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## CONCERNING A CALCULATION OF THE GRAND PARTITION FUNCTION OF A FLUID MODEL

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*The calculation method of the grand partition function of a simple fluid model in the frame of a generalized lattice model, where each cell may contain a random number of particles, is proposed. As an interaction potential between particles, the Morse potential is chosen. In course of calculations, the summation over the number of particles and the integration over their coordinates are performed. Using the simplest approximation, the equation of state valid in a wide temperature range is obtained. At temperatures lower than the critical one, the presence of horizontal plots on the pressure vs density curve is found.*

*Keywords:* coexistence curve, collective variables, reference system, simple fluid, equation of state.

### 1. Introduction

The behavior of many-particle systems in both gaseous and liquid phases has been attracting attention of scientists for over a century. The task of the microscopic description of such a behavior remains vital even today. Especially urgent is the problem of describing a fluid in a vicinity of and below the critical temperature  $T_c$ . Below  $T_c$ , two phases – gas at small density and liquid at large density – can coexist. The phenomenon of the transition of a system from the state in one phase to that in another one is called the first-order phase transition.

The significant contribution both to theoretical and experimental researches of the critical behavior of liquids was made by Leonid Bulavin. Particularly important results were received in experimental works, for example in observing the influence of an ionic admixture on the critical behavior of a binary mixture [1], applying SANS (small-angle neutron scattering) to explore the influence of a confinement on the critical behavior of an individual fluid [2]. The

outcomes of these investigations are presented in books [3, 4]. The critical properties of fluids are in the sphere of L. Bulavin's interests [5], especially the stratification processes in monotectic and eutectic metal fusions [6]. His works devoted to the development of the global isomorphism approach between the Lennard-Jones fluids and the lattice gas (LG) model for calculating the loci of critical points for such fluids [7] and deriving the explicit relations between the basic thermodynamic functions of the LG model and the continuum fluid [8] are well-known.

Nowadays, most approaches to the description of phase transitions and critical phenomena in fluids are based on scaling ideas, universality hypothesis, and renormalization group methods. The following theories are worth mentioning: methods taking into account the fluctuations within the van der Waals theory [9], field-theoretical approach, which appeared to be very powerful in describing the magnetic systems; complete scaling approach [10, 11], which is essentially a phenomenological theory; methods of integral equations, and, in particular, the self-consistent Ornstein–Zernike approximation (SCOZA) [12, 13];

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perturbation series expansion, for example, the hierarchic reference theory [14, 15]; non-perturbative renormalization group approach [16]; collective variables method [17, 18], numerical methods, and computer simulations.

The investigation of simple fluids is frequently carried out, by using the concept of a reference system. The system of hard spheres is often taken as a reference system. The full pair-interaction potential is usually chosen in the form of a function that does not possess the Fourier transform. The hard-sphere potential itself is such a function, as well as the widely considered Lennard-Jones potential or the more general Mie potential. However, the results can be found in the literature for the systems of many particles interacting via a pair potential possessing the Fourier transform. For instance, the Morse fluid has already been studied: within the integral equation approach [19] and by Monte Carlo simulations using both the  $NpT$  plus test particle method [20] and the grand-canonical transition matrix method [21]. The usage of such potentials may be sufficient for some purposes, for example, to describe the liquid-vapor coexistence in liquid metals [19, 21]. The description of such systems does not need the hard-sphere reference system. Consequently, all the interaction – short- and long-ranged – can be accounted in the framework of a unified approach within the collective variables method.

The objective of this paper is to propose a new method for calculating the grand partition function with interacting potential possessing the Fourier transform.

## 2. Problem Statement

Consider a classical system of identical particles interacting via a pairwise additive potential  $U(|\mathbf{R}|)$ , where  $\mathbf{R}$  is the distance in a three-dimensional space. It is assumed that, first, the interaction can be decomposed into two parts

$$U(R) = \Psi(R) - U_1(R), \quad (2.1)$$

where  $U_1(R)$  is the attractive part, and  $\Psi(R)$  is the repulsive one, and second, the full potential possesses a well-behaved Fourier transform.

A physical observable dependent on the particle coordinates is, in general, a functional of the micro-

scopic particle density defined as [17, 18]

$$\hat{n}(\mathbf{R}) = \sum_{j=1}^N \delta(\mathbf{R} - \mathbf{R}_j), \quad (2.2)$$

where  $\mathbf{R}_j$  is the coordinate of the  $j$ -th particle,  $N$  the number of particles in the system. Imposing boundary periodic conditions, one can represent  $\hat{n}(\mathbf{R})$  in the form of a Fourier series

$$\hat{n}(\mathbf{R}) = \frac{1}{V} \sum_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}}, \quad (2.3)$$

where  $\sum_{\mathbf{k}} = \sum_{k_x} \sum_{k_y} \sum_{k_z}$ ,  $k_i = \frac{2\pi}{L} n_i$ ,  $i = x, y, z$ ;  $n_i$  is an integer,  $V = L^3$  is the periodicity volume of all system's properties, and  $\int_V \hat{n}(\mathbf{R}) d\mathbf{R} = N$ . The Fourier transform  $\hat{\rho}_{\mathbf{k}}$  has the form

$$\hat{\rho}_{\mathbf{k}} = \sum_{j=1}^N \exp(-i\mathbf{k}\mathbf{R}_j), \quad \text{and} \quad \hat{\rho}_{\mathbf{k}=0} = N. \quad (2.4)$$

Let the system be open. The grand partition function (GPF) of the system with the interaction potential  $\tilde{U}_k$  has the form

$$\Xi = \sum_{N \geq 0} \frac{z^N}{N!} \int (d\mathbf{R}) \exp\left(-\frac{\beta}{2V} \sum_{\mathbf{k}} \tilde{U}_k \hat{\rho}_{\mathbf{k}} \hat{\rho}_{\mathbf{k}}\right). \quad (2.5)$$

Here,  $\tilde{U}_k = \int U(R) e^{i\mathbf{k}\mathbf{R}} d\mathbf{R}$  is the Fourier transform of the interaction potential  $U(R)$ ,  $z = \exp(\beta\mu')$  is the activity,  $\beta$  is the inverse temperature,  $\mu' = \mu + \beta^{-1} \ln[(2\pi m\beta^{-1})^{3/2}/h^3] + \frac{1}{2V} \sum_{\mathbf{k}} \tilde{U}_k$ , where we have used the equality  $U(0) = \sum_{\mathbf{k}} \tilde{U}_k/V$ .

To perform further calculations, let us consider the volume  $V$  to be conditionally split into  $N_B$  cells with volume  $v = V/N_B$ . Moreover,  $v = c^3$ , where  $c$  is the linear size of an elementary cell. Note that, in contrast to the lattice gas model (where it is assumed that a cell can contain one particle or doesn't contain any particle), a cell can contain a random number of particles within this approach. The problem of description of continuous systems (unlike lattice systems) is related to the fact that the values of a wave vector are not bounded from above, although they change discretely. The latter fact is connected with the restriction of a system to the space of coordinates in the volume  $V$ . In much the same way as in lattice systems (where the wave vector is discrete and bounded), some restrictions to the values of a

wave vector  $k < B$  are introduced in the majority of works on the description of fluid systems at a certain stage of calculations [25]. Herewith, the procedure of selecting  $B$  is ambiguous, and different authors use to choose  $B$  in different ways [18, 26].

The behavior of a system near the point of the first-order phase transition (PT) is determined by the interaction potential. When the latter tends to zero, one has a non-interactive gas, where the PT is absent. The Fourier transform of potential (2.1) has to decrease with increase in the wave vector as  $k^{-n}$ , where  $n \geq 4$ . That is why the value  $\tilde{U}(k) = \tilde{\Psi}(k) - \tilde{U}_1(k)$  is small enough for sufficiently large values of  $k$ . So, let us consider the behavior of a system containing  $N$  particles for some model potential  $\tilde{U}_B(k)$ , which coincides with  $\tilde{U}(k)$  for  $k \in [0, B)$  and equal to zero for each  $k \geq B$ . The value of  $B$  will be defined subsequently. At this stage of calculations, let us assume that  $B$  takes on a finite value.

The grand partition function with the interaction potential  $\tilde{U}_B(k)$  has the form

$$\Xi = \sum_{N \geq 0} \frac{z^N}{N!} \int (d\mathbf{R}) \exp \left( -\frac{\beta}{2V} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \tilde{U}_B(k) \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} \right). \quad (2.6)$$

The wave vector  $\mathbf{k}$  takes on the values

$$B_\Lambda = \left\{ \mathbf{k} = (k_x, k_y, k_z) \left| k_i = -\frac{\pi}{c} + \frac{2\pi}{c} \frac{n_i}{N_{B_i}}, \right. \right. \\ \left. \left. n_i = 1, 2, \dots, N_{B_i}; i = x, y, z; N_B = N_{B_x} N_{B_y} N_{B_z} \right\}. \quad (2.7)$$

In the collective variables (CV) representation [23], relation (2.6) can be written as

$$\Xi = \sum_{N \geq 0} \frac{z^N}{N!} \int (d\mathbf{R}) \times \\ \times (d\rho)^{N_B} e^{-\frac{\beta}{2V} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \tilde{U}_B(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}} J(\rho - \hat{\rho}), \quad (2.8)$$

where the function of transition to the CV  $\rho_{\mathbf{k}}$  is essentially a product of delta-functions

$$J(\rho - \hat{\rho}) = \prod_{\mathbf{k} \in \mathcal{B}_\Lambda} \delta(\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}}) = \\ = \int (d\nu)^{N_B} e^{2\pi i \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \nu_{\mathbf{k}} (\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})}. \quad (2.9)$$

The GPF in the form of (2.8) was originally proposed in [24] for a many-particle system with Coulomb interaction, but has not got enough attention since then. The calculation of (2.8) was made in works [17, 27], by using hard-spheres as a reference system. For this purpose, the hard-sphere repulsive interaction potential was added to the interaction potential (2.1). In the current work, any additional potential of interaction is used.

Before proceeding the calculation of (2.8), let us perform two identity transformations. The former is

$$e^{\beta \mu' N} = e^{\beta_c \mu^* N} \exp [\beta (\mu' - \mu^* (1 + \tau)) \hat{\rho}_0]. \quad (2.10)$$

Here,  $\mu^*$  is some fixed value of chemical potential,  $\beta_c = (k_B T_c)^{-1}$  is some inverse temperature, for which the identity  $\beta_c = \beta (1 + \tau)$  is valid, where

$$\tau = \frac{T - T_c}{T_c}. \quad (2.11)$$

In further calculations, the quantity  $\hat{\rho}_0$  in (2.10) will be substituted for  $\rho_0$ , since expression (2.8) contains the function  $J(\rho - \hat{\rho})$ , which allows one to perform this procedure.

