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PHASE BEHAVIOR OF A CELL FLUID MODEL WITH MODIFIED MORSE POTENTIAL

The present article gives a theoretical description of a first-order phase transition in the cell fluid model with a modified Morse potential and an additional repulsive interaction. In the framework of the grand canonical ensemble, the equation of state of the system in terms of chemical potential–temperature and terms of density–temperature is calculated for a wide range of the density and temperature. The behavior of the chemical potential as a function of the temperature and density is investigated. The maximum and minimum admissible values of the chemical potential, which approach each other with decreasing the temperature, are exhibited. The existence of a liquid-gas phase transition in a limited temperature range below the critical T_c is established.

Keywords: cell fluid model, coexistence curve, collective variables, equation of state, first-order phase transition.

1. Introduction

Construction of the equation of state is a topical problem of studying the phase behavior of a system of interacting particles. Nowadays, several such equations are, to a great extent, phenomenological in nature and well describe the properties of real substances. There are few approaches in which such equations were obtained at the level of microscopic description. Among them are methods based on investigating the behavior of the virial equation of state [1, 2]. The latter describes the behavior of systems at the thermodynamic boundary. Nevertheless, the consideration of higher virial coefficients causes problems in displaying the liquid branch of the phase diagram [3]. Another well-known approach to describe the phase behavior of fluids is the theory of integral equations. This method is mostly a numerical procedure for the structural analysis of a system based on the calculation of paired correlation functions. One of its implementations is the self-consistent Ornstein–Zernike approximation (SCOZA) [4, 5].

Previously [6–8], we proposed a cell fluid model applied to describe a first-order phase transition using different types of interaction potentials. Particularly in [6], the grand partition function was calculated, and the equation of state of a system with the Curie–Weiss potential was obtained. Without using any ap-

proximations, we established that such system possesses a cascade of first-order phase transitions describing a sequence of phases with increasing density. The emergence of multiple phase transitions, rather than a single one, was associated with particles being point-like. The explanation of the appearance of high-density phases in this model is such that a term forbidding the excessive concentration of particles in a cell is absent in the interaction potential. Usually, while describing the fluid systems, the hard-sphere (or soft-sphere) potential limiting the maximum density is used [9, 10]. In the present paper, a supplemental term of soft repulsion is included in the interaction potential, and, afterward, an appropriate equation of state is calculated. For this purpose, a modified Morse potential is used, which, along with the attractive and repelling components, contains a part describing the additional soft-wall repulsion. The inclusion of such a term in the interaction potential enables us to specify a distinct reference system, which makes it possible to calculate the Jacobian of the transition from density variables to collective variables. The set of collective variables is natural for describing the collective effects, including phase transitions.

The novelty of this work consists in the extension of the previously obtained results [11] over a wide temperature range (including the temperature at which the liquid-gas phase transition region ends). This is

made possible by the use of a modified interaction potential, which contains the additional soft repulsion.

2. A Model

Consider a system of N interacting particles located in the volume V . The potential of interaction is a function of the distance r between particles

$$U(r) = C_H \left\{ A e^{-n_0(r-R_0)/\alpha} + e^{-\gamma(r-R_0)/\alpha} - 2e^{-(r-R_0)/\alpha} \right\}. \quad (1)$$

In the last expression, R_0 is the equilibrium distance between two particles (location of the minima of the potential), α is the effective radius of interaction, γ, n_0 are some parameters of the model, C_H and A are the normalization constants. The location of the minima of the function $U(r)$ at $r = R_0$ can be found from the condition

$$\left. \frac{\partial U(r)}{\partial r} \right|_{R_0} = 0 \Rightarrow A = \frac{2-\gamma}{n_0}. \quad (2)$$

The depth of the potential well, which, according to [13], is equal to the energy of dissociation D

$$U(R_0) = -D. \quad (3)$$

The value of the constant C_H is determined from condition (3)

$$C_H = D \frac{n_0}{n_0 + \gamma - 2}. \quad (4)$$

Obviously, the interaction potential (1) has two parameters n_0 and γ , since the characteristic quantities R_0 , D , and α of a specific physical system are known from numerical computations and their comparison with experiments. In particular, for sodium (Na) [13], we have

$$R_0 = 5.3678 \text{ \AA}, \quad \frac{1}{\alpha} = 0.5504 \text{ \AA}^{-1}, \quad \frac{R_0}{\alpha} = 2.9544. \quad (5)$$

The constant of dissociation energy D for Na takes on a value [14]

$$D = 0.9241 \times 10^{-13} \text{ ergs.}$$

Note that, in the case of $n_0 \gg 1$, the former term in (1) corresponds to the hard core (it goes to infinity for any $r < R_0$ and turns to zero for $r > R_0$). The

case of $C_H \rightarrow D$ as $A \rightarrow 0$ yields the ordinary Morse potential [13].

