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BEHAVIOR OF A BINARY ASYMMETRIC MIXTURE OF INTERACTING PARTICLES IN THE SUPERCRITICAL REGION

We propose a method for describing the phase behavior of a system consisting of particles of two sorts. The interaction of each species is described by interaction potentials containing the repulsive and attractive components. Asymmetry is ensured by different values of the interaction potentials of each sort. The grand partition function of a binary mixture is calculated in the zero-mode approximation. A line of critical points, which correspond to different proportions of the components, is calculated for specific values of parameters of the interaction potential. We have obtained an equation that relates the introduced mixing parameter x to the concentration of the system. An explicit expression of the pressure of the binary mixture is derived as a function of the relative temperature and the mixing parameter x to plot the Widom line. It is established that, for boundary values of this parameter ($x = 0$ and $x = 1$), the equation of state of a mixture turns into equations of state of its separate species.

Keywords: asymmetric binary mixture, cell fluid model, collective variables, equation of state, Widom line.

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:

$$U_\delta(r) = C_H^{(\delta)} \Big\{ A_\delta e^{-n_0^{(\delta)}(r_\delta - R_0^{(\delta)})/\alpha_\delta} + \\ + e^{-\gamma_\delta (r_\delta - R_0^{(\delta)})/\alpha_\delta} - 2e^{-(r_\delta - R_0^{(\delta)})/\alpha_\delta} \Big\}. \quad (1)$$

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

$$C_H^{(\delta)} = D \frac{n_0^{(\delta)}}{n_0^{(\delta)} + \gamma_\delta - 2}; \quad A_\delta = \frac{2 - \gamma_\delta}{n_0^{(\delta)}}, \quad (2)$$

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 $\alpha_a = \alpha_b = \alpha$ 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 $\gamma_a \neq \gamma_b$ 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

$$U_{l_{12}}^{(\delta)} = C_H^{(\delta)} \Big\{ A_\delta e^{-\frac{n_0^{(\delta)}(l_{12}-c)}{\alpha_R c}} + e^{-\frac{\gamma_\delta (l_{12}-c)}{\alpha_R c}} - \\ - 2e^{-\frac{l_{12}-c}{\alpha_R c}} \Big\}. \quad (3)$$

Here, $\alpha_R = \alpha/R_0$ is a dimensionless quantity, $l_{12} = |\mathbf{l}_1 - \mathbf{l}_2|$ is a distance between the cell vectors $\mathbf{l}_1, \mathbf{l}_2 \in \Lambda$:

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

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

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

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

$$\Psi_\delta(k) = C_H^{(\delta)} A_\delta 8\pi e^{\frac{n_0^{(\delta)}}{\alpha_R}} \left(\frac{\alpha_R}{n_0^{(\delta)}} \right)^3 \left[1 + \left(\frac{\alpha_R}{n_0^{(\delta)}} ck \right)^2 \right]^{-2}, \\ \Phi_\delta^{(r)}(k) = C_H^{(\delta)} 8\pi e^{\gamma_\delta/\alpha_R} \left(\frac{\alpha_R}{\gamma_\delta} \right)^3 \left[1 + \left(\frac{\alpha_R}{\gamma_\delta} ck \right)^2 \right]^{-2}, \quad (6) \\ \Phi_\delta^{(a)}(k) = C_H^{(\delta)} 16\pi e^{1/\alpha_R} \alpha_R^3 \left[1 + (\alpha_R ck)^2 \right]^{-2}.$$

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:

$$\Xi = g_V^{(a)} g_V^{(b)} \exp\left[N_v \left(a_0 - \frac{\beta \tilde{\mu}_a^2}{2W_a(0)} \right) \right] \times \\ \times \exp\left[N_v \left(b_0 - \frac{\beta \tilde{\mu}_b^2}{2W_b(0)} \right) \right] \int (dt_{\mathbf{k}}^{(a)})^{N_v} \times \\ \times \exp\left[N_v^{\frac{1}{2}} \left(\frac{\tilde{\mu}_a}{W_a(0)} + a_1 \right) t_0^{(a)} + \frac{1}{2} \sum_{\mathbf{k} \in \mathcal{B}_c} D_a(k) t_{\mathbf{k}}^{(a)} t_{-\mathbf{k}}^{(a)} + \right. \\ \left. + \sum_{n=3}^{\infty} \frac{a_n}{n!} N_v^{\frac{2-n}{n}} \sum_{\substack{\mathbf{k}_1, ..., \mathbf{k}_n \\ \mathbf{k}_i \in \mathcal{B}_c}} t_{\mathbf{k}_1}^{(a)} \dots t_{\mathbf{k}_n}^{(a)} \delta_{\mathbf{k}_1 + ... + \mathbf{k}_n} \right] \times \\ \times \int (dt_{\mathbf{k}}^{(b)})^{N_v} \exp\left[N_v^{\frac{1}{2}} \left(\frac{\tilde{\mu}_b}{W_b(0)} + b_1 \right) t_0^{(b)} + \right. \\ + \frac{1}{2} \sum_{\mathbf{k} \in \mathcal{B}_c} D_b(k) t_{\mathbf{k}}^{(b)} t_{-\mathbf{k}}^{(b)} + \sum_{n=3}^{\infty} \frac{b_n}{n!} N_v^{\frac{2-n}{n}} \times \\ \left. \times \sum_{\substack{\mathbf{k}_1, ..., \mathbf{k}_n \\ \mathbf{k}_i \in \mathcal{B}_c}} t_{\mathbf{k}_1}^{(b)} ... t_{\mathbf{k}_n}^{(b)} \delta_{\mathbf{k}_1 + ... + \mathbf{k}_n} \right]. \quad (7)$$

Here, $\tilde{\mu}_\delta = \mu_\delta - \mu^*_\delta \beta_{\rm c}^{(\delta)}/\beta$, μ^*_δ is a constant, and $\beta_{\rm c}^{(\delta)}$ is the inverse critical temperature of species δ ($\delta = a, b$). The effective potentials of interaction [25] read

$$W_\delta(k) = \Phi_\delta^{(a)}(k) - \Phi_\delta^{(r)}(k) - \Psi_\delta(k) + \frac{\beta_{\rm c}^{(\delta)}}{\beta}\Psi_\delta(0),$$
$$D_a(k) = a_2 - \frac{1}{\beta W_a(k)}, \quad D_b(k) = b_2 - \frac{1}{\beta W_b(k)}. \tag{8}$$

$$g_V^{(\delta)} = \prod_{\mathbf{k}\in\mathcal{B}_{\rm c}} (2\pi\beta W_\delta(k))^{-1/2}. \tag{9}$$

The cumulants a_n are as follows:

$$\begin{aligned}
a_0 &= \ln T_0(\alpha_a^*, p_a),\\
a_1 &= \frac{T_1(\alpha_a^*, p_a)}{T_1(\alpha_a^*, p_a)},\\
a_2 &= \frac{T_2(\alpha_a^*, p_a)}{T_1(\alpha_a^*, p_a)} - a_1^2,\\
a_3 &= \frac{T_3(\alpha_a^*, p_a)}{T_1(\alpha_a^*, p_a)} - a_1^3 + 3a_1a_2,\\
a_4 &= \frac{T_4(\alpha_a^*, p_a)}{T_1(\alpha_a^*, p_a)} - a_1^4 - 6a_1^2a_2 - 4a_1a_3 - 3a_2^2,
\end{aligned} \tag{10}$$

where the special functions $T_n(\alpha_a^*, p_a)$ read

$$T_n(\alpha_a^*, p_a) = \sum_{m=0}^{\infty} \frac{(\alpha_a^*)^m}{m!} m^n e^{-p_a m^2}. \tag{11}$$

Here, $\alpha_a^* = v\exp[\beta_{\rm c}^{(a)}\mu_a^*]$, and the parameter p_a is expressed via the quantity $\Psi_a(0)$:

$$p_a = \frac{1}{2}\beta_{\rm c}^{(a)}\Psi_a(0). \tag{12}$$

So, it depends on the parameters $n_0^{(a)}$ and γ_a of the interaction potential $U_{l_{12}}^{(a)}$ given by (3).

