

THE BOLTZMANN DISTRIBUTION FUNCTION FOR EQUILIBRIUM FLUCTUATIONS

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A complex of issues related to the problem of proving the Boltzmann formula for the probability density (distribution) $w(\eta)$ of the values of a certain set of parameters η of an equilibrium system is investigated. The classical Boltzmann formula expresses this distribution through the non-equilibrium free energy of the system $F(\eta)$, which depends on the mentioned parameters. This is possible because after the occurrence of fluctuations, the system finds itself in a non-equilibrium state, which evolves further to equilibrium. The specified parameters are chosen according to the problem under consideration. In the theory of phase transitions, they are called the order parameters. Questions under consideration include definition and construction of the free energy $F(\eta)$ of a non-equilibrium system and distribution $w(\eta)$ for it in the microscopic theory. The approaches of Landau, Leontovich, and Peletminsky are discussed. It is proposed to investigate the results for states in the vicinity of equilibrium. The leading ideas of the research are considering the non-equilibrium state as being realized in the presence of an appropriate external field, using the Gibbs formula for the non-equilibrium system entropy, and applying the Boltzmann formula as a definition of the free energy of the non-equilibrium system. The article is a continuation of the authors' works and sets the task of clarifying some of their statements as well as simplifying and clarifying the calculations. Among other things, the following are discussed: the formula for the expansion of the free energy of the system in powers of the field, the simplification of the distribution $w(\eta)$ calculation, the normalization of the approximate expressions for the distribution $w(\eta)$, the possibilities of studying the free energy of the equilibrium system using our expression for the effective Landau Hamiltonian, the refinement of the calculation of the non-equilibrium free energy of a spatially inhomogeneous system, the investigation of new types of effective interactions with the Landau Hamiltonian.

Keywords: equilibrium fluctuations, effective Hamiltonian, non-equilibrium free energy, the Boltzmann principle, phase transitions of the second kind, correlation functions, fluctuations close to equilibrium, long wave fluctuations.

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1. Introduction

Studying the effect of fluctuations on physical phenomena in macroscopic systems is a leading task of statistical physics [1, 2]. The magnitude of fluctuations is measured by deviations of the observed values from their average values. It is easiest to study fluctuations in equilibrium systems that are completely described by Gibbs distributions. However, the complexity of macroscopic systems makes this apparatus practically unusable. The specification of macroscopic conditions in which the system is investigated is not of great importance [3]. It is easiest to study systems with fixed temperature T , volume V and number of particles N (TVN -states), which are described by the canonical Gibbs distribution. From the physical point of view, TpN -states (p is pressure) are closer to the experiment, but the Gibbs distribution required for this is more complex than the canonical one.

The complexity of macroscopic systems suggests a reduced description of fluctuations in an equilibrium system with a relatively small number of parameters η_a (a is the number of parameters). In the theory of phase transitions of the II kind, which was largely developed by Landau [4] (see also [1]), the parameters are called order parameters (this term will be used further on). The order parameters η_a are chosen to describe the most significant degrees of freedom (collective motions) of the system for the problem under consideration. Interest in the study of equilibrium fluctuations increased significantly after the works by Onsager [5], who expressed the fruitful opinion that systems after the occurrence of fluctuations evolve as an ordinary non-equilibrium system.

In an equilibrium *TVN*-state, the equilibrium distribution function $w(\eta)$ of parameter values η_a is defined through the canonical Gibbs distribution

$$w_0 = e^{-\frac{F_0 - \hat{H}}{T}}, \quad \text{Sp} w_0 = 1 \quad (1)$$

with the formulas

$$\begin{aligned} w(\eta) &= \text{Sp} w_0 \delta(\eta - \hat{\eta}), & \int d\eta w(\eta) &= 1; \\ \delta(\eta - \hat{\eta}) &\equiv \prod_a \delta(\eta_a - \hat{\eta}_a), & d\eta &\equiv \prod_a d\eta_a. \end{aligned} \quad (2)$$

Here and further, the caps denote the microscopic values of the corresponding physical quantities, Sp is integration operator over the phase variables of the system together with the multipliers, which is used in the normalization condition (1) of the canonical distribution and in the formulas for averages with it of the type $\bar{a} = \text{Sp} w_0 \hat{a}$. In applications, the Boltzmann formula

$$w(\eta) = A e^{-\frac{F(\eta)}{T}} \quad (3)$$

is considered valid for the distribution function $w(\eta)$ (see [1]). Here $F(\eta)$ is the free energy of a nonequilibrium state, which is described abbreviated by parameters η_a , A is the normalization factor. It is clear that the validity of this formula depends critically on the expression for the free energy $F(\eta)$ and the result should be compared with the expression for the distribution function $w(\eta)$, which is given by the microscopic theory on the basis of (2). A standard requirement for the nonequilibrium free energy is that it has a minimum at equilibrium

$$F(\eta) \geq F_0, \quad F(\eta_0) = F_0; \quad \eta_{a0} \equiv \text{Sp} w_0 \hat{\eta}_a. \quad (4)$$

The first research of the concept of the free energy of a non-equilibrium state belongs to Leontovich [6, 7]. It was based on the idea that nonequilibrium state can be equilibrium one in the presence of a suitable external field h_a . At the same time, the free energy of the non-equilibrium state was defined as the free energy of the equilibrium system in the mentioned field presence with the subsequent Legendre transformation giving the thermodynamic (TD) potential $F_L(\eta)$, for which the order parameters are own variables. At the same time, Leontovich proved that conditions (4) are fulfilled for the non-equilibrium potential $F_L(\eta)$. A little earlier [4] Landau built his theory of phase transitions of the II kind, based on some equilibrium thermodynamic potential dependent on order parameters η_a , the minimum of which describes the observed states. The authors tend to believe that Landau used the same potential $F_L(\eta)$, without giving any details.