To write a lattice form of the Morse potential (1), we use the following notations:

$$\begin{aligned} \tilde{\Phi}^{(r)}(r) &= C_H e^{-\gamma(r-R_0)/\alpha}, \\ \tilde{\Phi}^{(a)}(r) &= 2C_H e^{-(r-R_0)/\alpha}, \\ \tilde{\Psi}(r) &= C_H A e^{-n_0(r-R_0)/\alpha}. \end{aligned} \quad (6)$$

Then we define $l_{12} = |\mathbf{l}_1 - \mathbf{l}_2|$ as the distance between two cells l_1 and l_2 . According to [6], the volume of the system is conditionally divided into N_v cubic cells such that $V = c^3 \cdot N_v$, where c is the side, and $v = c^3$ is the volume of each cell. The set of cell vectors is defined as

$$\Lambda = \left\{ \mathbf{l} = (l_x, l_y, l_z) | l_i = c \cdot n_i; n_i = 1, 2, \dots, N_i; i = x, y, z; N_i = N_v^{1/3} \right\}. \quad (7)$$

In the thermodynamic limit as $V \rightarrow \infty$, $N_v \rightarrow \infty$, and $v = V/N_v = \text{const}$, we have

$$\begin{aligned} \tilde{\Phi}_{l_{12}}^{(r)} &= C_H e^{-\gamma(l_{12}-c)/\alpha_R c}, \\ \tilde{\Phi}_{l_{12}}^{(a)} &= 2C_H e^{-(l_{12}-c)/\alpha_R c}, \\ \tilde{\Psi}_{l_{12}} &= C_H A e^{-n_0(l_{12}-c)/\alpha_R c}. \end{aligned} \quad (8)$$

Here, $\alpha_R = \alpha/R_0$ is a dimensionless quantity. Let $l_{12} = xc$. Then expressions (8) take the following form:

$$\begin{aligned} \tilde{\Phi}^{(r)}(x) &= C_H e^{-\gamma(x-1)/\alpha_R}, \\ \tilde{\Phi}^{(a)}(x) &= 2C_H e^{-(x-1)/\alpha_R}, \\ \tilde{\Psi}(x) &= C_H A e^{-n_0(x-1)/\alpha_R}. \end{aligned} \quad (9)$$

The latter expressions coincide with (6), if one takes into account that $r = x R_0$, $\alpha_R = \alpha/R_0$. The Fourier transforms of the interaction potentials (8) are as follows:

$$\begin{aligned} \Phi^{(r)}(k) &= C_H 8\pi e^{\gamma/\alpha} \left(\frac{\alpha}{\gamma} \right)^3 \left(1 + \left(\frac{\alpha c}{\gamma} \right)^2 k^2 \right)^{-2}, \\ \Phi^{(a)}(k) &= C_H 16\pi e^{1/\alpha} \alpha^3 \left(1 + (\alpha c k)^2 \right)^{-2}, \\ \Psi(k) &= C_H A 8\pi e^{n_0/\alpha} \left(\frac{\alpha}{n_0} \right)^3 \left(1 + \left(\frac{\alpha c}{n_0} \right)^2 k^2 \right)^{-2}. \end{aligned} \quad (10)$$

To simplify notations, let α denote the quantity α_R . Moreover, all the quantities referred to a distance are measured in R_0 -units. It is easy to see that

$$\begin{aligned}\Phi^{(a)}(0) &= B\Phi^{(r)}(0), \quad B = 2\gamma^3 e^{(1-\gamma)/\alpha}, \\ \Psi(0) &= A_\gamma \Phi^{(r)}(0), \quad A_\gamma = Ae^{(n_0-\gamma)/\alpha} (\gamma/n_0)^3.\end{aligned}\quad (11)$$

For values (5) of the parameters R_0 and α , the quantity B expressed in (11) is small for the large values of γ ($\gamma \gg 1$). Moreover, $B \geq 1$, when $\gamma \leq \gamma_0$, where $\gamma_0 = 1.87047$. The behavior of the coefficient $B(\gamma)$ is important in the subsequent calculations, in particular, when determining the relation between the Fourier transforms of the repulsive $\Phi^{(r)}(0)$ and attractive $\Phi^{(a)}(0)$ interactions. In the range $\gamma < \gamma_0$, we have

$$\Phi^{(a)}(0) > \Phi^{(r)}(0).$$

This condition allows us to take advantage of the results of [12], where we obtained the following expression for the grand partition function of the cell fluid model:

$$\begin{aligned}\Xi &= \int (d\rho)^{N_v} \exp \left[\sqrt{N_v} \beta \tilde{\mu} \rho_0 + \frac{\beta}{2} \sum_{\mathbf{k} \in B_c} W(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] \times \\ &\times \prod_{l=1}^{N_v} \left(\sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} e^{-pm^2} e^{m\tilde{t}_1} \right).\end{aligned}\quad (12)$$

Here, $\alpha^* = ve^{\beta_c \mu^*}$, $\tilde{\mu} = \mu - \mu^*(1 + \tau)$. The effective interaction potential in the case of a modified Morse potential is as follows:

$$\begin{aligned}W(k) &= \Phi^{(a)}(k) - \Phi^{(r)}(k) - \Psi(k) + \\ &+ \frac{\beta_c}{\beta} \chi_0 \Phi^{(r)}(0) + \frac{\beta_c}{\beta} \Psi(0).\end{aligned}\quad (13)$$

Here, χ_0 , μ^* are some constants, and τ is the relative temperature,

$$\tau = (T - T_c)/T_c.\quad (14)$$

Here, T_c is the critical temperature which will be defined later on. It is easy to see that

$$W(0) = \Phi^{(r)}(0) [B - 1 + \chi_0 + \tau(\chi_0 + A_\gamma)].\quad (15)$$

The condition $W(0) > 0$ is met for all $\gamma < \gamma_0$. The parameter p from (12) has the form

$$p = \frac{\beta_c}{2} \Phi^{(r)}(0) [\chi_0 + A_\gamma].\quad (16)$$

Expressing the last factor in (12) as a cumulant series gives [12]

$$\begin{aligned}\Xi &= g_v \int (dt)^{N_v} \exp \left[-\frac{1}{2} \sum_{\mathbf{k} \in B_c} t_{\mathbf{k}} t_{-\mathbf{k}} / \beta W(k) \right] \times \\ &\times \prod_{l=1}^{N_v} \exp \left(\sum_{m=0}^{\infty} \frac{g_m \tilde{t}_1^m}{m!} \right).\end{aligned}\quad (17)$$

