\rho_{n+1}(t_1, p_1; \dots; t_n, p_n; s', p' \mid s_1, q_1; \dots \\ \dots; s_{n-1}, q_{n-1}; s', q_1'; s', q_2')\, dp'\, dq_1'\, dq_2'\, ds' + \\ + \rho_{n-1}(t_1, p_1; \dots; t_{n-1}, p_{n-1} \mid s_1, q_1; \dots; s_{n-1}, q_{n-1}) \times \\ \times \rho_1^{(0)}(t_n, p_n \mid s_n, q_n) + (t, p). \tag{AA2.18}$$

In the Fermi case the deduction of the equations for ρ_n repeats the above deduction in every detail. Due to the peculiarity of the definition of partial derivatives and the integration by parts the answer differs somewhat from

(AA2.18):

$$\rho_n(t_1,p_1;\dots;t_n,p_n \mid s_1,q_1;\dots;s_n,q_n) = g\int v(p',q_n \mid q_1',q_2')\times$$
$$\times\,\sigma(s'-s_n \mid q_n)\rho_{n+1}(t_1,p_1;\dots;t_n,p_n;s',p' \mid s_1,q_1;\dots$$
$$\dots;s_{n-1},q_{n-1};s',q_1';s',q_2')\,dp'\,dq_1'\,dq_2'\,ds' +$$
$$+\,\rho_{n-1}(t_1,p_1;\dots;t_{n-1},p_{n-1} \mid s_1,q_1;\dots;s_{n-1},q_{n-1})\times$$
$$\times\,\rho_1^{(0)}(t_n,p_n \mid s_n,q_n) \pm (t,p), \quad \text{(AA2.19)}$$

where $\pm(t,p)$ denotes the sum of summands obtained from

$$\rho_{n-1}(t_1,p_1;\dots \mid \dots s_{n-1},q_{n-1})\rho_1^{(0)}(t_n,p_n \mid s_n,q)$$

by alternation with respect to (t_i,p_i) and $\rho_1^{(0)}$ is the first Green function for free fermions equal to

$$\rho_1^{(0)}(t,p \mid s,q) = \delta(p-q)\sigma(t-s \mid p),$$

where

$$\sigma(t-s \mid p) = \frac{-\theta(t-s)e^{-(t-s)(\omega(p)-\mu)} + \theta(s-t)e^{-(\beta+t-s)(\omega(p)-\mu)}}{1+e^{-\beta(\omega(p)-\mu)}}.$$

Unlike the Bose case the Fermi Green functions are anti-periodic with respect to t_i, s_i with period β. That means that the value of ρ_n at s_i (or t_i) $= 0$ differs from the value of ρ_n at s_i (or t_i) $= \beta$ by a sign.

Equations (AA2.18) and (AA2.19) are analogous to the Kirkwood—Salzburg equations for correlation functions in the classical statistical physics. However, whereas in the Kirkwood—Salzburg equations use the activity $\zeta = e^{-\beta\mu}$ as a small parameter the equations (AA2.17) and (AA2.18) use on this row the constant g. We cannot investigate these equations by the Bogolyubov—Khatset—Ruelle method. Perhaps this is related with the principal fact the functions ρ_n might turn out to be infinitely differentiable with respect to g but not analytic in any neighborhood of the origin.

At present the nature of dependence of ρ_n on g is not studied (see [Ma]). And therefore the equations (AA2.18) and (AA2.19) are only used for formal expansions of ρ_n in the perturbation series g.

The possibility to pass to the limit as $|\Omega| \to \infty$ from the equations for prelimit functions $\rho_n^{(\Omega)}$ to the equations for ρ_n means that such a passage is possible for each summand in the perturbation theory series for $\rho_n^{(\Omega)}$ and as a result we get a perturbation theory series of limit functions ρ_n. This argument is considered as an heuristic proof of the relation $\rho_n = \lim\limits_{|\Omega|\to\infty} r_{m,n}^{(\Omega)}$.

