1. Introduction
A crucial part of the theory of phase transitions in multiparticle systems is the elaboration of functional methods. The study of microscopic mechanisms leading to the diversity of the phase behavior in mixtures is relevant for prognosticating the phase diagrams of systems containing particles of different species. The results obtained by both experimental and theoretical methods are essential in this regard. Among the former are the works [1–3] by L.A. Bulavin. We dedicate the present article to the occasion of his 75th birthday.

Theoretical approaches include publications [4, 5], where the description of multicomponent systems is carried out within the mean-field formalism, and work [6], where the study of a binary system is performed in a more general case. The compilation [7, 8] proposes an original approach to explain phase transitions and critical phenomena, which provides an exact functional representation of the grand partition function of a multicomponent model in the method of collective variables [9] with the reference system. There, a hard-sphere system is the reference system, and the interaction potential contains repulsive and attractive parts. The obtained results were generalized to the case of the Coulomb interaction (RPM) model [10]. In [11, 12], the behavior of a binary symmetric mixture was investigated in the framework of that approach near the critical point using non-Gaussian distributions.

More than 60 years ago, experiments on single fluids identified distinct liquid-like and gas-like structures under supercritical conditions [13]. Since then, the interest of the scientific community in the comprehensive study [14–16] of supercritical fluids for their widespread technological applications [17, 18] has been steadily increasing due to their high density, solubility, and transport properties. The line between gas-like and liquid-like structures – the Widom line [19] – is an extension to the coexistence curve in the supercritical region, which is characterized by maxima in the thermodynamic response functions. Over the past decade, this crossover line and the properties of supercritical single fluids have been actively investigated [20, 21]. Recently, M. Raju et al. have presented an evidence for the existence of Widom lines in binary mixtures from molecular dynamics simulations [22].
The aim of the present article is a description of the phase behavior of a binary fluid in the supercritical region using the cell fluid model [23, 24]. In contrast to the functional approaches mentioned above, we use a “soft repulsion” as a feature of the reference system. This provides calculating the grand partition function of the model within a single approach of the method of collective variables. The present work summarizes the results of [25] in the case of an asymmetric binary system. We have found that the critical temperature of the mixture is a function of its composition, described a method for calculating the equation of state of the mixture, and shown its pressure behavior along the Widom line.

2. Calculating the Grand Partition Function of a Binary Asymmetric System

We use the results of [25] to describe the properties of a binary system of particles. Let the volume $V$ contain $N_a$ particles of species $a$ and $N_b$ particles of species $b$. The interaction potentials between particles of each sort are modeled as follows:

$$U_\delta(r) = C_{H}^\delta \left\{ A_\delta e^{-n_0^{(a)}(r_\delta - R_0^{(a)})/\alpha_\delta} + e^{-\gamma_s(r_\delta - R_0^{(b)})/\alpha_s} - 2e^{-(r_\delta - R_0^{(b)})/\alpha_\delta} \right\}. \tag{1}$$

In the latter expression, the index $\delta = a, b$ labels the particle species. For the normalization constants

$$C_{H}^\delta = D \frac{n_0^{(a)}}{n_0^{(\delta)}}; \quad A_\delta = \frac{2 - \gamma_\delta}{n_0^{(\delta)}}, \tag{2}$$

we have the following conditions: 1) the minimum of $U_\delta(r)$ is at $r_\delta = R_0^{(\delta)}$, 2) its absolute value equals the energy of dissociation -- $D$. For simplicity, assume that $\alpha_\delta = \alpha_\delta = \alpha$ is the effective interaction radius, and $R_0^{(a)} = R_0^{(b)} = R_0$. Moreover, we use $R_0$-units to measure all the distance quantities. The interaction potentials $U_a(r)$ and $U_b(r)$ differ from each other by the parameters $\gamma_\delta \neq \gamma_\delta$ and $n_0^{(a)} \neq n_0^{(b)}$. The values of these parameters used in the present research are given in Appendix A. However, they might be changed to reflect other particular systems. The fluid system is henceforth modeled as a cell fluid [26], in which the total volume $V$ of the system is divided into $N_v$ cubic cells each of the side $c$ and the volume $v = c^3$. The lattice analog of (1) is expressed as

$$U_{112}^{(\delta)} = C_{H}^{(\delta)} \left\{ A_\delta e^{-n_0^{(112-a)}(r_{112} - R_0^{(112-a)})/\alpha_\delta} + e^{-\gamma_s(r_{112} - R_0^{(112-b)})/\alpha_s} - 2e^{-(r_{112} - R_0^{(112-b)})/\alpha_\delta} \right\}. \tag{3}$$

Here, $\alpha_R = \alpha/R_0$ is a dimensionless quantity, $l_{112} = |l_1 - l_2|$ is a distance between the cell vectors $l_1, l_2 \in \Lambda$:

$$\Lambda = \{ l = (l_x, l_y, l_z) | |l| = c n_i ; \ n_i = 1, 2, ..., N_i; \ i = x, y, z; \ N_i = (N_v)^{1/3} \}. \tag{4}$$

