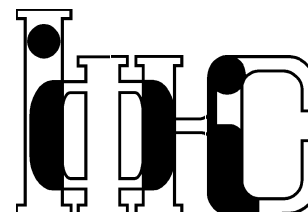


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ІНСТИТУТ
ФІЗИКИ
КОНДЕНСОВАНИХ
СИСТЕМ

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Оксана Андріївна Добуш
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До РОЗРАХУНКУ ВЕЛИКОЇ СТАТИСТИЧНОЇ СУМИ МОДЕЛІ ПЛИНУ

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M.P. Kozlovskii, O.A. Dobush, R.V. Romanik

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

ЛЬВІВ

УДК: 536.7; 539.6

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До розрахунку великої статистичної суми моделі плин

М.П. Козловський, О.А. Добуш, Р.В. Романік

Анотація. Запропоновано спосіб розрахунку великої статистичної суми моделі простого плин в рамках узагальненої граткової моделі, в кожному з вузлів якої може перебувати довільна кількість частинок. В якості потенціалу взаємодії між частинками використано потенціал Морзе. У процесі розрахунку виконано підсумовування за числом чатинок 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.

Concerning a calculation of the grand partition function of a fluid model

M.P. Kozlovskii, O.A. Dobush, R.V. Romanik

Abstract. The calculation method of the grand partition function of a simple fluid model in frames of generalized lattice model, where each cell may contain random number of particles, was proposed. As an interaction potential between particles the Morse potential was chosen. In course of calculations summation over number of particles and integration over it's coordinates were performed. Using a simplest approximation the state equation valid in wide temperature ranges was obtained. At temperatures lower than critical one, the presence of horizontal plots at curve of the pressure dependence on the density was established.

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1. Introduction

The behavior of many-particle system in both gaseous and liquid phases has been attracting attention of scientists for over a century. The task of microscopic description of such a behavior remains vital even today. Especially urgent is the problem of describing fluid in the 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 system transiting from the state in one phase to that in another is called the phase transition of the first order.

One of the most successful and extensively used, and undoubtedly the most known, is the Van der Waals (VdW) theory of phase transitions. Two phenomenological parameters of the theory along with the Maxwell rule, allows one to build the equation of state for fluid that elucidates the main properties of phase transitions. At the same time, the simplicity of the VdW theory is worth being stressed as it is nothing but a reasonable modification of the ideal-gas equation of state. It is obvious that this fact greatly contributed to the popularity of the theory and allowed us to obtain further insight into the physics of phase transitions. However, the VdW theory is of mean-field type and, therefore, does not account for fluctuations which heavily effect the behavior of a system near the critical point. Nonetheless, some authors made try to take into account the fluctuations within the VdW theory, see for instance [1].

Nowadays, most approaches to description of phase transitions and critical phenomena in fluids are based on scaling ideas, universality hypothesis, renormalization group methods. The following theories are worth mentioning: field-theoretical approach, which appeared to be very powerful in describing magnetic systems; complete scaling approach [2,3], which is essentially phenomenological theory; methods of integral equations, and in particular self-consistent Ornstein-Zernike approximation (SCOZA) [4, 5]; perturbation series expansion, for example hierarchical reference theory [6, 7]; non-perturbative renormalization group approach [8]; collective variables method [9]; numerical methods and computer simulations.

The investigation of simple fluids is frequently carried out 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-spheres potential is itself such a function, as well as widely considered Lenard-Jones potential, or more general Mie potentials. However, in literature the results can be found for systems of many particles inter-

acting via pair potential possessing the Fourier transform. For instance, the Morse fluid has already been studied: within the integral equation approach [10], by Monte Carlo simulations using both NpT plus test particle method [11] and the grand-canonical transition matrix method [12]. Usage of such potentials may be sufficient for some purposes, for example, to describe the liquid-vapor coexistence in liquid metals [10,12]. The description of such systems does not need the hard-spheres reference system and, 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 $U(|\vec{R}|)$, where \vec{R} is the distance in 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 microscopic particle density defined as

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

where \vec{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 $\hat{n}(\vec{R})$ in the form of Fourier series

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

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

N . The Fourier transform $\hat{\rho}_{\vec{k}}$ has the form

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

Let the system be open. The probability that an open system contains exactly N particles is defined by [13]

$$P_N = \frac{z'^N \int \exp(-\beta v_N(\vec{R}_1, \dots, \vec{R}_N)) (d\vec{R})}{N! \Xi},$$

where Ξ is the grand partition function (GPF) of the system:

$$\Xi = \sum_{N=0}^{\infty} \frac{z'^N}{N!} \int \exp(-\beta v_N(\vec{R}_1, \dots, \vec{R}_N)) (d\vec{R}). \quad (2.5)$$

Here $(d\vec{R}) = d\vec{R}_1 \dots d\vec{R}_N$, $z' = \exp(\beta\mu + \ln[(2\pi m\beta^{-1})^{3/2}/h^3])$, β is the inverse temperature, μ the chemical potential, m the mass of a particle, h the Planck constant. The potential energy v_N has the following form

$$v_N(\vec{R}_1, \dots, \vec{R}_N) = \sum_{1 \leq i < j \leq N} U(\vec{R}_{i,j}) \quad (2.6)$$

and can be represented in terms of $\hat{\rho}_{\vec{k}}$ as follows

$$v_N(\vec{R}_1, \dots, \vec{R}_N) = \frac{1}{2V} \sum_{\vec{k}} \tilde{U}_k \hat{\rho}_{\vec{k}} \hat{\rho}_{-\vec{k}} - \frac{1}{2} N U(0), \quad (2.7)$$

where $\tilde{U}_k = \int U(R) e^{i\vec{k}\vec{R}} d\vec{R}$ is the Fourier transform of the interaction potential $U(R)$.

Hence, the grand partition function with the interaction potential \tilde{U}_k has the form

$$\Xi = \sum_{N \geq 0} \frac{z'^N}{N!} \int (d\vec{R}) \exp \left(-\frac{\beta}{2V} \sum_{\vec{k}} \tilde{U}_k \hat{\rho}_{\vec{k}} \hat{\rho}_{-\vec{k}} \right). \quad (2.8)$$

Here $z = \exp(\beta\mu')$ is the activity, β is the inverse temperature, $\mu' = \mu + \beta^{-1} \ln[(2\pi m\beta^{-1})^{3/2}/h^3] + \frac{1}{2V} \sum_{\vec{k}} \tilde{U}_k$ where we have used the equality $U(0) = \sum_{\vec{k}} \tilde{U}_k / V$.

Performing further calculations let us consider volume V to be conditionally split into N_B cells of volume $v = V/N_B$, moreover $v = c^3$,

where c is a 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) within this approach a cell can contain random number of particles. The problem of description of continuous systems (unlike lattice systems) consist in the fact that values of the wave vector are not bounded above, although they change discretely. The latter fact is connected with system restriction to the space of coordinates of volume V . In much the same way as in lattice systems (where the wave vector is discrete and bounded) in the majority of works on description of fluid systems behavior at certain stage of calculations some restrictions to values of the wave vector $k < B$ are introduced [16]. Herewith the procedure of selecting B is ambiguous and different authors use to choose B in different ways [17].

The behavior of a system near the point of the phase transition (PT) is determined by the interaction potential. When the latter turns into zero one has a non-interactive gas where the PT is absent. The Fourier transform of the potential (2.1) have to decrease with increase of 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 behavior of a system containing N - particles for some model potential $\tilde{U}_B(k)$, which coincides with $\tilde{U}(k)$ for values $k \in [0, B)$ and equal to zero for each $k \geq B$. The value B will be defined subsequently. At this stage of calculations let us assume, that B takes on finite value.

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

$$\Xi = \sum_{N \geq 0} \frac{z^N}{N!} \int (d\vec{R}) \exp \left(-\frac{\beta}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \tilde{U}_B(k) \hat{\rho}_{\vec{k}} \hat{\rho}_{-\vec{k}} \right). \quad (2.9)$$

The wave vector \vec{k} takes on values

$$B_\Lambda = \left\{ \vec{k} = (k_x, k_y, k_z) \mid k_i = -\frac{\pi}{c} + \frac{2\pi}{c} \frac{n_i}{N_{B_i}}, \right. \\ \left. n_i = 1, 2, \dots, N_{B_i}; i = x, y, z; N_B = N_{B_x} N_{B_y} N_{B_z} \right\}. \quad (2.10)$$

In the collective variables (CV) representation [14] (2.9) is written as

$$\Xi = \sum_{N \geq 0} \frac{z^N}{N!} \int (d\vec{R}) (d\rho)^{N_B} \exp \left[-\frac{\beta}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \tilde{U}_B(k) \rho_{\vec{k}} \rho_{-\vec{k}} \right] J(\rho - \hat{\rho}), \quad (2.11)$$

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

$$J(\rho - \hat{\rho}) = \prod_{\vec{k} \in \mathcal{B}_\Lambda} \delta(\rho_{\vec{k}} - \hat{\rho}_{\vec{k}}) = \int (d\nu)^{N_B} e^{2\pi i \sum_{\vec{k} \in \mathcal{B}_\Lambda} \nu_{\vec{k}} (\rho_{\vec{k}} - \hat{\rho}_{\vec{k}})}. \quad (2.12)$$

The GPF in the form of Eq. (2.11) was originally proposed in [15] for a many-particle system with Coulomb interaction, but has not got enough attention since then.

