I.V. PYLYUK, O.A. DOBUSH

Institute for Condensed Matter Physics, Nat. Acad. of Sci. of Ukraine
(1, Svientsitskii Str., Lviv 79011, Ukraine)

EQUATION OF STATE OF A CELL FLUID MODEL WITH ALLOWANCE FOR GAUSSIAN FLUCTUATIONS OF THE ORDER PARAMETER [1]

The paper is devoted to the development of a microscopic description of the critical behavior of a cell fluid model with allowance for the contributions from collective variables with nonzero values of the wave vector. The mathematical description is performed in the supercritical temperature range $(T > T_c)$ in the case of a modified Morse potential with additional repulsive interaction. The method, developed here for constructing the equation of state of the system by using the Gaussian distribution of the order parameter fluctuations, is valid beyond an immediate vicinity of the critical point for wide ranges of the density and temperature. The pressure of the system as a function of the chemical potential and density is plotted for various fixed values of the relative temperature, both with and without considering the above-mentioned contributions. Compared with the results of the zero-mode approximation, the insignificant role of these contributions is indicated for temperatures $T > T_c$. At $T < T_c$, they are more significant.

K e y w o r d s: cell fluid model, equation of state, grand partition function, Morse potential, zero-mode approximation.

1. Introduction

We dedicate this paper to the 75th anniversary of Academician L.A. Bulavin, the outstanding Ukrainian physicist, who made a remarkable contribution to the development of the experimental base in the field of phase transitions and critical phenomena in simple and multicomponent liquid systems [1–4].

A large number of works are devoted to the description of the critical properties of liquid systems. The detailed bibliography can be found, for example, in books [5–8] and review papers [9, 10]. For decades, the interest in this problem persists, because the liquid near its critical points is the most convenient object, which simulates a class of systems with a large number of strongly interacting degrees of freedom [6, 7]. On the other hand, due to their specific properties, the critical fluids are frequently used in various technological processes [11]. In this regard, constructing the equation of state of critical fluids becomes an important applied task.

The main difficulty of a successive theoretical calculation of the equation of state by methods of statistical physics is the need for correctly accounting for the complex structure of the interparticle interaction. Therefore, when calculating, it is necessary to use simplified models, the scope of which is limited and is either established in each case, or based on internal characteristics of the model, or is determined

---

[1] This article is dedicated to the 75th anniversary of Academician L.A. Bulavin.

by comparison with the more accurate solutions and experimental results.

In our previous studies [12–14], we proposed a cell fluid model, which was used to describe a first-order phase transition applying different types of interaction potentials. In this work, a modified Morse potential with a term describing a soft wall repulsion is used to calculate the equation of state of the cell fluid model.

We consider a system of N interacting particles in the volume V conditionally divided into N_v cells ($V = vN_v$, $v = c^3$ is the cell volume, and c is the linear size of a cell) [14, 15]. Note that, in contrast to the lattice gas model (where it is assumed that the cell may or may not contain only one particle), in this approach, the cell may contain more than one particle. The interaction potential

$$U(r) = C_H \left\{ A e^{-n_0(r-R_0)/\alpha} + e^{-\gamma(r-R_0)/\alpha} - \right.$$

$$\left. -2e^{-(r-R_0)/\alpha} \right\} \tag{1}$$

of such cell fluid model involving the repulsive and attractive interactions (the second and third terms that form a Morse-type potential) includes an additional repulsive interaction (the first term) [16]. Here, R_0 corresponds to the minimum of the function $U(r)$, r is the distance between particles, α is the effective interaction radius, γ and n_0 are the parameters of the model, $A = (2 - \gamma)/n_0$, $C_H = Dn_0/(n_0 + \gamma - 2)$, and D determines the dissociation energy. The quantities R_0, α, and D are specific to a particular physical system. In the case of sodium (Na), we have [17, 18]

$$R_0 = 5.3678 \text{ Å}, \quad 1/\alpha = 0.5504 \text{ Å}^{-1},$$

$$R_0/\alpha = 2.9544, \quad D = 0.9241 \times 10^{-13} \text{ ergs.} \tag{2}$$

The following expressions form a lattice analog of potential (1):

$$\tilde{\Phi}_{l_{12}}^{(r)} = C_H e^{-\gamma(l_{12}-c)/(\alpha_R c)},$$

$$\tilde{\Phi}_{l_{12}}^{(a)} = 2C_H e^{-(l_{12}-c)/(\alpha_R c)}, \tag{3}$$

$$\tilde{\Psi}_{l_{12}} = C_H A e^{-n_0(l_{12}-c)/(\alpha_R c)},$$

where $l_{12} = |\mathbf{l}_1 - \mathbf{l}_2|$ is the distance between cells $\mathbf{l}_1$ and $\mathbf{l}_2$, $\alpha_R = \alpha/R_0$ is the dimensionless quantity. In what follows, we will use the Fourier transforms of

interaction potentials (3), which read

$$\Phi^{(r)}(k) = C_H 8\pi e^{\gamma/\alpha} \left(\frac{\alpha}{\gamma}\right)^3 \left[1 + \left(\frac{\alpha}{\gamma}\right)^2 c^2 k^2\right]^{-2},$$

$$\Phi^{(a)}(k) = C_H 16\pi e^{1/\alpha} \alpha^3 \left[1 + \alpha^2 c^2 k^2\right]^{-2}, \tag{4}$$

$$\Psi(k) = C_H A 8\pi e^{n_0/\alpha} \left(\frac{\alpha}{n_0}\right)^3 \left[1 + \left(\frac{\alpha}{n_0}\right)^2 c^2 k^2\right]^{-2}.$$

