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# THERMODYNAMIC PERTURBATION THEORY FOR CLASSICAL SYSTEMS BASED ON SELF-CONSISTENT FIELD MODEL

*A formulation of the thermodynamic perturbation theory for classical many-particle systems, which is based on a self-consistent field model as the main approximation, has been proposed. Systems of particles in a spatially homogeneous state and in external fields that increase or decrease as the distance from the surface changes are considered as an example. The application of the self-consistent field approach as the main approximation is found to enable the description of many-particle systems, in which the concentration of particles and the interactions between them are not low, as well as phase transitions in such systems.*

*Keywords*: perturbation theory, self-consistent field, thermodynamic quantities, dense gases and fluids.

## 1. Introduction

In the case where the energy contains rather small terms, which can be neglected in the main approximation, the perturbation theory is used to calculate thermodynamic quantities [1]. As the main approximation, the model of ideal gas is used most often. In this case, the role of small terms can be played, e.g., by the potential energy of particles in the external field or the particle-to-particle interaction if it is rather small. However, the choice of the ideal-gas model as the zeroth-order approximation demands that the particle-to-particle interaction should be weak, which does not allow the perturbation theory to be used to study the systems with broken symmetries, e.g., the transitions into the crystalline state, when the translational symmetry of the system becomes broken. Since the phenomena associated with the symmetry breaking result from the interaction between particles, it is important that this interaction should be somewhat taken into account already in the main approximation. Such a natural approximation that preserves a relative simplicity of description and simultaneously makes allowance for the particle-to-particle interaction is the model of self-consistent field, which is widely applied to study the phase transitions, in particular, between various modifications of simple crystals (see works [2, 3] and the references therein). Earlier [4], A.A. Vlasov paid attention to the importance of the account for self-consistent field effects, while describing the phenomenon of crystallization in a system of neutral classical particles. The application of the self-consistent field model turns out also important in the liquid-state theory [5, 6], where the energy of interaction between particles cannot be considered as a small correction to the kinetic energy. The self-consistent description is of special importance, while studying the inhomogeneous fluid states, in particular, the surface phenomena [7].

A version of thermodynamic perturbation theory, which is proposed in this work for many-particle systems described in the framework of classical mechanics, makes it possible to find corrections to the results obtained in the self-consistent field approximation. Moreover, as was shown with the use of the model of anharmonic quantum oscillator as an example [8, 9], the perturbation theory remains also relevant in the case where the interaction between particles is not weak. The proposed formulation is close to the approach used in the construction of a quantum-field perturbation theory for Fermi [10] and Bose [11] systems. In this work, a model of self-consistent field is formulated, and a nonlinear equation for the one-particle distribution function is obtained. The second-order corrections to the configuration integral and the free energy are found. The obtained general relations are used to consider a spatially homogeneous system and a system in external fields that either increase or decrease, as the distance from the surface increases. The developed approach can be used to describe dense gases and fluids, surface phenomena, and phase transitions.

## 2. Self-Consistent Field Model as the Main Approximation

Let us formulate the thermodynamic perturbation theory for classical systems that are characterized by the Hamiltonian

$$H(p,q) = T(p) + U(q), \tag{1}$$

where $p \equiv \{\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_N\}$ are the momenta; $q \equiv \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N\}$ the coordinates, $N$ the total number of particles,

$$T(p) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{2}$$

is the kinetic energy, and $m$ particle's mass. The potential energy $U(q)$ involves the interaction of particles with the external field $U_0(\mathbf{r})$ and the pair interaction between the particles,

$$U(q) = \sum_{i=1}^{N} U_0(\mathbf{r}_i) + \frac{1}{2} \sum_{i\neq j=1}^{N} U(\mathbf{r}_i, \mathbf{r}_j), \tag{3}$$

where $U(\mathbf{r}_i, \mathbf{r}_j) = U(\mathbf{r}_j, \mathbf{r}_i)$.