Before proceeding calculation of (2.11) let us perform two identity transformations. The former is

$$e^{\beta \mu' N} = e^{\beta_c \mu^* N} \exp [\beta (\mu' - \mu^* (1 + \tau)) \hat{\rho}_0]. \quad (2.13)$$

Here μ^* is a random fixed value of the 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

$$\tau = \frac{T - T_c}{T_c}. \quad (2.14)$$

In further calculations the quantity $\hat{\rho}_0$ in (2.13) will be substituted for ρ_0 , since expression (2.11) 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 $f \in [0, 1]$

$$\tilde{U}_B(k) = -\tilde{U}_1(k) + f \tilde{\Psi}(k) + (1 - f) \tilde{\Psi}(k). \quad (2.15)$$

Let us consider the summand

$$-\frac{\beta}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \tilde{U}_B(k) \rho_{\vec{k}} \rho_{-\vec{k}} = \frac{\beta}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} (\tilde{U}_1(k) - f \tilde{\Psi}(k)) \rho_{\vec{k}} \rho_{-\vec{k}} \\ - \frac{\beta(1-f)}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \tilde{\Psi}(k) \rho_{\vec{k}} \rho_{-\vec{k}} \quad (2.16)$$

and represent the latter in the form

$$-\frac{\beta_c(1-f)}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \tilde{\Psi}(k) \rho_{\vec{k}} \rho_{-\vec{k}} + \frac{\beta_c - \beta}{2V} (1-f) \sum_{\vec{k} \in \mathcal{B}_\Lambda} \tilde{\Psi}(k) \rho_{\vec{k}} \rho_{-\vec{k}}.$$

As a result one obtains for (2.16)

$$-\frac{\beta}{2V} \sum_{k \in \mathcal{B}_\Lambda} \tilde{U}_B(k) \rho_{\vec{k}} \rho_{-\vec{k}} = \frac{\beta}{2V} \sum_{k \in \mathcal{B}_\Lambda} \tilde{V}_B(k) \rho_{\vec{k}} \rho_{-\vec{k}} - \frac{\beta_c}{2V} (1-f) \sum_{k \in \mathcal{B}_\Lambda} \tilde{\Psi}(k) \rho_{\vec{k}} \rho_{-\vec{k}}, \quad (2.17)$$

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

$$\tilde{V}(k) = \tilde{U}_1(k) - f \tilde{\Psi}(k) + \tau(1-f) \tilde{\Psi}(k), \quad (2.18)$$

and the value $\tilde{\Psi}(k) > 0$. As in the case of the former transformation let us replace value $\rho_{\vec{k}}$ by $\hat{\rho}_{\vec{k}}$ in the last term of (2.17) and use a certain transformation

$$\exp \left[-\frac{\beta_c}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} (1-f) \tilde{\Psi}(k) \hat{\rho}_{\vec{k}} \hat{\rho}_{-\vec{k}} \right] = \tilde{g}_\Psi \int (d\varphi)^{N_B} \exp \left[-\frac{V}{2\beta_c} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\vec{k}} \varphi_{-\vec{k}}}{(1-f) \tilde{\Psi}(k)} + i \sum_{\vec{k} \in \mathcal{B}_\Lambda} \varphi_{\vec{k}} \hat{\rho}_{\vec{k}} \right]. \quad (2.19)$$

Here

$$\tilde{g}_\Psi = \prod_{\vec{k} \in \mathcal{B}_\Lambda} \left(2\pi \frac{\beta_c}{V} (1-f) \tilde{\Psi}(k) \right)^{-\frac{1}{2}}. \quad (2.20)$$

As a result of identity transformations appliance described above, the grand partition function (2.11) takes on the form

$$\Xi = \tilde{g}_\Psi \int \sum_{N=0}^{\infty} \frac{e^{\beta_c \mu^* N}}{N!} \int (d\rho)^{N_B} e^{\frac{\beta}{2V} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \tilde{V}(k) \rho_{\vec{k}} \rho_{-\vec{k}}} \times \int (d\varphi)^{N_B} e^{-\frac{V}{2\beta_c} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\vec{k}} \varphi_{-\vec{k}}}{(1-f) \tilde{\Psi}(k)}} \times \int (d\vec{R}) e^{i \sum_{\vec{k} \in \mathcal{B}_\Lambda} \varphi_{\vec{k}} \hat{\rho}_{\vec{k}}} \times \int (d\nu)^{N_B} e^{2\pi i \sum_{\vec{k} \in \mathcal{B}_\Lambda} \nu_{\vec{k}} (\rho_{\vec{k}} - \hat{\rho}_{-\vec{k}})} e^{\beta(\mu' - \mu^*(1+\tau)) \rho_0}. \quad (2.21)$$

To perform further calculations it is convenient to change variables

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

As a result the representation of the grand partition function in space of collective variables is obtained

$$\Xi = g_\Psi \int (d\rho)^{N_B} \exp \left\{ \beta[\mu' - \mu^*(1+\tau)] \rho_0 + \frac{\beta}{2} \sum_{\vec{k} \in \mathcal{B}_\Lambda} V(k) \rho_{\vec{k}} \rho_{-\vec{k}} \right\} \times \int (d\nu)^{N_B} (d\varphi)^{N_B} \exp \left[-\frac{1}{2\beta_c(1-f)} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\vec{k}} \varphi_{-\vec{k}}}{\Psi(k)} + 2\pi i \sum_{\vec{k} \in \mathcal{B}_\Lambda} \nu_{\vec{k}_1} \rho_{\vec{k}} \right] G(\bar{\nu}), \quad (2.22)$$

where such notions are introduced

$$V(k) = \tilde{V}(k)/v, \quad \Psi(k) = \tilde{\Psi}(k)/v. \quad (2.23)$$

the value g_Ψ has the form

$$g_\Psi = \tilde{g}_\Psi / \sqrt{N_B} = \prod_{k \in \mathcal{B}_\Lambda} \left(2\pi \frac{\beta_c}{v} (1-f) \Psi(k) \right)^{-1/2}. \quad (2.24)$$

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

$$G(\bar{\nu}) = \sum_{N=0}^{\infty} \frac{(z^*)^N}{N!} \int (d\vec{R}) \exp \left[-2\pi i \sum_{k \in \mathcal{B}_\Lambda} \bar{\nu}_{\vec{k}} \hat{\rho}_{\vec{k}} \right], \quad (2.25)$$

where the operator $\hat{\rho}_{\vec{k}}$ is given in (2.4), and for $\bar{\nu}_{\vec{k}}$ one has

$$\bar{\nu}_{\vec{k}} = \nu_{\vec{k}} - \varphi_{\vec{k}} / 2\pi. \quad (2.26)$$

It is possible to perform precise calculation of the expression (2.25), as we have already presented in [16]. For this purpose one should use an evident form of the operator $\hat{\rho}_{\vec{k}}$ expressed by (2.4)

$$G(\bar{\nu}) = \sum_{N=0}^{\infty} \frac{(z^*)^N}{N!} \int \dots \int d\vec{R}_1 \dots d\vec{R}_N \exp \left[-2\pi i \sum_{k \in \mathcal{B}_\Lambda} \bar{\nu}_{\vec{k}} \sum_{j=1}^N e^{-i\vec{k}\vec{R}_j} \right].$$

Summation over number of particles in the exponent can be written as a product of exponents, thus N typical integrals over the coordinate \vec{R} can be received

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

The latter expression can be summed using series expansion representation of an exponent

$$G(\bar{\nu}) = \exp \left[z^* \int d\vec{R} \exp \left[-2\pi i \sum_{k \in \mathcal{B}_\Lambda} \bar{\nu}_{\vec{k}} e^{-i\vec{k}\vec{R}} \right] \right].$$

The same representation can be used to perform series expansion in the integrand

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

It is easy to see, that integral over the coordinate \vec{R} correspond to the integral representation of the δ - function, so,

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

this result can be rewritten using the nodal representation in the form

$$G(\bar{\nu}) = \exp \left(\sum_{n=0}^{\infty} \frac{(2\pi i)^n}{n!} \alpha^* \sum_l \bar{\nu}_l^n \right) = \exp \left[\alpha^* \sum_l e^{2\pi i \bar{\nu}_l} \right], \quad (2.27)$$

where

$$\alpha^* = v e^{\beta_c \mu^*} = v z^*. \quad (2.28)$$

For the value $\bar{\nu}_l$ one has

$$\bar{\nu}_l = \nu_l - \varphi_l / 2\pi, \quad (2.29)$$

where

$$\nu_l = \frac{1}{\sqrt{N_B}} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \nu_{\vec{k}} e^{-i\vec{k}\vec{l}}, \quad \varphi_l = \frac{1}{\sqrt{N_B}} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \varphi_{\vec{k}} e^{-i\vec{k}\vec{l}}. \quad (2.30)$$

Taking into account (2.27), one obtains from (2.22)

$$\Xi = g_\Psi \int (d\rho)^{N_B} e^{\beta[\mu' - \mu^*(1+\tau)]\rho_0} \exp \left[\frac{\beta}{2} \sum_{\vec{k} \in \mathcal{B}_\Lambda} V(k) \rho_{\vec{k}} \rho_{-\vec{k}} \right] J(\rho), \quad (2.31)$$

where the expression for the Jacobian of transition $J(\rho)$ is

$$J(\rho) = \int (d\nu)^{N_B} e^{2\pi i \sum_{\vec{k} \in \mathcal{B}_\Lambda} \nu_{\vec{k}} \rho_{\vec{k}}} F(\nu) \quad (2.32)$$

where

$$F(\nu) = \int (d\varphi)^{N_B} e^{-\frac{1}{2\beta c} \sum_{\vec{k} \in \mathcal{B}_\Lambda} \frac{\varphi_{\vec{k}} \varphi_{-\vec{k}}}{(1-f)\Psi(k)}} e^{\alpha^* \sum_l e^{-2\pi i(\nu_l - \varphi_l/2\pi)}}. \quad (2.33)$$

The notation of the expression (2.33) is symbolic, since $\varphi_{\vec{k}}$ and $\nu_{\vec{k}}$ must be understood as the functions of variables $\varphi_{\vec{l}}$ and $\nu_{\vec{l}}$ according to the equalities (2.30).