Another approach to the construction of TD potentials of non-equilibrium systems was proposed by Landau [1] who called such a potential the effective Hamiltonian, which will be denoted by $H_L(\eta)$. In general, both terms are considered synonymous in modern literature (see, for example, [3, 8]). The Landau definition is based on the Boltzmann formula with a normalization factor, which is expressed in terms of the total free energy of the equilibrium system F_0

$$w(\eta) = e^{-\frac{F_0 - H_L(\eta)}{T}} \quad (5)$$

where $w(\eta)$ is given by formula (2). The normalization condition for $w(\eta)$ makes it possible to study the free energy of the system using the formula

$$e^{-\frac{F_0}{T}} = \int d\eta e^{-\frac{H_L(\eta)}{T}} \quad (6)$$

that is more realistic compared with the similar formula based on the canonical Gibbs distribution (1). The problem of calculating the effective Hamiltonian $H_L(\eta)$ is currently not solved, and formula (5) is used with a phenomenological expression for it [1, 8, 9].

Another approach to the construction of TD potentials of non-equilibrium systems is proposed in [10, 11] (see also [12]). The papers are based on the method of reduced description of non-equilibrium processes. Hereby the entropy of a non-equilibrium system is first introduced with the Gibbs formula using to the distribution function of the system in the reduced description.

The whole complex of issues raised above was discussed in our articles [13–15] and reports at several conferences with the aim of developing the microscopic theory. In particular, the relevance of such problem was noted in [16]. This paper aims to simplify the consideration of the mentioned works, to indicate the modern understanding of the discussed problems, and to present new results.

The work is structured in this way. Section 2 discusses the free energy of non-equilibrium systems. Section 2.1 discusses the microscopic implementation of the Landau–Leontovich definition of the free energy of a system. In Section 2.2, the definition of Landau–Leontovich is generalized to the case of spatially inhomogeneous systems. Section 3 discusses the problem of proving the Boltzmann formula for the distribution of equilibrium fluctuations. In clause 3.1, the distribution function of equilibrium fluctuations is calculated. Section 3.2 discusses the effective Landau Hamiltonian. In Section 3.3, the effective Hamiltonian of a subsystem of identical particles is considered as an application. Clause 3.4 derives the generalized Boltzmann formula.

2. Free energy of non-equilibrium systems

2.1. Microscopic implementation of the Landau–Leontovich definition

The concept of non-equilibrium thermodynamic (TD) potentials belongs to the basic ideas of modern theoretical physics. Interest in such problems increased after Landau created his theory of phase transitions of the II kind [1]. However, it is striking that, while investigating the extreme properties of the nonequilibrium TD Gibbs potential, Landau did not even use the term "non-equilibrium". The reason for this is that nonequilibrium TD potentials coincide with some equilibrium ones. In this subsection, the TVN -states are considered described by the canonical Gibbs distribution (1) and the nonequilibrium free energy of the system is discussed. The nonequilibrium state of the system is described by some parameters η_a (a is number), which, based on the theory of phase transitions, will be called order parameters. Then the non-equilibrium free energy will besides $\eta \equiv \{\eta_a\}$ depend on the temperature T , volume V and number of particles N . Landau's theory is purely phenomenological, and therefore the task of building a microscopic theory in which this theory is embedded is an urgent task (see, for example, [16]).

Further discussion of the non-equilibrium free energy construction procedure is carried out for a system subject to classical mechanics.

The basis of consideration is the canonical Gibbs distribution in the presence of an external field h_a

$$w = e^{\frac{F - [\hat{H} + \sum_a \hat{\eta}_a h_a]}{T}}, \quad \text{Sp} w = 1; \quad \eta_a \equiv \text{Sp} w \hat{\eta}_a. \quad (7)$$

This distribution according to Leontovich [6, 7] can be considered as non-equilibrium distribution function of the system, the state of which is described by the order parameters η_a defined in (7). Hereby it is possible to assume that the system consists of two subsystems: one in equilibrium with temperature T and one out of equilibrium, the state of which is described by the parameters η_a . The disequilibrium of the system is due to the fact that the order parameter is different from its equilibrium value $\eta_a \neq \eta_{a0} \equiv \text{Sp} w_0 \hat{\eta}_a$ (see [1, 4]).