A2.5. A relation of the thermodynamic potential and correlation functions with Green functions. In the quantum statistical physics the functions

$$r^{(\Omega)}_{m,n}(p_1,\dots,p_m \mid q_1,\dots,q_n) = \\ = |\Omega|^{\frac{m+n}{2}}\Xi^{-1}\operatorname{sp}(a^*(p_1)\dots a^*(p_m)a(q_1)\dots a(q_n)e^{-\beta H}).$$

are said to be *prelimit correlation functions*. As we will see the limit $r_{m,n} = \lim\limits_{|\Omega|\to\infty} r^{(\Omega)}_{m,n}$ exists. The functions $r_{m,n}$ are called *the limit correlation functions*. The importance of correlation functions in the quantum statistical physics is determined by the same arguments as in the classical one: If A is an arbitrary operator that can be represented as the normal series (AA2.1) then the mean value of A over the ensemble can be represented as $\langle A\rangle = \lim\limits_{|\Omega|\to\infty}\langle A\rangle_{|\Omega|}$, where

$$\langle A\rangle_{|\Omega|} = \frac{\operatorname{sp}(Ae^{-\beta H})}{\operatorname{sp} e^{-\beta H}} = \sum_{m,n}|\Omega|^{-(m+n)}\sum_{p_i,q_j}A_{m,n}(p_1,\dots,p_m \mid q_1,\dots,q_n)\times \\ \times r^{(\Omega)}_{m,n}(p_1,\dots,p_m \mid q_1,\dots,q_n).$$

The right-hand side contains an integral sum. Therefore

$$\langle A\rangle = \lim_{|\Omega|\to\infty}\langle A\rangle_{|\Omega|} = \sum_{m,n}\int A_{m,n}(p_1,\dots,p_m \mid q_1,\dots,q_n)\times \\ \times r_{m,n}(p_1,\dots,p_m \mid q_1,\dots,q_n)\,d^mp\,d^nq.$$

To prove the existence of the limit functions $r_{m,n}$ let us express the correlation functions in terms of the Green functions. It is more convenient to consider the functions

$$\tilde r^{(\Omega)}_{m,n} = |\Omega|^{\frac{m+n}{2}}\Xi^{-1}\operatorname{sp}(a(q_n)\dots a(q_1)a^*(p_1)\dots a^*(p_m)e^{-\beta H}).$$

instead of $r^{(\Omega)}_{m,n}$. The commutation relations between $a(p)$ and $a^*(p)$ imply the expression of $\tilde r^{(\Omega)}_{m,n}$ and $r^{(\Omega)}_{m,n}$ in terms of each other: In the Bose case

$$r^{(\Omega)}_{m,n}(p_1,\dots \mid \dots,q_n) = \tilde r^{(\Omega)}_{m,n}(p_1,\dots \mid \dots,q_n) + \\ + \delta_\Omega(p_m-q_n)\tilde r^{(\Omega)}_{m,n}(p_1,\dots,p_{m-1} \mid q_1,\dots,q_{n-1}) + \dots,$$

where $\delta_\Omega(p) = \begin{cases}\Omega & \text{as} \quad p=0,\\ 0 & \text{as} \quad p\neq 0,\end{cases}$ and $\lim\limits_{\Omega\to\infty}\delta_\Omega(p) = \delta(p)$,

where $\delta(p)$ is the Dirac δ-function.

In the Fermi case the expression for $r^{(\Omega)}_{m,n}$ in terms of $\tilde{r}^{(\Omega)}_{m,n}$ differs from the above by certain signs.

To prove the existence of the limit functions it suffices to establish the existence of similar limits $r_{m,n} = \lim\limits_{|\Omega|\to\infty} r^{(\Omega)}_{m,n}$. From the definition of prelimit Green functions we see that $\tilde{r}_{m,n} = \lim\limits_{|\Omega|\to\infty} \tilde{r}^{(\Omega)}_{m,n}$.

Therefore the existence of prelimit correlation functions follows from the existence of prelimit Green functions:

$$\tilde{r}^{(\Omega)}_{m,n}(p_1,\dots \mid \dots, q_n) = \rho^{(\Omega)}_{m,n}(0,p_1;\dots;0,p_m \mid \beta,q_1;\dots;\beta,q_n).$$

Let us express the thermodynamic potential in terms of the Green functions assuming that H is of the form (AA2.7). Set $\ln \Xi_{\Omega,N} = \Omega\Phi^{(N,\Omega)}$. Differentiating the integral (AA2.10) with respect to g we see that