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

3. The calculation of the Jacobian of transition

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

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

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

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

Here the value ϵ determines interaction on the distance R_0 between particles, where minimal value of $\Phi(r)$ can be reached, the parameter α describes an effective radius of attraction. Widespread use, and large number of results from numerical calculations [10–12] became the reason stipulated for the choice of exactly such $U(r)$. The Fourier transform of this potential has the form

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

where

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

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

One can find the Jacobian of transition to the collective variables $J(\rho)$ from (2.32) after calculating $F(\nu)$. It can be performed approximately

by means of substituting the value $\Psi(k)$ in (2.33) by its average value $\bar{\Psi}(k)$, for example, by the integral average

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

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

$$F(\nu) = \prod_l F_l(\nu), \quad (3.6)$$

where

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

Expression (3.7) can be represented in the form

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

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

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

where the value p

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

and for a one has

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

As a result

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

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

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

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

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

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

As a result one obtains

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

Here such special functions are used

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

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

Note that this special functions $T_n(\alpha^*, p)$ can be expressed by means of another special functions

$$W_n(\alpha^*, p) = (\alpha^*)^n \sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} e^{-p(n+m)^2}. \quad (3.16)$$

Herewith

$$\begin{aligned}
T_0(\alpha^*, p) &= W_0(\alpha^*, p), \\
T_1(\alpha^*, p) &= W_1(\alpha^*, p), \\
T_2(\alpha^*, p) &= W_1(\alpha^*, p) + W_2(\alpha^*, p), \\
T_3(\alpha^*, p) &= W_3(\alpha^*, p) + 3W_2(\alpha^*, p) + W_1(\alpha^*, p), \\
T_4(\alpha^*, p) &= W_4(\alpha^*, p) + 6W_3(\alpha^*, p) + 7W_2(\alpha^*, p) + W_1(\alpha^*, p), \\
T_5(\alpha^*, p) &= W_5(\alpha^*, p) + 10W_4(\alpha^*, p) + 25W_3(\alpha^*, p) + 15W_2(\alpha^*, p) \\
&\quad + W_1(\alpha^*, p), \\
T_6(\alpha^*, p) &= W_6(\alpha^*, p) + 15W_5(\alpha^*, p) + 65W_4(\alpha^*, p) + 90W_3(\alpha^*, p) \\
&\quad + 31W_2(\alpha^*, p) + W_1(\alpha^*, p). \tag{3.17}
\end{aligned}$$

Taking into account (3.12), one can obtain the following expression for the Jacobian of transition $J(\rho)$

$$J(\rho) = \prod_l J_l(\rho_l), \tag{3.18}$$

where

$$J_l(\rho_l) = \int_{-\infty}^{\infty} d\nu_l e^{2\pi i \nu_l \rho_l} \exp \left[\sum_{n=0}^{n_0} \frac{(-2\pi i)^n}{n!} \mathcal{M}_n \nu_l^n \right]. \tag{3.19}$$

There is a polynomial of degrees of a real variable ν_l in the index of the exponent. The convergency of the integral over this variable is provided by even powers. It is easy to see if represent (3.19) in the form

$$J_l(\rho_l) = \int_{-\infty}^{\infty} d\nu_l e^{2\pi i \nu_l \rho_l} e^{f(x)} (\cos f_1(x) - i \sin f_1(x)), \tag{3.20}$$

where

$$\begin{aligned}
f(x) &= -\frac{(2\pi)^2}{2} \mathcal{M}_2 x^2 + \frac{(2\pi)^4}{4!} \mathcal{M}_4 x^4 - \frac{(2\pi)^6}{6!} \mathcal{M}_6 x^6, \\
f_1(x) &= 2\pi \mathcal{M}_1 x - \frac{(2\pi)^3}{3!} \mathcal{M}_3 x^3 + \frac{(2\pi)^5}{5!} \mathcal{M}_5 x^5. \tag{3.21}
\end{aligned}$$

Here $n_0 = 6$ is assigned to provide definiteness, so to say the approximation used in [18] is applied.

The expression (3.20) can be represented in a form

$$\bar{J}_l(\rho_l) = \exp \left[-\sum_{n=0}^{n_0} \frac{a_n}{n!} \rho_l^n \right] \tag{3.22}$$

as a result of integration over variables ν_l . Herewith, coefficients a_n are real values and have a form

$$\begin{aligned}
a_0 &= \ln(2\pi) - \ln I_0, \quad a_1 = -J_1/I_0, \quad a_2 = I_2/I_0 + a_1^2, \\
a_3 &= J_3/I_0 - a_1^3 + 3a_1 a_2, \\
a_4 &= -I_4/I_0 + a_1^4 - 6a_1^2 a_2 + 4a_1 a_3 + 3a_2^2. \tag{3.23}
\end{aligned}$$

Here such notification are used

$$\begin{aligned}
I_n &= \int_{-\infty}^{\infty} dx x^n \cos(f_1(x)) e^{f(x)}, \\
J_n &= \int_{-\infty}^{\infty} dx x^n \sin(f_1(x)) e^{f(x)}. \tag{3.24}
\end{aligned}$$

As it was said above, convergency of the integrals expressed in (3.24) occurs for all values of

$$\mathcal{M}_2 > 0, \quad \mathcal{M}_4 < 0, \quad \mathcal{M}_6 > 0. \tag{3.25}$$

The condition $\mathcal{M}_6 > 0$ is sufficient for existence of quantities $I_n(\alpha^*, p)$ and $J_n(\alpha^*, p)$. The results of the calculations show that the value of $\mathcal{M}_2 > 0$ for any values of α^* and p . Note that $\alpha^* = ve^{\beta_c \mu^*}$ 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 the values of α^* and p is presented in Figure 1. It is easy to see, that there exists the region of values of the parameters $0 < \alpha^* < 25$ and $0,1 < p < 3$, which satisfy the condition (3.25). Here $\mathcal{M}_4 < 0$ both with $\mathcal{M}_6 > 0$, that allows one to find corresponding values of a_n .

An example of values of the cumulants \mathcal{M}_n and corresponding coefficients a_n for the case of $R_0/\alpha = 3, 7 \ln 2$, $\alpha^* = 11$ and $p = 0,11$ is given below. The choice of such values of the parameters is associated with the procedure of self-consistency, described in Appendix.

$$\begin{aligned}
\mathcal{M}_0 &= 6, 1362, \quad \mathcal{M}_1 = 4, 1588, \quad \mathcal{M}_2 = 2, 2040, \quad \mathcal{M}_3 = 0, 6023, \\
\mathcal{M}_4 &= -0, 1498, \quad \mathcal{M}_5 = -0, 0529, \quad \mathcal{M}_6 = 0, 1523; \\
a_0 &= -0, 1640, \quad a_1 = -2, 9664, \quad a_2 = 1, 8402, \quad a_3 = -2, 3378, \\
a_4 &= 6, 2845. \tag{3.26}
\end{aligned}$$

It should be noted, that obtained values of the coefficients (3.26) correspond to a pair of (in principle, random) parameters. One of them namely parameter p is defined by expression (3.10) and the value f , that

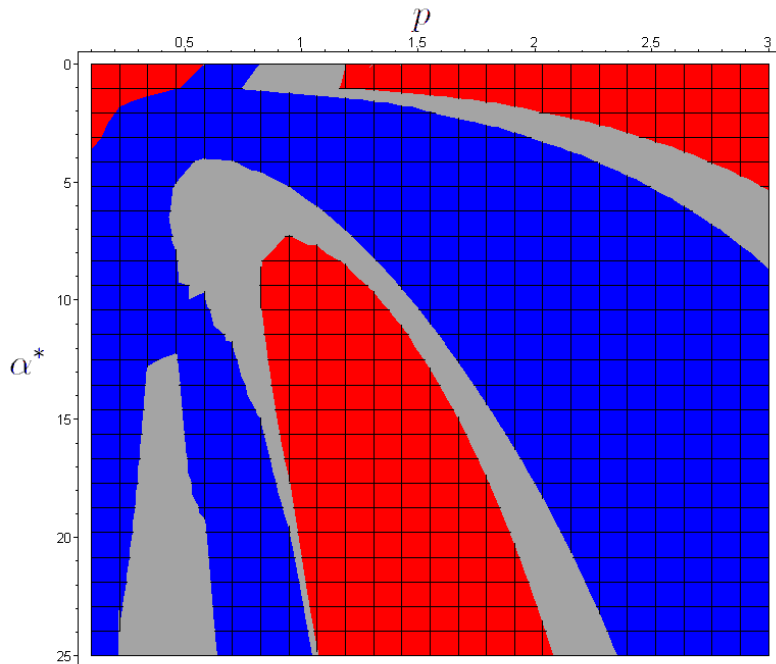


Figure 1. Regions of the cumulant values $\mathcal{M}_6 > 0$ (signed by 1) depending on the values α^* and p .

determines the reference system, and also by the value of the critical temperature $\beta_c = 1/kT_c$. So if some value of f ($f = 0,1488$) is set and T_c is determined, one can obtain only one fixed value of p (Appendix).