The external field h_a is included due to the mediocrity of the microscopic values $\hat{\eta}_a$ of the parameters η_a . The basic TD relation for the free energy F has the form

$$dF = -SdT + \sum_a \eta_a dh_a \quad (8)$$

and is built in the usual way on the basis of the 1st and 2nd laws of thermodynamics (TD), the definitions of internal E and free F energies, and the expression for the elementary work of the system δR when the field changes

$$\delta Q = dE + \delta R, \quad \delta Q = TdS, \quad (9)$$

$$E = \text{Sp} w (\hat{H} + \sum_a h_a \hat{\eta}_a), \quad F = E - TS, \quad \delta R = -\sum_a \eta_a dh_a$$

(see, for example, [1]). Let's make the Legendre transformation, which will allow us to introduce a new TD potential F_L

$$F_L = F - \sum_a h_a \eta_a. \quad (10)$$

which we will call the Landau–Leontovich free energy. For F_L the parameters η_a will be eigenvariables, since the basic relation of TD for F_L has the form

$$dF_L = -SdT - \sum_a h_a d\eta_a. \quad (11)$$

According to Leontovich [6, 7], the function $F_L(T, \eta)$ should be considered a non-equilibrium free energy, since he proved

$$F_L(T, \eta_0) = F_0, \quad F_L(T, \eta) \geq F_0; \quad \eta_{a0} \equiv \eta_a(T, h=0), \quad F_0 \equiv F(T, h=0). \quad (12)$$

Leontovich based his definition on the fact that the Gibbs distribution in the presence of a corresponding field w is simultaneously distribution function of a non-equilibrium state, the disequilibrium of which is connected with the fact that $\eta_a \neq \eta_{a0}$. Note that the approach of our work [10] also leads to the definition of the non-equilibrium free energy according to (10), since

$$F_L = E - TS, \quad S \equiv -\text{Sp} w \ln w,$$

where S is the non-equilibrium Gibbs entropy of the system, which is described by the non-equilibrium distribution function w , the first formula is the usual free energy definition.

In fact, Landau used a TD potential of the type $F_L(T, \eta)$ as a non-equilibrium TD potential. He certainly understood that the TD potential as a function of some parameters η_a can be obtained by the approach just described. Moreover, the idea of modeling the system's disequilibrium with an external field has always been widespread. Our reasoning is to some extent confirmed by the consideration of the phase transition between para- and ferromagnets in Landau's book [17] and in the textbook [18], the author of which collaborated with Landau. Landau did not discuss the notion of non-equilibrium TD potential in his works and did not use the corresponding term, most likely because F_L is an equilibrium TD potential, after all. He also did not discuss, on the basis of statistical mechanics, the status of the potential F_L as a function of the parameters η_a , although he considered that the potential has minimum in equilibrium in the absence of real external field (not auxiliary field for non-equilibrium modeling).

In fact, in his theory of phase transitions of the II kind, Landau defined the non-equilibrium TD potential in the presence of an external field by the formula

$$F_{\text{neq}}(T, \tilde{\eta}, h) = F_L(T, \tilde{\eta}) + \sum_a \tilde{\eta}_a h_a \quad (13)$$

(here we are not talking about the field that simulates the imbalance of the system!). In it, the notation of the parameters has been changed from η_a to $\tilde{\eta}_a$ in order to indicate that $\tilde{\eta}_a$ is an independent variable, the equilibrium value of which $\eta_a(T, h)$ is sought from the extremum condition of $F_{\text{neq}}(T, \tilde{\eta}, h)$

$$F_{\text{neq}}(T, \tilde{\eta}, h) \Big|_{\tilde{\eta}=\eta} = F, \quad \frac{\partial F_{\text{neq}}(T, \tilde{\eta}, h)}{\partial \tilde{\eta}_a} \Big|_{\tilde{\eta}=\eta} = 0. \quad (14)$$

Here, the first formula is another entry of relation (10), and the second one is a consequence of equality

$$(\partial F_L / \partial \eta_a)_h = -h_a, \quad (15)$$

which follows from (11). A certain summary related to the mentioned questions is summarized by Landau in the book [1], where formula (13) is also given. Weighing all the indicated circumstances, we believe that formula (13) can be called the Landau–Leontovich nonequilibrium free energy definition.

In his theory of phase transitions of the II kind, Landau [1, 4] postulated the expansion of the free energy $F_L(T, \eta)$ into a series of powers of order parameters for temperatures close to the transition temperature, when these parameters are small. The coefficients of such series remained unknown functions of the temperature T , the volume of the system V , and the number of particles N in it. In our work [13], in perturbation theory, the Landau function $F_L(T, \eta)$ near equilibrium was calculated when the value $\delta\eta_a = \eta_a - \eta_{a0}$ is small, where η_{a0} is the equilibrium value of the parameters η_a . It is clear that the Landau expansion is easy to find from our expansion, additionally considering the values to be small.