In the last expression, the Stratonovich–Hubbard transform has been already used for the factor in (12) containing the effective interaction potential, since $W(k) > 0$, as follows with (13). The quantity g_v in (17) is given by the formula

$$g_v = \prod_{\mathbf{k} \in B_c} (2\pi\beta W(k))^{-1/2},$$

and the variable $\tilde{t}_{\mathbf{k}}$ is

$$\tilde{t}_{\mathbf{k}} = t_{\mathbf{k}} + \beta_c \tilde{\mu} \sqrt{N_v} \delta_{\mathbf{k}}.\quad (18)$$

Moreover,

$$\tilde{t}_1 = \frac{1}{\sqrt{N_v}} \sum_{\mathbf{k} \in B_c} \tilde{t}_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{l}}.$$

The coefficients g_n from [8, 12] are as follows:

$$\begin{aligned}g_0 &= \ln T_0, \quad g_1 = T_1/T_0, \quad g_2 = T_2/T_0 - g_1^2, \\ g_3 &= T_3/T_0 - g_1^3 - 3g_1g_2, \\ g_4 &= T_4/T_0 - g_1^4 - 6g_1^2g_2 - 4g_1g_3 - 3g_2^2,\end{aligned}\quad (19)$$

where $T_n(p, \alpha^*)$ are the following special functions:

$$T_n(p, \alpha^*) = \sum_{m=0}^{\infty} \frac{(\alpha^*)^m}{m!} m^n e^{-pm^2}.\quad (20)$$

Since p fails to be a function of the temperature, the coefficients of the Jacobian of the transition to collective variables g_n do not depend on τ .

In the approximation of the ρ^4 model, we have [12]

$$\begin{aligned}\Xi &= g_v e^{N_v E_\mu} \int (d\rho)^{N_v} \times \\ &\times \exp \left[MN_v^{1/2} \rho_0 + \frac{1}{2} \sum_{\mathbf{k} \in B_c} \tilde{D}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + \right. \\ &\left. + \frac{g_4}{24} \frac{1}{N_v} \sum_{\substack{\mathbf{k}_1, \dots, \mathbf{k}_4 \\ \mathbf{k}_i \in B_c}} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} \right].\end{aligned}\quad (21)$$

The following notations are used in the last formula:

$$\begin{aligned} E_\mu &= g_0 - \frac{\beta \tilde{\mu}^2}{2W(0)} + n_c \left(g_1 + \frac{\tilde{\mu}}{W(0)} \right) + \frac{n_c^2}{2} \tilde{D}(0) + \frac{g_3^4}{8g_4^3}, \\ M &= \tilde{\mu}/W(0) + g_1 + n_c \tilde{D}(0) - \frac{1}{6} \frac{g_3^3}{g_4^2}, \\ \tilde{D}(k) &= \tilde{g}_2 - 1/\beta W(k), \\ \tilde{g}_2 &= g_2 - \frac{1}{2} \frac{g_3^2}{g_4}, \quad n_c = -g_3/g_4. \end{aligned} \quad (22)$$

Expression (21) is approximated only in the sense that it involves the contribution from the cumulants g_n of $n \leq 4$. The higher g_n (with $n \geq 5$) are considered to be zero. As shown in [15], this approximation qualitatively describes the behavior of a three-dimensional Ising model near the critical point. Since the simple fluids belong to the universality class of the Ising model, hopefully, the approximation used in (21) will allow us to describe the first-order phase transition in simple fluids, including the critical region.

3. Temperature Dependence and the Range of Model Parameters

To compute the values of g_n that are required to obtain the explicit form of (21), it is essential to have the parameters p and α^* . Consider the easiest case where

$$p = 1.0, \quad \alpha^* = 5.0. \quad (23)$$

The value of p is unambiguously determined by the parameters χ_0 and A_γ , which are a part of (16). The value of A_γ is a function of the parameter n_0 defined in (11), so the case of $p = 1$ corresponds to the well-defined χ_0 and n_0 . Let us find their magnitudes. According to (11), if

$$\gamma = 1.650, \quad (24)$$

then

$$n_0 = 1.521, \quad A_\gamma = 0.201; \quad \chi_0 = 0.070.$$

We now examine (21) applying the zero-mode approximation, just as it was done in [12]. The result is a grand partition function in the following form:

$$\Xi = g_v \exp[N_v(E_\mu + E(\bar{\rho}_0))], \quad (25)$$

where

$$E(\bar{\rho}_0) = M\bar{\rho}_0 + \frac{1}{2} \tilde{D}(0)\bar{\rho}_0^2 - \frac{a_4}{24} \bar{\rho}_0^4, \quad (26)$$

and the coefficient $a_4 = -g_4 > 0$. The quantity $\bar{\rho}_0$ is a solution of the equation $\partial E(\rho_0)/\partial \rho_0 = 0$, which is

$$\bar{M} + \tilde{D}(0)\bar{\rho}_0 - \frac{a_4}{6} \bar{\rho}_0^3 = 0. \quad (27)$$

Here, \bar{M} is some value of the chemical potential which corresponds to an extremum of the function $E(\rho_0)$. This extremum is the maximum (which is a condition of the Laplace method used to calculate (25)), if the inequality

$$\frac{\partial^2 E(\bar{\rho}_0)}{\partial \rho_0^2} \leq 0 \quad (28)$$

is fulfilled. The equality condition in (28) corresponds to the quantity

$$\rho_{0r}^2 = 2 \frac{\tilde{D}(0)}{a_4}. \quad (29)$$

Later on, we will see that ρ_{0r} describes a spinodal curve that is specified only in range $T < T_c$.