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

$$S_n(\alpha_b^*, p_b) = \sum_{m=0}^{\infty} \frac{(\alpha_b^*)^m}{m!} m^n e^{-p_b m^2} \tag{13}$$

are substituted for the functions $T_n(\alpha_a^*, p_a)$, $\alpha_b^* = v\exp[\beta_{\rm c}^{(b)}\mu_b^*]$, and p_b is as follows:

$$p_b = \frac{1}{2}\beta_{\rm c}^{(b)}\Psi_b(0). \tag{14}$$

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 $\rho_{\mathbf{k}}^{(\delta)}$, 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 ρ^4-model, make the change of variables to eliminate the third power of variables $\rho_{\mathbf{k}}^{(\delta)}$, and get

$$\Xi = g_v^{(a)} g_v^{(b)} \int (d\rho^{(a)})^{N_v} e^{N_v E_\mu^{(a)}} \exp[E(M_a, \rho_{\mathbf{k}}^{(a)})] \times$$
$$\times \int (d\rho^{(b)})^{N_v} e^{N_v E_\mu^{(b)}} \exp[E(M_b, \rho_{\mathbf{k}}^{(b)})]. \tag{15}$$

For $E_\mu^{(\delta)}$, we have

$$\begin{aligned}
E_\mu^{(a)} &= a_0 - \frac{\beta\tilde{\mu}_a^2}{2W_a(0)} + m_a\left(a_1 + \frac{\tilde{\mu}_a}{W_a(0)}\right) +\\
&+ \frac{1}{2}m_a^2 d_a(0) + \frac{a_3^4}{8a_4^3},\\
E_\mu^{(b)} &= b_0 - \frac{\beta\tilde{\mu}_b^2}{2W_b(0)} + m_b\left(b_1 + \frac{\tilde{\mu}_b}{W_b(0)}\right) +\\
&+ \frac{1}{2}m_b^2 d_b(0) + \frac{b_3^4}{8b_4^3},\\
\frac{\tilde{\mu}_a}{W_a(0)} &= M_a - a_1 - m_a d_a(0) + \frac{a_3^3}{a_4^2},\\
\frac{\tilde{\mu}_b}{W_b(0)} &= M_b - b_1 - m_b d_b(0) + \frac{b_3^3}{b_4^2},
\end{aligned} \tag{16}$$

here $m_a = -\frac{a_3}{a_4}$, $m_b = -\frac{b_3}{b_4}$. The functions $E(M_\delta, \rho_{\mathbf{k}}^{(\delta)})$ are given by

$$\begin{aligned}
E(M_a, \rho_{\mathbf{k}}^{(a)}) &= N_v^{\frac{1}{2}} M_a \rho_0^{(a)} + \frac{1}{2}\sum_{\mathbf{k}\in\mathcal{B}_{\rm c}} d_a(k)\rho_{\mathbf{k}}^{(a)}\rho_{-\mathbf{k}}^{(a)} +\\
&+ \frac{a_4}{24}\frac{1}{N_v}\sum_{\substack{\mathbf{k}_1,\ldots,\mathbf{k}_4\\ \mathbf{k}_i\in\mathcal{B}_{\rm c}}} \rho_{\mathbf{k}_1}^{(a)}\ldots\rho_{\mathbf{k}_4}^{(a)}\delta_{\mathbf{k}_1\ldots\mathbf{k}_4},\\
E(M_b, \rho_{\mathbf{k}}^{(b)}) &= N_v^{\frac{1}{2}} M_b \rho_0^{(b)} + \frac{1}{2}\sum_{\mathbf{k}\in\mathcal{B}_{\rm c}} d_b(k)\rho_{\mathbf{k}}^{(b)}\rho_{-\mathbf{k}}^{(b)} +\\
&+ \frac{b_4}{24}\frac{1}{N_v}\sum_{\substack{\mathbf{k}_1,\ldots,\mathbf{k}_4\\ \mathbf{k}_i\in\mathcal{B}_{\rm c}}} \rho_{\mathbf{k}_1}^{(b)}\ldots\rho_{\mathbf{k}_4}^{(b)}\delta_{\mathbf{k}_1\ldots\mathbf{k}_4}.
\end{aligned} \tag{17}$$