Hereinafter, to simplify the notation, α should be understood as the quantity α_R, and c is $c_R = c/R_0$. It is easy to see that

$$\Phi^{(a)}(0) = B\Phi^{(r)}(0), \quad B = 2\gamma^3 e^{(1-\gamma)/\alpha},$$

$$\Psi(0) = A_\gamma \Phi^{(r)}(0), \quad A_\gamma = A e^{(n_0-\gamma)/\alpha} (\gamma/n_0)^3. \tag{5}$$

This work logically complements the previous studies [16] devoted to the theoretical description of the first-order phase transition in the cell fluid model with potential (1). We use the phase space of collective variables. The term "collective variables" is a general name for a special class of variables specific of every individual physical system. For magnetic systems, the collective variables are the variables associated with the modes of spin moment density oscillations; for the ferroelectrics, with the cluster state oscillation modes; for the liquid-vapour system, with modes of the density deviation from the critical density, *etc.* The set of collective variables contains the variables whose average values are associated with order parameters. For this reason, the phase space of collective variables is most natural for describing a phase transition. The replacement of the original set of independent variables by the set of collective variables is accompanied by the introduction of a transition Jacobian. In [16], the equation of state of the system in terms of the chemical potential-temperature and density-temperature is calculated in the zero-mode approximation. The contributions from the collective variables $\rho_{\mathbf{k}}$ with nonzero values of the wave vector were not taken into account, when obtaining the equation of state of the cell fluid model. The purpose of this work is to develop a technique for constructing the equation of state of the model taking these contributions into account and to compare the results obtained with the account for a pressure and leaving out these contributions, as well as to assess the influence of the above-mentioned contributions on calculations. The equation of state obtained in

this paper is not applicable in an immediate vicinity of the critical point ($|\tau| < \tau^* \sim 10^{-2}$). Works [15, 19] are devoted to the construction of the equation of state in this narrow neighborhood of T_c with regard for the non-Gaussian fluctuations. A significant role in the development of this technique was played by works [20–24] devoted to describing the behavior of a three-dimensional Ising-like system near T_c with the use of the quartic measure density (the ρ^4 model).

2. Grand Partition Function of the System

The grand partition function of the cell fluid model in the approximation of the ρ^4 model is given by the formula [15]

$$\Xi = 2^{(N_v-1)/2} g_v e^{N_v E_\mu} \int (d\rho)^{N_v} \exp\left[M N_v^{1/2} \rho_0 + \right.$$

$$+ \frac{1}{2} \sum_{\mathbf{k} \in \mathcal{B}_c} \tilde{D}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} +$$

$$\left. + \frac{g_4}{24} \frac{1}{N_v} \sum_{\substack{\mathbf{k}_1,...,\mathbf{k}_4 \\ \mathbf{k}_i \in \mathcal{B}_c}} \rho_{\mathbf{k}_1}...\rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1+...+\mathbf{k}_4} \right] \quad (6)$$

with the following notations:

$$E_\mu = g_0 - \frac{\beta\tilde{\mu}^2}{2W(0)} + n_c\left(g_1 + \frac{\tilde{\mu}}{W(0)}\right) + \frac{n_c^2}{2}\tilde{D}(0) + \frac{g_3^4}{8g_4^3},$$

$$M = \tilde{\mu}/W(0) + g_1 + n_c\tilde{D}(0) - \frac{1}{6}\frac{g_3^3}{g_4^2},$$

$$\tilde{D}(k) = \tilde{g}_2 - 1/(\beta W(k)), \quad (7)$$

$$\tilde{g}_2 = g_2 - \frac{1}{2}\frac{g_3^2}{g_4}, \quad n_c = -g_3/g_4.$$

The quantity $\tilde{\mu}$ characterizes the chemical potential, and $\beta = 1/(kT)$ is the inverse temperature. Using expressions (4) and (5), we can write the total Fourier transform of the effective potential $W(k) = = \Phi^{(a)}(k) - \Phi^{(r)}(k) - \Psi(k) + \frac{\beta_c}{\beta}\chi_0\Phi^{(r)}(0) + \frac{\beta_c}{\beta}\Psi(0)$ in the form

$$W(k) = \Phi^{(r)}(0)\left\{ \frac{B}{\left[1 + \alpha^2 c^2 k^2\right]^2} - \frac{1}{\left[1 + \left(\frac{\alpha}{\gamma}\right)^2 c^2 k^2\right]^2} - \right.$$

$$\left. - \frac{A_\gamma}{\left[1 + \left(\frac{\alpha}{n_0}\right)^2 c^2 k^2\right]^2} + (1+\tau)(\chi_0 + A_\gamma) \right\}, \quad (8)$$

where χ_0 is some constant quantity, $\tau = (T - T_c)/T_c$ is the relative temperature, and T_c is the critical temperature. At $k = 0$, we obtain

$$W(0) = \Phi^{(r)}(0)\left[B - 1 + \chi_0 + \tau(\chi_0 + A_\gamma)\right]. \quad (9)$$