The critical temperature T_c is provided by solving the equation

$$\tilde{D}(0, T_c) = 0. \quad (30)$$

For the parameters given by (23) and (24), we have

$$\begin{aligned} k_B T_c &= \tilde{g}_2 W(0, T_c) = \tilde{g}_2 (B - 1 + \chi_0) \Phi^{(r)}(0), \\ k_B T_c &\approx 4.995 D. \end{aligned} \quad (31)$$

We now find the explicit form of the dependence of $\tilde{D}(0)$ on the temperature, using (22). In view of (15), we have

$$\frac{1}{\beta W(0)} = \tilde{g}_2 \gamma_\tau, \quad \gamma_\tau = \frac{1 + \tau}{1 + \omega_0 \tau}, \quad (32)$$

where \tilde{g}_2 is a constant which is independent of the temperature and defined by the microscopic parameters (5) and (23), and

$$\omega_0 = \frac{\chi_0 + A_\gamma}{B - 1 + \chi_0}. \quad (33)$$

Formula (22) yields the following expression:

$$\tilde{D}(0) = -\tau \frac{1 - \omega_0}{1 + \omega_0 \tau} \tilde{g}_2. \quad (34)$$

The computation of the coefficients g_n given by (19) implies that, under conditions (23), the value $\tilde{g}_2 < 1/2$. Therefore, $\omega_0 = 2\tilde{g}_2 < 1$. Consequently, the quantity $\tilde{D}(0) \leq 0$ for all $\tau \geq 0$, and $\tilde{D}(0) \geq 0$ in the case $\tau \leq 0$. This leads us to the conclusion that, in the temperature range $\tau > 0$, Eq. (29) has no real solutions for ρ_{0r} . Therefore, there are no restrictions on the quantity $\bar{\rho}_0$ as a solution of Eq. (27). However, in the case $\tau < 0$, there is a real quantity

$$\rho_{0r} = \left(2 \frac{\tilde{D}(0)}{a_4}\right)^{1/2}, \quad (35)$$

as well as the following restriction on the value of $\bar{\rho}_0$:

$$|\bar{\rho}_0| \geq \rho_{0r}. \quad (36)$$

The equality sign in (36) matches a spinodal curve that limits the stability region of the system.

The reduced form of Eq. (27) is given by

$$\bar{\rho}_0^3 + p_t \bar{\rho}_0 + q = 0, \quad (37)$$

where

$$p_t = -\frac{6\tilde{D}(0)}{a_4}; \quad q = -\frac{6\bar{M}}{a_4}. \quad (38)$$

The solution of (37) in the range $T > T_c$ is given by

$$\bar{\rho}_0 = \left(\frac{3\bar{M}}{a_4} + \sqrt{Q_t}\right)^{1/3} - \left(-\frac{3\bar{M}}{a_4} + \sqrt{Q_t}\right)^{1/3}, \quad (39)$$

where

$$Q_t = \left(-\frac{2\tilde{D}(0)}{a_4}\right)^3 + \left(\frac{3\bar{M}}{a_4}\right)^2. \quad (40)$$

For all $T > T_c$, the quantity $p_t > 0$. This suggests the existence of a unique real solution of (37). Using both a well-known relation

$$PV = k_B T \ln \Xi \quad (41)$$

and expression (25) gives the following explicit form of the equation of state in the case $T > T_c$:

$$\frac{Pv}{k_B T} = \frac{1}{N_v} \ln g_v + E_\mu(T) + \bar{M}\bar{\rho}_0 + \frac{1}{2}\tilde{D}(0)\bar{\rho}_0^2 - \frac{a_4}{24}\bar{\rho}_0^4. \quad (42)$$

The quantity $E_\mu(T)$ takes the form

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

$$\frac{\tilde{\mu}}{W(0)} = \bar{M} - g_1 - n_c\tilde{D}(0) + \frac{1}{6}g_3^3/g_4^2, \quad (43)$$

Note that, for all $\tau > 0$, there are no restrictions on the value of $\bar{\rho}_0$. Expression (42) for the pressure is a monotonically increasing function of the chemical potential and the temperature.

4. Region of Temperatures Below the Critical One

For all $\tau < 0$, Eq. (37) has three real solutions:

$$\begin{aligned} \rho_{01} &= 2\rho_{0r} \cos(\alpha_t/3), \\ \rho_{02} &= -2\rho_{0r} \cos\left(\alpha_t/3 + \frac{\pi}{3}\right), \\ \rho_{03} &= -2\rho_{0r} \cos\left(\alpha_t/3 - \frac{\pi}{3}\right), \end{aligned} \quad (44)$$

where ρ_{0r} is given by (35). The quantity α_t is provided by

$$\cos \alpha_t = \bar{M}/M_q. \quad (45)$$

Moreover,

$$M_q = -\frac{g_4}{3}\rho_{0r}^3 = \frac{a_4}{3} \left(\frac{2\tilde{D}(0)}{a_4}\right)^{3/2}. \quad (46)$$

Note that solutions (44) are valid in the case of $Q_t < 0$, where Q_t is defined in (40), that is, for all $|\bar{M}| < M_q$, where M_q is a solution of the equation $Q_t = 0$. The unique real solution $\bar{\rho}_0$ of Eq. (37) exists in the range $|\bar{M}| \geq M_q$. It is calculated similarly to (39), because the quantity $Q_t \geq 0$ for these values of \bar{M} :

$$\rho_{04} = \left(\frac{3}{a_4}\right)^{1/3} \left(A_1^{1/3} + A_2^{1/3}\right). \quad (47)$$

Here,

$$\begin{aligned} A_1 &= \bar{M} + \sqrt{\bar{M}^2 - M_q^2}, \\ A_2 &= \bar{M} - \sqrt{\bar{M}^2 - M_q^2}. \end{aligned} \quad (48)$$

The solution ρ_{04} defined in (47) is an extension of one of solutions (44). Moreover, for all $\bar{M} > 0$, ρ_{04} is a continuation of the solution ρ_{01} . In the region $\bar{M} < 0$, it coincides with ρ_{03} at $\bar{M} = -M_q$. The corresponding curves are shown in Fig. 1.