$$\begin{aligned}
\frac{\partial\Phi^{(N,\Omega)}}{\partial g} &= -|\Omega|^{-3}\Xi^{-1}_{\Omega,N}\frac{\beta}{N}\int \sum_{k,p_i,q_j} W(p_1,p_2 \mid q_1,q_2)\delta_\Omega(p_1+p_2-q_1-q_2)\times \\
&\times \overline{z}_k(p_1)\overline{z}_k(p_2)z_{k+1}(q_1)z_{k+1}(q_2)\times \\
&\times e^{-\frac{\beta}{N}\sum\limits_0^{N-1} H(\overline{z}_k,z_{k+1})+\sum\limits_0^{N-1}(\overline{z}_k-\overline{z}_{k+1})z_{k+1}} \prod_{k=1}^{N} d\overline{z}_k\, dz_k = \\
&= -\frac{\beta}{N}|\Omega|^{-5}\sum W(p_1,p_2 \mid q_1,q_2)\delta_\Omega(p_1+p_2-q_1-q_2)\times \\
&\times \rho_2^{(N,\Omega)}(k,p_1;k,p_2 \mid k+1,q_1;k+1,q_2) = \\
&= -\frac{\beta}{N}|\Omega|^{-4}\sum W(p_1,p_2 \mid q_1,q_2)\delta_\Omega(p_1+p_2-q_1-q_2)\times \\
&\qquad \times \sigma_2^{(N,\Omega)}(k,p_1;k,p_2 \mid k+1,q_1;k+1,q_2).
\end{aligned}$$

Hence

$$\begin{aligned}
\Phi^{(N,\Omega)} = \Phi_0^{(N,\Omega)} - \int_0^g \frac{\beta}{N}|\Omega|^{-4} &\sum_{k,p_i,q_j} W(p_1,p_2 \mid q_1,q_2)\times \\
&\times \rho_2^{(N,\Omega)}(\lambda\|k,p_1;k,p_2 \mid k+1,q_1;k+1,q_2)\, d\lambda.
\end{aligned}$$

In the right-hand side we have an expression obviously possessing a limit as

$N \to \infty$ and $|\Omega| \to \infty$. Passing to this limit we finally obtain

$$\Phi = \Phi_0 - \int\limits_{\substack{0<\lambda<g \\ 0<t<\beta}} W(p_1, p_2 \mid q_1, q_2) \times \\ \times \rho_2(\lambda \| t, p_1; t, p_2 \mid t, q_1; t, q_2)\, dp_1\, dp_2\, dq_1\, dq_2\, dt\, d\lambda,$$

where Φ_0 is the thermodynamic potential of free particles, explicitly

$$\Phi_0 = \mp \int \ln\bigl(1 \mp e^{-\beta(\omega(p)-\mu)}\bigr)\, dp,$$

where the upper sign corresponds to the Bose case and the lower one to the Fermi case. The argument λ of the functions ρ_2 and $\rho_2^{(N,\Omega)}$ means that they are computed for the Hamiltonian H of the form (AA2.7) at $g = \lambda$.

APPENDIX 3. **Review of rigorous results (R. A. Milnos)**

A3.1. The Lee-Yang theorem on the existence of the limit

$$\lim_{|\Omega|\to\infty} \ln \Xi(\Omega \mid \beta, \mu) = \Phi(\mu, \beta)$$

proved in the main text for the case of the pairwise finite potential is actually true for a much wider class of potentials. Let us indicate here a most natural (though far from exhausting) class of such potentials, see [DS], [BCD].

Theorem (Dobrushin). *Let $u(x)$ be a potential of the pairwise interaction. If there exist two positive decreasing functions $\varphi_1(x)$, $(0 < x < a_1)$ and $\varphi_2(x)$, $(a_1 < a_2 < x < \infty)$ such that*

1) $\int\limits_0^{a_1} t^{v-1}\varphi_1(t)\, dt = \infty$, $\int\limits_{a_2}^{\infty} t^{v-1}\varphi_2(t)\, dt < \infty$,

2)
$$u(x) \geq \varphi_1(|x|), \quad |x| < a_1,$$
$$u(x) \geq -\varphi_2(|x|), \quad |x| > a_2,$$

then for the system of particles that interacts by means of the potential $u(x)$ the Lee-Yang theorem holds.

A3.2. In the above assumptions on the potential $u(x)$ we also have the Van Hove theorem on the existence of the limit

$$\lim_{\substack{|\Omega|\to\infty \\ \frac{N}{|\Omega|}\to\gamma}} \frac{1}{N} \lim \frac{Z_N(\Omega)}{N!} = F(\gamma, \beta),$$

where $Z_N(\Omega)$ is the small statistical sum.

A3.3. Under the same conditions with respect to the potential $u(r)$ the following theorem holds.