Since the writing of the work [13], the authors have improved the understanding of the fundamental points of the theory and somewhat simplified the calculations. Their basis is an exact expression for the free energy in the presence of an external field

$$F = F_0 + \sum_a h_a \eta_{a0} - T \mathbf{G}(h), \quad \mathbf{G}(h) \equiv \sum_{s=2}^{\infty} \frac{(-1)^s}{s! T^s} \sum_{a_1 \dots a_s} h_{a_1} \dots h_{a_s} \langle \hat{\eta}_{a_1} \dots \hat{\eta}_{a_s} \rangle \quad (16)$$

in the form of a series in powers of the field, given in [3]. Here η_{a_0} and $\langle \hat{\eta}_{a_1} \dots \hat{\eta}_{a_n} \rangle$ are the average values of the parameters η_a and their correlation functions in the absence of the external field. The formula

$$(\partial F / \partial h_a)_T = \eta_a, \quad (17)$$

which follows from (8), is used to calculate the function $\eta_a(T, h)$ and its inverse $h_a(T, \eta)$. As a result, we obtained the Landau free energy $F_L(T, \eta)$ with accuracy up to contributions of the order $\delta\eta^4$ including [13], which gives microscopic expressions for the coefficients in the Landau expansion. Taking into account the dimensionality of the space of order parameters and symmetry of the system allows to simplify calculations and find further contributions. For example, when the order parameter is a three-dimensional vector and the system is isotropic, it is quite simple to calculate $F_L(T, \eta)$ with accuracy up to contributions of the order $\delta\eta^6$, which is discussed in some applications of Landau theory. A rather simple expression is obtained in the general theory in the Gaussian approximation [13]

$$F_L(T, \eta) = F_0 + \frac{T}{2} \sum_{a_1, a_2} A_{a_1 a_2}^{-1} \delta\eta_{a_1} \delta\eta_{a_2} + O(\delta\eta^3), \quad A_{a_1 a_2} \equiv \langle \hat{\eta}_{a_1} \hat{\eta}_{a_2} \rangle \quad (18)$$

where F_0 and $\langle \hat{\eta}_{a_1} \hat{\eta}_{a_2} \rangle$ are the free energy and the correlation function of the order parameters in the absence of the external field.

2.2. Free energy of spatially inhomogeneous non-equilibrium systems

Let us discuss how the developed theory is modified in a spatially inhomogeneous system, when the specified parameters η_a and the field h_a depend on the coordinates and in the formulas of the general theory it is possible to put

$$\eta_a = \eta_i(x), \quad h_a = h_i(x); \quad a = (i, x) \quad \sum_a \dots = \sum_i \int_V d^3x \dots \quad (19)$$

Here i is the quantity number, x is the radius vector (coordinates) of the space point (observation point), V is the volume of the system ($x \in V$). After that, the consideration of spatially inhomogeneous states differs from the general theory only by a certain detailing of notations. In particular, the new number of the order parameters $a = (i, x)$ is the combination of the new number i and the radius vector x .

When considering spatially inhomogeneous states, formula (18) for the non-equilibrium Landau free energy in the Gaussian approximation takes the form

$$F_L(T, \eta) = F_0 + \frac{T}{2} \sum_{i, i'} \int_V d^3x \int_V d^3x' A_{ix, i'x'}^{-1} \delta\eta_i(x) \delta\eta_{i'}(x') + O(\delta\eta^3) \quad (20)$$

where the notation of the type

$$a_1 = (i, x), \quad a_2 = (i', x') \rightarrow C_{a_1 a_2} = C_{ix, i'x'} \quad (21)$$

for the matrix is used. According to (18), (19), expression (21) for F_L includes a matrix

$$A_{ix, i'x'} = \langle \hat{\eta}_i(x) \hat{\eta}_{i'}(x') \rangle. \quad (22)$$

Using coordinates x as an order parameter number makes the theory mathematically complicated. For simplification, periodic boundary conditions can be imposed on the coordinate functions $\eta_i(x)$, $h_i(x)$. In terms of the Fourier transform for the function $f(x)$, on which the following conditions are imposed, we have

$$f(x) = \frac{1}{V} \sum_k f_k e^{ikx}, \quad f_k = \int_V d^3x f(x) e^{-ikx};$$

$$k_l = \frac{2\pi n_l}{V^{1/3}} \quad (l=1,2,3), \quad n_l = 0, \pm 1, \pm 2, \dots; \quad \sum_k \dots \xrightarrow{t\text{-lim}} \frac{V}{(2\pi)^3} \int d^3p \dots . \quad (23)$$

We will assume that the equilibrium state of the system in the absence of the external field is spatially homogeneous and therefore

$$\langle \hat{\eta}_i(x) \hat{\eta}_{i'}(x') \rangle = \langle \hat{\eta}_i(x+x'') \hat{\eta}_{i'}(x'+x'') \rangle, \quad (24)$$

where x'' is an arbitrary vector. Having introduced the Fourier components of the order parameter by formula (23), from (22) we obtain

$$A_{ix,i'x'} = \langle \hat{\eta}_i(x) \hat{\eta}_{i'}(x') \rangle = \frac{1}{V^2} \sum_{kk'} \langle \hat{\eta}_{ik} \hat{\eta}_{i'k'} \rangle e^{i(kx+k'x')}. \quad (25)$$