Note that

$$\begin{aligned} \lim_{\bar{M} \rightarrow M_q} \rho_{01} &= \lim_{\bar{M} \rightarrow M_q} \rho_{04}^{(p)} = 2\rho_{0r}, \\ \lim_{\bar{M} \rightarrow -M_q} \rho_{03} &= \lim_{\bar{M} \rightarrow -M_q} \rho_{04}^{(m)} = -2\rho_{0r}, \end{aligned} \quad (49)$$

where $\rho_{04}^{(p)}$ and $\rho_{04}^{(m)}$ correspond to (47) in either the region $M > 0$ or $M < 0$, respectively.

The equation of state at $T < T_c$ in terms of the chemical potential and temperature has the following form:

$$\frac{Pv}{k_B T} = \frac{1}{N_v} \ln g_V + E_\mu(\mu, T) + E(\rho_{01}) \times \Theta(M)\Theta(M_q - M) + E(\rho_{03})\Theta(-M)\Theta(M_q + M) + E(\rho_{04}^{(m)})\Theta(-M - M_q) + E(\rho_{04}^{(p)})\Theta(M - M_q), \quad (50)$$

where the function $E(\rho_0)$ is specified in (26), and the arguments of this function are expressed by (44) and (47). The quantity $E_\mu(\mu, T)$ is given by (43). The 3D plot of the pressure below T_c is represented in Fig. 2.

5. Relation between the Chemical Potential and the Density

The above-calculated equations of state (42) at $T > T_c$ and (50) at $T < T_c$ contain the dependence of the pressure on the temperature and the chemical potential. To obtain the pressure as a function of the temperature and density, we use the known relation for the average number of particles:

$$\langle N \rangle = \frac{\partial}{\partial \beta \mu} \ln \Xi. \quad (51)$$

Taking expression (25) into account, we have

$$\bar{n} = \frac{\langle N \rangle}{N_v} = \frac{\partial E_\mu}{\partial \beta \mu} + \frac{\partial E(\bar{\rho}_0)}{\partial \beta \bar{M}}. \quad (52)$$

The following equation which links the density of particles \bar{n} and the chemical potential \bar{M} is obtained using formulas (26) and (43):

$$\bar{n} = n_g - \bar{M} + \tilde{g}_2 \gamma_\tau \bar{\rho}_0, \quad (53)$$

where

$$n_g = g_1 + n_c \tilde{g}_2 - \frac{1}{6} g_3^3 / g_4^2. \quad (54)$$

Rewrite (53) in the form

$$\bar{\rho}_0 = (\bar{M} + \bar{n} - n_g) / \tilde{g}_2 \gamma_\tau. \quad (55)$$

This expression is actually the equation for ρ_0 , since \bar{M} contained in (53) is a function of the quantity $\bar{\rho}_0$. This follows from the equality (27), which specifies the extreme value of $\bar{\rho}_0(\tau, \bar{M})$. Substituting

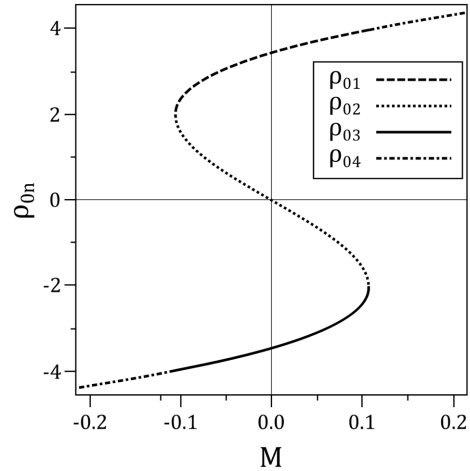


Fig. 1. Plot of solutions $\bar{\rho}_0$ (see (44)) at $\tau = -0.5$. There exist three real roots for $Q_t < 0$ and a unique real solution for $Q_t > 0$

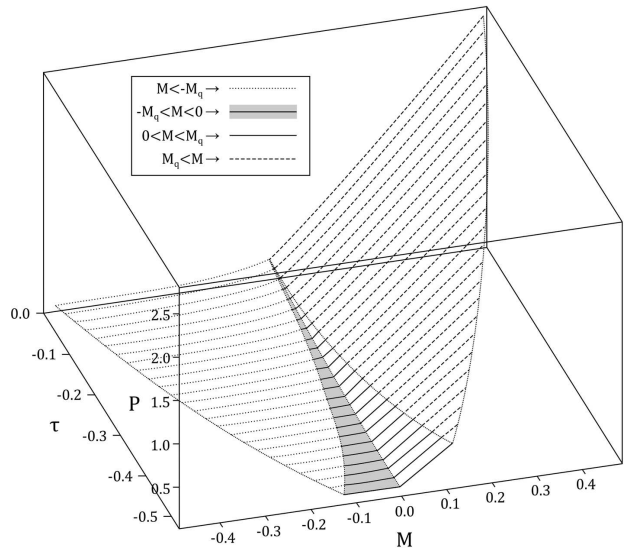


Fig. 2. 3D plot of the pressure as a function of the temperature and the chemical potential ($P = P(T, M)$) in the region $T < T_c$