The latter identity transformation consists in selecting some part from the repulsive component of the interaction potential by means of introducing some parameter  $f \in [0, 1]$ :

$$\tilde{U}_B(k) = -\tilde{U}_1(k) + f \tilde{\Psi}(k) + (1 - f) \tilde{\Psi}(k). \quad (2.12)$$

Let us consider the term

$$-\frac{\beta}{2V} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \tilde{U}_B(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} = \frac{\beta}{2V} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \tilde{V}_B(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \\ - \frac{\beta_c}{2V} (1 - f) \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \tilde{\Psi}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}, \quad (2.13)$$

where the effective potential  $\tilde{V}(k)$  takes the form

$$\tilde{V}(k) = \tilde{U}_1(k) - f \tilde{\Psi}(k) + \tau (1 - f) \tilde{\Psi}(k), \quad (2.14)$$

and the value  $\tilde{\Psi}(k) > 0$ . As in the case of the former transformation, let us replace  $\rho_{\mathbf{k}}$  by  $\hat{\rho}_{\mathbf{k}}$  in the last term of (2.13) and use the transformation

$$\exp \left[ -\frac{\beta_c}{2V} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} (1 - f) \tilde{\Psi}(k) \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} \right] = \\ = \tilde{g}_{\tilde{\Psi}} \int (d\varphi)^{N_B} e^{-\frac{V}{2\beta_c} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\mathbf{k}} \varphi_{-\mathbf{k}}}{(1-f)\tilde{\Psi}(k)} + i \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \varphi_{\mathbf{k}} \hat{\rho}_{\mathbf{k}}}. \quad (2.15)$$

Here,

$$\tilde{g}_\Psi = \prod_{\mathbf{k} \in \mathcal{B}_\Lambda} \left( 2\pi \frac{\beta_c}{V} (1-f) \tilde{\Psi}(k) \right)^{-1/2}. \quad (2.16)$$

As a result of the identity transformations described above, the grand partition function (2.8) takes on the form

$$\begin{aligned} \Xi &= \tilde{g}_\Psi \sum_{N=0}^{\infty} \frac{e^{\beta_c \mu^* N}}{N!} \int (d\rho)^{N_B} e^{\frac{\beta}{2V} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \tilde{V}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}} \times \\ &\times \int (d\varphi)^{N_B} e^{-\frac{V}{2\beta_c} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\mathbf{k}} \varphi_{-\mathbf{k}}}{(1-f)\tilde{\Psi}(k)}} \int (d\mathbf{R}) e^{i \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \varphi_{\mathbf{k}} \hat{\rho}_{\mathbf{k}}} \times \\ &\times \int (d\nu)^{N_B} e^{2\pi i \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \nu_{\mathbf{k}} (\rho_{\mathbf{k}} \rho_{-\mathbf{k}})} e^{\beta(\mu' - \mu^*(1+\tau))\rho_0}. \end{aligned} \quad (2.17)$$

To perform further calculations, it is convenient to change variables

$$\rho_{\mathbf{k}} = \sqrt{N_B} \rho'_{\mathbf{k}}; \quad \nu_{\mathbf{k}} = \nu'_{\mathbf{k}} / \sqrt{N_B}; \quad \varphi_{\mathbf{k}} = \varphi'_{\mathbf{k}} / \sqrt{N_B}.$$

As a result, the representation of the grand partition function in the space of collective variables can be obtained in the form

$$\begin{aligned} \Xi &= g_\Psi \int (d\rho)^{N_B} \times \\ &\times e^{\beta[\mu' - \mu^*(1+\tau)]\rho_0 + \frac{\beta}{2} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} V(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}} \int (d\nu)^{N_B} \times \\ &\times \int (d\varphi)^{N_B} e^{-\frac{1}{2\beta_c} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\mathbf{k}} \varphi_{-\mathbf{k}}}{(1-f)\tilde{\Psi}(k)} + 2\pi i \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \nu_{\mathbf{k}} \rho_{\mathbf{k}}} G(\bar{\nu}), \end{aligned} \quad (2.18)$$

where the ‘‘stresses’’ of new variables are omitted, and the following notation is introduced:

$$V(k) = \tilde{V}(k)/v, \quad \Psi(k) = \tilde{\Psi}(k)/v. \quad (2.19)$$

The quantity  $g_\Psi$  has the form

$$g_\Psi = \tilde{g}_\Psi / \sqrt{N_B} = \prod_{\mathbf{k} \in \mathcal{B}_\Lambda} \left( 2\pi \frac{\beta_c}{v} (1-f) \Psi(k) \right)^{-1/2}. \quad (2.20)$$

The value of  $G(\bar{\nu})$  is a result of the integration over coordinates and the summation over the number of particles in the expression

$$G(\bar{\nu}) = \sum_{N=0}^{\infty} \frac{(z^*)^N}{N!} \int (d\mathbf{R}) \exp \left[ -2\pi i \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \bar{\nu}_{\mathbf{k}} \hat{\rho}_{\mathbf{k}} \right], \quad (2.21)$$

where the operator  $\hat{\rho}_{\mathbf{k}}$  is given in (2.4). For  $\bar{\nu}_{\mathbf{k}}$ , we have

$$\bar{\nu}_{\mathbf{k}} = \nu_{\mathbf{k}} - \varphi_{\mathbf{k}}/2\pi. \quad (2.22)$$

It is possible to perform the precise calculation of expression (2.21), as we have already presented in [25]. For this purpose, one should use an evident form of the operator  $\hat{\rho}_{\mathbf{k}}$  expressed by (2.4). As a result, one obtains the expression

$$G(\bar{\nu}) = \exp \left[ \sum_{n=0}^{\infty} \frac{(-2\pi i)^n}{n!} z^* V \sum_{k_1 \dots k_n} \bar{\nu}_{\mathbf{k}_1} \dots \bar{\nu}_{\mathbf{k}_n} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n} \right].$$

It can be rewritten, by using the site representation in the form

$$G(\bar{\nu}) = e^{\sum_{l=0}^{\infty} \frac{(2\pi i)^l}{l!} \alpha^* \sum_l \bar{\nu}_l^l} = \exp \left[ \alpha^* \sum_l e^{2\pi i l \bar{\nu}_l} \right], \quad (2.23)$$

where

$$\alpha^* = v e^{\beta_c \mu^*} = v z^*. \quad (2.24)$$

For  $\bar{\nu}_l$ , we have

$$\bar{\nu}_l = \nu_l - \varphi_l/2\pi, \quad (2.25)$$

where

$$\nu_l = \frac{1}{\sqrt{N_B}} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \nu_{\mathbf{k}} e^{-i\mathbf{k}l}, \quad \varphi_l = \frac{1}{\sqrt{N_B}} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \varphi_{\mathbf{k}} e^{-i\mathbf{k}l}. \quad (2.26)$$

Taking (2.23) into account, relation (2.18) yields

$$\begin{aligned} \Xi &= g_\Psi \int (d\rho)^{N_B} e^{\beta[\mu' - \mu^*(1+\tau)]\rho_0} \times \\ &\times e^{\frac{\beta}{2} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} V(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}} J(\rho), \end{aligned} \quad (2.27)$$

where the expression for the Jacobian of the transition is

$$J(\rho) = \int (d\nu)^{N_B} e^{2\pi i \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \nu_{\mathbf{k}} \rho_{\mathbf{k}}} F(\nu), \quad (2.28)$$

where

$$F(\nu) = \int (d\varphi)^{N_B} e^{-\frac{1}{2\beta_c} \sum_{\mathbf{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\mathbf{k}} \varphi_{-\mathbf{k}}}{(1-f)\tilde{\Psi}(k)}} e^{\alpha^* \sum_l e^{-2\pi i (\nu_l - \frac{\varphi_l}{2\pi})}}. \quad (2.29)$$

The notation of expression (2.29) is symbolic, since  $\varphi_{\mathbf{k}}$  and  $\nu_{\mathbf{k}}$  must be understood as functions of the variables  $\varphi_1$  and  $\nu_1$  according to the equalities (2.26).

It is worth to say that the expressions given below are precise, since the integration over the particle coordinates  $R_i$  and the summation over the number of particles  $N$  are performed without using any interaction potentials and don't need any approximations.

### 3. Calculation of the Jacobian of the Transition

To perform further calculations, the interaction potential is to be specified. Let us choose (2.1) as the Morse potential, where  $U_1(r)$  is the attractive part,

$$U_1(r) = 2\epsilon e^{-(r-R_0)/\alpha}, \tag{3.1}$$

and  $\Psi(r)$  is the repulsive component:

$$\Psi(r) = \epsilon e^{-2(r-R_0)/\alpha}. \tag{3.2}$$

Here, the value of  $\epsilon$  determines the interaction at a distance  $R_0$  between particles, where the minimal value of  $\Phi(r)$  can be reached, and the parameter  $\alpha$  describes the effective radius of attraction. The widespread use and a large number of the results of numerical calculations [19–21] became the reason for the choice of  $U(r)$  exactly in such form. The Fourier transform of this potential has the form

$$U_1(k) = \frac{U_1(0)}{(1 + \alpha^2 k^2)^2}, \quad \Psi(k) = \frac{\Psi(0)}{(1 + \alpha^2 k^2/4)^2}, \tag{3.3}$$

where

$$U_1(0) = 16\pi\epsilon \left(\frac{\alpha}{c}\right)^3 e^{R_0/\alpha}, \quad \Psi(0) = \epsilon\pi \left(\frac{\alpha}{c}\right)^3 e^{2R_0/\alpha}. \tag{3.4}$$

It should be noted that the sign of  $U(0) = \Psi(0) - U_1(0)$  depends on the parameter  $R_0/\alpha$ . For each  $\ln 2 < R_0/\alpha < 4\ln 2$ , one has  $U(0) < 0$ , and, for larger  $R_0/\alpha$ ,  $U(0) > 0$ .

One can find the Jacobian  $J(\rho)$  of the transition to the collective variables from (2.28) after calculating  $F(\nu)$ . This can be performed approximately by substituting  $\Psi(k)$  in (2.33) by its average value  $\bar{\Psi}(k)$ , for example, by the integral average

$$\Psi(k) \rightarrow \bar{\Psi} \equiv \langle \Psi(k) \rangle = \frac{\int_0^B dk k^2 \Psi(k)}{\int_0^B dk k^2}. \tag{3.5}$$

In principle, another averaging can be used. After this operation, the expression for  $F(\nu)$  becomes factorized

$$F(\nu) = \prod_l F_l(\nu), \tag{3.6}$$

where

$$F_l(\nu) = \int d\varphi_l \exp \left[ \frac{-\varphi_l^2}{2\beta_c(1-f)\bar{\Psi}} \right] \times \exp \left[ \alpha^* e^{-2\pi i(\nu_l - \frac{\varphi_l}{2\pi})} \right]. \tag{3.7}$$

Expression (3.7) can be represented in the form

$$F_l(\nu) = \int_{-\infty}^{\infty} d\varphi_l e^{\frac{-\varphi_l^2}{2\beta_c(1-f)\bar{\Psi}}} \sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} e^{-2\pi i m(\nu_l - \frac{\varphi_l}{2\pi})}, \tag{3.8}$$

where the representation  $e^x = \sum_{m=0}^{\infty} \frac{x^m}{m!}$  is used. Obviously, the integration over  $\varphi_l$  in (3.8) can be performed:

$$\int_{-\infty}^{\infty} d\varphi_l e^{-a\varphi_l^2} e^{im\varphi_l} = (\pi/a)^{1/2} \exp[-pm^2], \tag{3.9}$$

where

$$p = \beta_c \bar{\Psi} (1-f)/2, \tag{3.10}$$

and

$$a = (2\beta_c(1-f)\bar{\Psi})^{-1}.$$

As a result, we have

$$F_l(\nu) = \sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} e^{-pm^2} e^{-2\pi i m \nu_l} (4\pi p)^{1/2}, \tag{3.11}$$

where the relation  $(\pi/a)^{1/2} = (4\pi p)^{1/2}$  is used.