Summing up the calculations performed above, functional representation of the grand partition function of a fluid model can be written. Substitution of (2.25) in the expression (3.22) leads to

$$\begin{aligned} \Xi = & g_{\Psi} e^{N_B \mathcal{M}_0} \int (d\rho)^{N_B} e^{\beta[\mu' - \mu^*(1+\tau)]\rho_0 \sqrt{N_B}} \\ & \times \exp \left[\frac{\beta}{2} \sum_k V(k) \rho_{\vec{k}} \rho_{-\vec{k}} \right] \prod_l \left(e^{-\sum_{n=0}^{n_0} \frac{\alpha_n}{n!} \rho_l^n} \right). \end{aligned} \quad (3.27)$$

Since $\rho_l = \frac{1}{\sqrt{N_B}} \sum_k \rho_{\vec{k}} e^{i\vec{k}l}$ is the nodal representation of the collective

variable $\rho_{\vec{k}}$ one has

$$\begin{aligned} \Xi = & g_{\Psi} e^{(\mathcal{M}_0 - a_0)N_B} \int (d\rho)^{N_B} \exp \left[\sqrt{N_B} \beta [\mu' - \mu^*(1+\tau)] \rho_0 \right. \\ & - a_1 \sqrt{N_B} \rho_0 - \frac{1}{2} \sum_k d(k) \rho_{\vec{k}} \rho_{-\vec{k}} - \frac{1}{3!} \frac{a_3}{\sqrt{N_B}} \sum_{k_1, \dots, k_3} \rho_{k_1, \dots, k_3} \delta_{k_1 + \dots + k_3} \\ & \left. - \frac{1}{4!} \frac{a_4}{N_B} \sum_{k_1, \dots, k_4} \rho_{k_1, \dots, k_4} \delta_{k_1 + \dots + k_4} \right]. \end{aligned} \quad (3.28)$$

Here the following notation is used

$$d(k) = a_2 - \beta V(k), \quad (3.29)$$

where $V(k)$, expressed by (2.20), is the Fourier transform of some effective interaction potential.

Further calculation of (3.28) can be performed, using the method of calculation of the grand partition function of the Ising model in external field proposed in [19]. Herewith the role of external field plays the value

$$h = \beta \mu' - \beta \mu^*(1+\tau) - a_1 \quad (3.30)$$

or

$$h = \frac{\beta_c}{1+\tau} \mu' - \beta_c \mu^* - a_1. \quad (3.31)$$

4. The grand partition function and the thermodynamic characteristics

The expression (3.28) allows one to calculate the dependence of pressure P on temperature T and chemical potential μ' applying a certain 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 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 a volume of an elementary cell and a parameter of the model in use.

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

One of the methods of calculating Ξ consist in substitution of variables in (3.28)

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

As a result one obtains

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

Here such notations are introduced

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

The value of shift n_c

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

and for $E_0(\mu)$ one obtains the expression

$$E_0(\mu) = \beta\mu' n_c - \beta\mu^*(1 + \tau)n_c - a_1 n_c - \frac{1}{2} d_2(0) n_c^2 + \frac{a_4}{8} n_c^4. \quad (4.8)$$

Note that the value $\tilde{d}(0)$ is expressed in terms of $d(0)$

$$\tilde{d}(0) = d(0) - \frac{a_4}{2} n_c^2. \quad (4.9)$$

Taking this into account one can find for $E_0(\mu)$

$$E_0(\mu) = \beta[\mu' - \mu^*(1 + \tau)]n_c - a_1 n_c - \frac{1}{2} \tilde{d}(0) n_c^2 - \frac{a_4}{8} n_c^4$$

or considering that

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

one has

$$E_0(\mu) = M n_c + \frac{1}{2} \tilde{d}(0) n_c^2 + \frac{a_4}{24} n_c^4. \quad (4.10)$$

In common with the former expression

$$\tilde{a}_1 = a_1 + \tilde{d}(0) n_c + \frac{a_4}{6} n_c^3. \quad (4.11)$$

The following expression can be written for the value M

$$M = \beta\mu - \beta\mu_c,$$

where

$$\beta\mu_c = \beta\mu^*(1 + \tau) + \tilde{a}_1 = \beta_c \mu^* + \tilde{a}_1.$$

Let us consider the simplest approximation in calculation of Ξ expressed by (3.28), the so called zero mode approximation ($\rho_k = 0$ for $k \neq 0$; $\rho_0 \neq 0$):

$$\ln \Xi_0 = \ln g_{\Psi} + N_B(\mathcal{M}_0 - a_0 + E_0(\mu)) + N_B E(\bar{\rho}_0), \quad (4.12)$$

where Ξ_0 denotes the grand partition function (4.5) in the approximation mentioned above

$$E(\bar{\rho}_0) = M \bar{\rho}_0 - \frac{1}{2} \tilde{d}(0) \bar{\rho}_0^2 - \frac{a_4}{24} \bar{\rho}_0^4, \quad (4.13)$$

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

$$M - \tilde{d}(0) \bar{\rho}_0 - \frac{a_4}{6} \bar{\rho}_0^3 = 0. \quad (4.14)$$

If several solutions $\bar{\rho}_0$ exist the one leading to maximal value of $E(\bar{\rho}_0)$ in (4.13) should be chosen.

The method of steepest descent is used for calculation of (4.12), 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

$$\bar{\rho}_0 > \rho_{00}, \quad \rho_{00} = \left(-\frac{2\tilde{d}(0)}{a_4} \right)^{1/2}. \quad (4.15)$$

Such situation takes place barely if $T < T_c$, where ρ_{00} is a real value. For all $T > T_c$ the equation (4.14) has only one solution.

5. The thermodynamic potential of a simple fluid in frames of the simplest approximation

All further calculations concern a case, in which fluctuation effects are not considered, so to say the approximation of zero model is in use. Taking into account the equality (4.14), 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

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

5.1. The case $T = T_c$

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

Assigning $\tilde{d}(0) = 0$, 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 using (4.14). In 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 case of $\tau = 0$ can be found using (4.2), (4.3), where the expression (5.5) is used as Ξ_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 the 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 case of $T = T_c$ one has the expression

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

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 the expression (5.10), by means of using the equality (5.8). In this case

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

The state equation at $T = T_c$ can be found using (5.4)

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

or excluding the chemical potential M_c , one obtains

$$\frac{Pv}{kT_c} = f_c + \frac{a_4}{24} \bar{n} (\bar{n} + n_c)^3 - \frac{a_4}{24} (\bar{n} + n_c)^4. \quad (5.14)$$

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

$$d\Omega = -SdT - PdV - Nd\mu, \quad (5.15)$$

and the pressure calculated in frames of this representation has the form

$$P = - \left(\frac{\partial \Omega}{\partial V} \right)_{T, \mu}. \quad (5.16)$$

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

$$dF = -Sd\tau - PdV + \mu d\bar{N}, \quad (5.17)$$

that is why the pressure is given by the expression

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, \bar{N}}. \quad (5.18)$$

According to (4.6) one has

$$\beta\mu' = M + \beta\mu^*(1 + \tau) - \tilde{a}_1, \quad (5.19)$$

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

$$F = -kT_c (V/v) \left[f_c + f_{2c} \bar{n} - \frac{a_4}{24} (\bar{n} - n_c)^4 \right], \quad (5.20)$$

where

$$f_{2c} = \tilde{a}_1 - \beta_c \mu^*. \quad (5.21)$$

Calculation of the pressure P using (5.18) and taking into account (5.20), results in (5.14). Just as it should be expected, calculation of the state equation at $T = T_c$ is not dependent on the way it was received (the formulas (5.16) and (5.18)) and has the form (5.14).

Critical value of the pressure can be found using (5.14) and binding $\bar{n} = n_c$. So one has

$$P_c = \frac{kT_c f_c}{v}, \quad (5.22)$$

where the value f_c is expressed in (4.11).

5.2. The case $T > T_c$

According to (4.16) expression for the simplest approximation of the grand partition function at $T > T_c$ has the form

$$\ln \Xi_0 = \ln g_\Psi + N_B (\mathcal{M}_0 - a_0 + E_0(\mu) + E(\bar{\rho}_0)), \quad (5.23)$$

where

$$E(\bar{\rho}_0) = M \bar{\rho}_0 - \frac{1}{2} \tilde{d}(0) \bar{\rho}_0^2 - \frac{a_4}{24} \bar{\rho}_0^4, \quad (5.24)$$

$$E_0(\mu) = M n_c + \frac{1}{2} \tilde{d}(0) n_c^2 + \frac{a_4}{24} n_c^4, \quad (5.25)$$

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

$$M - \tilde{d}(0) \bar{\rho}_0 - \frac{a_4}{6} \bar{\rho}_0^3 = 0. \quad (5.26)$$

Solution unicity of this equation, which is written in reduced form as

$$\bar{\rho}_0^3 + p \bar{\rho}_0 + q = 0, \quad (5.27)$$

where

$$p = \frac{6\tilde{d}(0)}{a_4}, \quad q = -\frac{6M}{a_4}, \quad (5.28)$$

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

$$Q = \left(\frac{2\tilde{d}(0)}{a_4} \right)^3 + \left(\frac{3M}{a_4} \right)^2. \quad (5.29)$$

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

$$\bar{\rho}_0 = \left(\frac{3M}{a_4} + \sqrt{Q} \right)^{1/3} + \left(\frac{3M}{a_4} - \sqrt{Q} \right)^{1/3}. \quad (5.30)$$

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

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

Note that region $M > 0$ refers to positive values of $\bar{\rho}_0 = \bar{n} - n_c$ and at $\bar{n} < n_c$ one obtains $M < 0$. Conversion of the chemical potential M into zero takes place at $\bar{n} = n_c$.