\bar{M} from (27) to (55), we obtain the equation for $\rho_{0n} = \rho_{0n}(\tau, \bar{n})$:

$$\rho_{0n}^3 + p_q \rho_{0n} + q_q = 0. \quad (56)$$

Here, the coefficients p_q and q_q are given by

$$p_q = -\frac{6}{a_4} (\tilde{g}_2 \gamma_\tau + \tilde{D}(0)); \quad q_q = \frac{6}{a_4} (\bar{n} - n_g). \quad (57)$$

Equation (56) allows us to find $\bar{\rho}_0$ as a function of the density \bar{n} and the temperature. It transforms the

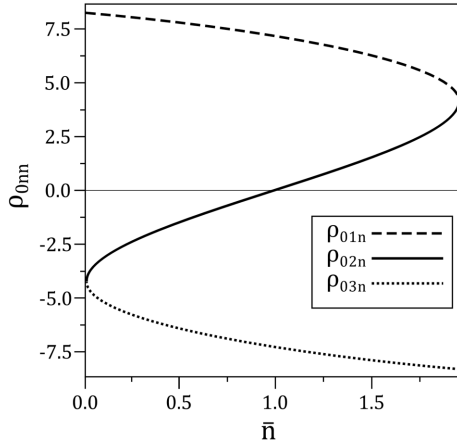


Fig. 3. Plot of the solutions ρ_{0nn} given by (60) as functions of the density

dependence of the solution of Eq. (37) on chemical potential to that on the density.

It is easy to see that, in view of (32) and (34), the coefficient p_q is a constant. We have

$$p_q = -\frac{6\tilde{g}_2}{a_4}. \quad (58)$$

It is negative and independent of the temperature. Therefore, for all $Q_q < 0$ given by

$$Q_q = (p_q/3)^3 + (q_q/2)^2, \quad (59)$$

Eq. (56) possesses three real solutions:

$$\begin{aligned} \rho_{01n} &= 2 \left(\frac{2\tilde{g}_2}{a_4} \right)^{1/2} \cos(\alpha_n/3), \\ \rho_{02n} &= -2 \left(\frac{2\tilde{g}_2}{a_4} \right)^{1/2} \cos(\alpha_n/3 + \pi/3), \\ \rho_{03n} &= -2 \left(\frac{2\tilde{g}_2}{a_4} \right)^{1/2} \cos(\alpha_n/3 - \pi/3). \end{aligned} \quad (60)$$

Here, either

$$\cos \alpha_n = \frac{n_g - \bar{n}}{n_\varphi}; \quad n_\varphi = \frac{2}{3} \left(\frac{2\tilde{g}_2^3}{a_4} \right)^{1/2}$$

or

$$\alpha_n = \arccos \left(\frac{n_g - \bar{n}}{n_\varphi} \right). \quad (61)$$

Solutions (60) are shown in Fig. 3. The extension of (56) to the region $Q_q > 0$ leads to the continuation of non-physical branches of the solutions ρ_{03n} and ρ_{01n} (see Fig. 3).

Note that both (37) and (56) are equations of the same type, but describe different dependences. We can find the solutions $\bar{\rho}_0(\tau, M)$ of (37) to determine the extrema of $E(\bar{\rho}_0)$ provided by (26), by applying the Laplace method [16] to calculate the grand partition function $\Xi(\tau, M)$. This is the way to obtain the equation of state (41) in terms of the temperature and chemical potential. Equation (56) allows us to find both the quantity $\bar{\rho}_0$ and, consequently, the pressure as functions of the density and temperature.

The difference between Eqs. (37) and (56) is also evident in the aspect of mathematics. Thus, the solutions ρ_{01} and ρ_{03} of Eq. (37) corresponding to $\max E(\bar{\rho}_0)$ are useful at $T < T_c$. The quantity ρ_{02} refers to $\min E(\bar{\rho}_0)$. Among the three solutions (56), only ρ_{02n} is physical. This solution shows that the density increases with the chemical potential. The other two solutions, ρ_{01n} and ρ_{03n} , show a decrease in the density (with growing chemical potential). Such a behavior does not fit the reality. The calculations should be carried out in the sequence suggested in the present paper. First, we find the solutions $\bar{\rho}_0(\tau, M)$ which give an explicit expression of the grand partition function $\Xi(\tau, M)$ as a function of the temperature and chemical potential. Only then, we search for $\bar{\rho}_0(\tau, \bar{n})$. This procedure gives the way to obtain both $\Xi(\tau, \bar{n})$ and the equation of state $P = P(\tau, \bar{n})$ in terms of the temperature and density.