Expression (3.11) can be represented in the form of a cumulant expansion

$$\bar{F}_l(\nu) = \exp \left[ \sum_{n=0}^{\infty} \frac{(-2\pi i)^n}{n!} \mathcal{M}_n \nu_l^n \right], \tag{3.12}$$

and the cumulants  $\mathcal{M}_n$  can be found as functions of  $\alpha^*$  and the parameter  $p$ . This calculation is to be performed for each  $\mathcal{M}_n$  according to the equalities

$$\left. \frac{\partial^n F_l(\nu)}{\partial \nu_l^n} \right|_{\nu_l=0} = \left. \frac{\partial^n \bar{F}_l(\nu)}{\partial \nu_l^n} \right|_{\nu_l=0}. \tag{3.13}$$

As a result, one obtains

$$\begin{aligned}
 e^{\mathcal{M}_0} &= (4\pi p)^{1/2} T_0(\alpha^*, p); \\
 \mathcal{M}_0 &= \frac{1}{2} \ln(4\pi p) + \ln T_0(\alpha^*, p), \\
 \mathcal{M}_1 &= T_1/T_0, \quad \mathcal{M}_2 = T_2/T_0 - \mathcal{M}_1^2, \\
 \mathcal{M}_3 &= T_3/T_0 - \mathcal{M}_1^3 - 3\mathcal{M}_1\mathcal{M}_2, \\
 \mathcal{M}_4 &= T_4/T_0 - \mathcal{M}_1^4 - 6\mathcal{M}_1^2\mathcal{M}_2 - 4\mathcal{M}_1\mathcal{M}_3 - 3\mathcal{M}_2^2, \\
 \mathcal{M}_5 &= T_5/T_0 - \mathcal{M}_1^5 - 10\mathcal{M}_1^3\mathcal{M}_2 - 10\mathcal{M}_1\mathcal{M}_2^2 - \\
 &\quad - 15\mathcal{M}_1\mathcal{M}_3 - 5\mathcal{M}_1\mathcal{M}_4 - 10\mathcal{M}_2\mathcal{M}_3, \\
 \mathcal{M}_6 &= T_6/T_0 - \mathcal{M}_1^6 - 15\mathcal{M}_1^4\mathcal{M}_2 - 20\mathcal{M}_1^3\mathcal{M}_3 - \\
 &\quad - 15\mathcal{M}_1^2\mathcal{M}_4 - 45\mathcal{M}_1^2\mathcal{M}_2^2 - 60\mathcal{M}_1\mathcal{M}_2\mathcal{M}_3 - \\
 &\quad - 6\mathcal{M}_1\mathcal{M}_5 - 15\mathcal{M}_2^3 - 15\mathcal{M}_2\mathcal{M}_4 - 10\mathcal{M}_3^2. \quad (3.14)
 \end{aligned}$$

Here, we used the special functions

$$T_n(\alpha^*, p) = \sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} m^n e^{-pm^2}. \quad (3.15)$$

They have form of a rapidly convergent series, since the parameter  $p$  from (3.10) takes on only positive values, and  $\alpha^* = v \exp(\beta_c \mu^*)$ .

In view of (3.12), one can obtain the following expression for the Jacobian:

$$J(\rho) = \prod_l J_l(\rho_l), \quad (3.16)$$

where

$$J_l(\rho_l) = \int_{-\infty}^{\infty} d\nu_l e^{2\pi i \nu_l \rho_l} \exp \left[ \sum_{n=0}^{n_0} \frac{(-2\pi i)^n}{n!} \mathcal{M}_n \nu_l^n \right] h. \quad (3.17)$$

There is a polynomial in degrees of a real variable  $\nu_l$  in the index of the exponent. The convergence of the integral in this variable is provided by even powers. It is easy to see, by representing (3.17) in the form

$$J_l(\rho_l) = \int_{-\infty}^{\infty} d\nu_l e^{2\pi i \nu_l \rho_l} e^{f(x)} (\cos[f_1(x)] - i \sin[f_1(x)]), \quad (3.18)$$

where

$$f(x) = -\frac{(2\pi)^2}{2} \mathcal{M}_2 x^2 + \frac{(2\pi)^4}{4!} \mathcal{M}_4 x^4 - \frac{(2\pi)^6}{6!} \mathcal{M}_6 x^6,$$

$$f_1(x) = 2\pi \mathcal{M}_1 x - \frac{(2\pi)^3}{3!} \mathcal{M}_3 x^3 + \frac{(2\pi)^5}{5!} \mathcal{M}_5 x^5. \quad (3.19)$$

Here,  $n_0 = 6$  is assigned to provide the definiteness. So, the approximation used in [27] is applied.

Expression (3.18) can be represented in the form

$$\bar{J}_l(\rho_l) = \exp \left[ - \sum_{n=0}^{n_0} \frac{a_n}{n!} \rho_l^n \right] \quad (3.20)$$

as a result of the integration over variables  $\nu_l$ . Herewith, the coefficients  $a_n$  are real values and have form

$$\begin{aligned}
 a_0 &= \ln(2\pi) - \ln I_0, \quad a_1 = -J_1/I_0, \quad a_2 = I_2/I_0 + a_1^2, \\
 a_3 &= J_3/I_0 - a_1^3 + 3a_1 a_2, \quad (3.21)
 \end{aligned}$$

$$a_4 = -I_4/I_0 + a_1^4 - 6a_1^2 a_2 + 4a_1 a_3 + 3a_2^2.$$

Here, the following notations are used:

$$\begin{aligned}
 I_n &= \int_{-\infty}^{\infty} dx x^n \cos[f_1(x)] e^{f(x)}, \\
 J_n &= \int_{-\infty}^{\infty} dx x^n \sin[f_1(x)] e^{f(x)}. \quad (3.22)
 \end{aligned}$$

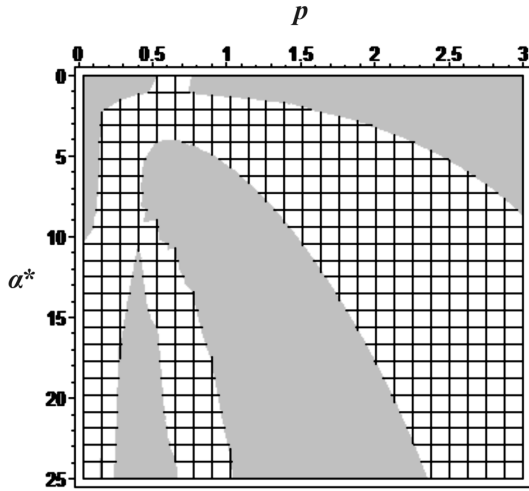
As was said above, the convergence of the integrals in (3.22) occurs for all values of

$$\mathcal{M}_2 > 0, \quad \mathcal{M}_4 < 0, \quad \mathcal{M}_6 > 0. \quad (3.23)$$

The condition  $\mathcal{M}_6 > 0$  is sufficient for the existence of the quantities  $I_n(\alpha^*, p)$  and  $J_n(\alpha^*, p)$ . The results of calculations show that  $\mathcal{M}_2 > 0$  for any values of  $\alpha^*$  and  $p$ . Note that  $\alpha^* = v e^{\beta_c \mu^*}$  and  $p$  from expression (3.10) take on real positive values.

The cumulants  $\mathcal{M}_4$  and  $\mathcal{M}_6$  are real, but they may take on both positive and negative values. The dependence of these cumulants on  $\alpha^*$  and  $p$  is presented in Fig. 1. It is easy to see that there exists the region of the values of parameters  $0 < \alpha^* < 25$  and  $0.1 < p < 3$ , which satisfy condition (3.23). Here,  $\mathcal{M}_4 < 0$  and  $\mathcal{M}_6 > 0$ , which allows one to find the corresponding values of  $a_n$ .

An example of the values of cumulants  $\mathcal{M}_n$  and the corresponding coefficients  $a_n$  for  $R_0/\alpha = 3.7 \ln 2$ ,  $\alpha^* = 11$ , and  $p = 0.11$  is given below. The choice of



**Fig. 1.** Regions of the cumulant values  $\mathcal{M}_6 > 0$  (white colour) depending on  $\alpha^*$  and  $p$

such values of parameters is associated with the procedure of self-consistency described in Appendix. We take

$$\begin{aligned} \mathcal{M}_0 &= 6.1362, \mathcal{M}_1 = 4.1588, \mathcal{M}_2 = 2.2040, \\ \mathcal{M}_3 &= 0.6023, \mathcal{M}_4 = -0.1498, \mathcal{M}_5 = -0.0529, \\ \mathcal{M}_6 &= 0.1523, \\ a_0 &= -0.1640, a_1 = -2.9664, a_2 = 1.8402, \\ a_3 &= -2.3378, a_4 = 6.2845. \end{aligned} \quad (3.24)$$

It should be noted that the obtained values of coefficients (3.24) correspond to a pair of parameters. One of them, namely the parameter  $p$ , is defined by expression (3.10) and the value of  $f$ , which determines the reference system, and by the critical temperature  $\beta_c = 1/kT_c$ . So, if some value of  $f$  ( $f = 0.1488$ ) is set, and if  $T_c$  is determined, one can obtain only one fixed value of  $p$  (Appendix).

Summing up the calculations performed above, we can write a functional representation of the grand partition function of a fluid model. The substitution of (3.20) in (2.27) gives

$$\begin{aligned} \Xi &= g_\Psi e^{N_B \mathcal{M}_0} \int (d\rho)^{N_B} e^{\sqrt{N_B} \beta [\mu' - \mu^* (1 + \tau)] \rho_0} \times \\ &\times \exp \left[ \frac{\beta}{2} \sum_k V(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] \prod_l \left( e^{-\sum_{n=0}^{n_0} \frac{a_n}{n!} \rho_l^n} \right). \end{aligned} \quad (3.25)$$

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Since  $\rho_l = \frac{1}{\sqrt{N_B}} \sum_k \rho_{\mathbf{k}} e^{i\mathbf{k}l}$  is the site representation of the collective variable  $\rho_{\mathbf{k}}$ , one has

$$\begin{aligned} \Xi &= g_\Psi e^{(\mathcal{M}_0 - a_0) N_B} \int (d\rho)^{N_B} \times \\ &\times \exp \left[ \sqrt{N_B} (\beta [\mu' - \mu^* (1 + \tau)] - a_1) \rho_0 - \right. \\ &- \frac{1}{2} \sum_k d(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{1}{3!} \frac{a_3}{\sqrt{N_B}} \times \\ &\times \sum_{k_1, \dots, k_3} \rho_{k_1, \dots, k_3} \delta_{k_1 + \dots + k_3} - \\ &\left. - \frac{1}{4!} \frac{a_4}{N_B} \sum_{k_1, \dots, k_4} \rho_{k_1, \dots, k_4} \delta_{k_1 + \dots + k_4} \right]. \end{aligned} \quad (3.26)$$

$$\text{Here, } d(k) = a_2 - \beta V(k), \quad (3.27)$$

where  $V(k)$  expressed by (2.19) is the Fourier transform of some effective interaction potential.