Comparing (24) with (25) shows that $\langle \hat{\eta}_{ik} \hat{\eta}_{i'k'} \rangle$ is different from zero only if $k' = -k$ and because

$$\langle \hat{\eta}_{ik} \hat{\eta}_{i'k'} \rangle = A_{i'i'}(k) \delta_{k',-k}, \quad A_{ix,i'x'} = \frac{1}{V^2} \sum_k A_{i'i'}(k) e^{ik(x-x')}, \quad A_{i'i'}(k) \equiv \langle \hat{\eta}_{ik} \hat{\eta}_{i',-k} \rangle, \quad (26)$$

$$A_{i'i'}(k) = A_{i'i}(-k), \quad A_{i'i}^*(k) = A_{i'i}(-k).$$

Note that all coordinate functions in the TD limit are different from 0 and ∞ . When moving to the TD limit, the sums over the wave vectors are replaced by an integral proportional to the volume of the system V . Therefore, formula (26) shows that the matrix $A_{i'i'}(k) \equiv \langle \hat{\eta}_{ik} \hat{\eta}_{i',-k} \rangle$ is proportional to the volume V in the TD limit. A simple calculation based on (26) now shows that

$$A_{ix,i'x'}^{-1} = \sum_k A_{i'i'}^{-1}(k) e^{ik(x-x')} \quad (27)$$

where $A_{i'i'}^{-1}(k)$ is the matrix inverted to $A_{i'i'}(k)$. The obtained expression for the quantity $A_{ix,i'x'}^{-1}$ allows to represent the Landau free energy (20) in the form

$$F_L(T, \eta) = F_0 + \frac{T}{2} \sum_{i'i'} \sum_k A_{i'i'}^{-1}(k) \delta\eta_{i,-k} \delta\eta_{i'k} + O(\delta\eta^3). \quad (28)$$

The main problems of the theory of phase transitions are related to the long-wave behavior of the system, that is to η_{ik} , to the order parameters for small wave vectors k . For this purpose, it is sufficient to investigate the Landau free energy for non-zero values $\delta\eta_{ik}$ only for small k . In this case, the function $A_{i'i'}^{-1}(k)$ can be expanded into a series in powers of the vector k . The specific form of this expansion depends on the symmetry of the system. In the simplest case, we have

$$A_{i'i'}^{-1}(k) = 2\delta_{i'i'}(a + gk^2) / TV \quad (29)$$

where the values a and g are some functions of the temperature T that do not depend on the volume (see the discussion after (26)). Taking into account this result, formula (22) gives the well-known Landau expression for the free energy of the system in the spatially inhomogeneous case

$$F_L = F_0 + \int_V d^3x \left[a \sum_i \delta\eta_i(x)^2 + g \sum_i \frac{\partial \delta\eta_i(x)}{\partial x_n} \frac{\partial \delta\eta_i(x)}{\partial x_n} \right] \quad (30)$$

proposed by him for phenomenological reasons [1]. A similar expression for non-equilibrium free energies was first introduced by Landau in [19]. Thus, we have discussed the basic concepts related constructions of non-equilibrium TD potentials. A generalization of the theory for the case of spatially inhomogeneous states has been developed.

3. The proof problem for the Boltzmann formula

3.1. Distribution function of equilibrium fluctuations

The study of equilibrium fluctuations became an important task of modern statistical physics after the research by Onsager [5], who formulated a fruitful idea about equilibrium fluctuations as an important class of non-equilibrium states. The main tool of such research is Boltzmann's formula (3) for the distribution function $w(\eta)$ of the values of some parameters $\eta \equiv \{\eta_a\}$ that describe the system state (a numbers the parameters). The list of such parameters is determined by the needs of the theory. Focusing on the needs of the theory of phase transitions of the II kind, we will call these parameters the order parameters.

Since no matter in what macroscopic conditions the situation is studied [3], we will limit ourselves to the consideration of TVN -states with using the canonical Gibbs distribution (1). The standard definition of the distribution function of order parameters $w(\eta)$ is given by formulas (2). The function $w(\eta)$ was found in our work [14], but later its approach was simplified. Our consideration begins with the expansion of expression (2) into the Fourier integral

$$\begin{aligned} w(\eta) &= \text{Sp } w_0 \delta(\eta - \hat{\eta}) = \frac{1}{(2\pi)^s} \int du \text{Sp } w_0 e^{i \sum_a u_a (\eta_a - \hat{\eta}_a)} = \\ &= \frac{1}{(2\pi)^s} e^{\frac{F_0}{T}} \int du e^{i \sum_a u_a \eta_a} \text{Sp } e^{-\frac{\hat{H} + \sum_a i u_a T \hat{\eta}_a}{T}} \quad (du \equiv \prod_a du_a). \end{aligned} \quad (31)$$

This expression can be written using the canonical Gibbs distribution w (7) in the presence of the external field h_a in terms of the free energy as a function of the field $F(h)$

$$e^{\frac{F(h)}{T}} = \text{Sp } e^{-\frac{\hat{H} + \sum_a h_a \hat{\eta}_a}{T}} \quad (32)$$

that gives

$$w(\eta) = \frac{1}{(2\pi)^s} \int du e^{i \sum_a u_a \eta_a} e^{\frac{F_0 - F(iuT)}{T}}. \quad (33)$$

As a result, the equilibrium distribution of the order parameters takes its final form

$$w(\eta) = \frac{1}{(2\pi)^s} \int du e^{\mathbf{G}(iuT)} e^{i \sum_a u_a \delta \eta_a}, \quad \delta \eta_a \equiv \eta_a - \eta_{a0}. \quad (34)$$

We are not aware of literary references to this result, that is, it was obtained by us in [14] for the first time.