The coefficients g_n, which appear in (7), are given by the formulas [14, 25]

$$g_0 = \ln T_0, \quad g_1 = T_1/T_0, \quad g_2 = T_2/T_0 - g_1^2,$$

$$g_3 = T_3/T_0 - g_1^3 - 3g_1 g_2, \quad (10)$$

$$g_4 = T_4/T_0 - g_1^4 - 6g_1^2 g_2 - 4g_1 g_3 - 3g_2^2.$$

The special functions $T_n(p, \alpha^*)$ are as follows:

$$T_n(p, \alpha^*) = \sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} m^n e^{-pm^2}. \quad (11)$$

Here, $p = \beta_c \Phi^{(r)}(0)[\chi_0 + A_\gamma]/2$, and $\alpha^* \sim v$ (see [16]). The expression of the grand partition function (6) also includes the quantity

$$g_v = \prod_{\mathbf{k} \in \mathcal{B}_c} (2\pi\beta W(k))^{-1/2}, \quad (12)$$

which is a function of the inverse temperature β and the Fourier transform of the effective potential $W(k)$. The wave vector $\mathbf{k}$ runs all the values inside the Brillouin zone

$$\mathcal{B}_c = \left\{ \mathbf{k}=(k_1, k_2, k_3) \middle| k_i = -\frac{\pi}{c} + \frac{2\pi}{c}\frac{n_i}{N_a}; \right.$$

$$\left. n_i = 1, 2, ..., N_a; i = 1, 2, 3; N_v = N_a^3 \right\}.$$

Singling out terms with $k = 0$ from the sums over $\mathbf{k}$ in (6), we obtain

$$\Xi = 2^{(N_v-1)/2} \Xi' g_v \exp[N_v(E_\mu + E(\bar{\rho}_0))], \quad (13)$$

where

$$E(\bar{\rho}_0) = \bar{M}\bar{\rho}_0 + \frac{1}{2}\tilde{D}(0)\bar{\rho}_0^2 - \frac{a_4}{24}\bar{\rho}_0^4, \quad (14)$$

moreover, the coefficient $a_4 = -g_4 > 0$. The quantity $\bar{\rho}_0$ can be determined from the condition $\partial E(\rho_0)/\partial\rho_0 = 0\big|_{\rho_0=\bar{\rho}_0}$, which leads to the equation

$$\bar{M} + \tilde{D}(0)\bar{\rho}_0 - \frac{a_4}{6}\bar{\rho}_0^3 = 0. \quad (15)$$

Here, $\bar{M}$ is the chemical potential, which corresponds to an extremum of the function $E(\bar{\rho}_0)$. At $T > T_c$, the real solution of (15) takes the form

$$\bar{\rho}_0 = \left(\frac{3\bar{M}}{a_4} + \sqrt{Q_t}\right)^{1/3} - \left(-\frac{3\bar{M}}{a_4} + \sqrt{Q_t}\right)^{1/3},$$

$$Q_t = \left(-\frac{2\tilde{D}(0)}{a_4}\right)^3 + \left(\frac{3\bar{M}}{a_4}\right)^2.$$

For the component Ξ' of the grand partition function, we have

$$\Xi' = \int (d\rho)^{N_v-1} \exp\left[-\frac{1}{2}\sideset{}{'}\sum_{\mathbf{k}\in\mathcal{B}_c} \tilde{d}(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - \right.$$
$$-\frac{a_4}{4}\frac{1}{N_v}\rho_0^2 \sideset{}{'}\sum_{\mathbf{k}\in\mathcal{B}_c} \rho_{\mathbf{k}}\rho_{-\mathbf{k}} - $$
$$\left.-\frac{a_4}{24}\frac{1}{N_v} \sideset{}{'}\sum_{\substack{\mathbf{k}_1,\ldots,\mathbf{k}_4 \\ \mathbf{k}_i\in\mathcal{B}_c}} \rho_{\mathbf{k}_1}\cdots\rho_{\mathbf{k}_4}\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_4}\right], \quad (16)$$

where $\tilde{d}(k) = -\tilde{D}(k)$. The prime next to the sum sign means that the term with $k = 0$ is missing.

Carrying out the integration in (16) with respect to the variables $\rho_{\mathbf{k}}$ with $k \neq 0$ with the use of the Gaussian distribution of fluctuations as the basis one, we obtain the following expression in the zero-order approximation:

$$\Xi' = \prod_{k\neq 0}^{\mathcal{B}_c} (\pi/\tilde{d}_A(k))^{1/2}. \quad (17)$$

Here,

$$\tilde{d}_A(k) = \tilde{d}(k) + A', \quad (18)$$

and

$$\tilde{d}(k) = 1/(\beta W(k)) - \tilde{g}_2. \quad (19)$$

The quantity A' is given by the formula

$$A' = \frac{a_4}{4}(1 + 2\langle\rho_0^2\rangle)N_v^{-1} \sideset{}{'}\sum_{\mathbf{k}\in\mathcal{B}_c}\langle\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle. \quad (20)$$

It should be noted that, in the calculations, we applied the approximation

$$\sideset{}{'}\sum_{\substack{\mathbf{k}_1,\ldots,\mathbf{k}_4 \\ \mathbf{k}_i\in\mathcal{B}_c}} \rho_{\mathbf{k}_1}\cdots\rho_{\mathbf{k}_4}\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_4} \approx 3\sideset{}{'}\sum_{\mathbf{k}_1\in\mathcal{B}_c}\langle\rho_{\mathbf{k}_1}\rho_{-\mathbf{k}_1}\rangle \times$$
$$\times \sideset{}{'}\sum_{\mathbf{k}_2\in\mathcal{B}_c}\rho_{\mathbf{k}_2}\rho_{-\mathbf{k}_2}. \quad (21)$$