Theorem (Dobrushin–Minlos). *For all γ there exists a continuous derivative $\dfrac{\partial F}{\partial \gamma}$ and the limit $\lim\limits_{\substack{N\to\infty \\ \frac{N}{\Omega}\to\gamma}} \dfrac{Z_{N+1}}{NZ_N}$, and this limit is equal to $\lim\limits_{\substack{N\to\infty \\ \frac{N}{\Omega}\to\gamma}} \dfrac{Z_{N+1}}{NZ_N} = e^{F+\gamma}\dfrac{\partial F}{\partial \gamma}$.*

This theorem implies in particular that the thermodynamic pressure is continuous:

$$p(\gamma,\beta) = \frac{\partial}{\partial \frac{1}{\gamma}}\Big(\frac{1}{\gamma}F(\gamma,\beta)\Big).$$

A3.4. The phase transition is at the moment only studied for certain lattice systems. The simplest of them is *the Ising model* with the attraction whose potential is of the form

$$u(r) = \begin{cases} \varepsilon < 0, & |r| = 1, \\ 0, & |r| > 1. \end{cases}$$

For the Ising model in dimension ≥ 2 it is shown that for a certain value of the chemical potential $\mu = \mu_0$ and sufficiently large values of β there exists a first type phase transition (Dobrushin, Griffits). Besides, the detailed structure of typical configurations in the small canonical ensemble at the values of density inside the interval of phase transition is studied (Minlos-Sinai). The existence of phase transition for other systems on the lattice with attraction between particles (or more generally with attraction prevailing over repulsion) is established in works by Berezin and Sinai and Dobrushin.

To this we should add that for the Ising model (both with attraction and repulsion) for a certain value of chemical potential the function $\Phi(\mu_0, \beta)$ (and also a number of other thermodynamic characteristics of the system) are explicitly computed in the well known work by Onzager [O] (and further generalized in the works by Kaufmann, Yang, Berezin and others; for a review, see [M1]). The explicit analytic expressions obtained enable one to find a critical point β_0 the boundary value of the values of β for which the phase transition of first type exists.

A3.5. For the systems of quantum numbers (both bosons and fermions) whose operator of energy is of the form (26.1), (26.2), the Van Hove and Li-Yang theorems are proved for a rather broad class of potentials (real) and a wide class of boundary conditions that determine the energy operator for a system in a finite vessel. It is also proved that the limit thermodynamic

potentials do not actually depend on the choice of these boundary conditions (I. Novikov). The continuity of the pressure (see above) is also established in the quantum case (Ginibre).

A3.6. In the quantum systems with the energy operator of form (26.1), (26.2) for the small values of activity z the existence of the limit correlation functions $r_n(x_1, \dots, x_n \mid y_1, \dots, y_n)$ is proved. This result is obtained by reducing the quantum ensemble to the classical ensemble of Wiener trajectories with later usage of the technique of Kirkwood–Salzburg equations in the same way one performs this for the classical systems.

For the further bibliographic references concerning the questions studied here see the book by Ruelle [R].

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MR0496246 (58 #14819): Prior to 1976 the only general method of establishing the existence of phase transitions was a method developed by R. L.

Dobrushin [Teor. Verojatnost. i Primenen. 10 (1965), 209–230] and R. B. Griffiths [Phys. Rev. (2) 136 (1964), A437-A439; MR0189681 (32 #7103)], on the basis of original ideas of R. Peierls [Proc. Cambridge Philos. Soc. 32 (1936), 477–481; Zbl 14, 336]. In 1976, J. Fröhlich, the second author and T. Spencer [Comm. Math. Phys. 50 (1976), no. 1, 79–95; MR0421531 (54 #9530)] published an independent method and applied it to various Ising and classical Heisenberg models. The paper under review extends this method to several quantum mechanical models and proves, for example, that transitions occur in the spin-1, nearest neighbour, quantum Heisenberg antiferromagnet on a cubic lattice in three or more dimensions. (Previously N. D. Mermin and H. Wagner [Phys. Rev. Lett. 17 (1966), 1133–1136] had proved the absence of such transitions in one and two dimensions.) Less information is obtained for ferromagnetic models although phase transitions are shown to occur for the X-Y spin $\frac{1}{2}$ model with nearest neighbour interactions in three or more dimensions.

{Reviewer's remarks: In a prepublication version of this paper the authors claimed to have resolved the classic problem of the existence of a spontaneous magnetization for the three-dimensional Heisenberg ferromagnet, but apparently Fröhlich discovered an error in the proof. Unfortunately, the published version still retains traces of this earlier misapprehension and it is regrettable that the paper was not revised and edited more severely. For example, much of the discussion of the ferromagnetic models remains speculative and of questionable value. The principal achievement appears to be the reduction of the physically reasonable property of nonzero spontaneous magnetization to a property the authors call Gaussian domination. But there does not appear to be any reason, heuristic or otherwise, to believe that this property is true for ferromagnets. Nevertheless, the results for anti-ferromagnets are of great interest, as is much of the methodology. For example, critical phenomena are discussed in terms of long range order for the Duhamel two-point function in place of the usual two-point function.}

Reviewed by Derek W. Robinson

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