The quantities $d_\delta(k)$ are expressed by

$$d_a(k) = \tilde{a}_2 - \frac{1}{\beta W_a(k)}, \quad \tilde{a}_2 = a_2 - \frac{a_3^2}{2a_4},$$
$$d_b(k) = \tilde{b}_2 - \frac{1}{\beta W_b(k)}, \quad \tilde{b}_2 = b_2 - \frac{b_3^2}{2b_4}. \tag{18}$$

According to (6), we have

$$\Phi_\delta^{(a)}(0) = B_\delta \Phi_\delta^{(r)}(0),$$
$$\Psi_\delta^{(a)}(0) = A_\gamma^{(\delta)} \Phi_\delta^{(r)}(0),$$
$$B_\delta = 2\gamma_\delta^3 \exp\left[\frac{1-\gamma_\delta}{\alpha_R}\right], \tag{19}$$
$$A_\gamma^{(\delta)} = A_\delta \left(\frac{\gamma_\delta}{n_0^{(\delta)}}\right)^3 \exp\left[\frac{n_0^{(\delta)} - \gamma_\delta}{\alpha_R}\right].$$

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

$$p_a = \frac{1}{2}\beta_{\rm c}^{(a)} \Phi_a^{(r)}(0) A_\gamma^{(a)}, \quad p_b = \frac{1}{2}\beta_{\rm c}^{(b)} \Phi_b^{(r)}(0) A_\gamma^{(b)}, \tag{20}$$

and

$$W_a(0) = \Phi_a^{(r)}(0)[B_a - 1 + \tau_a A_\gamma^{(a)}],$$
$$W_b(0) = \Phi_b^{(r)}(0)[B_b - 1 + \tau_b A_\gamma^{(b)}]. \tag{21}$$

The quantites τ_a and τ_b are the relative temperatures of pure components of the mixture (separately for species a and b, respectively):

$$\tau_a = \frac{T - T_{\rm c}^{(a)}}{T_{\rm c}^{(a)}}, \quad \tau_b = \frac{T - T_{\rm c}^{(b)}}{T_{\rm c}^{(b)}}. \tag{22}$$

Obviously, the critical temperature of the mixture $T_{\rm c}$ is different from $T_{\rm c}^{(\delta)}$. Taking that into account, we write the following:

$$\tau_a = \frac{\tau T_{\rm c}}{T_{\rm c}^{(a)}} + \frac{T_{\rm c} - T_{\rm c}^{(a)}}{T_{\rm c}^{(a)}},$$
$$\tau_b = \frac{\tau T_{\rm c}}{T_{\rm c}^{(b)}} + \frac{T_{\rm c} - T_{\rm c}^{(b)}}{T_{\rm c}^{(b)}}, \tag{23}$$

where τ is the relative temperature of the mixture:

$$\tau = \frac{T - T_{\rm c}}{T_{\rm c}}. \tag{24}$$

From (22) and (24), we obtain

$$W_a(0) = \Phi_a^{(r)}(0)\left[B_a - 1 + \tau A_\gamma^{(a)} \frac{T_{\rm c}}{T_{\rm c}^{(a)}} + \frac{T_{\rm c} - T_{\rm c}^{(a)}}{T_{\rm c}^{(a)}} A_\gamma^{(a)}\right],$$
$$W_b(0) = \Phi_b^{(r)}(0)\left[B_b - 1 + \tau A_\gamma^{(b)} \frac{T_{\rm c}}{T_{\rm c}^{(b)}} + \frac{T_{\rm c} - T_{\rm c}^{(b)}}{T_{\rm c}^{(b)}} A_\gamma^{(b)}\right]. \tag{25}$$