Expression (20) and the relations

$$\langle\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle = \frac{1}{\tilde{d}_A(k)},$$
$$\langle\rho_0^2\rangle = \begin{cases} 0, & T \geq T_c, \\ -\dfrac{6\tilde{d}(0)}{a_4}, & T < T_c \end{cases} \quad (22)$$

allow us to find the equation for A'. It is obtained by the transition to a spherical Brillouin zone and replacing the summation over the wave vectors by the integration with respect to $\mathbf{k}\in\mathcal{B}_c$. The equation for A' is as follows:

$$A' = A'_\tau \int\limits_0^{\mathcal{B}_c} \frac{\beta W(k)k^2}{1 - \beta W(k)(\tilde{g}_2 - A')}dk, \quad (23)$$

where

$$A'_\tau = \begin{cases} \dfrac{3}{4}a_4\dfrac{c^3}{\pi^3}, & T \geq T_c, \\ \dfrac{3}{4}a_4\dfrac{c^3}{\pi^3}\left(1 - \dfrac{12\tilde{d}(0)}{a_4}\right), & T < T_c. \end{cases} \quad (24)$$

The quantity A' is included in the coefficient $\tilde{d}_A(k)$ (18), through which the component of the grand partition function Ξ' (17) is expressed. The component Ξ' and the quantity g_v (12) are contained in the expression for Ξ (13). Let us write the expressions for the logarithms Ξ' and g_v, which will be needed to calculate the equation of state of the system.

In view of the relation

$$\frac{1}{2}\sideset{}{'}\sum_{\mathbf{k}\in\mathcal{B}_c}\ln\tilde{d}_A(k) = \frac{3}{2}N_v\frac{c^3}{\pi^3}\int\limits_0^{\mathcal{B}_c}k^2\ln\left[\frac{1}{\beta W(k)} - \tilde{g}_2 + A'\right]dk, \quad (25)$$

we find the following expression for $\ln\Xi'$:

$$\ln\Xi' = N_v L_{\Xi'}(T). \quad (26)$$

Here,

$$L_{\Xi'}(T) = \frac{1}{2}\ln\pi - \frac{3}{2}\frac{c^3}{\pi^3}\int\limits_0^{\mathcal{B}_c}k^2\ln\left[\frac{1}{\beta W(k)} - \tilde{g}_2 + A'\right]dk. \quad (27)$$