In the thermodynamic limit $V \to \infty$, $N_v \to \infty$, $v = V/N_v = \text{const}$. The Fourier transform of (3) has the form

$$\Phi_\delta(k) = \Psi_\delta(k) + \Phi_\delta^{(r)}(k) - \Phi_\delta^{(o)}(k), \tag{5}$$

where both $\Phi_\delta^{(r)}(k)$ and $\Psi_\delta(k)$ are the repulsive parts of the interaction between species $\delta$, and $\Phi_\delta^{(o)}(k)$ is the attraction. We have

$$\Phi_\delta(k) = C_{H}^{(\delta)} 8\pi e^{\gamma_s/\alpha_s} \left( \frac{\alpha_R}{\gamma_s} \frac{n_0^{(a)}}{n_0^{(\delta)}} \right)^2 \left[ 1 + \left( \frac{\alpha_R}{\gamma_s} \frac{n_0^{(a)}}{c} \right)^2 \right]^{-2}, \tag{6}$$

$$\Phi_\delta^{(r)}(k) = C_{H}^{(\delta)} 16\pi e^{\gamma_s/\alpha_s} \left( \frac{\alpha_R}{\gamma_s} \frac{n_0^{(a)}}{c} \right)^2 \left[ 1 + \left( \alpha_R c k \right)^2 \right]. \tag{7}$$

Recall that $\delta = a, b$. According to the results of [25], we write the expression for the grand partition function of a binary cell fluid model as follows:
Here, \( \tilde{\mu}_\delta = \mu_4 - \mu_3^* \beta^{(5)} / \beta, \) \( \mu_3^* \) is a constant, and \( \beta^{(5)} \) is the inverse critical temperature of species \( \delta \) \((\delta = a, b)\). The effective potentials of interaction \([25]\) read

\[
W_\delta(k) = \Phi_\delta^{(0)}(k) - \Phi_\delta^{(1)}(k) - \Psi_\delta(k) + \frac{\beta^{(5)}}{\beta} \Psi_\delta(0),
\]

\[
D_\delta(k) = a_2 - \frac{1}{\beta W_\delta(k)}, \quad D_\delta(k) = b_2 - \frac{1}{\beta W_\delta(k)}.
\]

The cumulants \( a_n \) are as follows:

\[
a_0 = \ln T_0(\alpha^*_a, p_a),
\]

\[
a_1 = T_1(\alpha^*_a, p_a) / T_0(\alpha^*_a, p_a),
\]

\[
a_2 = T_2(\alpha^*_a, p_a) / T_1(\alpha^*_a, p_a) - a_1^2,
\]

\[
a_3 = T_3(\alpha^*_a, p_a) / T_2(\alpha^*_a, p_a) - a_1^3 + 3a_1a_2,
\]

\[
a_4 = T_4(\alpha^*_a, p_a) / T_3(\alpha^*_a, p_a) - a_1^4 - 6a_1^2a_2 - 4a_1a_3 - 3a_2^2,
\]

where the special functions \( T_n(\alpha^*_a, p_a) \) read

\[
T_n(\alpha^*_a, p_a) = \sum_{m=0}^{\infty} \frac{(\alpha^*_a)^m}{m!} m^n e^{-p_a m^2}.
\]

Here, \( \alpha^*_a = v \exp[\beta^{(0)} / \mu_a] \), and the parameter \( p_a \) is expressed via the quantity \( \Psi_a(0) \):

\[
p_a = \frac{1}{2} \beta^{(0)} \Psi_a(0).
\]

So, it depends on the parameters \( n_0^{(a)} \) and \( \gamma_a \) of the interaction potential \( U_1^{(a)} \) given by (3).

The cumulants \( b_n \) are expressed by the formulas similar to (9), where the special functions \( S_n(\alpha^*_b, p_b) \)

\[
S_n(\alpha^*_b, p_b) = \sum_{m=0}^{\infty} \frac{(\alpha^*_b)^m}{m!} m^n e^{-p_b m^2}
\]

are substituted for the functions \( T_n(\alpha^*_a, p_a) \), \( \alpha^*_b = v \exp[\beta^{(0)} / \mu_b] \), and \( p_b \) as is follows:

\[
p_b = \frac{1}{2} \beta^{(0)} \Psi_b(0).
\]

At the present stage, expression (7) for the grand partition function does not contain any approximations, but has infinite series in the exponent. To deal with this case, we use the traditional approximation for the phase transition theory, assuming that \( a_n \) and \( b_n \) with \( n \geq 5 \) are zero. In general, the calculation scheme below allows us to account for the higher powers of the variable \( \rho_k^{(5)} \), as we did in [27] when investigating the second-order phase transition for the Ising model.