The further calculation of (3.26) can be performed, by using the method of calculation of the grand partition function of the Ising model in an external field proposed in [28]. Herewith, the role of an external field is played by

$$h = \beta \mu' - \beta \mu^* (1 + \tau) - a_1. \quad (3.28)$$

#### 4. The Grand Partition Function and the Thermodynamic Characteristics

Expression (3.26) allows one to calculate the dependence of the pressure  $P$  on the temperature  $T$  and the chemical potential  $\mu'$ , by applying the relation

$$PV = kT \ln \Xi. \quad (4.1)$$

The average number of particles  $\bar{N}$  can be found, if the grand partition function is known:

$$\bar{N} = \frac{\partial \ln \Xi}{\partial \beta \mu}. \quad (4.2)$$

The latter expression allows one to express the chemical potential in terms of the number of particles or relative density

$$\bar{n} = \frac{\bar{N}}{N_B} = \left( \frac{\bar{N}}{V} \right) v, \quad (4.3)$$

where  $v$  is the volume of an elementary cell and a parameter of the model in use.

Uniting equalities (4.1) and (4.2), one can find the dependence of the pressure on the temperature  $T$  and the relative density  $\bar{n}$ , which is to be the equation of state of the model under study.

One of the methods of calculation of  $\Xi$  consists in the substitution of variables in (3.26):

$$\rho_{\mathbf{k}} = \eta_{\mathbf{k}} + n_c \sqrt{N_B} \delta_{\mathbf{k}}. \quad (4.4)$$

As a result, one obtains

$$\begin{aligned} \Xi = & g_{\Psi} e^{N_B(\mathcal{M}_0 - a_0 + E_0(\mu))} \times \\ & \times \int \exp \left[ M \sqrt{N_B} \eta_0 - \frac{1}{2} \sum_{\mathbf{k}} \tilde{d}(k) \eta_{\mathbf{k}} \eta_{-\mathbf{k}} - \right. \\ & \left. - \frac{a_4}{4!} \frac{1}{\sqrt{N_B}} \sum_{k_1, \dots, k_4} \eta_{k_1} \dots \eta_{k_4} \delta_{k_1 + \dots + k_4} \right] (d\eta)^{N_B}. \quad (4.5) \end{aligned}$$

Here, we introduced the notations

$$\begin{aligned} M &= \beta\mu' - \beta\mu^*(1 + \tau) - \tilde{a}_1, \\ \tilde{a}_1 &= a_1 + n_c d(0) - n_c^3 \frac{a_4}{3}, \\ \tilde{d}(k) &= \tilde{a}'_2 - \beta V(k), \\ \tilde{a}'_2 &= a_2 - n_c^2 \frac{a_4}{2}. \end{aligned} \quad (4.6)$$

The value of shift

$$n_c = -a_3/a_4. \quad (4.7)$$

For  $E_0(\mu)$ , one obtains the expression

$$E_0(\mu) = Mn_c + \frac{1}{2} \tilde{d}(0) n_c^2 + \frac{a_4}{24} n_c^4. \quad (4.8)$$

In common with the former expression, we have

$$\tilde{a}_1 = a_1 + \tilde{d}(0) n_c + \frac{a_4}{6} n_c^3. \quad (4.9)$$

Let us consider the simplest approximation in the calculation of  $\Xi$  expressed by (3.26), the so-called zero-mode approximation ( $\rho_k = 0$  for  $k \neq 0$ ;  $\rho_0 \neq 0$ ):

$$\ln \Xi_0 = \ln g_{\Psi} + N_B(\mathcal{M}_0 - a_0 + E_0(\mu)) + E(\bar{\rho}_0), \quad (4.10)$$

where  $\Xi_0$  denotes the grand partition function (4.5) in the approximation mentioned above, and

$$E(\bar{\rho}_0) = M\bar{\rho}_0 - \frac{1}{2} \tilde{d}(0) \bar{\rho}_0^2 - \frac{a_4}{24} \bar{\rho}_0^4, \quad (4.11)$$

where  $\bar{\rho}_0$  is a solution of the equation

$$M - \tilde{d}(0) \bar{\rho}_0 - \frac{a_4}{6} \bar{\rho}_0^3 = 0. \quad (4.12)$$

If several solutions  $\bar{\rho}_0$  exist, the one leading to the maximal value of  $E(\bar{\rho}_0)$  in (4.11) should be chosen.

The method of steepest descent is used for the calculation of (4.10). That is why the second derivative of  $E(\bar{\rho}_0)$  has to be negative, and, consequently, every solution  $\bar{\rho}_0$  has to satisfy the condition

$$\bar{\rho}_0 > \rho_{00}, \quad \rho_{00} = \left( -\frac{2\tilde{d}(0)}{a_4} \right)^{1/2}. \quad (4.13)$$

Such situation takes place barely if  $T < T_c$ , where  $\rho_{00}$  is a real value. For all  $T > T_c$ , Eq. (4.12) has only one solution.

### 5. Thermodynamic Potential of a Simple Fluid in Frames of the Simplest Approximation

All further calculations concern the case where the fluctuation effects are not considered. So, the zero model approximation is in use. In view of equality (4.12), it should be noted that, in case of  $M = 0$ , the critical temperature  $T_c$  is determined from the condition

$$\tilde{d}(0) \Big|_{T=T_c} = 0. \quad (5.1)$$

Using (4.6), one can find

$$\beta_c = \frac{\tilde{a}'_2}{V(0, T_c)}, \quad kT_c = \frac{V(0, T_c)}{\tilde{a}'_2}. \quad (5.2)$$

For  $T \neq T_c$ , one obtains

$$\tilde{d}(0) = \tilde{a}_2 \frac{\tau}{1 + \tau}, \quad \text{where } \tilde{a}_2 = \tilde{a}'_2 \frac{16e^{-R_0/\alpha} - 1}{16e^{-R_0/\alpha} - f}. \quad (5.3)$$

#### 5.1. The case $T = T_c$

It should be noted at once that the correct investigation of the behavior of a simple fluid at  $\tau = 0$  should be carried out, by considering the fluctuation effects, which cause the emergence of the renormalization group symmetry. But even in frames of a simplified consideration, the value  $T_c$  should be fixed (at least approximately), and then, only, the behavior of the system at temperatures different from  $T_c$  should be examined.



Assigning  $\tilde{d}(0) = 0$  and using (4.1), one obtains

$$PV = kT_c \ln \Xi_c, \quad (5.4)$$

where

$$\ln \Xi_c = \ln g_{\Psi}^{(c)} + N_B (\mathcal{M}_0 - a_0 + E_{0c}(\mu) + E_c(\bar{\rho}_{0c})). \quad (5.5)$$

Here,

$$E_{0c}(\mu) = M_c n_c + \frac{a_4}{24} n_c^4; \quad E_c(\bar{\rho}_0) = M_c \bar{\rho}_{0c} - \frac{a_4}{24} \bar{\rho}_{0c}^4.$$

The value  $\bar{\rho}_{0c}$  is determined, by using (4.12). In the case of  $\tau = 0$ , one can find

$$\bar{\rho}_{0c} = \left( \frac{6M_c}{a_4} \right)^{1/3}. \quad (5.6)$$

The average number of particles in the case of  $\tau = 0$  can be found, by using (4.2) and (4.3), where expression (5.5) is used as  $\Xi_c$ . One has

$$\bar{n} = n_c + \bar{\rho}_{0c}. \quad (5.7)$$

So, one can find an evident dependence of the chemical potential  $M_c$  on the density at  $T = T_c$  from equalities (5.6) and (5.7):

$$M_c = \frac{a_4}{6} (\bar{n} - n_c)^3. \quad (5.8)$$

Let us find the grand thermodynamic potential  $\Omega(T_0, \mu)$  of a fluid:

$$\Omega = -kT \ln \Xi. \quad (5.9)$$

In the case of  $T = T_c$ , one has the expression

$$\Omega = -kT N_B \left[ f_c + \bar{n} M_c - \frac{a_4}{24} (\bar{n} - n_c)^4 \right], \quad (5.10)$$

where

$$f_c = \frac{1}{N_B} \ln g_{\Psi} + \mathcal{M}_0 - a_0 + \frac{a_4}{4!} n_c^4. \quad (5.11)$$

The chemical potential  $M_c$  can be excluded from expression (5.10), by using equality (5.8). In this case,

$$\Omega = -kT N_B \left[ f_c + \frac{a_4}{6} \bar{n} (\bar{n} - n_c)^3 - \frac{a_4}{24} (\bar{n} - n_c)^4 \right]. \quad (5.12)$$

The equation of state at  $T = T_c$  can be found, by using (5.4) and excluding the chemical potential  $M_c$ :

$$\frac{Pv}{kT_c} = f_c + \frac{a_4}{24} \bar{n} (\bar{n} - n_c)^3 - \frac{a_4}{24} (\bar{n} - n_c)^4. \quad (5.13)$$

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Let us find the free energy  $F = \Omega + \mu \bar{N}$  of a fluid. The grand thermodynamic potential is a function of the temperature, volume, and chemical potential:

$$d\Omega = -SdT - PdV - Nd\mu. \quad (5.14)$$

The pressure calculated in frames of this representation has the form

$$P = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu}. \quad (5.15)$$

The free energy is a function of the temperature, volume, and average number of particles:

$$dF = -Sd\tau - PdV + \mu d\bar{N}. \quad (5.16)$$

That is why the pressure is given by the expression

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T, \bar{N}}. \quad (5.17)$$

According to (4.6), one has

$$\beta \mu' = M + \beta \mu^* (1 + \tau) - \tilde{a}_1. \quad (5.18)$$

So, at  $T = T_c$ , one can find  $F = \Omega + N_B \bar{n} \mu$  or

$$F = -kT_c \frac{V}{v} \left[ f_c + f_{2c} \bar{n} - \frac{a_4}{24} (\bar{n} - n_c)^4 \right], \quad (5.19)$$

where

$$f_{2c} = \tilde{a}_1 - \beta_c \mu^*. \quad (5.20)$$

The calculation of the pressure  $P$  with regard for (5.17) and (5.19) results in (5.13). As should be expected, the calculation of the equation of state at  $T = T_c$  is not dependent on the way it was deduced (formulas (5.15) and (5.17)) and has the form (5.13).