Dependence of the chemical potential M on the density at $T > T_c$ can be defined directly from (5.26), taking into account that $\bar{\rho}_0 = \bar{n} - n_c$. Then

$$M = \tilde{d}(0)(\bar{n} - n_c) + \frac{a_4}{6} (\bar{n} - n_c)^3. \quad (5.31)$$

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

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

$$\Omega = -kTN_B \left[f_c + \frac{1}{2} \tilde{d}(0) n_c^2 + M \bar{n} - \frac{1}{2} \tilde{d}(0) (\bar{n} - n_c)^2 - \frac{a_4}{24} (\bar{n} - n_c)^4 \right], \quad (5.32)$$

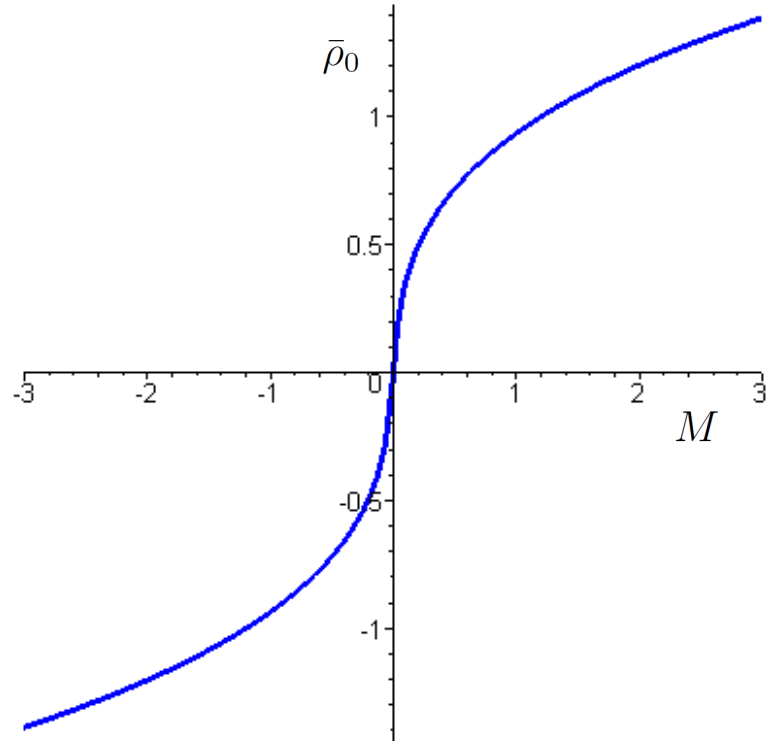


Figure 2. Dependence of the solution $\bar{\rho}_0$ on the chemical potential M at $T > T_c$ in case of $R_0/\alpha = 3, 7 \ln 2, \alpha^* = 11$ and $p = 0,11$.

where

$$f_c = \frac{1}{N_B} \ln g_\Psi + \mathcal{M}_0 - a_0 + \frac{a_4}{24} n_c^4 + \frac{1}{2} \tilde{d}(0) n_c^2. \quad (5.33)$$

Corresponding to (5.32) the free energy doesn't contain chemical potential and has the form

$$F = -kT (V/v) \left[f_c + f_2 \bar{n} - \frac{1}{2} \tilde{d}(0) n_c^2 - \frac{1}{2} \tilde{d}(0) (\bar{n} - n_c)^2 - \frac{a_4}{24} (\bar{n} - n_c)^4 \right]. \quad (5.34)$$

where

$$f_2 = \tilde{a}_1 - \beta \mu^* (1 + \tau). \quad (5.35)$$

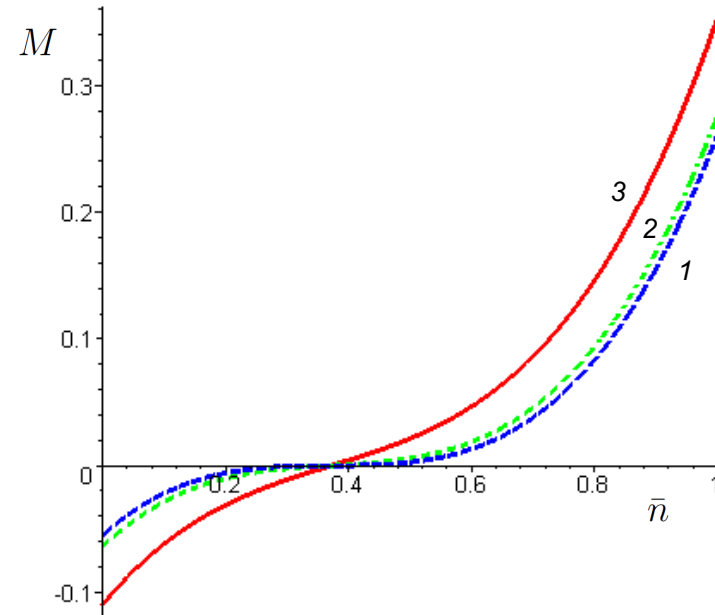


Figure 3. Dependence of the M on the density \bar{n} at $T > T_c$ for temperatures $\tau_1 = 0.01$ (curve 1), $\tau_2 = 0.1$ (curve 2), $\tau_3 = 1$ (curve 3).

The state equation at $T > T_c$ has the form

$$\frac{Pv}{kT} = f_c + \frac{\tilde{a}_2}{2} \frac{\tau}{1 + \tau} n_c^2 + \bar{n} M - \frac{\tilde{a}_2}{2} \frac{\tau}{1 + \tau} (\bar{n} - n_c)^2 - \frac{a_4}{24} (\bar{n} - n_c)^4. \quad (5.36)$$

Substitution of the value M expressed by (5.31), leads to

$$\frac{Pv}{kT} = f_c + \frac{\tilde{a}_2}{2} \frac{\tau}{1 + \tau} \bar{n}^2 + \frac{a_4}{6} (\bar{n} - n_c)^3 - \frac{a_4}{24} (\bar{n} - n_c)^4. \quad (5.37)$$

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

The expression (5.37) allows one to depict 3-dimensional diagram of pressure dependence on the average density and reduced temperature τ in the region $T \geq T_c$ (Figure 5).

The state equation expressed by (5.37) can be represented in reduced

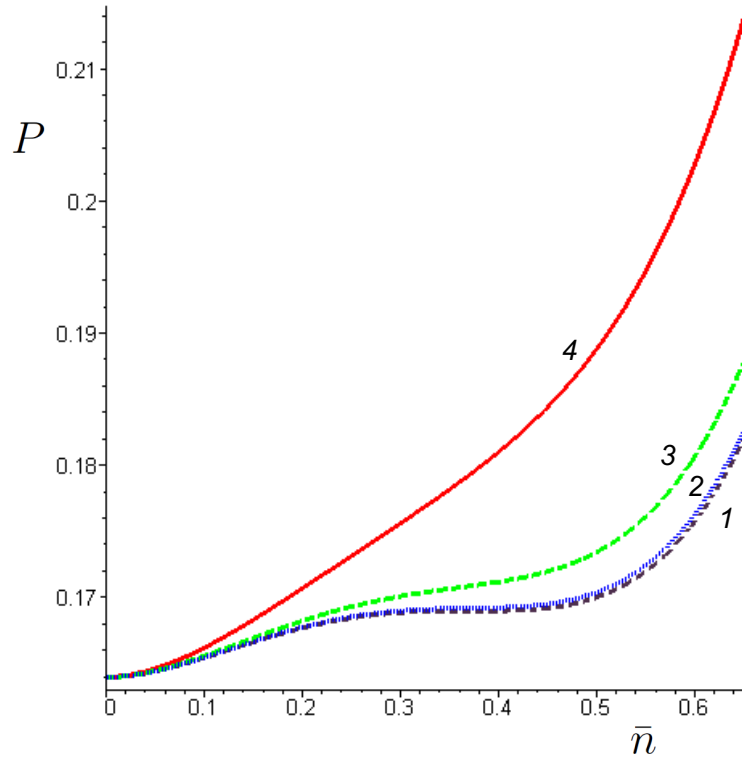


Figure 4. Dependence of the pressure P on the density \bar{n} at $\tau = 0$ (curve 1), $\tau = 0.01$ (curve 2), $\tau = 0.1$ (curve 3) and $\tau = 1.5$ (curve 4).

form. For this purpose the following values are introduced

$$\tilde{P} = \frac{P}{P_c}, \quad t = \frac{T}{T_c}, \quad \eta = \frac{\bar{n}}{n_c}. \quad (5.38)$$

Then (5.37) takes on the form

$$\tilde{P} = 1 + P_1(t-1)\eta^2 + P_2(1+3\eta)(\eta-1)^3, \quad (5.39)$$

where such notations are used

$$P_1 = \frac{\tilde{a}_2 n_c^2}{2f_c}, \quad P_2 = \frac{\tilde{a}_2 n_c^4}{24f_c}. \quad (5.40)$$

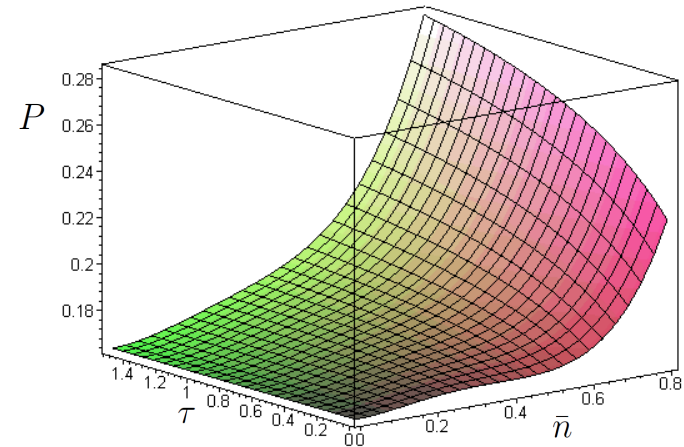


Figure 5. Dependence of the pressure P on the average density \bar{n} and the reduced temperature τ in the region $T > T_c$.