For small $\delta \eta_a$, the distribution function can be represented in the standard exponential form, which can be compared with the Boltzmann formula (3). In particular, from (34) with accuracy up to the quadratic contributions, we approximately have

$$w(\eta) = A_0 \exp \left[\frac{1}{A_0} \sum_a A_a \delta \eta_a - \frac{1}{2} \sum_{a,b} D_{ab} \delta \eta_a \delta \eta_b + O(\delta \eta^3) \right] \quad (35)$$

where denoted

$$A_0 \equiv \frac{1}{(2\pi)^s} \int du e^{\mathbf{G}(iuT)}, \quad A_{a_1 \dots a_n} \equiv \frac{i^n}{(2\pi)^s n!} \int du e^{\mathbf{G}(iuT)} u_{a_1} \dots u_{a_n}, \quad (36)$$

$$D_{ab} \equiv \frac{2}{A_0} \left(\frac{1}{2A_0} A_a A_b - A_{ab} \right).$$

Note that formula (35) expresses a rather complicated result, since the function $\mathbf{G}(h)$ depends on all the correlation functions of order parameters. In addition, the function $w(\eta)$ is normalized according to (35) only when taking into account all terms of the series in the exponent. In the Gaussian approximation, the distribution $w(\eta)$ should be written in the form

$$w_2(\eta) \equiv C \exp \left[\frac{1}{A_0} \sum_a A_a \delta \eta_a - \frac{1}{2} \sum_{a,b} D_{ab} \delta \eta_a \delta \eta_b \right] \quad (37)$$

and the multiplier should be determined from the normalization condition.

3.2. The effective Landau Hamiltonian

To study the influence of equilibrium fluctuations on the thermodynamics of a system, Landau proposed [1] the definition of the free energy of non-equilibrium states of the system $H_L(\eta)$ (the effective Hamiltonian of the system, as it was proposed to call it) by the Boltzmann formula (5) with a normalization factor, which is expressed through the total free energy of the equilibrium system F_0 . This definition, taking into account expression (2) for the distribution of equilibrium values of the order parameters $w(\eta)$, can be written in the form

$$H_L(\eta) = -T \ln \text{Sp} e^{-\frac{\hat{H}}{T}} \delta(\eta - \hat{\eta}). \quad (38)$$

This function allows to calculate the free energy of the system F_0 using the formula

$$F_0 = -T \ln \int d\eta e^{-\frac{H_L(\eta)}{T}}, \quad (39)$$

since accordingly (1)

$$\int d\eta e^{-\frac{H_L(\eta)}{T}} = \text{Sp} e^{-\frac{\hat{H}}{T}} = e^{-\frac{F_0}{T}}.$$

Unfortunately, at present, examples of calculating the effective Hamiltonian using formula (38) are unknown. Therefore, formula (39) is used only with the phenomenological expression for $H_L(\eta)$ (see, for example, [2, 9, 11]).

However, we have found an exact expression (34) for the function $w(\eta)$, which gives the formula for the effective Hamiltonian $H_L(\eta)$

$$H_L(\eta) = F_0 - T \ln w(\eta), \quad (40)$$

which can be written in the form of expansion in powers of $\delta\eta_a$. But expression (13) cannot be used directly to calculate the free energy of the system F_0 based on formula (39), because it contains F_0 and transforms (39) into an identity. At the same time, the approximate expression for $w(\eta)$ taking into account the first contributions $A_{a_1 \dots a_n}$ gives an approximate expression for $H_L(\eta)$, which, based on formula (11), makes it possible to investigate the contribution of the quantities $A_{a_1 \dots a_n}$ to the free energy F_0 . This approach is better than using a phenomenological expression for $H_L(\eta)$ because it expresses the result not through phenomenological coefficients, but through correlation functions $\langle \hat{\eta}_{a_1} \dots \hat{\eta}_{a_n} \rangle$. In this sense, the contribution F_{02} to the free energy F_0 from the Hamiltonian in the Gaussian approximation $H_{L2}(\eta)$ should be estimated by the formula

$$F_{02} = -T \ln \int d\eta e^{-\frac{H_{L2}(\eta)}{T}} \quad (41)$$

where

$$H_{L2}(\eta) = -T \left[\frac{1}{A_0} \sum_a A_a \delta\eta_a - \frac{1}{2} \sum_{a,b} D_{ab} \delta\eta_a \delta\eta_b \right], \quad (42)$$

since, respectively (35) and (40),

$$H_L(\eta) = F - T \left[\ln A_0 + \frac{1}{A_0} \sum_a A_a \delta\eta_a - \frac{1}{2} \sum_{a,b} D_{ab} \delta\eta_a \delta\eta_b + O(\delta\eta^3) \right]. \quad (43)$$

It should be noted that the obtained formulas (34), (35) for the distribution function $w(\eta)$ and expressions (40), (43) for the effective Hamiltonian $H_L(\eta)$ are not available in the literature known to us.