The critical value of pressure can be found, by using (5.13) and the relation  $\bar{n} = n_c$ . So, one has

$$P_c = \frac{kT_c f_c}{v}, \quad (5.21)$$

where the value of  $f_c$  is given in (5.11).

## 5.2. The case $T > T_c$

According to (4.10), the expression for the simplest approximation of the grand partition function at  $T > T_c$  has the form

$$\ln \Xi_0 = \ln g_{\Psi} + N_B (\mathcal{M}_0 - a_0 + E_0(\mu) + E(\bar{\rho}_0)), \quad (5.22)$$

where

$$E(\bar{\rho}_0) = M\bar{\rho}_0 - \frac{1}{2}\tilde{d}(0)\bar{\rho}_0^2 - \frac{a_4}{24}\bar{\rho}_0^4, \quad (5.23)$$

$$E_0(\mu) = Mn_c + \frac{1}{2}\tilde{d}(0)n_c^2 + \frac{a_4}{24}n_c^4, \quad (5.24)$$

and  $\bar{\rho}_0$  is the solution of Eq. (4.12). The uniqueness of the solution of this equation, which is written in reduced form as

$$\bar{\rho}_0^3 + p\bar{\rho}_0 + q = 0, \quad (5.25)$$

where

$$p = \frac{6\tilde{d}(0)}{a_4}, \quad q = -\frac{6M}{a_4}, \quad (5.26)$$

is provided with the positive discriminant (here,  $\tilde{d}(0) > 0$ )

$$Q = \left(\frac{2\tilde{d}(0)}{a_4}\right)^3 + \left(\frac{3M}{a_4}\right)^2. \quad (5.27)$$

It should be noted that the sign of  $Q$  doesn't depend on the sign of the chemical potential. Among all the solutions, only one is real:

$$\bar{\rho}_0 = \left(\frac{3M}{a_4} + \sqrt{Q}\right)^{1/3} + \left(\frac{3M}{a_4} - \sqrt{Q}\right)^{1/3}. \quad (5.28)$$

This equation defines (with respect to (5.7)) the dependence of the chemical potential  $M$  on the density and the temperature.

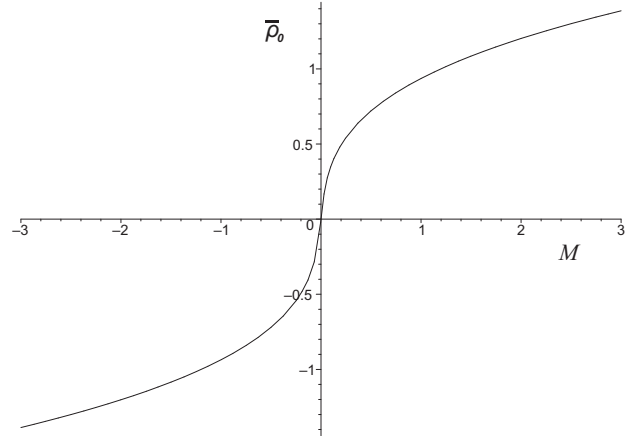
The diagram of the dependence of  $\bar{\rho}_0$  on  $M$  is presented in Fig. 2 at  $T > T_c$ .

Note that the region  $M > 0$  is referred to the positive values of  $\bar{\rho}_0 = \bar{n} - n_c$ . At  $\bar{n} < n_c$ , one obtains  $M < 0$ . The conversion of the chemical potential  $M$  into zero takes place at  $\bar{n} = n_c$ .

The dependence of the chemical potential  $M$  on the density at  $T > T_c$  can be defined directly from (5.25), taking into account that  $\bar{\rho}_0 = \bar{n} - n_c$ . Then

$$M = \tilde{d}(0)(\bar{n} - n_c) + \frac{a_4}{6}(\bar{n} - n_c)^3. \quad (5.29)$$

In contrast to (5.8), the linear term in the density is present here, and it becomes a main one in the high-temperature region. As  $T \rightarrow T_c$ , the cubic dependence of  $M$  on the density is obtained (Fig. 3).



**Fig. 2.** Dependence of the solution  $\bar{\rho}_0$  on the chemical potential  $M$  at  $T > T_c$  in the case where  $R_0/\alpha = 3.7 \ln 2$ ,  $\alpha^* = 11$ , and  $p = 0.11$

The grand thermodynamic potential of a fluid at  $T > T_c$  has the form

$$\Omega = -kTN_B \left[ f_c + \frac{\tilde{d}(0)}{2}n_c^2 + M\bar{n} - \frac{\tilde{d}(0)}{2}(\bar{n} - n_c)^2 - \frac{a_4}{24}(\bar{n} - n_c)^4 \right], \quad (5.30)$$

where

$$f_c = \frac{1}{N_B} \ln g_\Psi + \mathcal{M}_0 - a_0 + \frac{a_4}{24}n_c^4 + \frac{1}{2}\tilde{d}(0)n_c^2. \quad (5.31)$$

Corresponding to (5.30), the free energy doesn't contain the chemical potential and has the form

$$F = -kT \frac{V}{v} \left[ f_c + f_2\bar{n} - \frac{\tilde{d}(0)}{2}n_c^2 - \frac{\tilde{d}(0)}{2}(\bar{n} - n_c)^2 - \frac{a_4}{24}(\bar{n} - n_c)^4 \right], \quad (5.32)$$

where

$$f_2 = \tilde{a}_1 - \beta\mu^*(1 + \tau). \quad (5.33)$$

The equation of state at  $T > T_c$  can be found, by using (5.30) and substituting the value  $M$  expressed by (5.29):

$$\frac{Pv}{kT} = f_c + \frac{\tilde{a}_2}{2} \frac{\tau}{1 + \tau} \bar{n}^2 + \frac{a_4}{6}(\bar{n} - n_c)^3 - \frac{a_4}{24}(\bar{n} - n_c)^4. \quad (5.34)$$

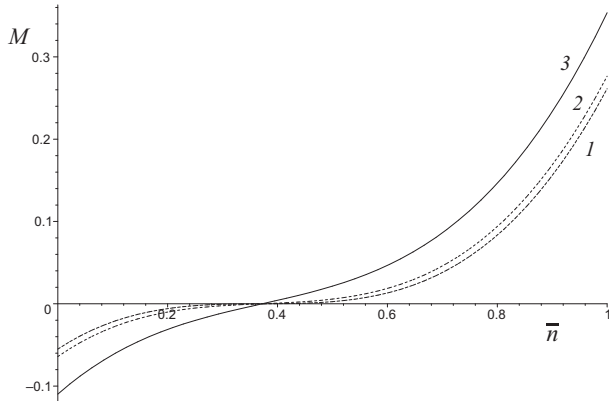


Fig. 3. Dependence of  $M$  on the density  $\bar{n}$  at  $T > T_c$  for temperatures  $\tau_1 = 0.01$  (curve 1),  $\tau_2 = 0.1$  (curve 2),  $\tau_3 = 1$  (curve 3)

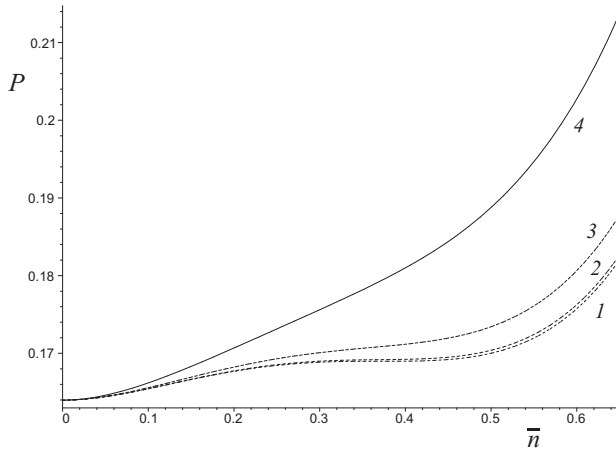


Fig. 4. Dependence of the pressure  $P$  on the density  $\bar{n}$  at  $\tau = 0$  (curve 1),  $\tau = 0.01$  (curve 2),  $\tau = 0.1$  (curve 3), and  $\tau = 1.5$  (curve 4)

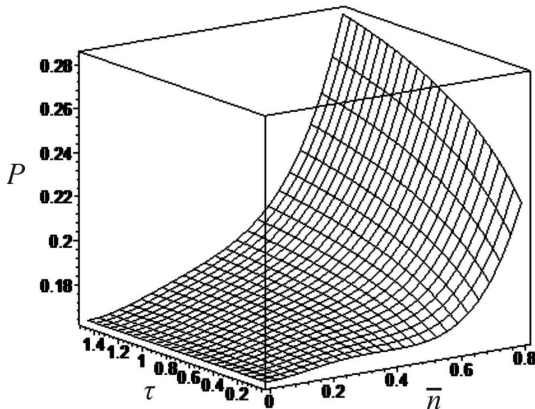


Fig. 5. Dependence of the pressure  $P$  on the average density  $\bar{n}$  and the reduced temperature  $\tau$  in the region  $T > T_c$

The dependence of the pressure on the density  $\bar{n}$  at temperatures  $T \geq T_c$  is presented in Fig. 4.

Expression (5.34) allows one to depict a 3-dimensional diagram of the pressure as a function of the average density and the reduced temperature  $\tau$  in the region  $T \geq T_c$  (Fig. 5).

The equation of state expressed by (5.34) can be represented in a reduced form. For this purpose, the following values are introduced:

$$\tilde{P} = \frac{P}{P_c}, \quad t = \frac{T}{T_c}, \quad \eta = \frac{\bar{n}}{n_c}. \quad (5.35)$$

Then (5.34) takes on the form

$$\tilde{P} = 1 + P_1(t-1)\eta^2 + P_2(1+3\eta)(\eta-1)^3, \quad (5.36)$$

where the following notations are used:

$$P_1 = \frac{\tilde{a}_2 n_c^2}{2f_c}, \quad P_2 = \frac{\tilde{a}_2 n_c^4}{24f_c}. \quad (5.37)$$

The curve of dependence (5.36) of the pressure on the density  $\eta$  has the inflexion point at  $\eta = 1$  and  $T = T_c$  and reaches its minimum at  $\eta = 0$ , which follows from the relations

$$\frac{\partial \tilde{P}}{\partial \eta} = 2\eta(P_1(t-1) + 6P_2(\eta-1)^2), \quad (5.38)$$

$$\frac{\partial^2 \tilde{P}}{\partial \eta^2} = 2P_1(t-1) + 12P_2(1-4\eta+3\eta^2). \quad (5.39)$$

It is easy to see that, for all  $t > 1$ , the first derivative turns into zero at  $\eta = 0$  only. In the case of  $t = 1$ , there is an additional inflexion point  $\eta = 1$ . Indeed, at  $t = 1$  and  $\eta = 1$ , the second derivative also turns into zero.

## 6. Equation of State at $T < T_c$

As was shown above, the pressure  $\tilde{P}$  expressed in (5.36) is a gradually increasing function of the density  $\eta$  in the temperature region  $T > T_c$ . It is expected to observe the first-order phase transition at temperatures  $T < T_c$ , that must show to turn the susceptibility into infinity for the certain values of density.