The curve of pressure dependence (5.39) on the density η has an inflexion point at $\eta = 1$ and $T = T_c$ and reaches minimum at $\eta = 0$, that follows from the relations

$$\frac{\partial \tilde{P}}{\partial \eta} = 2\eta \left(P_1(t-1) + 6P_2(\eta-1)^2 \right) \quad (5.41)$$

$$\frac{\partial^2 \tilde{P}}{\partial \eta^2} = 2P_1(t-1) + 12P_2(1-4\eta+3\eta^2). \quad (5.42)$$

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

6. The state equation at $T < T_c$

As it was shown above, at temperature region $T > T_c$, where T_c is defined by (5.2), in a system consisting of N non-interactive particles the phase transition is absent. The pressure \tilde{P} expressed in (5.39) is

gradually increasing function of density η . It is expected to observe the first order phase transition at temperatures $T < T_c$, that must show to turn susceptibility into infinity for 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 just here

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

where

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

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 case of $T > T_c$ the equation (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 calculation of (6.1) is performed using the method of steepest descent, which foresees such a condition.

The equation (6.3) can be written in reduced form

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

where the coefficients p and q are defined in (4.28).

Let us find the marginal value of the chemical potential $|M_q|$, at which the equality $Q = 0$ is fulfilled. According to (5.29) one has

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

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

Let us consider in detail case of $Q \geq 0$ at $T < T_c$, where single root exists. Using (5.30) at $|M| = M_q$ one can find

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

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

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

where

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

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

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

The state equation of a fluid at $T < T_c$ for all $M > M_q$ has the form (5.37), where the value $\tau < 0$. Under such conditions 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 Figure 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 case of large negative values of the 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 $\bar{n} < n_1$ gaseous phase of a fluid occurs and realizes for all $M < -M_q$ (Figure 6, solid line 1).

Density region $n_1 < \bar{n} < n_2$ corresponds to the chemical potential $|M| < M_q$, where $Q < 0$. The equation (5.27) has three real roots in this case

$$\bar{\rho}_{01} = 2\rho_{0r} \cos \frac{\alpha}{3}, \quad (6.12)$$

$$\bar{\rho}_{02} = -2\rho_{0r} \cos \left(\frac{\alpha}{3} + \frac{\pi}{3} \right),$$

$$\bar{\rho}_{03} = -2\rho_{0r} \cos \left(\frac{\alpha}{3} - \frac{\pi}{3} \right),$$

where

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

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

$$\alpha = \arccos \frac{M}{M_q} \equiv \frac{\pi}{2} - \arcsin \frac{M}{M_q}. \quad (6.14)$$

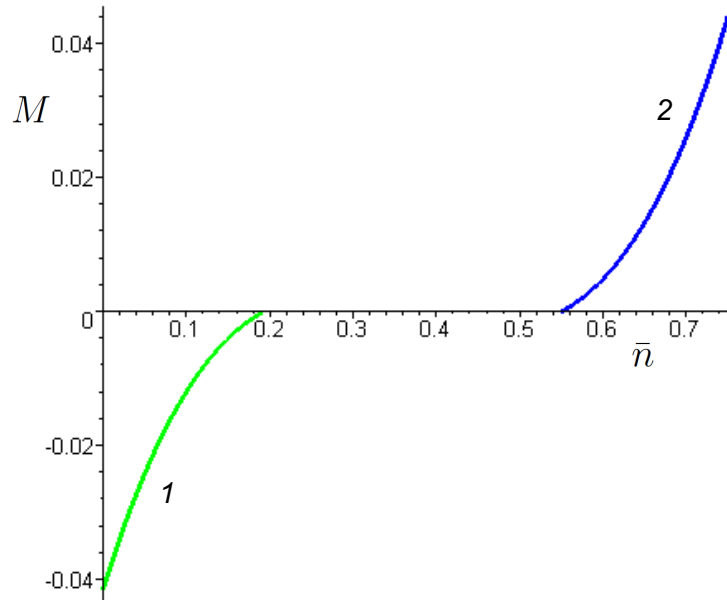


Figure 6. Accordance between the density of a fluid and values of the chemical potential M ; solid line 1 – gaseous phase; 2 – liquid phase.

In case of $M = M_q$ one has $\alpha = 0$, so,

$$\lim_{M \rightarrow -M_q} \bar{\rho}_{01} = \rho_1^{(+)} = \left(-\frac{8\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{\frac{1}{2}} \equiv n_g, \quad (6.15)$$

$$\lim_{M \rightarrow -M_q} \bar{\rho}_{02} = \lim_{M \rightarrow -M_q} \bar{\rho}_{03} = \rho_2^{(+)} = - \left(-\frac{6\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{\frac{1}{2}}.$$

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

Case $M = -M_q$ gives $\alpha = \pi$. Herewith

$$\rho_1^{(-)} = \rho_2^{(-)} = \bar{\rho}_s = \left(-\frac{2\tilde{a}_2\tau}{a_4(1+\tau)} \right)^{\frac{1}{2}}, \quad (6.16)$$

$$\rho_3^{(-)} = \lim_{M \rightarrow -M_q} \bar{\rho}_{03} = -\rho_1^{(+)} = -n_g.$$

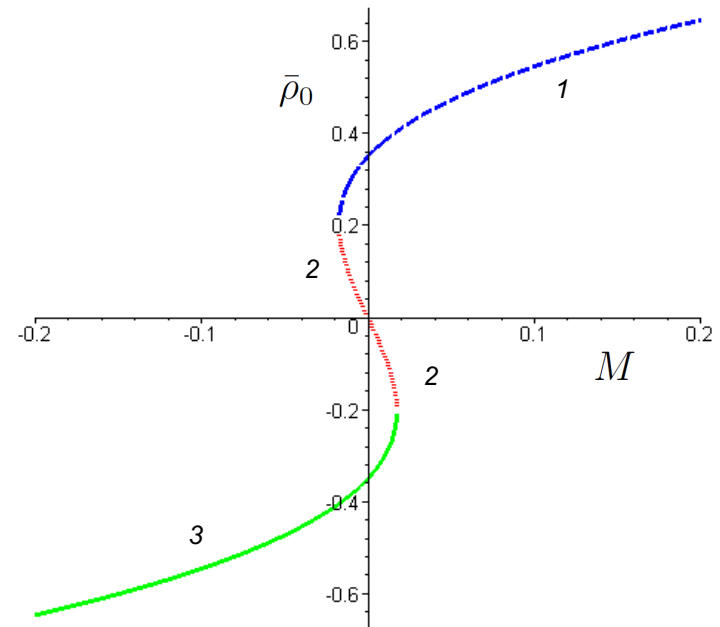


Figure 7. Dependence of the roots (5.12) on the chemical potential values $|M| < M_q$, curve 1 corresponds to the solution $\bar{\rho}_{01}$, curve 2 – $\bar{\rho}_{02}$, curve 3 – $\bar{\rho}_{03}$

The solution $\bar{\rho}_{03}$ results at $M = -M_q$ to the density

$$n_1 = n_c - n_g. \quad (6.17)$$

In general case the dependence of roots $\bar{\rho}_{0i}$ from (6.12) on the values of the chemical potential in the region $|M| < M_q$ is depicted on Figure 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.

These dependencies $\bar{\rho}_{0i} = \bar{\rho}_{0i}(M)$ can be used to presented in Figure 8. It is easy to see, that root $\bar{\rho}_{01}$ correspond to the maximum of $E(\bar{\rho}_{0i})$ as far as the chemical potential decreases from M_q to zero and, when M changes from zero to $-M_q$, maximal value of $E(\bar{\rho}_{0i})$ occurs at $\bar{\rho}_{03}$.

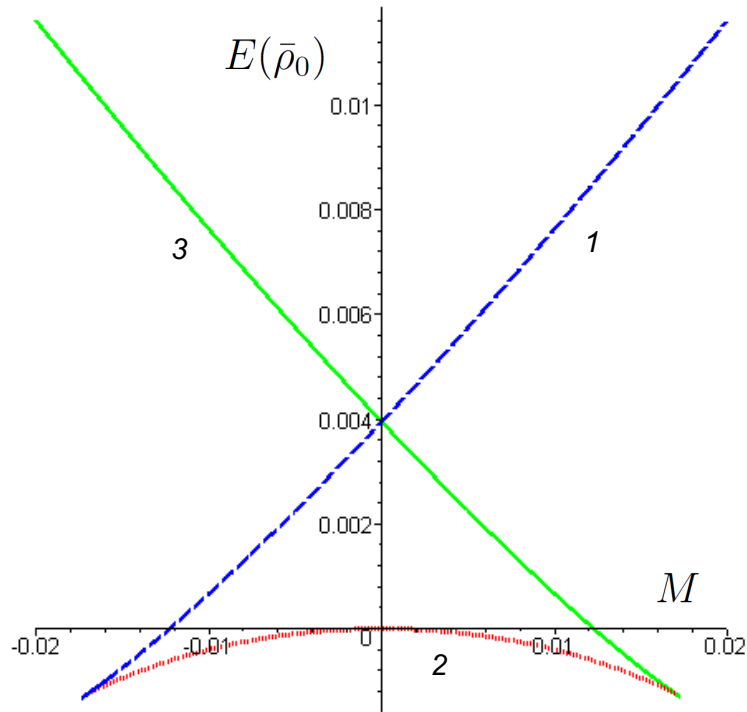


Figure 8. Dependence of the function $E(\bar{\rho}_0)$ exponent on the chemical potential M .