In the boundary case, either $T_{\rm c} = T_{\rm c}^{(a)}$ or $T_{\rm c} = T_{\rm c}^{(b)}$, the expressions given by (25) transform into (21). The quantities $T_{\rm c}^{(\delta)}$ are defined from the conditions $d_\delta(0) = 0$ and are equal to

$$k_{\rm B} T_{\rm c}^{(a)} = \tilde{a}_2 W_a(0, T_{\rm c}^{(a)}) = \tilde{a}_2 \Phi_a^{(r)}(0)(B_a - 1),$$
$$k_{\rm B} T_{\rm c}^{(b)} = \tilde{b}_2 W_b(0, T_{\rm c}^{(b)}) = \tilde{b}_2 \Phi_b^{(r)}(0)(B_b - 1). \tag{26}$$

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

$$\Phi_a^{(r)}(0) A_\gamma^{(a)} = 2p_a k_{\rm B} T_{\rm c}^{(a)},$$
$$\Phi_b^{(r)}(0) A_\gamma^{(b)} = 2p_b k_{\rm B} T_{\rm c}^{(b)} \tag{27}$$

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 $\rho_{\mathbf{k}}$ at $\mathbf{k} = 0$. The contributions from $\rho_{\mathbf{k}}$ at $\mathbf{k} \neq 0$ are important near the critical point. Let us investigate the role of $\rho_0^{(\delta)}$ 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:

$$\Xi_0 = g_V^{(a)} g_V^{(b)} \exp\left[N_v\left(E_\mu^{(a)} + E_\mu^{(b)} + E_a(\bar{\rho}_a) + E_b(\bar{\rho}_b)\right)\right]. \tag{28}$$

The expressions of $E_\mu^{(\delta)}$ are given in (16). For $E_0(\bar{\rho}_\delta)$, we have

$$E_a(\bar{\rho}_a) = M_a \bar{\rho}_a + \frac{1}{2} d_a(0) \bar{\rho}_a^2 + \frac{a_4}{24} \bar{\rho}_a^4,$$
$$E_b(\bar{\rho}_b) = M_b \bar{\rho}_b + \frac{1}{2} d_b(0) \bar{\rho}_b^2 + \frac{b_4}{24} \bar{\rho}_b^4. \tag{29}$$

It is convenient to use the Laplace method [28] to calculate (28). Thereby, the values $\bar{\rho}_a$ and $\bar{\rho}_b$ correspond

to maxima of the function $E_0(\bar{\rho}_a)$ and $E_0(\bar{\rho}_b)$, respectively. So, the following equations determine $\bar{\rho}_a$ and $\bar{\rho}_b$:

$$\begin{aligned} &M_a + d_a(0)\bar{\rho}_a + \frac{a_4}{6}\bar{\rho}_a^3 = 0, \\ &M_b + d_b(0)\bar{\rho}_b + \frac{b_4}{6}\bar{\rho}_b^3 = 0. \end{aligned} \tag{30}$$

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:

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

It is easy to see that

$$\begin{aligned} &\rho_+ = \bar{\rho}_a + \bar{\rho}_b, \\ &x = \frac{\bar{\rho}_a}{\bar{\rho}_a + \bar{\rho}_b}, \quad 1 - x = \frac{\bar{\rho}_b}{\bar{\rho}_a + \bar{\rho}_b}. \end{aligned} \tag{32}$$

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 ρ_+ and x, expressions (29) have the form

$$\begin{aligned} &E_a(x,\rho_+) = M_a x\rho_+ + \frac{1}{2}d_a(0)x^2\rho_+^2 + \frac{a_4}{24}x^4\rho_+^4, \\ &E_b(x,\rho_+) = M_b(1-x)\rho_+ + \frac{1}{2}d_b(0)(1-x)^2\rho_+^2 + \\ &+ \frac{b_4}{24}(1-x)^4\rho_+^4. \end{aligned} \tag{33}$$

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

$$\begin{aligned} &M_{ab} = xM_a + (1-x)M_b, \\ &D_{ab} = x^2 d_a(0) + (1-x)^2 d_b(0), \\ &a_+ = -x^4 a_4 - (1-x)^4 b_4. \end{aligned} \tag{35}$$