Let us calculate the grand partition function (4.5) in the simplest approximation at  $T < T_c$ . The following expression is valid:

$$\ln \Xi_0 = \ln g'_\Psi N_B (\mathcal{M}_0 - a_0 + E_0(\mu)) + N_B E(\bar{\rho}_{0i}). \quad (6.1)$$

Here,

$$E_0(\bar{\rho}_{0i}) = M\bar{\rho}_{0i} - \frac{\tilde{a}_2}{2} \frac{\tau}{\tau+1} \bar{\rho}_{0i}^2 - \frac{a_4}{24} \bar{\rho}_{0i}^4, \quad (6.2)$$

herewith  $\bar{\rho}_{0i}$  are solutions of the equation

$$M - \tilde{a}_2 \frac{\tau}{1+\tau} \bar{\rho}_{0i} - \frac{a_4}{6} \bar{\rho}_{0i}^3 = 0. \quad (6.3)$$

Unlike the case of  $T > T_c$ , Eq. (6.3) can possess more than one real root. In this case for  $E(\bar{\rho}_{0i})$  in expression (6.2), one should choose  $\bar{\rho}_{0i}$  corresponding to the maximal value of  $E(\bar{\rho}_{0i})$ , since the calculation of (6.1) is performed, by using the method of steepest descent, which foresees such a condition.

Equation (6.3) can be written in a reduced form:

$$\bar{\rho}_{0i}^3 + p\bar{\rho}_{0i} + q = 0, \quad (6.4)$$

where the coefficients  $p$  and  $q$  are defined in (5.26).

Let us find the marginal value of the chemical potential  $|M_q|$ , at which the equality  $Q = 0$  is fulfilled. According to (5.27), one has

$$M_q = \frac{a_4}{3} \left( -\frac{2\tilde{d}(0)}{a_4} \right)^{3/2}. \quad (6.5)$$

For all values of  $|M| > M_q$ , the discriminant  $Q > 0$ , and Eq. (6.4) has the single real root. In the case of  $|M| < M_q$  ( $Q < 0$ ), there are three real solutions.

Let us consider the case of  $Q \geq 0$  at  $T < T_c$ , where the single root exists, in detail. Using (5.28) at  $|M| = M_q$ , one can find

$$\bar{\rho}_{0r} = \left( \frac{24}{a_4} M_q \right)^{1/3}. \quad (6.6)$$

Since  $\bar{\rho}_{0i} = \bar{n} - n_c$ , the value of density  $n_c$ , which realizes at the value of the chemical potential  $|M| = M_q$ , can be found as

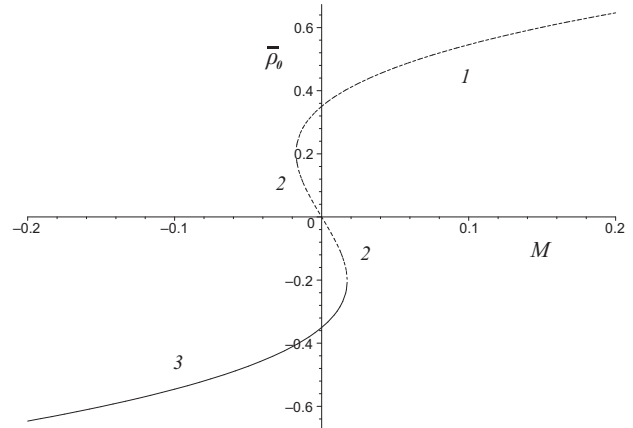
$$n_2 = n_c + n_g, \quad (6.7)$$

where

$$n_g = \left( -\frac{8\tilde{a}_2}{a_4} \frac{\tau}{\tau+1} \right)^{1/2}. \quad (6.8)$$

In the course of a further increase in the chemical potential  $M$  ( $|M| > M_q$ ) at  $T < T_c$ , the density can be defined from the relation

$$\bar{n} = n_c + \left( \frac{3M}{a_4} + Q^{1/2} \right)^{1/3} + \left( \frac{3M}{a_4} - Q^{1/2} \right)^{1/3}. \quad (6.9)$$



**Fig. 6.** Accordance between the density of a fluid and the values of chemical potential  $M$ ; the gaseous phase – solid line 1; the liquid phase – 2

The equation of state of a fluid at  $T < T_c$  for all  $M > M_q$  has the form (5.34), where the value  $\tau < 0$ . Under such conditions, the fluid exists in a liquid state (at  $T < T_c$ ), where the following dependence of the chemical potential  $M = M_2$  on the density ( $\bar{n} \geq n_2$ ) occurs (see Fig. 6, solid line 2):

$$M_2 = \frac{\tilde{a}_2\tau}{1+\tau} (\bar{n} - n_c) + \frac{a_4}{6} (\bar{n} - n_c)^3. \quad (6.10)$$

In the case of the large negative values of chemical potential  $M$  ( $M \leq -M_q$ ), the average density  $n_1$ , expressed below, corresponds to the value  $M = -M_q$ :

$$n_1 = n_c - n_g. \quad (6.11)$$

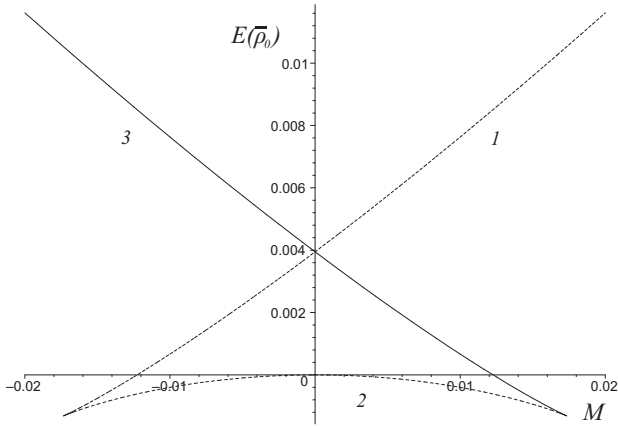
For all  $\bar{n} < n_1$ , the gaseous phase of a fluid occurs and realizes for all  $M < -M_q$  (Fig. 6, solid line 1).

The region  $n_1 < \bar{n} < n_2$  corresponds to the chemical potential  $|M| < M_q$ , where  $Q < 0$ . Equation (5.25) has three real roots in this case:

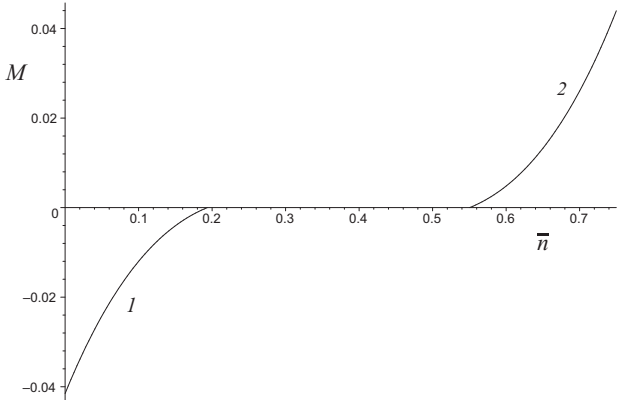
$$\begin{aligned} \bar{\rho}_{01} &= 2\rho_{0r} \cos \frac{\alpha}{3}, \\ \bar{\rho}_{02} &= -2\rho_{0r} \cos \left( \frac{\alpha}{3} + \frac{\pi}{3} \right), \\ \bar{\rho}_{03} &= -2\rho_{0r} \cos \left( \frac{\alpha}{3} - \frac{\pi}{3} \right), \end{aligned} \quad (6.12)$$

where

$$\rho_{0r} = \left( -\frac{2\tilde{d}(0)}{a_4} \right)^{1/2}, \quad (6.13)$$



**Fig. 7.** Dependence of roots (6.12) on the chemical potential  $|M| < M_q$ , curve 1 corresponds to the solution  $\bar{\rho}_{01}$ , curve 2 –  $\bar{\rho}_{02}$ , curve 3 –  $\bar{\rho}_{03}$



**Fig. 8.** Dependence of the function  $E(\bar{\rho}_{0i})$  on the chemical potential  $M$

and the angle  $\alpha$  is defined from the condition  $\cos \alpha = \frac{M}{M_q}$  and is equal to

$$\alpha = \arccos \frac{M}{M_q}. \tag{6.14}$$

In the case of  $M = M_q$ , one has  $\alpha = 0$ . So,

$$\begin{aligned} \lim_{M \rightarrow -M_q} \bar{\rho}_{01} &= \rho_1^{(+)} = \left( -\frac{8\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{1/2} \equiv n_g, \\ \lim_{M \rightarrow -M_q} \bar{\rho}_{02} &= \lim_{M \rightarrow -M_q} \bar{\rho}_{03} = \\ &= \rho_2^{(+)} = -\left( -\frac{6\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{1/2}. \end{aligned} \tag{6.15}$$

Comparing (6.15) with (6.8), one can find that the solution  $\rho_1^{(+)}$  coincides with  $n_g$  and corresponds to the density of a liquid phase  $n_2$ .

The case where  $M = -M_q$  gives  $\alpha = \pi$ . Herewith,

$$\begin{aligned} \rho_1^{(-)} &= \rho_2^{(-)} = \bar{\rho}_s = \left( -\frac{2\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{1/2}, \\ \rho_3^{(-)} &= \lim_{M \rightarrow -M_q} \bar{\rho}_{03} = -\rho_1^{(+)} = -n_g. \end{aligned} \tag{6.16}$$

At  $M = -M_q$ , the solution  $\bar{\rho}_{03}$  results in the density

$$n_1 = n_c - n_g. \tag{6.17}$$

In the general case, the dependence of roots  $\bar{\rho}_{0i}$  from (6.12) on the values of chemical potential in the region  $|M| < M_q$  is depicted in Fig. 7. Herewith, the solutions  $\bar{\rho}_{01}$  and  $\bar{\rho}_{03}$  have both positive and negative branches and coincide at  $M = 0$ . The root  $\bar{\rho}_{02}$  takes on negative values only.

The dependences  $\bar{\rho}_{0i} = \bar{\rho}_{0i}(M)$  are presented in Fig. 8. It is easy to see that the root  $\bar{\rho}_{01}$  corresponds to the maximum of  $E(\bar{\rho}_{0i})$ , as far as the chemical potential decreases from  $M_q$  to zero. When  $M$  changes from zero to  $-M_q$ , the maximal value of  $E(\bar{\rho}_{0i})$  occurs at  $\bar{\rho}_{03}$ .