So the state equation at temperature ranges $T < T_c$ has to be written in the form

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

where $\Theta(M)$ is the Heaviside function, which is equal to one at $M > 0$, turns into zero at $M < 0$ and equal to 1/2 at $M = 0$. It should be noted that the equality (6.12) foresees existence of two marginal values of the roots $\bar{\rho}_{0i}$ when the chemical potential M approaches to zero.

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

where

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

When the chemical potential approaches to zero from below one has

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

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

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

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

The expression for the grand thermodynamic potential at temperature ranges $T < T_c$, 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 corresponds to the value $D_{13}(M)$

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

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, that corresponds to (6.8).

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

where

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

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

$$D_{13}(\bar{n}) = - \left(\frac{\tilde{a}_2}{2} \frac{\tau}{1+\tau} (\bar{n} - n_c)^2 + \frac{a_4}{24} (\bar{n} - n_c)^4 \right) \Theta(n^{(-)} - \bar{n}) - \left(\frac{\tilde{a}_2}{2} \frac{\tau}{1+\tau} (\bar{n} - n_c)^2 + \frac{a_4}{24} (\bar{n} - n_c)^4 \right) \Theta(\bar{n} - n^{(+)}). \quad (6.27)$$

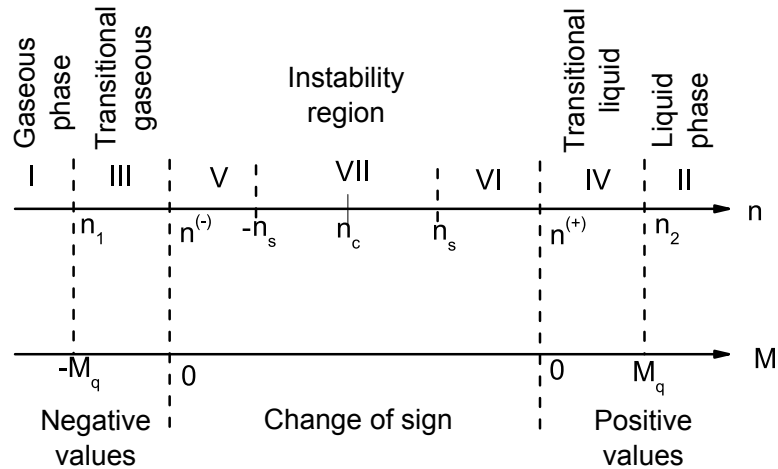


Figure 9. Relation between density ranges of a simple fluid at $T < T_c$ and the chemical potential values $M = \beta\mu - \beta\mu_c$.

In such a way, a simple fluid system stays in gaseous or liquid state, as far as the chemical potential increases. It depends on the value of the latter. As it was shown above, at $T < T_c$ and negative values of $M < -M_q$ only a single root of the equation (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 meets the pure gaseous phase (Figure 9). As far as the chemical potential increases $-M_q < M \leq 0$ the equation (6.4) has three real solutions, however only one of them $\bar{\rho}_{03}$ realizes. It can be seen from the following non-equalities

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

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

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

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 state equation of a fluid has the form

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

where

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

the value $n_t = 0$ at $T > T_c$, and 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 case of $n_t = 0$ the sum of theta-functions in (6.15) turns into unity

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

The transition occurs between gaseous and liquid phases characterized by densities that maximize the expression (6.30). Their values can be found from the following 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 the expression (6.30). Solving the equation (6.36) with respect to temperature, allows one to obtain the expression

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

which can serve as the base for the binodal construction (the coexistence curve) in temperature-density coordinates which is presented in

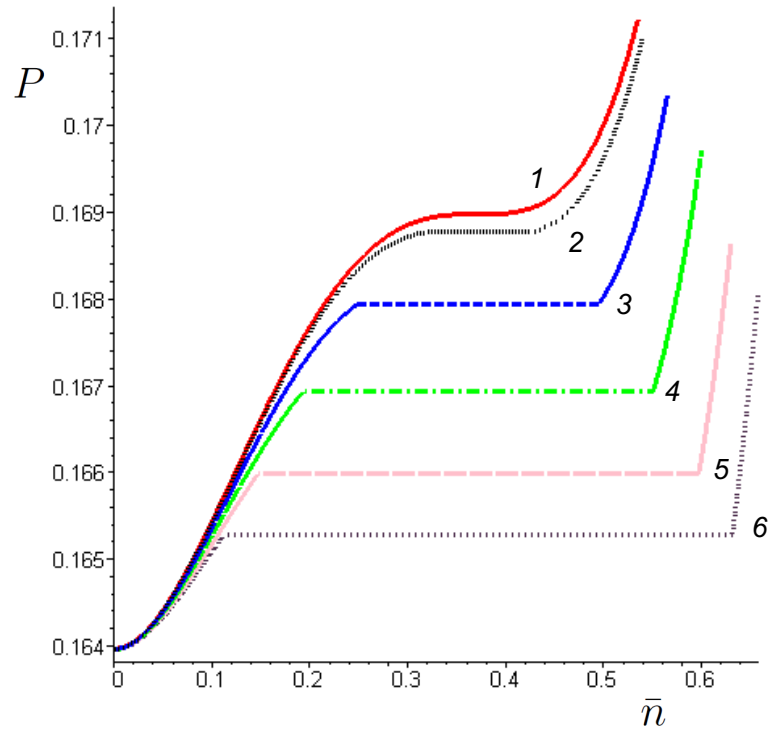


Figure 10. Dependence of the pressure P on the density \bar{n} at $\tau = 0$ (curve 1), $\tau = -0.01$ (curve 2), $\tau = -0.05$ (curve 3), $\tau = -0.1$ (curve 4), $\tau = -0.15$ (curve 5), $\tau = -0.2$ (curve 6).

Figure 11. The equation for the spinodal, so as to say the curve of marginal states of a system, defining the boundaries of instability region, can be found from extremum condition for the state equation (6.30):

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

which leads to the following equation

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

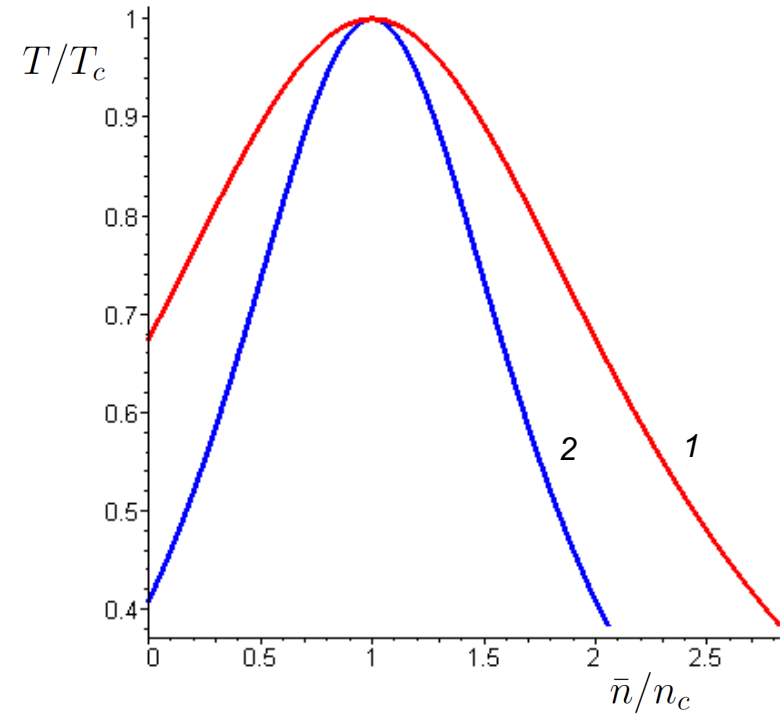


Figure 11. Binodal (1) and spinodal (2) in reduced temperature-density coordinates.

or

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

whence the spinodal curve can be obtained. It is also presented in Figure 11.

7. Appendix

Determination of the value B , that characterize the model potential

$$U(k) = \begin{cases} U_B(k) = \Psi(k) - U_1(k) & \text{at } |k| \leq B \\ 0 & \text{at } |k| > B \end{cases} \quad (7.1)$$

Here

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

Let us perform transition to reduced form. Let it be $r' = r/R_0$, then

$$\Psi(r') = \epsilon e^{-2(r'-1)/\alpha_R}, \quad U_1(r') = 2\epsilon e^{-(r'-1)/\alpha_R}, \quad (7.2)$$

where

$$\alpha_R = \alpha/R_0. \quad (7.3)$$

So, there are two parameters of the interaction potential ϵ (as a dimension unit) and α_R . The Fourier transforms

$$\begin{aligned} \Psi(k) &= \Psi(0) (1 + \alpha_R^2 k^2/4)^{-2}, & \Psi(0) &= \epsilon \pi \alpha_R^3 e^{2/\alpha_R}, \\ U_1(k) &= U_1(0) (1 + \alpha_R^2 k^2)^{-2}, & U_1(0) &= 16\epsilon \pi \alpha_R^3 e^{1/\alpha_R}. \end{aligned} \quad (7.4)$$

Herewith the following condition is satisfied

$$U_1(0) = \Psi(0) 16e^{-1/\alpha_R}. \quad (7.5)$$

The condition to determine the value B has the form

$$\int_B^\infty V(k) k^2 dk = 0, \quad (7.6)$$

where

$$V(k) = U_1(k) - f\Psi(k) + \tau(1-f)\Psi(0) \left(1 + \frac{\alpha_R^2 k^2}{4}\right)^{-2}. \quad (7.7)$$

Let us assign $\tau = 0$.