In terms of ρ_+ and x, the grand potential of the mixture reads

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

In order to minimize it with respect to ρ_+, 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 τ, while the relative temperatures τ_a and τ_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 μ_a and μ_b. Using the quantity M_{ab} (or M_a, M_b) is 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

$$D_{ab}(x,T_{\mathrm{c}}) = 0 \tag{39}$$

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

$$x^2\left[\tilde{a}_2 - \frac{1}{\beta_{\mathrm{c}}W_a(0,T_{\mathrm{c}})}\right] + (1-x)^2\left[\tilde{b}_2 - \frac{1}{\beta_{\mathrm{c}}W_b(0,T_{\mathrm{c}})}\right] = 0. \tag{40}$$

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

$$\begin{aligned} &\tilde{a}_2 W_a(0,T_{\mathrm{c}}) = T_{ca} + 2\tilde{a}_2 p_a T_{\mathrm{c}}, \\ &\tilde{b}_2 W_b(0,T_{\mathrm{c}}) = T_{cb} + 2\tilde{b}_2 p_b T_{\mathrm{c}}, \end{aligned} \tag{41}$$

where

$$\begin{aligned} &T_{ca} = T_{\mathrm{c}}^{(a)}(1 - 2\tilde{a}_2 p_a), \\ &T_{cb} = T_{\mathrm{c}}^{(b)}(1 - 2\tilde{b}_2 p_b). \end{aligned} \tag{42}$$

Then we rewrite (40) as follows:

$$æ\tilde{a}_2 W_a(0,T_c)\tilde{b}_2 W_b(0,T_c) - x^2 T_c \tilde{b}_2 W_b(0,T_c)/\tilde{b}_2 - \\ -(1-x)^2 T_c \tilde{a}_2 W_a(0,T_c)/\tilde{a}_2 = 0. \quad (43)$$

Here, expression (40) is multiplied by $W_a(0,T_c) \times \times W_b(0,T_c) \neq 0$ and, for æ, reads

$$æ = \frac{x^2}{\tilde{b}_2} + \frac{(1-x)^2}{\tilde{a}_2}. \quad (44)$$

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

$$f_2 T_c^2 + f_1 T_c + f_0 = 0, \quad (45)$$

where

$$f_2 = 4æ p_a p_b \tilde{a}_2 \tilde{b}_2 - 2x^2 p_b - 2(1-x)p_a, \\ f_1 = 2æ(\tilde{a}_2 p_a T_{cb} + \tilde{b}_2 p_b T_{ca}) - x^2 \frac{T_{cb}}{\tilde{b}_2} - \\ - (1-x)^2 \frac{T_{ca}}{\tilde{a}_2}, \\ f_0 = æ T_{ca} T_{cb}. \quad (46)$$

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

$$\rho_+^3 + p_s \rho_+ + q_s = 0, \quad (47)$$

where

$$p_s = -\frac{6D_{ab}(x,T)}{a_+}, \quad q_s = -\frac{6M_{ab}}{a_+}. \quad (48)$$

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

$$\rho_+ = \left(\frac{3}{a_+}\right)^{1/3} \left(A^{1/3} + B^{1/3}\right), \quad (49)$$

where

$$A = M_{ab} + \sqrt{M_{ab}^2 - M_{0s} D_{ab}^3}, \\ B = M_{ab} - \sqrt{M_{ab}^2 - M_{0s} D_{ab}^3}. \quad (50)$$

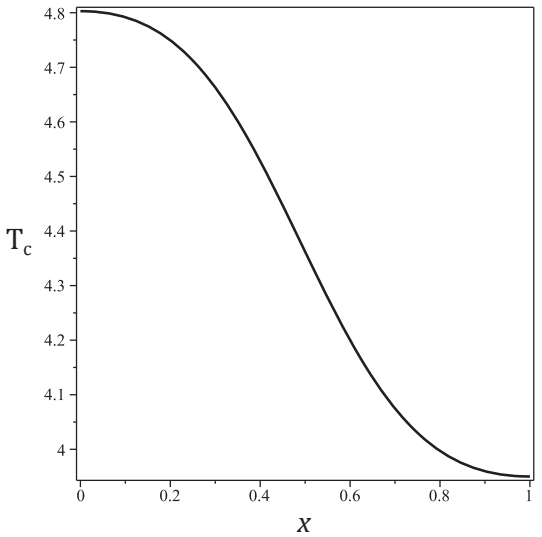

Fig. 1. Plot of the line of critical temperatures of the binary mixture

In these expressions,

$$M_{0s} = \frac{8}{9a_+}. \quad (51)$$

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

$$D_{ab} = x^2 \left(\frac{T_c}{W_a(0,T_c)} - \frac{T}{W_a(0)}\right) + \\ + (1-x)^2 \left(\frac{T_c}{W_b(0,T_c)} - \frac{T}{W_b(0)}\right). \quad (52)$$