The partition function equals $Z = \int e^{-\beta H(p,q)} d\Gamma$, where $d\Gamma = dp\, dq/(N! h^{3N})$, $h$ is Planck's constant, and $\beta = T^{-1}$ is the inverse temperature. After the integration over the momenta, the partition function reads

$$Z = \left(\frac{2\pi m T}{h^2}\right)^{3N/2} \frac{Z_Q}{N!},$$

where

$$Z_Q = \int e^{-\beta U(q)} dq \tag{4}$$

is the configuration integral. The density of probability to find the system in a state with the set of coordinates $\{q\}$ equals

$$w(q) = \frac{\exp\left[-\beta U(q)\right]}{Z_Q}. \tag{5}$$

In most cases, it is the particle-to-particle interaction that is considered as a perturbation. This approach is justified for rarefied systems with weak interaction. For dense systems with strong interaction, this approximation is invalid. In this case, it is convenient to reformulate the perturbation theory by extracting the self-consistent field and excluding it from the perturbation, as was done for quantum-mechanical Fermi and Bose many-particle systems in works [10,11]. Therefore, the interaction between particles is approximately taken into account already in the main approximation.

Before constructing the perturbation theory, let us introduce a self-consistent field into the theory by presenting interaction (3) in the form

$$U(q) = V(q) + W(q), \tag{6}$$

where

$$\begin{aligned} V(q) &\equiv \sum_{i=1}^{N} U_0(\mathbf{r}_i) + \tilde{U}(q) + E_0, \\ W(q) &\equiv U_2(q) - \tilde{U}(q) - E_0. \end{aligned} \tag{7}$$

Here, $U_2(q) \equiv \frac{1}{2}\sum_{i\neq j=1}^{N} U(\mathbf{r}_i, \mathbf{r}_j)$ is the potential energy of pair interaction, and $\tilde{U}(q) = \sum_{i=1}^{N} \tilde{U}(\mathbf{r}_i)$ is the potential energy of particles in a self-consistent field; the specific form for the latter will be found later. The energy $V(q)$ is regarded as the main approximation, and $W(q)$ as a perturbation. Since,

$$V(q) \equiv \sum_{i=1}^{N} V(\mathbf{r}_i) + E_0,$$

where

$$V(\mathbf{r}_i) \equiv U_0(\mathbf{r}_i) + \tilde{U}(\mathbf{r}_i),$$

the configuration integral (4) in the main approximation looks like

$$Z_Q^{(0)} = e^{-\beta E_0} z^N, \tag{8}$$

where $z \equiv \int e^{-\beta V(\mathbf{r})} d\mathbf{r}$. In this approximation, the probability to find the system in a configuration with the coordinates $\{q\}$ can be presented as a product of one-particle distribution functions $f(\mathbf{r}) = e^{-\beta V(\mathbf{r})}$, i.e.

$$w^{(0)}(q) = \prod_{i=1}^{N} f(\mathbf{r}_i). \tag{9}$$

The distribution function is normalized by the condition $\int f(\mathbf{r}) d\mathbf{r} = 1$.

## 3. Equation for Distribution Function

Let us define a self-consistent field from the requirement that the approximating potential energy $V(q)$ should be close to the exact one as much as possible. With that end in view, let us introduce the functional

$$I \equiv \langle U(q) - V(q) \rangle = \langle W(q) \rangle \tag{10}$$

and vary it with respect to the one-particle distribution function, demanding that $\delta I = 0$. Hereafter, the angular brackets mean the averaging with the probability density (9). As a result, we obtain the following expression for the potential energy of a particle in the self-consistent field:

$$\tilde{U}(\mathbf{r}) = (N-1) \int U(\mathbf{r}, \mathbf{r}') f(\mathbf{r}')\, d\mathbf{r}'. \tag{11}$$

Note that the same expression for the potential energy can also be obtained from the requirement of the minimum for the free energy calculated in the framework of the self-consistent field model. Relation (11) together with the definition of one-particle distribution function, $f(\mathbf{r}) = e^{-\beta V(\mathbf{r})}/z$, brings about the equation

$$f(\mathbf{r}) = z^{-1} \exp\Biggl\{-\beta \Biggl[U_0(\mathbf{r}) + \\ + (N-1) \int U(\mathbf{r}, \mathbf{r}') f(\mathbf{r}')\, d\mathbf{r}'\Biggr]\Biggr\}, \tag{12}$$

where $z \equiv \int \exp\{-\beta[U_0(\mathbf{r}) + \tilde{U}(\mathbf{r})]\} d\mathbf{r}$. The obtained nonlinear integral equation allows us to find the distribution function and, hence, the potential energy of a particle in the self-consistent field (11). This equation can also have solutions dependent on the coordinates in the case where the external field is absent and, therefore, can describe phase transitions with a violation of the translational symmetry; for instance, transitions into the crystalline state. Note that an equation of type (12) was proposed in [4]. Later on, it was used for the description of the crystalline state and polymorphic transformations [2, 3]. The application of the Bogolyubov variational principle makes it possible to develop the variational method of solution of the self-consistent field equation (12) [2, 3].