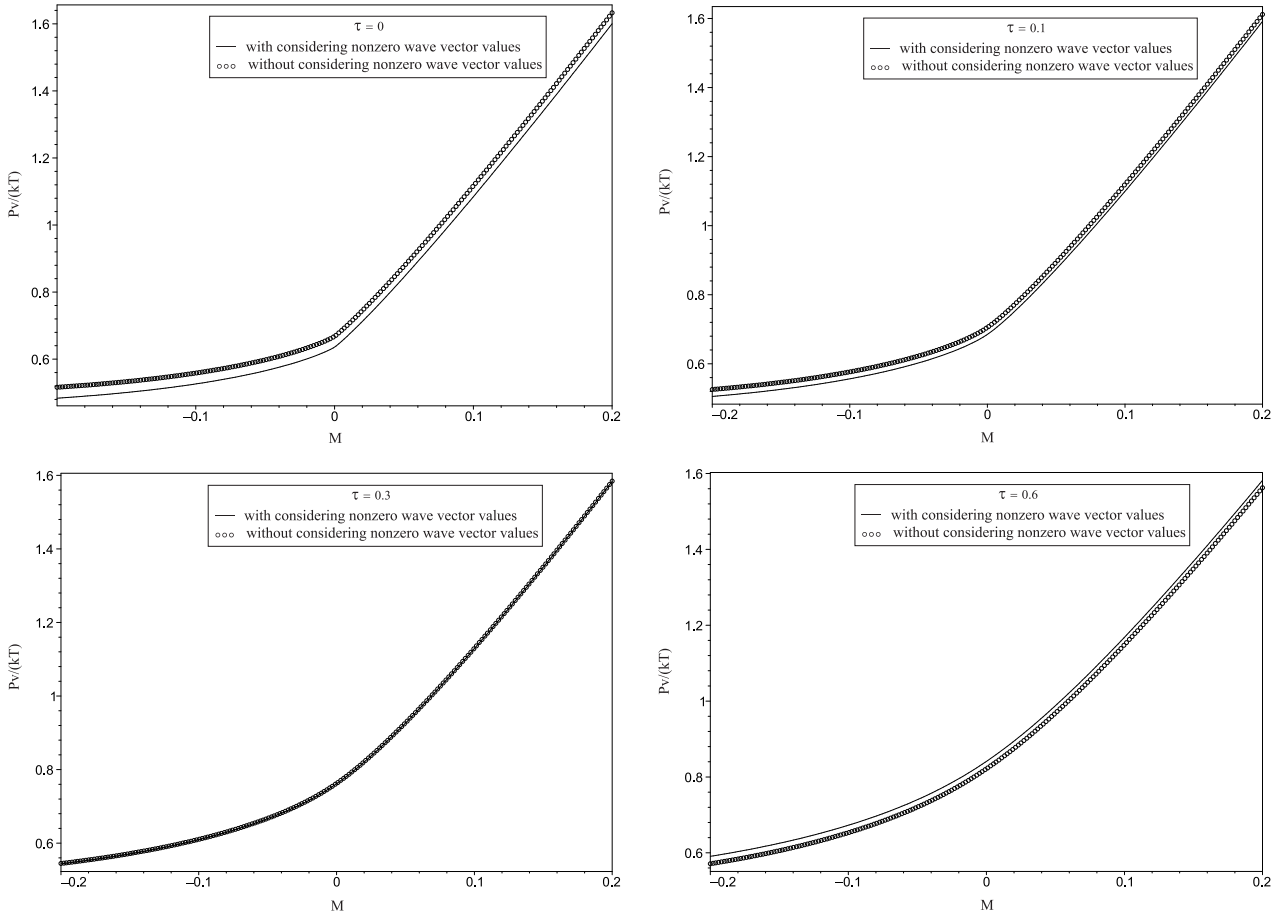For $\ln g_v$, we finally get

$$\ln g_v = N_v L_{g_v}(T), \quad (28)$$

Fig. 1. Dependence of $Pv/(kT)$ on the chemical potential M for various values of the relative temperature τ without accounting for the contributions from the quantities $L_{\Xi'}(T)$ and $L_{g_v}(T)$ (circles) and taking the mentioned contributions into account (solid curves)

where

$$L_{g_v}(T) = -\frac{1}{2}\ln(2\pi) - \frac{3}{2}\frac{c^3}{\pi^3}\int\limits_0^{\mathcal{B}_c} k^2 \ln\left[\frac{W(k)}{kT}\right]dk. \quad (29)$$

Expressions (26)–(29) allow us to find the sum $\ln\Xi' + \ln g_v$. This sum together with the term $N_v \ln 2/2$ appearing in Ξ (13) from the first multiplier will additionally be included in the equation of state of the cell fluid model, which was obtained in [16] in the zero-mode approximation (the mean-field approximation) for potential (1). It characterizes the contribution from the collective variables with nonzero values of the wave vector. The values of the quantities $\tilde{d}(0)$ and A', as well as $L_{\Xi'}$ (27), L_{g_v} (29), and their sum $L_{\Xi'g_v} = L_{\Xi'} + L_{g_v}$, are given in the Table for various τ. Hereinafter, the calculations are performed for

Values of $\tilde{d}(0)$, A', and contributions from the quantities Ξ' and g_v to the pressure of the system at different temperatures τ

τ	$\tilde{d}(0)$	A'	$L_{\Xi'}$	L_{g_v}	$L_{\Xi'g_v}$	$L_{\Xi'g_v}+\frac{\ln 2}{2}$
-0.5	-0.081	0.247	0.459	-0.759	-0.300	0.047
-0.3	-0.040	0.194	0.733	-0.977	-0.244	0.103
-0.1	-0.011	0.097	0.929	-1.061	-0.132	0.215
0	0	0.030	1.054	-1.087	-0.033	0.314
0.1	0.010	0.031	1.086	-1.107	-0.021	0.326
0.3	0.026	0.033	1.135	-1.135	0.000	0.346
0.5	0.039	0.035	1.169	-1.155	0.014	0.360

the following set of parameters:

$$p = 1.0, \quad \alpha^* = 5.0, \quad v = 1.0;$$
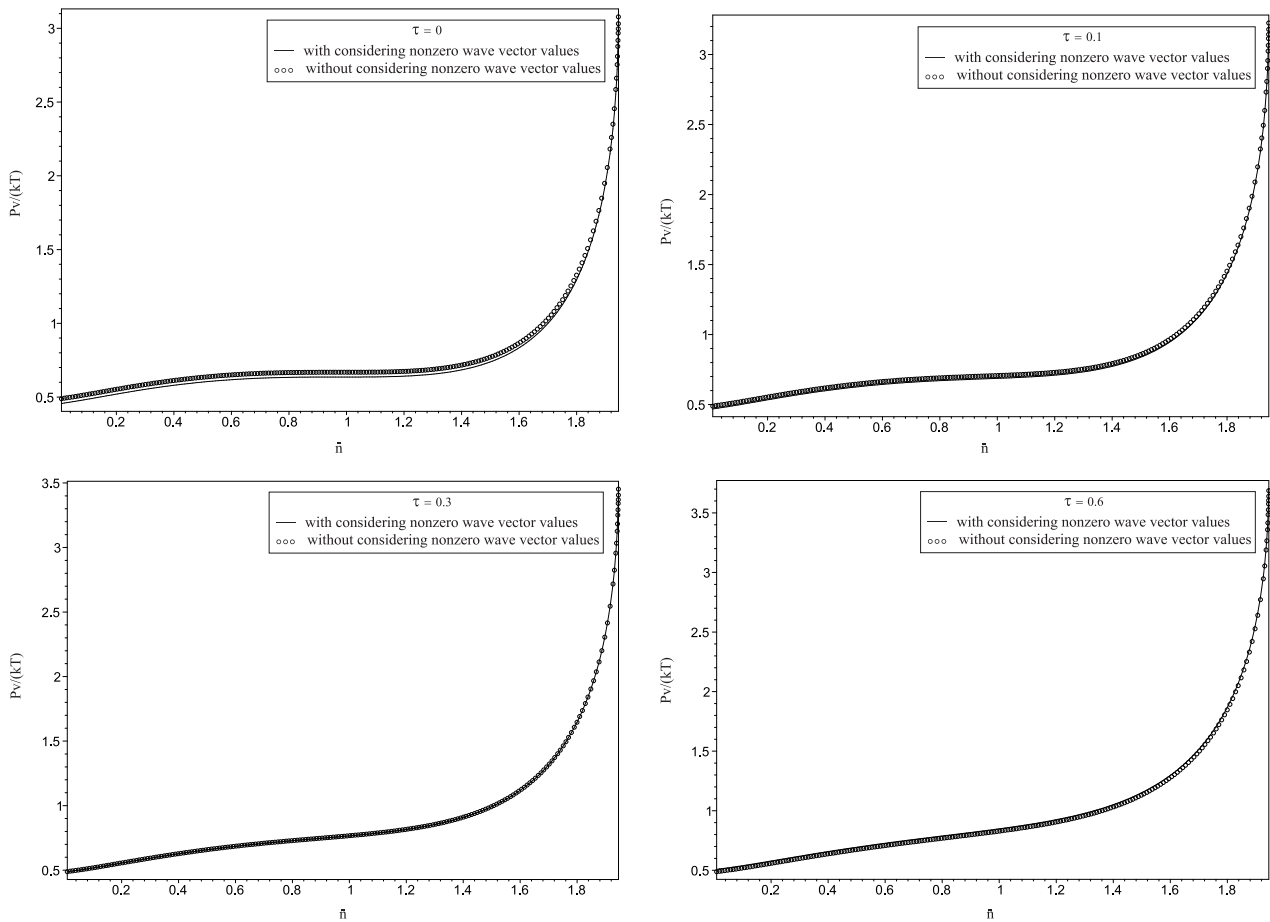$$\gamma = 1.330, \quad \chi_0 = 0.070. \quad (30)$$