3.3. The effective Hamiltonian of a subsystem of identical particles

Let's apply the developed theory to the construction of the effective Landau Hamiltonian $H_{L_s}(x_1 \dots x_s)$ for s -particle subsystem of the system of N identical point

particles, when the phase variables x_1, \dots, x_s of particles play the role of parameters η_a . Denoting the probability density of these phase variables by $w_s(x_1 \dots x_s)$, definition (5) of the Hamiltonian $H_{L_s}(x_1 \dots x_s)$ can be written in the form

$$w_s(x_1 \dots x_s) = e^{\frac{F_0 - H_{L_s}(x_1 \dots x_s)}{T}}. \quad (44)$$

The function $w_s(x_1 \dots x_s)$ can be expressed through the s -particle distribution function $f_s(x_1 \dots x_s)$ introduced by Bogolyubov [2]. Using the details of the designations of the monograph [12] in terms of the canonical Gibbs distribution $w_N^c(x_1 \dots x_N)$, we have

$$f_s(x_1 \dots x_s) = \frac{1}{(N-s)!} \int dx_{s+1} \dots dx_N w_N^c(x_1 \dots x_s, x_{s+1} \dots x_N), \quad (45)$$

$$w_N^c(x_1 \dots x_N) \equiv e^{\frac{F_0 - H_N(x_1 \dots x_N)}{T}}, \quad \frac{1}{N!} \int dx_1 \dots dx_N w_N^c(x_1 \dots x_N) = 1$$

and therefore

$$w_s(x_1 \dots x_s) = \frac{(N-s)!s!}{N!} f_s(x_1 \dots x_s), \quad \frac{1}{s!} \int dx_1 \dots dx_s w_s(x_1 \dots x_s) = 1 \quad (46)$$

($h^\nu dx_a$ is the product of the differentials of the phase variables of the a -particle, ν is the number of degrees of freedom of a particle, h is the Planck constant).

Bogolyubov [2] constructed a perturbation theory for calculating the function $f_s(x_1 \dots x_s)$ in the approximation of the low density of the system $n \equiv N/V$ for a system of point identical particles, when in our formulas $x_a \equiv (\mathbf{x}_a, \mathbf{p}_a)$, $dx_a \equiv d^3\mathbf{x}_a d^3\mathbf{p}_a / h^3$. In the thermodynamic limit, it was found that

$$f_s(x_1 \dots x_s) = e^{-\frac{U_s}{T}} \chi_s(\mathbf{x}_1 \dots \mathbf{x}_s) \prod_{1 \leq a \leq s} w(\mathbf{p}_a), \quad w(\mathbf{p}) \equiv \frac{n}{(2\pi m T)^{3/2}} e^{-\frac{\mathbf{p}^2}{2mT}};$$

$$\ln \chi_s = n \int d^3\mathbf{x}_{s+1} \left[\prod_{1 \leq a \leq s} (1 + f_{a,s+1}) - 1 - \sum_{1 \leq a \leq s} f_{a,s+1} \right] + O(n^2); \quad (47)$$

$$U_s \equiv \sum_{1 \leq a < b \leq s} \Phi_{ab}, \quad \Phi_{ab} \equiv \Phi(|\mathbf{x}_a - \mathbf{x}_b|), \quad f_{ab} \equiv e^{-\frac{\Phi(|\mathbf{x}_a - \mathbf{x}_b|)}{T}} - 1$$

where $\Phi(r)$ is the potential of pair interaction of particles. In this case, the effective Landau Hamiltonian is given by the formula

$$H_{L_s} = (F - F_{s0}) + (H_s - T \ln \chi_s) \quad (48)$$

where denoted

$$H_s = \sum_{1 \leq a \leq s} \frac{\mathbf{p}_a^2}{2m} + U_s, \quad F_{s0} = -T \ln \frac{(2\pi m T)^{3s/2} V^s}{s!}. \quad (49)$$

For large s value F_{s_0} is the free energy of the ideal gas of the particles of the system. Thus, the effective Landau Hamiltonian H_{L_s} of the low-density gas of s -particle system differs from the Hamiltonian function H_s of the s -particle system by the term $-T \ln \chi_s$ of the first order of smallness.

The expression (48) for the effective Hamiltonian is rather complicated since it contains contributions from multiparticle interactions. Similarly to (41), (42), it is possible to estimate the contribution of the three-particle effective interaction to the free energy, in particular.