## 4. Second-Order Correction to Free Energy

To an accuracy of the second-order terms, the configuration integral (4) can be written in the form

$$Z_Q = z^N e^{-\beta E_0} \left[1 - \beta \langle W(q) \rangle + \frac{\beta^2}{2!} \langle W(q)^2 \rangle \right]. \tag{13}$$

The undetermined quantity $E_0$ is selected according to the requirement that the first-order correction should be equal to zero, $\bigl\langle W(q) \bigr\rangle = 0$. Therefore, $E_0 \equiv \bigl\langle U_2(q) \bigr\rangle - \bigl\langle \tilde{U}(q) \bigr\rangle$ or

$$E_0 = -\frac{N(N-1)}{2} \int U(\mathbf{r}, \mathbf{r}') f(\mathbf{r}) f(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}'. \tag{14}$$

As a result, perturbation (7) looks like

$$W(q) \equiv [U_2(q) - \langle U_2(q) \rangle] - \Bigl[\tilde{U}(q) - \Bigl\langle \tilde{U}(q) \Bigr\rangle\Bigr], \tag{15}$$

so that

$$\bigl\langle W^2(q) \bigr\rangle = \\ = \Bigl[\bigl\langle U_2^2(q) \bigr\rangle - \bigl\langle U_2(q) \bigr\rangle^2\Bigr] + \Bigl[\bigl\langle \tilde{U}^2(q) \bigr\rangle - \bigl\langle \tilde{U}(q) \bigr\rangle^2\Bigr] - \\ - 2\Bigl[\bigl\langle U_2(q)\, \tilde{U}(q) \bigr\rangle - \bigl\langle U_2(q) \bigr\rangle \bigl\langle \tilde{U}(q) \bigr\rangle\Bigr], \tag{16}$$

where the averaging, as was done earlier, is carried out with the probability density (9). Hence, a correction to the main approximation emerges only in the second order. To calculate it, we must determine mean-square fluctuations of the self-consistent and pair potential energies. Note that those quantities are proportional to the number of particles.

Let us introduce the notations for the averaged potential energy of two-particle interaction and its square:

$$\begin{aligned} &\bigl\langle U(1,2) \bigr\rangle \equiv \int U(\mathbf{r}, \mathbf{r}') f(\mathbf{r}) f(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}', \\ &\bigl\langle U^2(1,2) \bigr\rangle \equiv \int U^2(\mathbf{r}, \mathbf{r}') f(\mathbf{r}) f(\mathbf{r}')\, d\mathbf{r}\, d\mathbf{r}', \\ &\bigl\langle U(1,2) U(1,3) \bigr\rangle \equiv \\ &\equiv \int U(\mathbf{r}, \mathbf{r}') U(\mathbf{r}, \mathbf{r}'') f(\mathbf{r}) f(\mathbf{r}') f(\mathbf{r}'')\, d\mathbf{r}\, d\mathbf{r}'\, d\mathbf{r}''. \end{aligned} \tag{17}$$

In view of Eq. (17), the average self-consistent and pair potential energies are given by the formulas

$$\big\langle\tilde U(q)\big\rangle = 2\,\big\langle U_2(q)\big\rangle = N(N-1)\big\langle U(1,2)\big\rangle, \qquad (18)$$

and the averages of the squares and the products of those potential energies look like

$$\big\langle\tilde U^2(q)\big\rangle = N(N-1)^2\big\langle U(1,2)U(1,3)\big\rangle + \\ + N(N-1)^3\big\langle U(1,2)\big\rangle^2, \qquad (19)$$

$$\big\langle U_2^2(q)\big\rangle = \frac{1}{2}N(N-1)\big\langle U^2(1,2)\big\rangle + \\ + N(N-1)(N-2)\big\langle U(1,2)U(1,3)\big\rangle + \\ + \frac{1}{4}N(N-1)(N-2)(N-3)\big\langle U(1,2)\big\rangle^2, \qquad (20)$$

$$\big\langle\tilde U(q)U_2(q)\big\rangle = N(N-1)^2\big\langle U(1,2)U(1,3)\big\rangle + \\ + \frac{1}{2}N(N-1)^2(N-2)\big\langle U(1,2)\big\rangle^2. \qquad (21)$$

As a result, we obtain

$$\big\langle W^2(q)\big\rangle = \frac{N(N-1)}{2}\times \\ \times\Big[\big\langle U^2(1,2)\big\rangle - 2\big\langle U(1,2)U(1,3)\big\rangle + \big\langle U(1,2)\big\rangle^2\Big]. \qquad (22)$$

Note that, while calculating the averaged quantities, the cumulant expansion method [12] can be applied.