Fig. 2. Pressure as a function of the average density for various values of the relative temperature. The results were obtained by accounting for the contributions from the collective variables with nonzero values of the wave vector (solid curves) and without them (circles)

The value of the ratio R_0/α is given in (2). For the quantities n_0 and A_γ, taking (30) into account, we have

$$n_0 = 1.541, \quad A_\gamma = 0.521. \tag{31}$$

Let us go over to calculating the equation of state of the system.

3. Equation of State of the Model with Allowance for Gaussian Fluctuations

Applying the well-known relation
$$PV = kT \ln \Xi \tag{32}$$

and the formula (13), we find the explicit form of the equation of state for $T > T_c$ that is either

$$\frac{PV}{kT} = \ln \Xi' + \ln g_v + N_v \left[\frac{1}{2} \ln 2 + E_\mu(M, T) + \right.$$

$$\left. + \bar{M}\bar{\rho}_0 + \frac{1}{2}\tilde{D}(0)\bar{\rho}_0^2 - \frac{a_4}{24}\bar{\rho}_0^4 \right] \tag{33}$$

or

$$\frac{Pv}{kT} = L_{\Xi'}(T) + L_{g_v}(T) + \frac{1}{2}\ln 2 + E_\mu(M, T) +$$

$$+ \bar{M}\bar{\rho}_0 + \frac{1}{2}\tilde{D}(0)\bar{\rho}_0^2 - \frac{a_4}{24}\bar{\rho}_0^4. \tag{34}$$

Here,

$$E_\mu(M, T) = g_0 - \frac{\beta W(0)}{2}\left(\frac{\tilde{\mu}}{W(0)}\right)^2 + \bar{M}n_c -$$

$$- \frac{n_c^2}{2}\tilde{D}(0) - \frac{1}{24}\frac{g_3^4}{g_4^3}, \tag{35}$$

$$\frac{\tilde{\mu}}{W(0)} = \bar{M} - g_1 - n_c\tilde{D}(0) + \frac{1}{6}\frac{g_3^3}{g_4^2}.$$

The expression for the pressure (34) at $T > T_c$ is a monotonically increasing function of $\bar{M}$ [the variable M in the formalism of the grand canonical ensemble in coordinates (τ, M)] (see Fig. 1).

Equation (34) describes the dependence of the pressure on the temperature and chemical potential. Let us now go over to obtaining the dependence of the pressure on temperature and density.

With regard for the expression of the grand partition function (13), we can find the average number of particles

$$\bar{N} = \frac{\partial \ln \Xi}{\partial \beta \mu} \tag{36}$$

or the average density

$$\bar{n} = \frac{\bar{N}}{N_v}. \tag{37}$$

Considering relations (14) and (35), we get the equation

$$\bar{n} = n_g - \bar{M} + \tilde{g}_2 \gamma_\tau \bar{\rho}_0 \tag{38}$$

connecting the density of particles $\bar{n}$ with the chemical potential $\bar{M}$. Here,

$$n_g = g_1 + n_c \tilde{g}_2 - \frac{1}{6} g_3^3/g_4^2,$$
$$\gamma_\tau = \frac{1 + \tau}{1 + \omega_0 \tau}, \quad \omega_0 = \frac{\chi_0 + A_\gamma}{B - 1 + \chi_0}. \tag{39}$$

Substituting $\bar{M}$ from (15) in expression (38), we arrive at the cubic equation for $\bar{\rho}_0$ (see [16]). Among the three solutions of this equation, only one solution

$$\rho_{02n} = -2 \left(\frac{2\tilde{g}_2}{a_4} \right)^{1/2} \cos\left(\alpha_n/3 + \pi/3 \right) \tag{40}$$

has a physical sense. Here,

$$\alpha_n = \arccos\left(\frac{n_g - \bar{n}}{n_\varphi} \right), \quad n_\varphi = \frac{2}{3} \left(\frac{2\tilde{g}_2^3}{a_4} \right)^{1/2}. \tag{41}$$