So, we restrict the problem to the approximation of the \( \rho^s \)-model, make the change of variables to eliminate the third power of variables \( \rho_k^{(5)} \), and get

\[
\Xi = \sqrt{n} g_v \int (dp^{(a)}) e^{N \nu \rho^{(a)}} \exp[E(M_a, \rho_k^{(a)})] \times \int (dp^{(b)}) e^{N \nu \rho^{(b)}} \exp[E(M_b, \rho_k^{(b)})].
\]

For \( E^{(a)} \), we have

\[
E^{(a)} = a_0 - \frac{\beta \tilde{\mu}_a^2}{2W_a(0)} + m_a \left( a_1 + \frac{\tilde{\mu}_a}{W_a(0)} \right) + \frac{1}{2} m_a^2 d_a(0) + \frac{a_1^4}{8a_2},
\]

\[
E^{(b)} = b_0 - \frac{\beta \tilde{\mu}_b^2}{2W_b(0)} + m_b \left( b_1 + \frac{\tilde{\mu}_b}{W_b(0)} \right) + \frac{1}{2} m_b^2 d_b(0) + \frac{b_1^4}{8b_2},
\]

\[
\tilde{\mu}_a = \frac{M_a - a_1}{m_a d_a(0)} + \frac{a_1^3}{a_2^2},
\]

\[
\tilde{\mu}_b = \frac{M_b - b_1}{m_b d_b(0)} + \frac{b_1^3}{b_2^2},
\]

here \( m_a = -\frac{a_2}{a_1}, m_b = -\frac{b_2}{b_1} \). The functions \( E(M_a, \rho_k^{(5)}) \) are given by

\[
E(M_a, \rho_k^{(a)}) = N^{\frac{1}{2}} M_a p_0^{(a)} + \frac{1}{2} \sum_{k \in \mathcal{B}_c} d_u(k) \rho_k^{(a)} \rho_{-k}^{(a)} + \frac{a_4}{24 N^2} \sum_{k_1, \ldots, k_4} \rho_{k_1}^{(a)} \rho_{k_2}^{(a)} \rho_{k_3}^{(a)} \rho_{k_4}^{(a)} \delta_{k_1 \ldots k_4},
\]

\[
E(M_b, \rho_k^{(b)}) = N^{\frac{1}{2}} M_b p_0^{(b)} + \frac{1}{2} \sum_{k \in \mathcal{B}_c} d_u(k) \rho_k^{(b)} \rho_{-k}^{(b)} + \frac{b_4}{24 N^2} \sum_{k_1, \ldots, k_4} \rho_{k_1}^{(b)} \rho_{k_2}^{(b)} \rho_{k_3}^{(b)} \rho_{k_4}^{(b)} \delta_{k_1 \ldots k_4}.
\]

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The quantities $d_3(k)$ are expressed by

$$d_a(k) = \tilde{a}_2 - \frac{1}{\beta W_a(k)}, \quad \tilde{a}_2 = a_2 - \frac{a_2^2}{2a_4},$$

$$d_b(k) = \tilde{b}_2 - \frac{1}{\beta W_b(k)}, \quad \tilde{b}_2 = b_2 - \frac{b_2^2}{2b_4}. \quad (18)$$

According to (6), we have

$$\Phi^{(a)}_\delta(0) = B_\delta \Phi^{(r)}_\delta(0),$$

$$\Psi^{(a)}_\delta(0) = A^{(a)}_\gamma \Phi^{(r)}_\delta(0),$$

$$B_\delta = 2^{3/2} \exp \left( \frac{1 - \gamma_\delta}{\alpha_R} \right),$$

$$A^{(a)}_\gamma = A_\delta \left( \frac{\gamma_\delta}{\gamma_0(0)} \right)^3 \exp \left[ \frac{n_0(0) - \gamma_\delta}{\alpha_R} \right]. \quad (19)$$

So, we can rewrite $p_a$ and $p_b$ given by (12) and (14) as follows:

$$p_a = \frac{1}{2} \beta c \Phi^{(r)}_\delta(0) \xi^{(a)}_\gamma,$$

$$p_b = \frac{1}{2} \beta c \Phi^{(r)}_\delta(0) \xi^{(b)}_\gamma, \quad (20)$$

and

$$W_a(0) = \Phi^{(r)}_\delta(0) [B_a - 1 + \tau_a \xi^{(a)}_\gamma],$$

$$W_b(0) = \Phi^{(r)}_\delta(0) [B_b - 1 + \tau_b \xi^{(b)}_\gamma]. \quad (21)$$

The quantities $\tau_a$ and $\tau_b$ are the relative temperatures of pure components of the mixture (separately for species $a$ and $b$, respectively):

$$\tau_a = \frac{T - T^{(a)}_c}{T^{(a)}_c}, \quad \tau_b = \frac{T - T^{(b)}_c}{T^{(b)}_c}. \quad (22)$$