To the second-order accuracy, the free energy $F = -T\ln Z$ is determined by the formula

$$F = E_0 - NT\left[1+\ln\frac{z}{N}\left(\frac{2\pi mT}{h^2}\right)^{3/2}\right] - \frac{1}{2T}\big\langle W^2(q)\big\rangle. \qquad (23)$$

The first two terms in Eq. (23) correspond to the free energy $F_0$ in the self-consistent field approximation. With regard for Eq. (14), this quantity looks like

$$F_0 = -\frac{N(N-1)}{2}\int U(\mathbf r,\mathbf r')f(\mathbf r)f(\mathbf r')\,d\mathbf r\,d\mathbf r' - \\ - NT\left[1+\ln\frac{z}{N}\left(\frac{2\pi mT}{h^2}\right)^{3/2}\right]. \qquad (24)$$

## 5. Spatially Homogeneous System

As was mentioned above, the formulation proposed for the perturbation theory is most efficient for the theoretical researches of spatially inhomogeneous systems in external fields or in states with a broken translational symmetry. However, let us first consider the most simple case of a spatially homogeneous system, by supposing that $U_0(\mathbf r) = 0$ and $U(\mathbf r,\mathbf r') = U(|\mathbf r-\mathbf r'|)$. In this case, the distribution function and the self-consistent field do not depend on coordinates, so that

$$f=\frac{1}{V},\quad z = Ve^{-\beta\tilde U}, \\ \tilde U = \frac{N-1}{V}U_{\rm I},\quad E_0 = -\frac{N(N-1)}{2V}U_{\rm I}, \qquad (25)$$

and

$$\big\langle U(1,2)\big\rangle = \frac{U_{\rm I}}{V},\quad \big\langle U^2(1,2)\big\rangle = \frac{U_{\rm II}}{V}, \\ \big\langle U(1,2)U(1,3)\big\rangle = \frac{U_{\rm I}^2}{V^2}, \qquad (26)$$

where $V$ is the volume of the system, and

$$U_{\rm I} = 4\pi\int_0^\infty U(r)r^2dr,\quad U_{\rm II} = 4\pi\int_0^\infty U^2(r)r^2dr. \qquad (27)$$

At short distances, particles strongly repulse one another. Therefore, integrals (27) diverge for model potentials growing at short distances, such as the Lennard-Jones potential [5,6]. The role of short-range forces for classical many-particle systems was considered in work [12].

Note that the application of model potentials infinitely growing at short distances, for which the Fourier image is absent, gives rise to considerable difficulties. In particular, such potentials do not allow one to calculate the scattering length, in terms of which the scattering cross-section at low energies is expressed. A requirement of atomic hardness at arbitrary high pressures is too strict, because there must exist a pressure, at which the atom would be "destroyed", i.e. it would cease to exist as a separate structural unit. Therefore, in our opinion, it is natural and physically substantiated to use potentials that are finite at short distances. It should also be noted that the quantum-chemical calculations give potentials, to which this property is inherent [13, 14].

In the simplest case, the following potential can be used:

$$U(r) = \begin{cases} U_m, & r < r_0, \\ 0, & r > r_0, \end{cases} \tag{28}$$

(the "semitransparent" sphere model), for which

$$U_{\mathrm{I}} = \frac{4\pi}{3} U_m r_0^3, \quad U_{\mathrm{II}} = \frac{4\pi}{3} U_m^2 r_0^3. \tag{29}$$

Note that the quantity $U_{\mathrm{I}}$ is directly coupled with the observable scattering length $a_0 = mU_{\mathrm{I}}/(4\pi\hbar^2)$. In our case (the self-consistent field model), the free energy in the thermodynamic limit $N \to \infty$, $V \to \infty$, and $n = N/V = \mathrm{const}$ looks like

$$F_0 = N\left\{\frac{nU_{\mathrm{I}}}{2} - T\left[1 + \ln\frac{1}{n}\left(\frac{2\pi mT}{h^2}\right)^{3/2}\right]\right\}. \tag{30}$$