Relations (38) and (40) allow us to express the chemical potential $\bar{M}$ in terms of the average density $\bar{n}$. We have

$$\bar{M} = \rho_{02n} \tilde{g}_2 \gamma_\tau - (\bar{n} - n_g). \tag{42}$$

The equation of state of the cell fluid model at $T > T_c$ in terms of the temperature and density takes the form

$$\frac{Pv}{kT} = L_{\Xi'}(T) + L_{g_v}(T) + \frac{1}{2} \ln 2 + E_\mu(n, T) +$$
$$+ \bar{M}\bar{\rho}_0 + \frac{1}{2} \tilde{D}(0)\bar{\rho}_0^2 - \frac{a_4}{24} \bar{\rho}_0^4. \tag{43}$$

The expression for $\bar{M}$ from (42) should be substituted in (43), as well as in the solution $\bar{\rho}_0$ of equation (15) and in the relations

$$E_\mu(n, T) = g_0 - \frac{1}{2\tilde{g}_2 \gamma_\tau} \left(\frac{\tilde{\mu}}{W(0)} \right)^2 + \bar{M}n_c -$$
$$- \frac{n_c^2}{2} \tilde{D}(0) - \frac{1}{24} \frac{g_3^4}{g_4^3}, \tag{44}$$

$$\frac{\tilde{\mu}}{W(0)} = \bar{M} - n_g + n_c \tilde{g}_2 \gamma_\tau.$$

The behavior of pressure (43) with increasing the density $\bar{n}$ is shown in Fig. 2 for various τ.

4. Conclusions

In the temperature range $T > T_c$, the procedure for constructing the equation of state of the cell fluid model is developed with regard for Gaussian fluctuations of the order parameter. The Gaussian fluctuation distribution is used as the basis one, when calculating contributions from the collective variables with nonzero values of the wave vector.

The contributions to the pressure of the system from the collective variables $\rho_{\mathbf{k}}$ with $k \neq 0$ are calculated for temperatures below and above the critical one T_c (see the quantities $L_{\Xi'}$, L_{g_v}, and $L_{\Xi' g_v}$ in Table). As is seen from the Table, the quantity $L_{\Xi'}$ (27) increases with the temperature, whereas L_{g_v} (29) decreases. The total contribution of $L_{\Xi' g_v} = L_{\Xi'} + L_{g_v}$ to the pressure at temperatures $T < T_c$ ($\tau < 0$) is more significant compared with the case of $T > T_c$ ($\tau > 0$). This is evidenced by the magnitude (module) of the total contribution $L_{\Xi' g_v}$ for various τ (see the Table).

The equation of state of the cell fluid model is obtained in terms of the chemical potential-temperature and density-temperature with allowance for the above-mentioned contributions. The comparison of the behavior of system's pressure in the presence and absence of these contributions, which is shown in Fig. 1 and Fig. 2, indicates the insignificant role of contributions in the case of $T > T_c$. For example, the magnitude of the total contribution to the pressure from the

collective variables with nonzero values of the wave vector (from $L_{\Xi' g_v}$) with changing the density $\bar{n}$ at $\tau = 0.1$ (Fig. 2) does not exceed 4.5%. At $\tau = 0.3$ and $\tau = 0.6$, this magnitude of the contribution becomes even smaller.

A specific feature of the proposed description lies in the possibility to use exclusively the microscopic characteristics of a fluid (parameters of the interaction potential) for calculating the macroscopic quantities (pressure and other thermodynamic quantities). The results of studies obtained at $T > T_c$ for the given values of potential parameters show that Gaussian fluctuations of the order parameter with nonzero wave vectors make insignificant changes in the pressure of the cell fluid model. The evolution of the pressure with increasing the chemical potential or density is the same as in the case of the zero-mode approximation, when the collective variables with only zero values of the wave vector are taken into account. We can neglect Gaussian fluctuations in the studied ranges of the density and temperature.

Thus, it is established that, in the region of supercritical temperatures $(T > T_c)$, the inclusion of Gaussian fluctuations has a negligible effect on the equation of state of the cell fluid model. Therefore, at $T > T_c$, the zero-mode approximation is enough for calculating the equation of state.

1. L.A. Bulavin, V. Kopylchuk, V. Garamus, M. Avdeev, L. Almasy, A. Hohryakov. SANS studies of critical phenomena in ternary mixtures. *Appl. Phys. A: Materials Sci. and Proc.* **74**, s546 (2002).

2. Y.B. Melnichenko, G.D. Wignall, D.R. Cole, H. Frielinghaus, L.A. Bulavin. Liquid-gas critical phenomena under confinement: Small-angle neutron scattering studies of CO_2 in aerogel. *J. Mol. Liq.* **120**, 7 (2005).

3. A.V. Chalyi, L.A. Bulavin, V.F. Chekhun, K.A. Chalyy, L.M. Chernenko, A.M. Vasilev, E.V. Zaitseva, G.V. Khrapijchyk, A.V. Siverin, M.V. Kovalenko. Universality classes and critical phenomena in confined liquid systems. *Condens. Matter Phys.* **16**, 23008 (2013).

4. M.V. Ushcats, L.A. Bulavin, V.M. Sysoev, V.Y. Bardik, A.N. Alekseev. Statistical theory of condensation – Advances and challenges, *J. Mol. Liq.* **224**, 694 (2016).