So, the equation of state in the temperature range  $T < T_c$  has to be written in the form

$$\bar{n} = n_c + \bar{\rho}_{01}\Theta(M) + \bar{\rho}_{03}\Theta(-M), \tag{6.18}$$

where  $\Theta(M)$  is the Heaviside function. It should be noted that equality (6.12) foresees the existence of two marginal values of roots  $\bar{\rho}_{0i}$ , when the chemical potential  $M$  approaches zero. We have

$$n^{(+)} = \lim_{M \rightarrow 0} \bar{n} = n_c + \lim_{M \rightarrow 0} \bar{\rho}_{01} = n_c + n_t, \tag{6.19}$$

where

$$n_t = \left( -\frac{6\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{1/2}. \tag{6.20}$$

When the chemical potential approaches zero from below, one has

$$n^{(-)} = \lim_{M \rightarrow -0} \bar{n} = n_c + \lim_{M \rightarrow -0} \bar{\rho}_{03} = n_c - n_t. \tag{6.21}$$

So, the change of the sign of the chemical potential  $M$  in the temperature range  $T < T_c$  tends to the fluid density leap, which has a size

$$\Delta \bar{n} = n^{(+)} - n^{(-)} = 2n_t. \tag{6.22}$$

It should be noted that at temperatures  $T > T_c$ , such leap is absent, since there exists only the single root  $\bar{\rho}_0$ , at which the value of  $E(\bar{\rho}_0)$  reaches its maximum. The change of the sign of the chemical potential  $M$  converts the value of  $\bar{\rho}_0$  into itself.

The expression for the grand thermodynamic potential at temperatures  $T < T_c$ , where the first-order phase transition occurs, has the form

$$\Omega = -kTN_B \left[ f_c + \frac{n_c^2}{2} \frac{\tilde{a}_2\tau}{1-\tau} + n_c M + D_{13}(M) \right]. \quad (6.23)$$

Here, the chemical potential  $|M| < M_q$ , and the following expression holds:

$$D_{13}(M) = \left( -\frac{\tilde{a}_2}{2} \frac{\tau}{1+\tau} \bar{\rho}_{01}^2 - \frac{a_4}{24} \bar{\rho}_{01}^4 \right) \Theta(M-) - \left( -\frac{\tilde{a}_2}{2} \frac{\tau}{1+\tau} \bar{\rho}_{03}^2 - \frac{a_4}{24} \bar{\rho}_{03}^4 \right) \Theta(-M). \quad (6.24)$$

Using the Laplace transformation  $F = \Omega + \mu\bar{N}$ , it is possible to find the free energy of a fluid in the region of the first-order phase transition, which corresponds to (6.8):

$$F = -kT \frac{V}{v} \left[ f_c + \frac{n_c^2}{2} \frac{\tilde{a}_2\tau}{1+\tau} + \bar{n} \left( f_2 - n_c \frac{\tilde{a}_2\tau}{1+\tau} \right) + D_{13}(\bar{n}) \right], \quad (6.25)$$

where

$$f_2 = \tilde{a}_1 - \beta_c \mu^* (1 + \tau). \quad (6.26)$$

For  $D_{13}(\bar{n})$ , one has

$$D_{13}(\bar{n}) = - \left( \frac{\tilde{a}_2}{2} \frac{\tau}{1+\tau} (\bar{n} - n_c)^2 + \frac{a_4}{4!} (\bar{n} - n_c)^4 \right) \Theta(n^{(-)} - \bar{n}) - \left( \frac{\tilde{a}_2}{2} \frac{\tau}{1+\tau} (\bar{n} - n_c)^2 + \frac{a_4}{4!} (\bar{n} - n_c)^4 \right) \Theta(\bar{n} - n^{(+)}). \quad (6.27)$$

In such a way, a simple fluid stays in the gaseous or liquid state, as far as the chemical potential increases. This depends on its value. As was shown above, at  $T < T_c$  and the negative values of  $M < -M_q$ , only the single root of Eq. (6.4) occurs. This situation corresponds to the densities  $\bar{n} < n_1$  ( $n_1 = n_c - n_g$ , and  $n_g$  is expressed by (6.8)). This range of densities corresponds to the pure gaseous

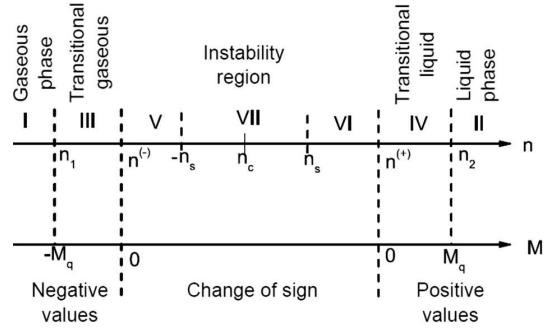


Fig. 9. Relation between the density ranges of a simple fluid at  $T < T_c$  and the values of chemical potential  $M = \beta\mu - \beta\mu_c$

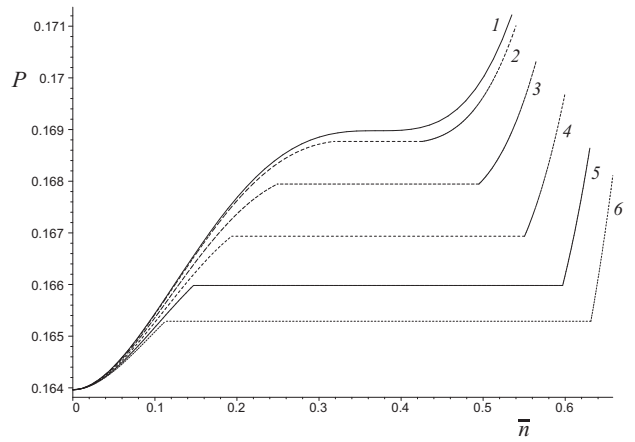


Fig. 10. Dependence of the pressure  $P$  on the density  $\bar{n}$  at  $\tau = 0$  (curve 1),  $\tau = -0.01$  (curve 2),  $\tau = -0.05$  (curve 3),  $\tau = -0.1$  (curve 4),  $\tau = -0.15$  (curve 5),  $\tau = -0.2$  (curve 6)

phase (Fig. 9). As far as the chemical potential increases  $-M_q < M \leq 0$ , Eq. (6.4) has three real solutions. However, only one of them  $\bar{\rho}_{03}$  realizes. This can be seen from the inequalities

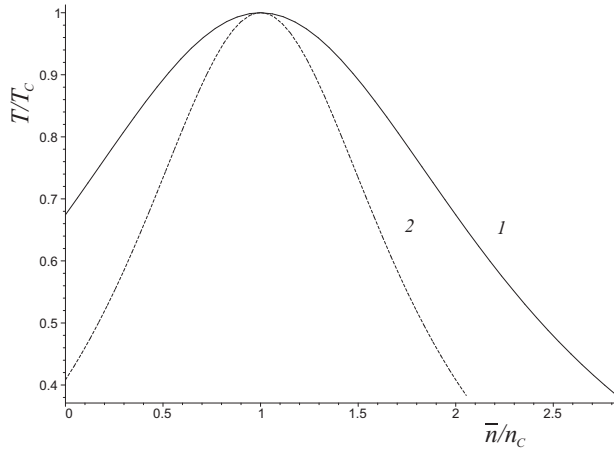
$$E(\bar{\rho}_{03}) > E(\bar{\rho}_{02}), \quad \bar{\rho}_{03} > \bar{\rho}_{02}. \quad (6.28)$$

This situation is just for all  $n_1 < \bar{n} < n^{(-)}$ .

The density  $n^{(-)}$  is the largest value for a fluid at  $M < 0$  and temperatures  $T < T_c$ .

The transition of  $M$  from  $-0$  to  $+0$  causes the density leap from  $n^{(-)}$  to  $n^{(+)}$ . For all  $n^{(+)} \leq \bar{n} < n_2$ , the chemical potential takes on the values  $0 \leq M < M_q$ . There are three real roots of Eq. (6.4) for these values of  $M$ , with  $\bar{\rho}_{01}$  expressed in (6.12). We have

$$E(\bar{\rho}_{01}) > E(\bar{\rho}_{02}); \quad E(\bar{\rho}_{01}) > E(\bar{\rho}_{03}). \quad (6.29)$$



**Fig. 11.** Binodal (1) and spinodal (2) in the reduced temperature-density coordinates

This situation takes place for all  $n^{(+)} < \bar{n} < n_2$ . The stable liquid phase with densities  $\bar{n} > n_2$  corresponds to the case of  $M > M_q$ .

The generalized equation of state of a fluid has the form

$$\begin{aligned} \frac{Pv}{kT} = & \left[ f_c + \frac{\tilde{a}_2}{2} \frac{\tau}{1+\tau} n_c^2 + \right. \\ & \left. + \frac{a_4}{6} \bar{n} (\bar{n} - n_c)^3 - \frac{a_4}{24} (\bar{n} - n_c)^4 \right] \times \\ & \times \left[ \Theta(n^{(-)} - \bar{n}) + \Theta(\bar{n} - n^{(+)}) \right], \end{aligned} \quad (6.30)$$

where

$$n^{(-)} = n_c - n_t, \quad n^{(+)} = n_c + n_t. \quad (6.31)$$

At  $T > T_c$ ,  $n_t = 0$ , whereas, at  $T < T_c$ , one has

$$n_t = \left( -\frac{6\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{1/2}. \quad (6.32)$$

It should be noted that, in the case of  $n_t = 0$ , the sum of theta-functions in (6.15) turns into unity:

$$\Theta(n_c - \bar{n}) + \Theta(\bar{n} - n_c) = 1. \quad (6.33)$$

The transition occurs between the gaseous and liquid phases characterized by densities that maximize expression (6.30). Their values can be found from the condition

$$\left. \frac{\partial(Pv/kT)}{\partial \bar{n}} \right|_{M=0,T} = 0, \quad (6.34)$$

which leads to the equation

$$\frac{\tilde{a}_2\tau}{1+\tau} (\bar{n} - n_c) + \frac{a_4}{6} (\bar{n} - n_c)^3 = 0. \quad (6.35)$$

The solutions

$$\bar{n} = n_c \pm \left( -\frac{6\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{1/2} \quad (6.36)$$

satisfy the condition of maximum of expression (6.30). Solving Eq. (6.36) with respect to the temperature allows one to obtain the expression

$$\frac{T_b}{T_c} = \frac{6\tilde{a}_2}{6\tilde{a}_2 + a_4 n_c^2 (\bar{n}/n_c - 1)^2}, \quad (6.37)$$

which can serve as the base for the binodal construction (the coexistence curve) in the temperature-density coordinates, which is presented in Fig. 11. The equation for the spinodal or the curve of marginal states of the system, defining the boundaries of the instability region, can be found from the extremum condition for the equation of state (6.30):

$$\left. \frac{\partial(Pv/kT)}{\partial \bar{n}} \right|_T = 0, \quad (6.38)$$

which leads to the equation

$$\bar{n} = n_c \pm \left( -\frac{2\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{1/2} \quad (6.39)$$

or

$$\frac{T_s}{T_c} = \frac{2\tilde{a}_2}{2\tilde{a}_2 + a_4 n_c (\bar{n}/n_c - 1)^2}. \quad (6.40)$$

From whence, the spinodal curve can be obtained. It is presented in Fig. 11.

## 7. Conclusions

Using the general principles of statistical mechanics in frames of the grand canonical ensemble, the calculation method of the grand partition function of a simple fluid is proposed. A system of  $N$  particles in a volume  $V$  with periodic boundary conditions is concerned. As an interaction potential between particles, the Morse potential was chosen.