Obviously, the critical temperature of the mixture $T_c$ is different from $T^{(a)}_c$. Taking that into account, we write the following:

$$\tau_a = \frac{\tau T_c}{T^{(a)}_c} + \frac{T_c - T^{(a)}_c}{T^{(a)}_c},$$

$$\tau_b = \frac{\tau T_c}{T^{(b)}_c} + \frac{T_c - T^{(b)}_c}{T^{(b)}_c}, \quad (23)$$

where $\tau$ is the relative temperature of the mixture:

$$\tau = \frac{T - T_c}{T_c}. \quad (24)$$

From (22) and (24), we obtain

$$W_a(0) = \Phi^{(r)}_\delta(0) \left[ B_a - 1 + \tau A^{(a)}_\gamma \frac{T_c - T^{(a)}_c}{T^{(a)}_c} + \frac{T_c - T^{(a)}_c}{T^{(a)}_c} \right],$$

$$W_b(0) = \Phi^{(r)}_\delta(0) \left[ B_b - 1 + \tau A^{(b)}_\gamma \frac{T_c - T^{(b)}_c}{T^{(b)}_c} + \frac{T_c - T^{(b)}_c}{T^{(b)}_c} \right]. \quad (25)$$

In the boundary case, either $T_c = T^{(a)}_c$ or $T_c = T^{(b)}_c$, the expressions given by (25) transform into (21). The quantities $T^{(a)}_c$ are defined from the conditions $d_a(0) = 0$ and are equal to

$$k_B T^{(a)}_c = a_2 W_a(0, T^{(a)}_c) = 2 \Phi^{(r)}_\delta(0) (B_a - 1),$$

$$k_B T^{(b)}_c = b_2 W_b(0, T^{(b)}_c) = 2 \Phi^{(r)}_\delta(0) (B_b - 1). \quad (26)$$

Note that, because of (21), we can use the equalities

$$\Phi^{(r)}_\delta(0) A^{(a)}_\gamma = 2 p_a k_B T^{(a)}_c,$$

$$\Phi^{(r)}_\delta(0) A^{(b)}_\gamma = 2 p_b k_B T^{(b)}_c \quad (27)$$

to find the critical temperature of the mixture.

3. The Zero-Mode Approximation

Recently in [25], we have shown that the zero-mode approximation describes well the phase behavior of a one-component fluid. It is a mean-field-type approximation considering the contribution from the variable $\rho_k$ at $k = 0$. The contributions from $\rho_k$ at $k \neq 0$ are important near the critical point. Let us investigate the role of $\rho_0^{(d)}$ in the formation of a phase diagram of the mixture.

The grand partition function of the mixture in the zero-mode approximation is as follows:

$$\Xi_0 = g^{(a)}_V g^{(b)} \exp \left[ N_\gamma \left( E^{(a)}_\mu + E^{(b)}_\mu + E_a(\tilde{\rho}_a) + E_b(\tilde{\rho}_b) \right) \right]. \quad (28)$$

The expressions of $E^{(d)}_\mu$ are given in (16). For $E_0(\tilde{\rho}_0)$, we have

$$E_a(\tilde{\rho}_a) = M_a \tilde{\rho}_a + \frac{1}{2} d_a(0) \tilde{\rho}_a^2 + \frac{a_4}{24} \tilde{\rho}_a^4,$$

$$E_b(\tilde{\rho}_b) = M_b \tilde{\rho}_b + \frac{1}{2} d_b(0) \tilde{\rho}_b^2 + \frac{b_4}{24} \tilde{\rho}_b^4. \quad (29)$$

It is convenient to use the Laplace method [28] to calculate (28). Thereby, the values $\tilde{\rho}_a$ and $\tilde{\rho}_b$ correspond
to maxima of the function $E_0(\hat{\rho}_a)$ and $E_0(\hat{\rho}_b)$, respectively. So, the following equations determine $\hat{\rho}_a$ and $\hat{\rho}_b$:

$$M_a + d_a(0)\hat{\rho}_a + \frac{a_4}{6}\hat{\rho}_a^3 = 0,$$

$$M_b + d_b(0)\hat{\rho}_b + \frac{b_4}{6}\hat{\rho}_b^3 = 0. \tag{30}$$

Equalities (27) define the critical temperatures of each subsystem, which are calculated in [25]. Expression (28) contains independent contributions from the particles of different species.