The first term in Eq. (30) corresponds to the contribution given to the free energy by the particle-to-particle interaction. Taking into account that

$$\left\langle W^2(q)\right\rangle = N\frac{nU_{\mathrm{II}}}{2}, \tag{31}$$

the second-order correction to the free energy is obtained as follows:

$$F_2 = -N\frac{nU_{\mathrm{II}}}{4T}. \tag{32}$$

The perturbation theory is applicable, if $F_2 \ll F_0$. Here, there are two possibilities. If $nU_{\mathrm{I}} \gg T$, the following two conditions should be satisfied simultaneously:

$$\frac{T}{U_m} \ll (r_0/l)^3, \quad \frac{T}{U_m} \gg 1, \tag{33}$$

where $l = n^{-1/3}$ is the average distance between particles, $\Lambda \equiv \sqrt{2\pi\hbar^2/(mT)}$ is the thermal wavelength of the particle, and $r_0$ is a characteristic radius of the interparticle potential. For the classical description to be applicable, the inequality $\Lambda \ll l$ has to be satisfied. In view of the definition of scattering length, conditions (33) can be rewritten in the form

$$\frac{r_0^3}{a_0\Lambda^2} \gg 1, \quad \frac{l^3}{a_0\Lambda^2} \ll 1. \tag{34}$$

Theoretically, they can be obeyed, in principle, at very high densities, when $r_0 \gg l$, but this can hardly be realized in practice.

In the other limiting case, $nU_{\mathrm{I}} \ll T$, which is equivalent to $l^3 \gg a_0\Lambda^2$, it is necessary that

$$nU_{\mathrm{II}} \ll T^2, \quad l^3 \gg \frac{a_0^2\Lambda^4}{r_0^3}. \tag{35}$$

These requirements are satisfied at low densities. One should pay attention that the particle-to-particle interaction itself, which is characterized by the scattering length, is not assumed to be small, because the conditions for the perturbation theory to be applicable are determined by the relations between the characteristic lengths $a_0$, $r_0$, $l$, and $\Lambda$.

With regard for the second-order correction, the pressure is described by the formula

$$p = nT + \frac{n^2}{2}\left(U_{\mathrm{I}} - \frac{U_{\mathrm{II}}}{2T}\right) = nT\big[1 + B(T)n\big]. \tag{36}$$

From whence, the following expression for the virial coefficient is obtained:

$$B(T) = \frac{1}{2T}\left(U_{\mathrm{I}} - \frac{U_{\mathrm{II}}}{2T}\right). \tag{37}$$

As was marked above (see Eq. (33)), if $nU_{\mathrm{I}} \gg T$, there must be $U_{\mathrm{II}}/T \ll U_{\mathrm{I}}$, so the sign of virial coefficient in this case is determined by the sign of $U_{\mathrm{I}}$ (Eq. (27)) or the scattering length. At $T \gg nU_{\mathrm{I}}$, the contributions to $B(T)$ from $U_{\mathrm{I}}$ and $U_{\mathrm{II}}$ can be of the same order. In this case, Eq. (37) can be used to determine the Boyle temperature $T_{\mathrm{B}}$, at which $B(T_{\mathrm{B}}) = 0$:

$$T_{\mathrm{B}} = \frac{U_{\mathrm{II}}}{2U_{\mathrm{I}}} = \frac{U_m}{2}. \tag{38}$$

If $bn \ll 1$, where $b = 16\pi r_0^3/3$, Eq. (36) can be rewritten in the form of the van der Waals equation,

$$\big(p + an^2\big)\big(1 - bn\big) = nT, \tag{39}$$

where $a = (2\pi/3)r_0^3 U_m[8T/U_m + U_m/2T - 1]$. In the van der Waals theory, the parameter $a$ is positive and independent of the temperature. In our case, the sign of $a$ is determined by the sign of the particle-to-particle interaction. At the repulsion, $U_m > 0$, so that $a > 0$ as well. In addition, in the used approximation, $a$ depends on the temperature. However, for potential (28), its sign is not changed, as the temperature varies.