3.4. The generalized Boltzmann formula

By definition, the Boltzmann formula expresses the distribution function of the order parameters of a system in equilibrium $w(\eta)$ through the free energy of a nonequilibrium state $F(\eta)$, which occurs in fluctuation and is described by the same parameters. In this section, we set the problem of expressing the distribution function $w(\eta)$ in terms of the Landau free energy $F_L(\eta)$, which, according to the Landau–Leontovich definition, is the free energy of the nonequilibrium state under consideration. We take $w(\eta)$ in the form (33)

$$w(\eta) = \frac{1}{(2\pi)^s} \int du e^{i \sum_a u_a \eta_a} e^{-\frac{F_0 - F(iuT)}{T}}$$

where $F(h)$ is the free energy of the system in the external field h_a presence. According to (1.4), the Landau free energy $F_L(\eta)$ as a function of order parameters is given by formula (10)

$$F_L(\eta) = F(h(\eta)) - \sum_a h_a(\eta) \eta_a, \quad (50)$$

in which $h_a(\eta)$ are functions reversed to the average values $\eta_a(h)$ of order parameters η_a in the presence of the field h_a . The last two formulas give the following expression for the distribution function $w(\eta)$ through the free energy of the non-equilibrium state $F_L(\eta)$

$$w(\eta) = \frac{1}{(2\pi)^s} \int du e^{i \sum_a u_a [\eta_a - \eta_a(iuT)]} e^{-\frac{1}{T} [F_0 - F_L(\eta(iuT))]}.$$

Successive substitutions of variables when integrating $u_a = h_a / iT$, $h_a = h_a(\tilde{\eta})$, simplify this expression and give formulas that can be called generalized Boltzmann formulas

$$w(\eta) = \frac{1}{(2\pi i)^s} \int dh e^{\frac{1}{T} \sum_a h_a [\eta_a - \eta_a(h)]} e^{-\frac{1}{T} [F_0 - F_L(\eta(h))]}, \quad (51)$$

$$w(\eta) = \frac{1}{(2\pi i)^s} \int d\tilde{\eta} \frac{\partial h}{\partial \tilde{\eta}} e^{\frac{1}{T} \sum_a h_a(\tilde{\eta}) [\eta_a - \tilde{\eta}_a]} e^{-\frac{1}{T} [F_0 - F_L(\tilde{\eta})]}$$

where $\partial h / \partial \tilde{\eta}$ is the corresponding Jacobi determinant. The closest to the standard form of the Boltzmann formula is the second expression (51).

Conclusions

The article is a continuation of the works of the authors [13–15] and sets the task of clarifying some of their statements and simplifying and clarifying the calculations. It discusses equilibrium fluctuations and non-equilibrium states, in which the system is when exiting fluctuations. Fluctuations and non-equilibrium states are described reduced by a relatively small number of parameters η_a , the list of which is determined by the problem under consideration. In the most important application of the discussed scheme to the theory of phase transitions of the II kind, they are called order parameters. This work considers macroscopic equilibrium states described by the canonical Gibbs distribution and characterized by non-equilibrium free energy at the developed fluctuations. The paper discusses the entire complex of issues devoted to the proof and substantiation of Boltzmann's formula for the distribution $w(\eta)$ of reduced description parameters of the equilibrium system. We obtained an exact expression for this function, not found in the literature. At the same time, we have simplified the derivation of the final expression for the distribution compared to [14, 15] and correctly estimated its importance.

The standard Boltzmann formula relates the distribution $w(\eta)$ to the free energy of the non-equilibrium state $F(\eta)$, which occurs in an equilibrium fluctuation. Therefore, we pay a lot of attention to its construction. In the work, the free energy of the non-equilibrium state according to Leontovich $F_L(\eta)$ is called the free energy of the equilibrium state in the presence of an external field that simulates the non-equilibrium state of the system with subsequent Legendre transformation that makes the order parameters its own variables. Leontovich proposed this definition by proving that the function $F_L(\eta)$ has a minimum in equilibrium. Our analysis showed that Landau also used some function as the free energy of the nonequilibrium state. Unlike Landau and Leontovich, we calculated the free energy around the equilibrium state of the system in microscopic theory. The calculations of our work [14] have been refined. Note that our results are more general since Landau studied the function $F_L(\eta)$ only near the phase transition point where the order parameters are small. We also introduced the free energy of a non-equilibrium state in the presence of an external field (a similar formula was used by Landau) and indicated that it has an extremum in equilibrium (here we are not talking about an external field that simulates a non-equilibrium state).

Among other results of our work related to the free energy of a non-equilibrium state, we note that Peletminsky's definition of the entropy of a non-equilibrium system confirms Leontovich's result. We have also developed a generalization of Leontovich's definition for spatially inhomogeneous states of the system when the order parameters depend on the coordinates. At the same time, an expression for non-equilibrium free energy with gradients of order parameters was obtained, which was first proposed by Landau for phenomenological reasons. Based on our exact expressions for the distribution $w(\eta)$ and non-equilibrium free energy $F_L(\eta)$, we obtained a generalized Boltzmann formula that does not have its standard structure, as expected. The quantities $w(\eta)$, $F_L(\eta)$, in our microscopic theory, are expressed through all the correlation functions of the order parameters. It can be shown that, taking into account only binary correlations, the Boltzmann formula is valid in its standard form [16].

The work also explores Landau's idea to determine the non-equilibrium free energy (the effective Hamiltonian of the system $H_L(\eta)$, according to Landau's terminology) directly from the Boltzmann formula. However, we did not manage to fully implement

Landau's definition. Only the exact expression is obtained $H_L(\eta) = F_0 - T \ln w(\eta)$, where F_0 is the equilibrium free energy of the system in the external field absence. This expression does not make it possible to calculate the free energy F_0 from the Hamiltonian $H_L(\eta)$, since the normalization condition will lead to the identity.

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