Now, we introduce the mixing parameter $x$ as follows:

$$\hat{\rho}_a = x\rho_+ , \quad \hat{\rho}_b = (1 - x)\rho_+ . \tag{31}$$

It is easy to see that

$$\rho_+ = \hat{\rho}_a + \hat{\rho}_b , \quad x = \frac{\hat{\rho}_a}{\hat{\rho}_a + \hat{\rho}_b} , \quad 1 - x = \frac{\hat{\rho}_b}{\hat{\rho}_a + \hat{\rho}_b} . \tag{32}$$

The mixing parameter $x$ is like the concentration in a different space. In Section 4, we show the relation between the parameter $x$ and the concentration of a solution. In terms of $\rho_+$ and $x$, expressions (29) have the form

$$E_a(x, \rho_+) = M_a x \rho_+ + \frac{1}{2} d_a(0) x^2 \rho_+^2 + \frac{a_4}{24} x^4 \rho_+^4 ,$$

$$E_b(x, \rho_+) = M_b (1 - x) \rho_+ + \frac{1}{2} d_b(0) (1 - x)^2 \rho_+^2 + \frac{b_4}{24} (1 - x)^4 \rho_+^4 + \frac{b_4}{24} (1 - x)^4 \rho_+^4 . \tag{33}$$

Their sum (see (28)) is as follows:

$$E_{ab}(x, \rho_+) = M_{ab} + \frac{1}{2} D_{ab} \rho_+^2 - a_+ \rho_+^4 , \tag{34}$$

where we use notations

$$M_{ab} = xM_a + (1 - x)M_b ,$$

$$D_{ab} = x^2 d_a(0) + (1 - x)^2 d_b(0) , \tag{35}$$

$$a_+ = -x^4 a_4 - (1 - x)^4 b_4 .$$

In terms of $\rho_+$ and $x$, the grand potential of the mixture reads

$$\Omega = -k_B T \ln \Xi_0(x, \rho_+) . \tag{36}$$

In order to minimize it with respect to $\rho_+$, we have to solve the equation

$$\frac{\partial E_{ab}(x, \rho_+)}{\partial \rho_+} = 0 , \tag{37}$$

namely,

$$M_{ab} = -D_{ab}(x, \tau) \rho_+ + \frac{a_+}{6} \rho_+^3 . \tag{38}$$

An equation of this type also holds for a single system. Equation (38) is peculiar for the coefficients $D_{ab}(x, T)$ and $a_+(x)$ which are functions of the mixing parameter $x$. Moreover, $D_{ab}$ also depends on the relative temperature of the mixture $\tau$, while the relative temperatures $\tau_a$ and $\tau_b$ characterize pure species $a$ and $b$, respectively.

The effective chemical potential of the mixture $M_{ab}$ is a variable of the same type as either $M_a$ for the subsystem of particles of species $a$, or $M_b$ for species $b$. Each of them associate with $\mu_a$ and $\mu_b$. Using the quantity $M_{ab}$ (or $M_a$, $M_b$), convenient, because the first-order phase transition occurs at $M_a = 0$ for the subsystem of particles of species $a$, $M_b = 0$ for the subsystem of particles of species $b$ and $M_{ab} = 0$ for the mixture of particles of both species $a$ and $b$.

Both Eqs. (38) and (30) are of the same type. Therefore, the condition

$$D_{ab}(x, T_c) = 0 \tag{39}$$

defines the critical temperature of the liquid-gas phase transition of a binary system. Taking (35) into account, we obtain the equation for $T_c = T_c(x)$:

$$x^2 \left[ \tilde{a}_2 - \frac{1}{\beta_c \Xi_a(0, T_c)} \right] + (1 - x)^2 \left[ \tilde{b}_2 - \frac{1}{\beta_c \Xi_b(0, T_c)} \right] = 0 . \tag{40}$$

We use (26) and (27) to solve the latter equation and get

$$\tilde{a}_2 \Xi_a(0, T_c) = T_{ca} + 2\tilde{a}_2 p_a T_c , \tag{41}$$

$$\tilde{b}_2 \Xi_b(0, T_c) = T_{cb} + 2\tilde{b}_2 p_b T_c , \tag{42}$$

where

$$T_{ca} = T_c^{(a)} (1 - 2\tilde{a}_2 p_a) , \tag{42}$$

$$T_{cb} = T_c^{(b)} (1 - 2\tilde{b}_2 p_b) .$$
Then we rewrite (40) as follows:

$$w_2 w_a(0, T_c) b_2 W_b(0, T_c) - x^2 T_c b_2 W_b(0, T_c) + (1 - x)^2 T_c a_2 W_a(0, T_c) / a_2 = 0.$$  

(43)

Here, expression (40) is multiplied by $W_a(0, T_c) \times W_b(0, T_c) \neq 0$ and, for $w_2$, we read

$$w_2 = \frac{x^2}{b_2} + \frac{(1 - x)^2}{a_2}.$$  

(44)

Substituting expressions (41) in formula (43), we obtain the quadratic equation

$$f_2 T_c^2 + f_1 T_c + f_0 = 0,$$  

(45)

where

$$f_2 = 4 w_2 p_0 a_2 b_2, f_1 = 2 x^2 p_0 - 2(1 - x) p_a,$$

(46)

$$f_0 = a_2 T_c.$$  

The critical temperature of the mixture as a function of the mixing parameter $x \in [0, 1]$ is shown in Fig. 1.

The parameters of the interaction used for the plotting are given in Appendix 5. Note that, at $x = 0$, we have a single system of species $b$, for which $T_c^{(b)} = 4.8028$. The case $x = 1$ means the existence of a single system of species $a$, for which $T_c^{(a)} = 3.9502$.