The expression for the entropy $S = -(\partial F/\partial T)_V$ that takes the second-order correction into account looks like

$$S = N\left[\frac{5}{2} + \ln\frac{1}{n}\left(\frac{2\pi mT}{h^2}\right)^{3/2}\right] - N\frac{nU_{\mathrm{II}}}{4T^2}. \tag{40}$$

Here, the second term gives a correction to the Sackur–Tetrode formula due to the interaction [15]. The contribution inserted by this correction decreases, as the temperature grows. Note that the results presented above for the trivial spatially homogeneous case can also be obtained with the help of the standard thermodynamic perturbation theory [1]. In the latter case, the account for the first-order correction turns out equivalent to the self-consistent field approximation. The difference of this approach from the standard one consists in that the contribution of self-consistent field effects is not assumed to be small in comparison with the results obtained in the framework of the ideal gas model. In this special case, the second-order corrections in both approaches coincide. The application of the developed approach is not reduced to the standard perturbation theory and plays a considerable role in the description of spatially inhomogeneous states and phase transitions with a violation of the translational symmetry.

## 6. System in Homogeneous External Field

Let us apply our approach to the consideration of a system in an external field. The self-consistent equation (12) can be presented in the form

$$f(\mathbf{r}) = \tilde{f}(\mathbf{r}) \exp\big[\beta(\mu - \mu_0)\big] \times \\ \times \exp\left[-\beta(N-1)\int U(\mathbf{r},\mathbf{r}')f(\mathbf{r}')d\mathbf{r}'\right], \tag{41}$$

where the chemical potential $\mu$ is defined by the formula $z = e^{-\beta\mu}$. Here, we introduced the distribution function of particles in an external field in the absence of the interaction between particles, $\tilde{f}(\mathbf{r}) = \exp\{-\beta[U_0(\mathbf{r}) - \mu_0]\}$, and $e^{-\beta\mu_0} = \int e^{-\beta U_0(\mathbf{r})}d\mathbf{r}$.

Let a many-particle system with the interparticle potential $U(\mathbf{r},\mathbf{r}') = U(|\mathbf{r}-\mathbf{r}'|)$, being embedded into the field $U_0(x)$, occupy the half-space $x > 0$. Here, two possibilities must be distinguished. In the first case, the potential $U_0(x)$ increases with the coordinate $x$. The homogeneous field $U_0(x) = gx$ is an example. In this field, the distribution function tends to zero at infinity. Hence, all particles are mainly concentrated near the surface, and the particle concentration falls down, as the distance grows. In the second case, the absolute value of the field diminishes, as the distance grows, and tends to zero at infinity. The potential of the van der Waals forces $U_0(x) = -\alpha/x^3$ [16] is an example. Here, the particle concentration far from the surface tends to an average concentration that would be in the spatially homogeneous system. The account for those forces is of importance, while studying the influence of boundaries on the fluid properties, in particular, while researching the superfluid helium films and boundary phenomena in them [17].

First, let us consider the case where $U_0(x)$ is a growing function, and $f(x) \to 0$ at $x \to \infty$. In this case, it is convenient to change to a new distribution function $f_1(x) = Sf(x)$ normalized by the condition $\int_0^\infty f_1(x)dx = 1$, where $S$ is the area of the surface $x = 0$. Then, the self-consistent potential (11) is determined by the relation

$$\tilde{U}(x) = \frac{(N-1)}{S}\int\limits_0^\infty \underline{U}(|x-x'|)f_1(x')\,dx', \tag{42}$$

where

$$\underline{U}(|x-x'|) \equiv \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} U\Big(\sqrt{(x-x')^2+y'^2+z'^2}\Big)dy'dz'. \tag{43}$$

The self-consistent Eq. (41) looks like

$$\frac{f_1(x)}{\tilde{f}_1(x)} = \exp\Bigg\{-\beta\Bigg[\mu_0 - \mu + \\ + (N-1)S^{-1}\int\limits_0^\infty \underline{U}(|x-x'|)f_1(x')dx'\Bigg]\Bigg\}. \tag{44}$$