The evident form of the integral (7.5) can be calculated. So the following expression is obtained

$$f = 16e^{-1/\alpha_R} \int_B^\infty \frac{k^2 dk}{(1 + \alpha_R^2 k^2)^2} / \int_B^\infty \frac{k^2 dk}{\left(1 + \frac{\alpha_R^2 k^2}{4}\right)^2}. \quad (7.8)$$

That is why

$$\begin{aligned} f &= \frac{16}{8} e^{-1/\alpha_R} \left[\frac{\pi}{2} + \frac{B\alpha_R}{1 + B^2\alpha_R^2} - \operatorname{arctg}(B\alpha_R) \right] \\ &\times \left[\frac{\pi}{2} + \frac{B\alpha_R/2}{1 + B^2\alpha_R^2/4} - \operatorname{arctg}(B\alpha_R/2) \right]^{-1}. \end{aligned} \quad (7.9)$$

The parameter p expressed by (3.10) has the form

$$p = \beta_c \bar{\Psi}(1-f)/2 \quad (7.10)$$

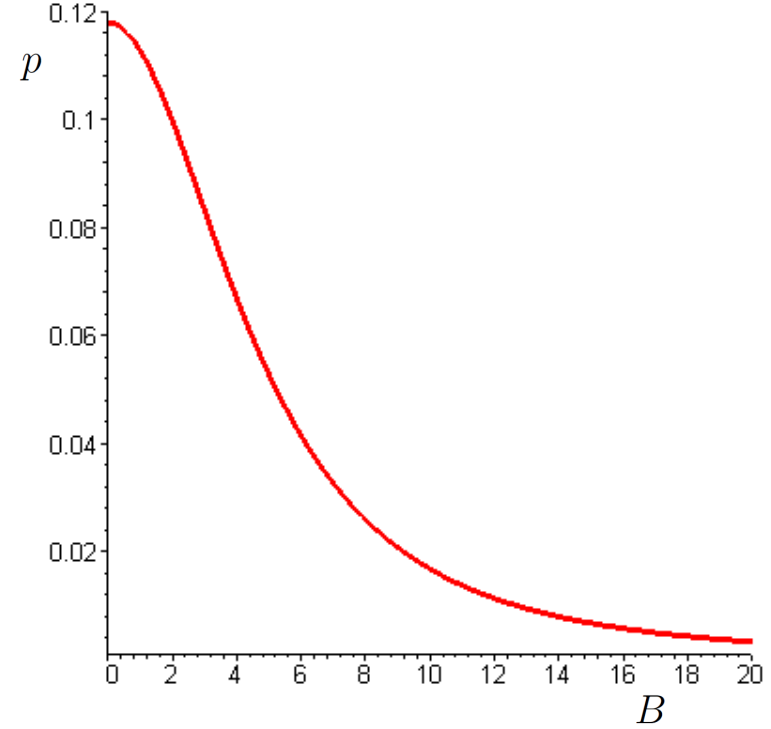


Figure 12. Change of the parameter p depending on the value B at $R_0/\alpha = 3, 7 \ln 2$.

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 fixed value of α_R (the characteristic of a substance) the latter is determined only by the parameter f (see Figure 12).

$\bar{\Psi}$ can be found as an average value of $\Psi(k)$ at $k \in [0, B]$

$$\bar{\Psi} = \frac{3}{2} \Psi(0) \left(\frac{2}{\alpha_R B} \right)^3 \left(\operatorname{arctg} \frac{\alpha_R B}{2} - \frac{1}{2} \frac{B\alpha_R}{1 + \alpha_R^2 B^2/4} \right) = \Psi(0) \chi_R, \quad (7.11)$$

where

$$\chi_R = \frac{3}{2} \left(\frac{2}{\alpha_R B} \right)^3 \left(\operatorname{arctg} \frac{\alpha_R B}{2} - \frac{1}{2} \frac{B\alpha_R}{1 + \alpha_R^2 B^2/4} \right). \quad (7.12)$$

It is easy to see, that the value χ_R is a function of B (or f) at fixed α_R .

In case of fixed $f = 0.1488$, at which $B = 1,258$ one has $\chi_R = 0,932$, that correspond to the value P_R

$$P_R = 0.11, \quad (7.13)$$

which is calculated using (6.9) in the simplest approximation, where β_c is expressed by (5.2)

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

So

$$P_R = \frac{a_2\Psi(0)\chi_R}{2V(0, T_c)}(1 - f) \quad (7.14)$$

since

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

that is why

$$P_R = \frac{\tilde{a}_2}{2} \frac{1 - f}{16e^{1/\alpha_R} - f} \chi_R. \quad (7.15)$$

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

Conclusion. One should chose a substance to be observed, that means to fix the parameter α_R (for example $\alpha_R = 0,3899$ referring to $R_0/\alpha = 3,7 \ln 2$). The range of possible values of parameter f defining the reference system changes within the limits $0 < f < 0.154$ (see. Figure 13). In this range $V(0) > 0$, that is necessary condition for appliance of analytical calculation methods, specifically the method of CV. In this case reference system includes main part of repulsive potential.

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

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

To co-ordinate the “primeval” parameter p which has the value (7.9), one has to chose the value

$$f = 0,1488, \quad (7.16)$$

corresponding to $p = 0,11$. The latter has to coincide with the value of p expressed by (7.10) at $\alpha^* = 11$. If the initial value $p \neq 0,11$, any α^* exist for (7.15) to coincide with the result of calculating p using the formula (7.10).

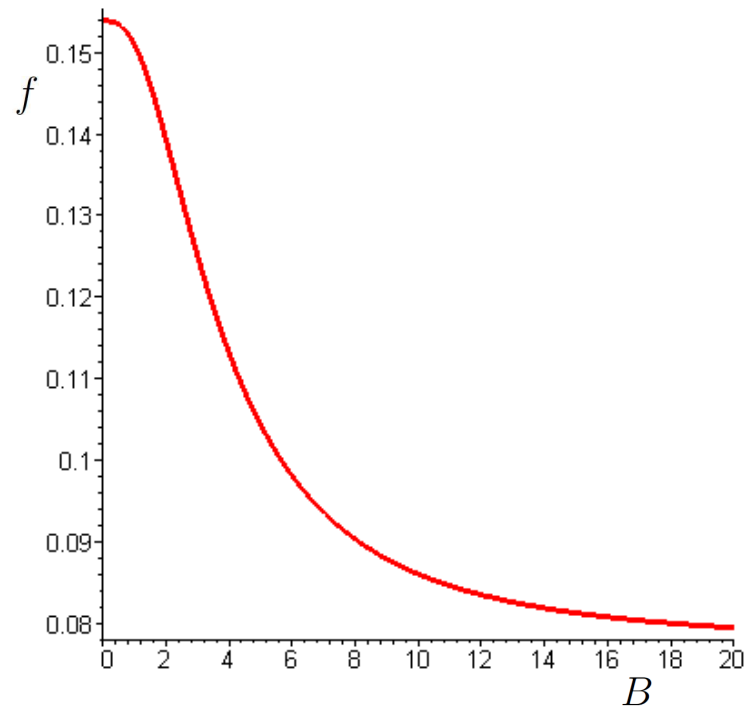


Figure 13. Change of the parameter f depending on the value B at $R_0/\alpha = 3,7 \ln 2$.

8. 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 model was proposed. A system of N – particles in volume V with periodic boundary conditions was concerned. As an interaction potential between particles the Morse potential was chosen.

In course of calculating the grand partition function the reference system, formed from a part of repulsive component of interaction potential, was used. It was established that due to selection of the reference system one can perform summation over number of particles N and integration over their coordinates. As a result the evident form of the Jacobian of transition from a set of variables, characterizing individual particles, to collective variables, which average values are connected with the order

parameter of the first order phase transition, was obtained. Coefficients of the Jacobian of transition, that is a polynomial over a series of collective variables in the exponent argument, expressed via the special functions $T_n(\alpha^*, p)$ were introduced. The latter are represented in the form of rapidly convergent series. The special functions arguments α^* and p are real positive values. The former α^* is related to some fixed value of the chemical potential μ^* , the latter argument p is proportional to the reference system potential.

We received 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 random number of particles. It is general and valid both far from the critical point and directly in its vicinity.

We considered simplest approximation which is valid out of a vicinity of the critical point. The equation of state received in this work describes a behavior of a simple fluid system in wide temperature ranges below and above the critical one T_c . In temperature ranges $T < T_c$ the presence of rectilinear plots at the curve of pressure dependence on density is established. It describes a density loop at the first order phase transition. A curve that circumflex these rectilinear plots allowed us to obtain the binodal line. Also the spinodal curve as the instability region of a system at temperatures lower than the critical one was found.

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

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CONTACT INFORMATION:

Institute for Condensed Matter Physics
of the National Academy of Sciences of Ukraine
1 Svientsitskii Str., 79011 Lviv, Ukraine
Tel: +38(032)2761978; Fax: +38(032)2761158
E-mail: cmp@icmp.lviv.ua <http://www.icmp.lviv.ua>