The reduced form of Eq. (38) is

$$\rho^3 + \rho \rho_a + q_a = 0,$$  

(47)

where

$$\rho_a = -6 D_{ab}(x, T) a_+^{-1}, \quad q_a = -6 M_{ab} a_+^{-1}.$$  

(48)

For all $\tau > 0$, Eq. (47) has a single solution

$$\rho = \left(\frac{3}{a_+}\right)^{1/3} (A^{1/3} + B^{1/3}),$$  

(49)

where

$$A = M_{ab} + \sqrt{M_{ab}^2 - M_{0a} D_{ab}},$$

$$B = M_{ab} - \sqrt{M_{ab}^2 - M_{0a} D_{ab}}.$$  

(50)

In these expressions,

$$M_{0a} = \frac{8}{9 a_+}.$$  

(51)

We find the temperature dependence of $D_{ab}$ from (35). Write an identity $D_{ab} = D_{ab}(x, T) - D_{ab}(x, T_c)$, namely, according to (39), subtract zero from $D_{ab}$. Then

$$D_{ab} = x^2 \left(\frac{T}{W_a(0, T_c)} - \frac{T}{W_a(0)}\right) +$$

$$+ (1 - x)^2 \left(\frac{T}{W_a(0, T_c)} - \frac{T}{W_b(0)}\right).$$  

(52)

In view of the relation

$$\tilde{a}_2 W_a(0) = T_{ca} + 2 \tilde{a}_2 p_a T_c =$$

$$= \tilde{a}_2 W_a(0) + 2 \rho \tilde{a}_2 p_a T_c,$$

$$\tilde{b}_2 W_b(0) = T_{cb} + 2 \tilde{b}_2 p_b T_c =$$

$$= \tilde{b}_2 W_b(0) + 2 \rho b_2 p_b T_c,$$  

(53)

we obtain $D_{ab}$ in a more compact form

$$D_{ab} = x^2 \tau \left(\frac{W_a(0, T_c)}{a_2 W_a(0, T_c) \beta_a W_b(0) +} - 2 \rho a_2 p_a \right)$$

$$+ (1 - x)^2 \tau \left(\frac{W_b(0, T_c)}{b_2 W_b(0, T_c) \beta_b W_a(0) +} - 2 \rho b_2 p_b \right).$$  

(54)

The coefficient $D_{ab}$ is negative for all $\tau > 0$ and positive at $T < T_c$. It is proportional to $\tau$, like a similar coefficient in the case of a single system [25].
by using the well-known formula
\[ \rho(T) \text{ of the method suggested in work [25].} \]

The solutions \( \rho \) of Eq. (47) are similar to solutions of the analogous equation in the case of a single system (see [25]). The difference is that the critical temperature of the mixture depends on the mixing parameter \( x \), as well as the coefficient \( a_+ = a_+(x) \). The latter case is shown in Fig. 2.

In the temperature range \( T < T_c \), Eq. (47) has three real solutions, which can be found with the use of the method suggested in work [25].

The solutions \( \rho_+ \) are functions of the temperature \( T \), the effective chemical potential \( M_{ab} \), and the mixing parameter \( x \). Therefore, it is possible to visualize the function \( \rho_+(T, M_{ab}, x) \) only as separate projections on the surfaces:

\[
\begin{align*}
\rho_+ &\big|_{T = \text{const}} = \rho_+^{(1)}(M_{ab}, x), \\
\rho_+ &\big|_{x = \text{const}} = \rho_+^{(2)}(M_{ab}, T), \\
\rho_+ &\big|_{M_{ab} = \text{const}} = \rho_+^{(3)}(T, x).
\end{align*}
\]

Each of these projections reflects a particular physical process. The quantity \( \rho_+^{(3)} \) is of importance, since it determines the Widom line of a binary mixture. It is easy to verify that, for all \( T > T_c \) at \( M_{ab} = 0 \), we have \( \rho_+(M_{ab} = 0) = 0 \). Then we find the pressure, by using the well-known formula

\[ PV = k_B T \ln \Xi. \]

**Fig. 2.** Plot of the coefficient \( a_+ \) given in (35) as a function of \( x \)

We obtain

\[ P v = k_B T \left[ \frac{1}{N_v} \ln (g_v^{(a)} g_v^{(b)}) + E_W^{(a)} + E_W^{(b)} \right], \]

where, according to (16), we have

\[
\begin{align*}
E_W^{(a)} &= a_0 - \frac{\beta}{2} (\mu_a^{(W)})^2 + m_a (a_1 + \mu_a^{(W)}) + \\
&\quad + \frac{m_a^2 d_a(0)}{2} + \frac{a_1^4}{8a_4^3}, \\
E_W^{(b)} &= b_0 - \frac{\beta}{2} (\mu_b^{(W)})^2 + m_b (b_1 + \mu_b^{(W)}) + \\
&\quad + \frac{m_b^2 d_b(0)}{2} + \frac{b_1^4}{8b_4^3},
\end{align*}
\]

moreover,

\[
\begin{align*}
\mu_a^{(W)} &= -a_1 - m_a d_a(0) + \frac{a_1^3}{a_4}, \\
\mu_b^{(W)} &= -b_1 - m_b d_b(0) + \frac{b_1^3}{b_4}.
\end{align*}
\]