In the thermodynamic limit–$N \to \infty$ and $S \to \infty$, provided that $N/S = \text{const}$–and in the self-consistent field approximation (see Eq. 24), the free energy per unit area equals

$$\frac{F_0}{S} = -\frac{n_s^2}{2}\int \underline{U}(|x-x'|)f_1(x)f_1(x')\,dxdx' - \\ - Tn_s\left[1 + \ln\frac{z_1}{n_s}\left(\frac{2\pi mT}{h^2}\right)^{3/2}\right], \tag{45}$$

where $n_s = N/S$ is the surface concentration of particles, and $z_1 = \int_0^\infty \exp\left\{-\beta\left[U_0(x) + \tilde{U}(x)\right]\right\}dx$. The second-order correction to the free energy is

$$\frac{F_2}{S} = -\frac{n_s^2}{4T}\int\limits_0^\infty\int\limits_0^\infty U_*(|x-x'|)f_1(x)f_1(x')\,dxdx', \tag{46}$$

where

$$U_*(|x-x'|) \equiv \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} U^2\Big(\sqrt{(x-x')^2+y'^2+z'^2}\Big)dy'dz'. \tag{47}$$

If the potential is short-range, and if the distribution function changes little at distances of the order of the potential radius, the obtained relations can be written in a simpler form. By approximating potentials (43) and (47) by delta-functions, $\underline{U}(|x-x'|) = \upsilon_0\delta(x-x')$ and $U_*(|x-x'|) = \upsilon_*\delta(x-x')$, we obtain the following formulas for the self-consistent potential (42) and the correction to the free energy (46):

$$\begin{aligned}&\tilde{U}(x) = \upsilon_0\frac{(N-1)}{S}f_1(x),\\&\frac{F_2}{S} = -\upsilon_*\frac{n_s^2}{4T}\int\limits_0^\infty f_1^2(x)dx.\end{aligned}\tag{48}$$

## 7. System in the van der Waals Force Field

Let us also consider the case of a potential that falls down, as the distance $x\to\infty$. Now, the influence of the potential disappears at large distances. Therefore, it is convenient to write down the distribution function in the form

$$f_1(x) = f_{1\infty} + \chi(x),\tag{49}$$

where we extracted the value of distribution function at large distances, $f_{1\infty}$, so that $\chi(x)\to 0$ at $x\to\infty$. The self-consistent potential is presented similarly, so that the distribution function and the self-consistent potential are determined at infinity by the relations

$$f_{1\infty} = z_1^{-1}\exp\left(-\beta\tilde{U}_\infty\right),\ \tilde{U}_\infty = \frac{(N-1)\tilde{v}_0}{S}f_{1\infty},\tag{50}$$

where $\tilde{v}_0 = 2\int_0^\infty U(|x|)dx$. The contributions to the distribution function and the potential that vanish at infinity satisfy the equations

$$\chi(x) = f_{1\infty}\Big\{e^{-\beta[U_0(x)+\tilde{U}_\chi(x)]} - 1\Big\},\tag{51}$$

$$\begin{aligned}\tilde{U}_\chi(x) = &-f_{1\infty}\frac{(N-1)}{S}\int\limits_x^\infty \underline{U}(|x'|)dx' +\\&+\frac{(N-1)}{S}\int\limits_{-x}^\infty \underline{U}(|x'|)\chi(x'+x)\,dx'.\end{aligned}\tag{52}$$

Taking into account that

$$z_1 = e^{-\beta\tilde{U}_\infty}\left[\frac{V}{S} + \frac{1}{f_{1\infty}}\int\limits_0^\infty\chi(x)dx\right],\tag{53}$$

we obtain

$$f_{1\infty} = \frac{S}{V}\left[1 - \int\limits_0^\infty\chi(x)dx\right].\tag{54}$$

Note that

$$n_s = \frac{N}{S}\int\limits_0^\infty\chi(x)dx\tag{55}$$

is the surface concentration of particles in the area, where the potential $U_0(x)$ acts, and the quantity $\int_0^\infty\chi(x)dx = Sn_s/N \equiv N_s/N$ is the ratio between the number of "near-surface" particles and the total number of particles in the system. In terms of those notations, we have

$$\begin{aligned}&f_{1\infty} = \frac{S}{V}\left(1-\frac{N_s}{N}\right),\\&z_1 = \frac{V}{S}\,e^{-\beta\tilde{U}_\infty}\left(1-\frac{N_s}{N}\right)^{-1}.\end{aligned}\tag{56}$$