In the zero-mode approximation, Eq. (25) of the ρ^4 -model (21) leads to a restriction on the quantity $\rho_{0n}(\tau, \bar{n})$ defined in (60) (see Fig. 3):

$$-\bar{\rho} < \rho_{0n} < \bar{\rho}, \quad (62)$$

where

$$\bar{\rho} = (2\tilde{g}_2/a_4)^{1/2}. \quad (63)$$

Consider this situation in more details. For this purpose, we rewrite Eq. (53) as

$$\bar{M} = \tilde{g}_2 \gamma_\tau \rho_{0n} - (\bar{n} - n_g). \quad (64)$$

The quantity \bar{M} [which is a variable in the framework of the grand canonical ensemble in terms of (τ, M)] becomes a function of the density \bar{n} and the temperature τ . To transform the results represented in terms of (τ, M) to those in terms of (τ, \bar{n}) , we use formula (64), where the solution ρ_{02n} from (60) is applied to ρ_{0n} . To simplify notations, we denote $\rho_{02n} = \rho_n$. Since the right-hand side of (64) is a finite quantity, the quantity \bar{M} is also limited

by two boundary curves. The former corresponds to $\rho_n = -\bar{\rho}$. Then (64) gives

$$M^* = \lim_{\rho_n \rightarrow -\bar{\rho}} \bar{M} = -\tilde{g}_2 \gamma_\tau \bar{\rho} - (n_{\min} - n_g). \quad (65)$$

The following relation is used in the last formula:

$$\lim_{\rho_n \rightarrow -\bar{\rho}} \bar{n} = n_{\min}. \quad (66)$$

The other limit provides an upper boundary curve, where $\rho_n \rightarrow \bar{\rho}$, and the density $\bar{n} \rightarrow n_{\max}$:

$$M^{**} = \lim_{\rho_n \rightarrow \bar{\rho}} \bar{M} = \tilde{g}_2 \gamma_\tau \bar{\rho} - (n_{\max} - n_g). \quad (67)$$

Here,

$$\lim_{\rho_n \rightarrow \bar{\rho}} \bar{n} = n_{\max}. \quad (68)$$

Figure 4 illustrates the temperature dependences of M^* and M^{**} . Evidently, there is no gas-liquid phase transition below the value n_{\min} which specifies the lowest possible density for some temperature T^* . Thus, in the approximation of the ρ^4 -distribution, the cell fluid model has a certain region of admissible density values:

$$n_{\min} \leq \bar{n} \leq n_{\max}. \quad (69)$$

It is easy to see that there is some temperature

$$\tau^* = -0.618, \quad (70)$$

at which the following equality is fulfilled:

$$M^* = M^{**} = 0. \quad (71)$$

This temperature corresponds to some fixed density values

$$\begin{aligned} n_{\max} &= n_g + n_\varphi, \\ n_{\min} &= n_g - n_\varphi, \end{aligned} \quad (72)$$

where

$$n_\varphi = \bar{\rho} \tilde{g}_2 \gamma_\tau (\tau^*). \quad (73)$$

Clearly, in view of the condition $n_{\min} \geq 0$, the following inequality should be held:

$$n_g \geq n_\varphi. \quad (74)$$

This condition is met for the parameter set (23). We use parameters (24) to describe sodium and find

$$\begin{aligned} n_g &= 0.977; & n_{\max} &= 1.946; \\ n_\varphi &= 0.968; & n_{\min} &= 0.009. \end{aligned} \quad (75)$$

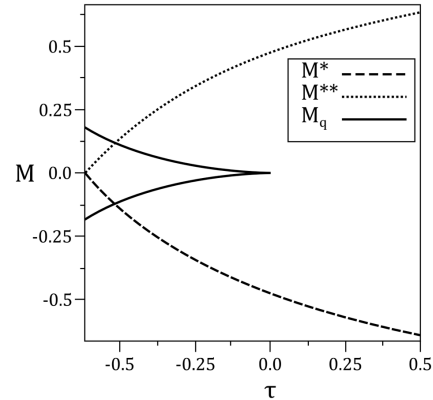


Fig. 4. Boundary values of the chemical potential M (M_q , M^{**} – the upper limit, M^* – the lower limit)

The quantity n_{\min} increases, as the parameter α^* decreases. For instance, the equalities $p = 1$ and $\alpha^* = 4$ give

$$\begin{aligned} n_g &= 0.884; & n_{\max} &= 1.652; \\ n_\varphi &= 0.767; & n_{\min} &= 0.117. \end{aligned} \quad (76)$$

In the case $p = 1$, $\alpha^* = 3$, and

$$\begin{aligned} n_g &= 0.832; & n_{\max} &= 1.505; \\ n_\varphi &= 0.673; & n_{\min} &= 0.158. \end{aligned} \quad (77)$$

We note that each set of parameters p and α^* corresponds to particular values of the characteristic densities.

At $T > T_c$, the equation of state of the cell fluid model in terms of the density has the form

$$\begin{aligned} \frac{Pv}{k_B T} &= \frac{1}{N_v} \ln g_v + E_\mu^{(2)}(n, T) + \bar{M} \rho_n + \\ &+ \frac{\tilde{D}(0)}{2} \rho_n^2 - \frac{a_4}{24} \rho_n^4, \end{aligned} \quad (78)$$

where

$$\bar{M} = \rho_n \tilde{g}_2 \gamma_\tau - (\bar{n} - n_g) \quad (79)$$

is a function of the density and temperature. We use formula (43) to find

$$\frac{\tilde{\mu}}{W(0)} = \bar{M} - n_g + n_c \tilde{g}_2 \gamma_\tau, \quad (80)$$

where n_g is defined in (54). Therefore,

$$\begin{aligned} E_\mu^{(2)}(n, T) &= g_0 - \frac{1}{2\tilde{g}_2 \gamma_\tau} \left(\frac{\tilde{\mu}}{W(0)} \right)^2 + n_c \bar{M} - \\ &- \frac{1}{2} n_c^2 \tilde{D}(0) - \frac{1}{24} \frac{g_3^4}{g_4^3}. \end{aligned} \quad (81)$$