The temperature dependence hides in the quantities \( d_0(0) \). It is easy to see from the above formulas that the pressure along the Widom line is a function of the relative temperature \( \tau \) and the parameter \( x \). The dependence on \( x \) eventuates from \( d_0(0) \) containing the critical temperature \( T_c(x) \), which is a function of the mixing parameter:

\[
\begin{align*}
d_a(0) &= -\tau \tilde{\alpha} T_c \frac{1 - \omega_{0a} p_c^{(a)}}{1 + \omega_{0a} \tau_a}, \\
&= -\tilde{\alpha} T_c \frac{T_c^{(a)}}{T_c^{(a)}} \frac{1 - \omega_{0a} p_c^{(a)}}{1 + \omega_{0a} \tau_a}, \\
d_b(0) &= -\tau \tilde{\beta} T_c \frac{1 - \omega_{0b} p_c^{(b)}}{1 + \omega_{0b} \tau_b}, \\
&= -\tilde{\beta} T_c \frac{T_c^{(b)}}{T_c^{(b)}} \frac{1 - \omega_{0b} p_c^{(b)}}{1 + \omega_{0b} \tau_b},
\end{align*}
\]

where \( \tau_a \) and \( \tau_b \) are given in (22). For \( \omega_k \), we have

\[
\omega_{0a} = 2\tilde{\alpha}, \quad \omega_{0b} = 2\tilde{\beta}.
\]

At \( x = 0 \) and \( x = 1 \), we get, respectively, the Widom lines of a single subsystem of species \( b \) and \( a \). For all \( x \in (0, 1) \), the set of Widom lines forms a surface represented in Fig. 3.
4. The Equation for Density

The general principles of statistical mechanics give the equation for average numbers of particles of both species \( \langle N_a \rangle \) and \( \langle N_b \rangle \). Denote

\[
n_a = \frac{\langle N_a \rangle}{N_v}, \quad n_b = \frac{\langle N_b \rangle}{N_v}.
\]

Then, according to [23, 25], we have

\[
n_a = \frac{1}{N_v} \frac{\partial \ln \Xi}{\partial \mu_a}, \quad n_b = \frac{1}{N_v} \frac{\partial \ln \Xi}{\partial \mu_b}.
\]

With regard for (28), we find

\[
n_a = -M_a + n_c^{(a)} + \tilde{a}_2 \gamma a \rho_n, \quad n_b = -M_b + n_c^{(b)} + \tilde{b}_2 \gamma b \rho_n.
\]

The quantities \( M_a, M_b \) are given in (30), which means that they are functions of \( \tau \) and \( \rho_n \). Equalities (30) yield

\[
x^3 \rho_n^3 + g_a x \rho_n + q_a = 0,
\]

where

\[
g_a = \frac{6 \tilde{a}_2}{a_4}, \quad q_a = \frac{6(n_c^{(a)} - n_a)}{a_4}.
\]

From (66), we have

\[
(1 - x)^3 \rho_n^3 + g_b (1 - x) \rho_n + q_b = 0,
\]

where

\[
g_b = \frac{6 \tilde{b}_2}{b_4}, \quad q_b = \frac{6(n_c^{(b)} - n_b)}{b_4}.
\]

Before writing the solutions of Eqs. (64) and (66), we introduce the total density of the mixture \( n_+ \) and the concentration \( \eta \) using the equations

\[
n_a = \eta n_+, \quad n_b = (1 - \eta) n_+.
\]

Then

\[
n_+ = n_a + n_b, \quad \eta = \frac{n_a}{n_+}, \quad 1 - \eta = \frac{n_b}{n_+}.
\]

From (64), we have

\[
x \rho_n = -2 \tilde{a} \cos \left( \frac{\alpha_n + \pi}{3} \right).
\]

From (66), we have

\[
\alpha_n = \arccos \left( \frac{n_c^{(a)} - \eta n_+}{n_c^{(a)}} \right), \quad \tilde{a} = \left( \frac{2 \tilde{a}_2}{a_4} \right)^{1/2}.
\]

From (66), we have

\[
(1 - x) \rho_n = -2 \tilde{b} \cos \left( \frac{\beta_n + \pi}{3} \right),
\]

where

\[
\beta_n = \arccos \left( \frac{n_c^{(b)} - (1 - \eta) n_+}{n_c^{(b)}} \right), \quad \tilde{b} = \left( \frac{2 \tilde{b}_2}{b_4} \right)^{1/2}.
\]