The presentation of the distribution function in the form (49) allows the free energy to be divided into the bulk and surface components: $F_0 = F_{0V}+F_{0S}$, where

$$\frac{F_{0V}}{N} = -\left\{\frac{nw_0}{2V} + T\left[1+\ln\frac{1}{n}\left(\frac{2\pi mT}{h^2}\right)^{3/2}\right]\right\} + n\tilde{v}_0,\tag{57}$$

$$\begin{aligned}\frac{F_{0S}}{N} = &T\ln\left(1-\frac{N_s}{N}\right) - n\left(w_1 + \tilde{v}_0\frac{N_s}{N} - \frac{w_0}{V}\frac{N_s}{N}\right) -\\&-\frac{n}{2}\left(w_2 - \frac{2w_1}{V}\frac{N_s}{N} + \frac{w_0}{V^2}\frac{N_s^2}{N^2}\right),\end{aligned}\tag{58}$$

$n = N/V$, and

$$\begin{aligned}&w_0 = \int U(|\mathbf{r}-\mathbf{r}'|)\,d\mathbf{r}d\mathbf{r}',\\&w_1 = S^{-1}\int U(|\mathbf{r}-\mathbf{r}'|)\,\chi(x')\,d\mathbf{r}d\mathbf{r}',\\&w_2 = S^{-2}\int U(|\mathbf{r}-\mathbf{r}'|)\,\chi(x)\chi(x')\,d\mathbf{r}d\mathbf{r}'.\end{aligned}\tag{59}$$

The evaluation of those quantities gives

$$w_0\sim U_\eta V,\ w_1\sim U_\eta(N_s/N),\ w_2\sim(U_\eta/V)(N_s/N)^2,$$

where $U_\eta\sim\int U(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'$.

The second-order correction to the free energy also consists of the bulk and surface contributions, $F_2 = F_{2V} + F_{2S}$, where

$$\frac{F_{2V}}{N} = -\frac{n}{4T}\frac{w_{0*}}{V},$$
$$\frac{F_{2S}}{N} = -\frac{n}{4T}\left[2\left(w_{1*} - \frac{w_{0*}}{V}\frac{N_s}{N}\right) + \right. \tag{60}$$
$$\left. + \left(w_{2*}V - 2w_{1*}\frac{N_s}{N} + \frac{w_{0*}}{V}\frac{N_s^2}{N^2}\right)\right],$$

and the quantities $w_{0*}$, $w_{1*}$, and $w_{2*}$ can be determined using formulas (59), in which $U(|\mathbf{r}-\mathbf{r}'|)$ in the integrands is replaced by $U^2(|\mathbf{r}-\mathbf{r}'|)$. The obtained relations can be used to study the behavior of dense gases and fluids near their boundaries with solids, as well as the surface phenomena [7].

## 8. Conclusions

In this work, the thermodynamic perturbation theory based on a self-consistent field model as the main approximation is formulated for classical systems. The model of ideal gas, which is usually used as the main approximation, is not suitable for the description of systems with a high density and a not weak particle-to-particle interaction, e.g., dense gases and fluids. In dense systems, every particle permanently interacts with a large number of other particles. Therefore, such concepts as the mean free path and two-particle collisions, which are used in the kinetic theory of gases, cannot be applied, e.g., to fluids. On the contrary, the idea of self-consistent field corresponds well to the physical situation in dense systems. In addition, the approximate account for the interaction between particles makes it possible, in principle, to describe phase transitions already in the main approximation. The proposed approach can be efficient, while describing systems with a large number of particles under inhomogeneous conditions, for instance, near a surface or a boundary with a solid. In dense systems, besides pair interactions, a substantial contribution can be made by ternary and higher-order interactions [3, 18]. Although the perturbation theory was developed here, by taking only the pair interaction into account, the equations obtained can be generalized in a natural way to the case of ternary forces.

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### ТЕРМОДИНАМІЧНА ТЕОРІЯ ЗБУРЕНЬ ДЛЯ КЛАСИЧНИХ СИСТЕМ В НАБЛИЖЕННІ САМОУЗГОДЖЕНОГО ПОЛЯ

Резюме

Запропоновано формулювання термодинамічної теорії збурень для багаточастинкової системи класичних частинок, що засноване на виборі у ролі головного наближення моделі самоузгодженого поля. Як приклад використання запропонованого підходу, розглянуто систему частинок у просторово-однорідному стані і в зовнішніх полях, що зростають і спадають з відстанню від поверхні. Підкреслено, що використання моделі самоузгодженого поля як основного наближення дає можливість опису багаточастинкових систем з не малою густиною і не слабкою міжчастинковою взаємодією, а також фазових переходів в них.