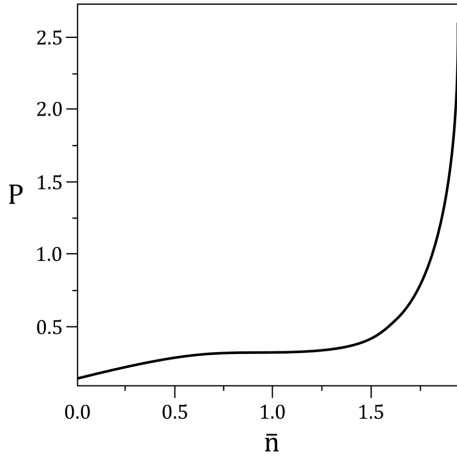


Fig. 5. Plot of the pressure as a function of the density at $T = T_c$

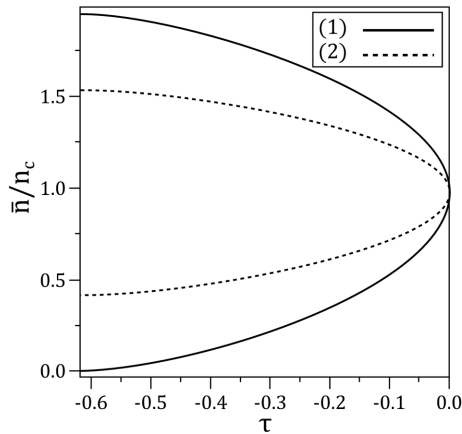


Fig. 6. Coexistence curve (1) and the spinodal (2) of the model investigated in the present research

The plot of the pressure as a function of the density at $T = T_c$ is represented in Fig. 5. It shows that n_g is the critical density.

6. Phase Behavior of the Cell Fluid Model

In Sections 3 and 4, the equation $P = P(\tau, M)$ is obtained for the temperature regions above and below the critical temperature. Section 5 states that the region of the chemical potential M is limited by two characteristic curves M^* (65) and M^{**} (67), respectively,

$$M^* \leq M \leq M^{**}. \tag{82}$$

Figure 2 shows the 3D plot of the equation of state $P(\tau, M)$ for the temperatures $T < T_c$. It has a frac-

ture along with the line $M = 0$, which indicates a first-order phase transition, since the first derivative of the pressure with respect to the chemical potential M on the line $M = 0$ will be different from the left- and right-hand sides. In addition, Fig. 4 shows the line $M_q(\tau)$, which delimits regions of the surface $P(\tau, M)$, in which there are either one or three real solutions of Eq. (37) with the unknown $\bar{\rho}_0$. Finding $\bar{\rho}_0$ makes it possible to calculate the grand partition function of the cell fluid model and to establish the existence of a first-order phase transition in it. Figure 6 illustrates the coexistence curve and the spinodal of the present model. Each of these curves ends at a temperature $T = T^* < T_c$.

7. Conclusions

The results of the present research state that the cell fluid model is suitable for the description of a first-order phase transition. The interaction potential of such a model, in addition to the attractive and repulsive interactions (such as the Morse potential), should include an additional repulsive interaction (in a reference system). The use of the supplementary interaction enables studying a phase behavior of the model in wide ranges of the density and the temperature.

A feature of the proposed approach is the use of the grand canonical ensemble, in which the temperature and the chemical potential are independent variables. First, the equation of state of the cell fluid model is obtained in terms of these variables and then transposed to the temperature-density plane. For this purpose, we derived and solved the equation, which relates the average number of particles (density) to the chemical potential. The solutions are functions of the temperature. Such dependence is found to be substantially nonlinear. Moreover, it implies the limited lower and upper ranges of the density and the chemical potential. We have proved that the minimum and maximum admissible values of the chemical potential approach each other below the critical temperature. The estimated value of the temperature T^* , at which they coincide, is $T^* \approx 0.38T_c$ (for the sodium-specific interaction potential parameters given in [14]). The conclusion on the existence of a first-order phase transition in the temperature region $T^* < T < T_c$, as well as the absence of the liquid-gas phase transition in the temperature region $T \leq T^*$, is obvious. The temperature T^* can be interpreted as the triple point temperature. We obtain both the

maximum density value n_{max} for the liquid phase and the minimum density value in the gaseous phase n_{min} (formula (68)). Each of these densities corresponds to the temperature specified in formula (66).

The proposed method for calculating the phase behavior can be extended to other systems with the known parameters of interaction potentials.

The equation obtained in this paper is not suitable near the critical point ($\tau < \tau^* \approx 10^{-2}$). In this case, one should count the effects of long-range fluctuations, since they play a major role in the description of the critical region above and below the critical point. In this regard, there are theoretical approaches [4, 17–19] and experiments [20–22] confirming the presence of the non-classical critical exponents of compressibility, heat capacity, correlation length, etc. We have also considered fluctuations (within the approach represented in the present paper) based on the calculation of the grand thermodynamic potential and on the consideration of the contributions of the collective variables $\rho_{\mathbf{k}}$ with $|\mathbf{k}| \neq 0$ [11].

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ФАЗОВА ПОВЕДІНКА МОДЕЛІ КОМІРКОВОГО ПЛІНУ З МОДИФІКОВАНИМ ПОТЕНЦІАЛОМ МОРЗЕ
Резюме

У роботі здійснено теоретичний опис фазового переходу першого роду коміркової моделі плинку із модифікованим потенціалом Морзе та додатковою відштовхувальною взаємодією. У формалізмі великого канонічного ансамблю розраховано рівняння стану системи у змінних хімпотенціал-температура та густина-температура для широкого діапазону густини і температури. Досліджено поведінку хімічного потенціалу як функції температури та густини. Виявлено максимально і мінімально допустимі значення хімпотенціалу, які наближаються одне до одного зі зменшенням температури. Встановлено існування фазового переходу рідина-газ в обмеженій області температур нижче критичної T_c .