5. J.-P. Hansen, I.R. McDonald. *Theory of Simple Liquids: With Applications to Soft Matter* (Academic Press, 2013).

6. A.R.H. Goodwin, J.V. Sengers, C.J. Peters. *Applied Thermodynamics of Fluids* (Royal Society of Chemistry, 2010).

7. M.A. Anisimov. *Critical Phenomena in Liquids and Liquid Crystals* (Gordon and Breach, 1991).

8. L.A. Bulavin. *Critical Properties of Liquids* (ACMI, 2002) (in Ukrainian).

9. J.V. Sengers, J.M.H. Levelt Sengers. Thermodynamic behavior of fluids near the critical point. *Ann. Rev. Phys. Chem.* **37**, 189 (1986).

10. M.A. Anisimov, J.V. Sengers. Critical region. In: *Equations of State for Fluids and Fluid Mixtures.* Edited by J.V. Sengers, R.F. Kayser, C.J. Peters, H.J. White, jr. (Elsevier, 2000), pp. 381–434.

11. D.Yu. Zalepugin, N.A. Tilkunova, I.V. Chernyshova, V.S. Polyakov. Development of technologies based on supercritical fluids. *Supercritical Fluids: Theory and Practice* **1**, 27 (2006) (in Russian).

12. Y. Kozitsky, M. Kozlovskii, O. Dobush. Phase transitions in a continuum Curie-Weiss system: A quantitative analysis. In: *Modern Problems of Molecular Physics.* Edited by L.A. Bulavin, A.V. Chalyi (Springer, 2018), pp. 229–251.

13. M.P. Kozlovskii, O.A. Dobush. Phase transition in a cell fluid model. *Condens. Matter Phys.* **20**, 23501 (2017).

14. M.P. Kozlovskii, O.A. Dobush, I.V. Pylyuk. Using a cell fluid model for the description of a phase transition in simple liquid alkali metals. *Ukr. J. Phys.* **62**, 865 (2017).

15. M.P. Kozlovskii, I.V. Pylyuk, O.A. Dobush. The equation of state of a cell fluid model in the supercritical region. *Condens. Matter Phys.* **21**, 43502 (2018).

16. M.P. Kozlovskii, O.A. Dobush. Phase behavior of a cell fluid model with modified Morse potential. *Ukr. J. Phys.* **65**, 428 (2020).

17. R.C. Lincoln, K.M. Koliwad, P.B. Ghate. Morse-potential evaluation of second- and third-order elastic constants of some cubic metals. *Phys. Rev.* **157**, 463 (1967).

18. J.K. Singh, J. Adhikari, S.K. Kwak. Vapor–liquid phase coexistence curves for Morse fluids. *Fluid Phase Equilib.* **248**, 1 (2006).

19. I.V. Pylyuk. Fluid critical behavior at liquid–gas phase transition: Analytic method for microscopic description. *J. Mol. Liq.* **310**, 112933 (2020).

20. M.P. Kozlovskii, I.V. Pylyuk, O.O. Prytula. Critical behaviour of a three-dimensional one-component magnet in strong and weak external fields at $T > T_c$. *Physica A* **369**, 562 (2006).

21. M.P. Kozlovskii, I.V. Pylyuk, Z.E. Usatenko. Method of calculating the critical temperature of three-dimensional Ising-like system using the non-Gaussian distribution. *Phys. Stat. Sol. (b)* **197**, 465 (1996).

22. M.P. Kozlovskii, R.V. Romanik. Influence of an external field on the critical behavior of the 3D Ising-like model. *J. Mol. Liq.* **167**, 14 (2012).

23. M.P. Kozlovskii. Free energy of 3D Ising-like system near the phase transition point. *Condens. Matter Phys.* **12**, 151 (2009).

24. M.P. Kozlovskii, I.V. Pylyuk. Entropy and specific heat of the 3D Ising model as functions of temperature and micro-

scopic parameters of the system. *Phys. Stat. Sol. (b)* **183**, 243 (1994).

25. M. Kozlovskii, O. Dobush. Representation of the grand partition function of the cell model: The state equation in the mean-field approximation. *J. Mol. Liq.* **215**, 58 (2016).

I.В. Пилюк, О.А. Добуш

РІВНЯННЯ СТАНУ КОМІРКОВОЇ
МОДЕЛІ ПЛИНУ З ВРАХУВАННЯМ ГАУСОВИХ
ФЛУКТУАЦІЙ ПАРАМЕТРА ПОРЯДКУ

Р е з ю м е

Роботу присвячено розвитку мікроскопічного опису критичної поведінки коміркового флюїду, при якому враховуються внески від колективних змінних з відмінними від нуля значеннями хвильового вектора. Математичний опис здійснено у діапазоні надкритичних температур ($T > T_c$) для випадку модифікованого потенціалу Морзе з додатковою відштовхувальною взаємодією. Розвинутий спосіб побудови рівняння стану системи з використанням гаусового розподілу флуктуацій параметра порядку справедливий поза безпосереднім околом критичної точки для широкого діапазону густини і температури. Приведено графіки залежностей тиску системи від хімічного потенціалу та густини для різних значень відносної температури як із врахуванням вищевказаних внесків, так і без їх врахування. Для температур $T > T_c$ вказано на незначну роль цих внесків у порівнянні з результатами наближення нульової моди. При $T < T_c$ внески у тиск системи відіграють суттєвішу роль.