The sum of expressions (70) and (72) equals

\[
\rho_n = -2 \tilde{a} \cos \left( \frac{\alpha_n + \pi}{3} \right) - 2 \tilde{b} \cos \left( \frac{\beta_n + \pi}{3} \right).
\]

Note that \( \rho_n \) fails to be a function of the temperature. It has a restricted range, since \( \tilde{a} \) and \( \tilde{b} \) are finite quantities. The subtraction of (70) and (72) gives the equation

\[
x = \frac{1}{2} \left[ 1 + \frac{\tilde{a} \cos \left( \frac{\alpha_n + \pi}{3} \right) - \tilde{b} \cos \left( \frac{\beta_n + \pi}{3} \right)}{\tilde{a} \cos \left( \frac{\alpha_n + \pi}{3} \right) + \tilde{b} \cos \left( \frac{\beta_n + \pi}{3} \right)} \right],
\]

which allows us to find the relation between the mixing parameter \( x \) and the concentration \( \eta \) for an arbitrary value of the total density \( n_+ \).
5. Conclusions
In this article, we represent the investigation of the behavior of a binary asymmetric mixture at 
\( T > T_c \). Among the results is a two-dimensional analog of the Widom line for different values of the mixing parameter \( x \in [0,1] \). The equation of state of the system, which includes the dependence on the parameter \( x \), is calculated. This parameter links to the concentration and is also used to determine the critical temperature of the mixture. In the boundary cases \( x = 0 \) and \( x = 1 \), the formulas obtained here describe separately the subsystems of particles of species \( b \) and \( a \), respectively. In the case of \( x \in (0,1) \), we have a mixture of components, that is characterized by the critical temperature \( T_c \) (see Fig. 1). The Widom line shifts on the surface shown in Fig. 3, as the composition of the mixture changes.

APPENDIX A
Parameters of the Model
The following values of the interaction potential parameters are used for numerical calculations and plots.
For both species, \( a_s = \alpha_b = \alpha \), as well as \( R_0^{(a)} = R_0^{(b)} = R_0 = 5.3678 \), \( \alpha = 1.8167 \), \( \alpha_R = 0.3385 \), \( \gamma_b = 1.6500 \), \( n_0^{(a)} = 1.7255 \), \( \gamma_a = 1.6500 \), \( n_0^{(b)} = 1.7613 \).
The values (A2) give
\[ p_a = 1, \quad \alpha_a^* = 5, \]
see (12). This set of parameters eventuates in the following values of the coefficients \( a_s \) (see (11) and (18)): \( a_0 = 1.1220, \quad a_1 = 0.7506, \quad a_2 = 0.3413, \quad a_3 = 0.0265, \quad a_4 = -0.0407, \quad \tilde{a}_2 = 0.3500 \).
The values of the parameters \( \gamma_b \) and \( n_0^{(b)} \) of the potential \( U_b(r) \) differ from \( \gamma_a \) and \( n_0^{(a)} \):
\[ \gamma_b = 1.6000, \quad n_0^{(b)} = 1.7613. \]
They give
\[ p_b = 1, \quad \alpha_b^* = 5.5 \]
and the following values of the coefficients \( b_n \):
\[ b_0 = 1.1951, \quad b_1 = 0.7832, \quad b_2 = 0.3437, \quad b_3 = 0.0231, \quad b_4 = -0.0302, \quad \tilde{b}_2 = 0.3526. \]

The normalization constants given in (2) equal
\[ C_H^{(a)} = 1.2544, \quad A_a = 0.2217, \]
\[ C_H^{(b)} = 1.2938, \quad A_b = 0.2742. \]
The values of the critical temperatures of separate single systems of species \( a \) and species \( b \) are
\[ k_B T_c^{(a)} = 3.9502, \quad k_B T_c^{(b)} = 4.8028. \]

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ПОВЕДІНКА БІНАРНОЇ АСІМЕТРИЧНОЇ СУМІШІ ВЗАЄМОДІЮЧИХ ЧАСТИНОК В НАДКРИТИЧНІЙ ОБЛАСТІ

Резюме

Запропоновано метод опису фазової поведінки системи, яка складається із частинок двох сортів. Взаємодія кожного із сортів описується властивим йому потенціалом взаємодії, що містить відштовхувальну та притягальну частини. Асиметрічність забезпечується різними значеннями параметрів потенціалів взаємодії кожного із сортів. Проведено розрахунок великої статистичної суми бінарної системи в наближенні нульової моди. Для конкретних значень параметрів потенціалу взаємодії розраховано лінію критичних точок, які відповідають різним пропорціям компонент. Отримано рівняння, яке пов’язує введені нами параметри змішування μ і рівень концентрації системи. Знайдено явний вигляд виразу для тиску бінарної системи як функції відносної температури та параметра змішування μ для побудови лінії Відома. Встановлено, що для граничних значень цього параметра (μ = 0 і μ = 1) рівняння стану суміші переходять у рівняння стану однієї з окремих компонент.