In the course of calculating the grand partition function, the reference system formed from a part of the repulsive component of the interaction potential

was used. It is established that, due to the selection of the reference system, one can perform the summation over the number of particles  $N$  and the integration over their coordinates. As a result, the evident form of the Jacobian of the transition from a set of variables, characterizing individual particles, to the collective variables, whose average values are connected with the order parameter of the first-order phase transition, is obtained. Coefficients of the Jacobian of the transition, which is a polynomial over a series of collective variables in the exponent expressed via the special functions  $T_n(\alpha^*, p)$ , are introduced. The latter are represented in the form of rapidly convergent series. The arguments of special functions  $\alpha^*$  and  $p$  are real positive values. The former  $\alpha^*$  is related to some fixed value of chemical potential  $\mu^*$ , the latter argument  $p$  is proportional to the reference system potential.

We have obtained a representation of the grand partition function corresponding to some lattice model. But, in contrast to the lattice gas model, it foresees that a cell can contain a random number of particles. The representation is general and valid both far from the critical point and directly in its vicinity.

We have considered the simplest approximation, which is valid out of a vicinity of the critical point. The equation of state obtained in this work describes a behavior of a simple fluid system in wide temperature ranges below and above the critical temperature  $T_c$ . At temperatures  $T < T_c$ , the presence of rectilinear plots at the pressure vs density curve is established. It describes a density jump at the first-order phase transition. A curve circumflex these rectilinear plots allows us to obtain the binodal line. In addition, the spinodal curve as the instability region of a system at temperatures lower than the critical one is found.

The usage of higher-order approximations for the calculation of the equation of state is the subject of a separate research.

## APPENDIX

Determination of the value of  $B$  which characterizes the model potential

$$U(k) = \begin{cases} U_B(k) = \Psi(k) - U_1(k) & \text{at } |k| \leq B, \\ 0 & \text{at } |k| > B. \end{cases} \quad (8.1)$$

Here,

$$\Psi(r) = \epsilon e^{-2(r-R_0)/\alpha}, \quad U_1(r) = 2\epsilon e^{-(r-R_0)/\alpha}.$$

Let us perform the transition to a reduced form. Let  $r' = r/R_0$ . Then

$$\Psi(r') = \epsilon e^{-2(r'-1)/\alpha_R}, \quad U_1(r') = 2\epsilon e^{-(r'-1)/\alpha_R}, \quad (8.2)$$

where

$$\alpha_R = \alpha/R_0. \quad (8.3)$$

So, there are two parameters of the interaction potential:  $\epsilon$  (as a dimension unit) and  $\alpha_R$ . The Fourier transforms

$$\Psi(k) = \Psi(0) (1 + \alpha_R^2 k^2/4)^{-2}, \quad \Psi(0) = \epsilon \pi \alpha_R^3 e^{2/\alpha_R},$$

$$U_1(k) = U_1(0) (1 + \alpha_R^2 k^2)^{-2}, \quad (8.4)$$

$$U_1(0) = 16\epsilon \pi \alpha_R^3 e^{1/\alpha_R}.$$

Herewith, the following condition is satisfied:

$$U_1(0) = \Psi(0) 16e^{-1/\alpha_R}. \quad (8.5)$$

The condition to determine the value of  $B$  has the form

$$\int_B^\infty V(k) k^2 dk = 0, \quad (8.6)$$

where

$$V(k) = U_1(k) - f\Psi(k) + \tau(1-f)\Psi(0) \left(1 + \frac{\alpha_R^2 k^2}{4}\right)^{-2}. \quad (8.7)$$

This allows us to assign  $\tau = 0$ .

The evident form of integral (8.5) can be calculated. So, the following expression is obtained:

$$f = 16e^{-1/\alpha_R} \int_B^\infty \frac{k^2 dk}{(1 + \alpha_R^2 k^2)^2} \Big/ \int_B^\infty \frac{k^2 dk}{\left(1 + \frac{\alpha_R^2 k^2}{4}\right)^2}. \quad (8.8)$$

That is why

$$f = \frac{16}{8} e^{-1/\alpha_R} \frac{\left[\frac{\pi}{2} + \frac{B\alpha_R}{1+B^2\alpha_R^2} - \text{arctg}(B\alpha_R)\right]}{\left[\frac{\pi}{2} + \frac{B\alpha_R/2}{1+B^2\alpha_R^2/4} - \text{arctg}(B\alpha_R/2)\right]}. \quad (8.9)$$

The parameter  $p$  expressed by (3.10) has the form

$$p = \beta_c \bar{\Psi}(1-f)/2 \quad (8.10)$$

and is dependent on the average value of the repulsive potential  $\bar{\Psi} = \langle \Psi(k) \rangle$  at ranges  $[0, B]$ , where  $B = B(\alpha_R, f)$ . At a fixed value of  $\alpha_R$  (the characteristic of a substance), the latter is determined only by the parameter  $f$  (see Fig. 12).

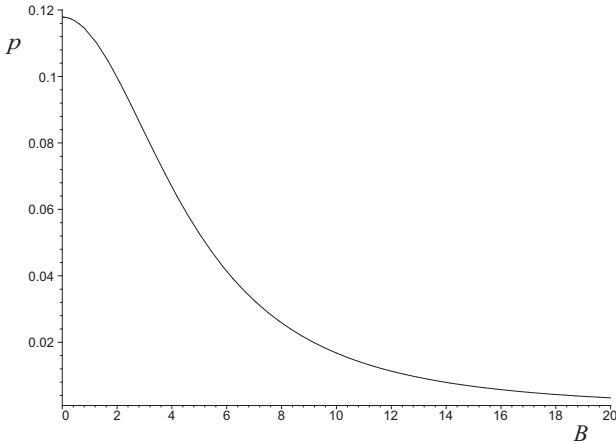
We will find  $\bar{\Psi}$  as the average value of  $\Psi(k)$  at  $k \in [0, B]$ :

$$\bar{\Psi} = \Psi(0)\chi_R, \quad (8.11)$$

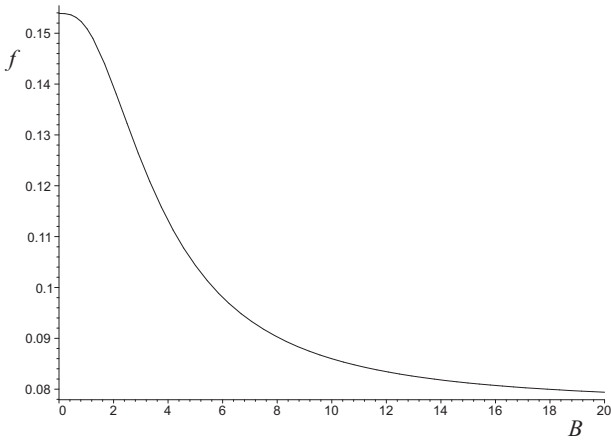
where

$$\chi_R = \frac{3}{2} \left(\frac{2}{\alpha_R B}\right)^3 \left(\text{arctg} \frac{B\alpha_R}{2} - \frac{1}{2} \frac{B\alpha_R}{1 + \alpha_R^2 B^2/4}\right). \quad (8.12)$$





**Fig. 12.** Changes of the parameter  $p$  depending on the value  $B$  at  $R_0/\alpha = 3.7 \ln 2$



**Fig. 13.** Changes of the parameter  $f$  depending on  $B$  at  $R_0/\alpha = 3.7 \ln 2$

It is easy to see that the value of  $\chi_R$  is a function of  $B$  (or  $f$ ) at fixed  $\alpha_R$ .

In the case of fixed  $f = 0.1488$ , at which  $B = 1.258$ , one has  $\chi_R = 0.932$ , which corresponds to

$$P_R = 0.11, \tag{8.13}$$

which is calculated, by using (8.9) in the simplest approximation, where (see (5.2))

$\beta_c = \tilde{a}_2/V(0, T_c)$ , then

$$P_R = \frac{\alpha_2 \Psi(0) \chi_R}{2V(0, T_c)} (1 - f). \tag{8.14}$$

Since

$$V(0, T_c) = U_1(0) - f\Psi(0) = \Psi(0) \left( 16e^{-1/\alpha_R} - f \right),$$

we have

$$P_R = \frac{\tilde{a}_2}{2} \frac{1 - f}{16e^{1/\alpha_R} - f} \chi_R. \tag{8.15}$$

So, the parameter  $p$ , which defines the special functions (3.15), depends on  $f$  and the parameter  $\alpha^* = ve^{\beta\mu^*}$ . The parameter ( $\alpha^*$ ) defines the values of  $\tilde{a}_2$ .

Conclusion. One should choose a substance to be observed, which means to fix the parameter  $\alpha_R$  (for example,  $\alpha_R = 0.3899$  referring to  $R_0/\alpha = 3.7 \ln 2$ ). The possible values of parameter  $f$  defining the reference system change within the limits  $0 < f < 0.154$  (see Fig. 13). In this range,  $V(0) > 0$ , that is the necessary condition to apply analytical calculation methods, specifically the method of CV. In this case, the reference system includes the main part of the repulsive potential

$$\Psi_{RS} = (1 - f)\Psi(k),$$

where  $0.846 < (1 - f) < 1$ .

To co-ordinate the “primeval” parameter  $p$  which has value (8.9), one has to choose the value

$$f = 0.1488, \tag{8.16}$$

corresponding to  $p = 0.11$ . The latter has to coincide with the value of  $p$  expressed by (8.10) at  $\alpha^* = 11$ . If the initial value  $p \neq 0.11$ , any  $\alpha^*$  exist for (8.15) to coincide with the result of calculation of  $p$  by formula (8.10). The critical temperature (5.2)  $kT_c = 3.8135$  corresponds to these values of parameters for the model.

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*М.П. Козловський, О.А. Добуш, Р.В. Романік*ДО РОЗРАХУНКУ ВЕЛИКОЇ  
СТАТИСТИЧНОЇ СУМИ МОДЕЛІ ПЛИНУ

Резюме

Запропоновано спосіб розрахунку великої статистичної суми моделі простого плинку в рамках узагальненої ґраткової моделі, в кожному з вузлів якої може перебувати довільна кількість частинок. В ролі потенціалу взаємодії між частинками використано потенціал Морзе. У процесі розрахунку виконано підсумовування за числом частинок та інтегрування за їхніми координатами. У найпростішому наближенні отримано рівняння стану, яке справедливе для широкого діапазону температур. Для температур, нижчих, ніж критична, встановлено наявність горизонтальних ділянок на кривій залежності тиску від густини.

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Резюме

Предложен способ расчета большой статистической суммы модели простого флюида в рамках обобщенной решеточной модели, в каждом из узлов которой может находиться произвольное количество частиц. В качестве потенциала взаимодействия между частицами использован потенциал Морзе. В процессе расчета выполнено суммирование по числу частиц и интегрирование по их координатам. В простейшем приближении получено уравнение состояния, которое справедливо для широкого диапазона температур. Для температур ниже, чем критическая, установлено наличие горизонтальных участков на кривой зависимости давления от плотности.