In view of the relation

$$\tilde{a}_2 W_a(0) = T_{ca} + 2\tilde{a}_2 p_a T = \\ = \tilde{a}_2 W_a(0,T_c) + 2\tau \tilde{a}_2 p_a T_c, \\ \tilde{b}_2 W_b(0) = T_{cb} + 2\tilde{b}_2 p_b T = \\ = \tilde{b}_2 W_b(0,T_c) + 2\tau \tilde{b}_2 p_b T_c, \quad (53)$$

we obtain D_{ab} in a more compact form

$$D_{ab} = x^2 \tau \frac{W_a(0,T_c) - 2p_a}{\beta_c W_a(0,T_c) \beta_c W_b(0)} + \\ + (1-x)^2 \tau \frac{W_b(0,T_c) - 2p_b}{\beta_c W_b(0,T_c) \beta_c W_a(0)}. \quad (54)$$

The coefficient D_{ab} is negative for all $\tau > 0$ and positive at $T < T_c$. It is proportional to τ, like a similar coefficient in the case of a single system [25].

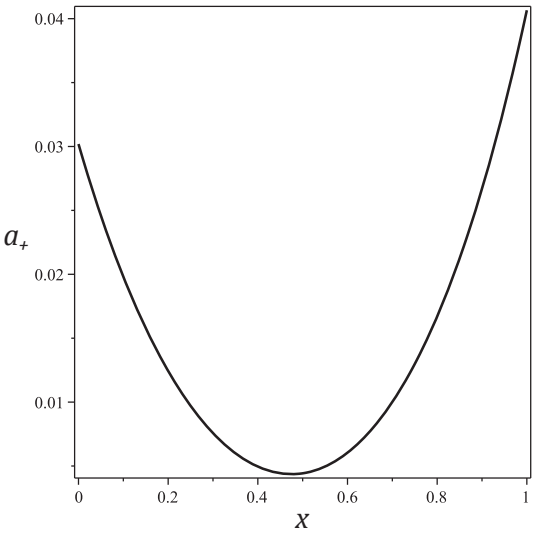

Fig. 2. Plot of the coefficient a_+ given in (35) as a function of x

Solutions 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 $T < T_{\rm c}$, Eq. (47) has three real solutions, which can be found with the use of the method suggested in work [25].

The solutions ρ_+ 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:

$$\begin{aligned}
&\rho_+\big|_{T=\text{const}} = \rho_+^{(1)}(M_{ab}, x),\\
&\rho_+\big|_{x=\text{const}} = \rho_+^{(2)}(M_{ab}, T),\\
&\rho_+\big|_{M_{ab}=\text{const}} = \rho_+^{(3)}(T, x).
\end{aligned} \tag{55}$$

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 $T > T_{\rm c}$ at $M_{ab} = 0$, we have $\rho_+(M_{ab} = 0) = 0$. Then we find the pressure, by using the well-known formula

$$PV = k_{\rm B}T \ln \Xi.$$

We obtain

$$Pv = k_{\rm B}T \left[\frac{1}{N_v} \ln (g_v^{(a)} g_v^{(b)}) + E_W^{(a)} + E_W^{(b)}\right], \tag{56}$$

where, according to (16), we have

$$\begin{aligned}
&E_W^{(a)} = a_0 - \frac{\beta}{2}(\mu_a^{(W)})^2 + m_a(a_1 + \mu_a^{(W)}) +\\
&+ \frac{m_a^2}{2} d_a(0) + \frac{a_3^4}{8a_4^3},\\
&E_W^{(b)} = b_0 - \frac{\beta}{2}(\mu_b^{(W)})^2 + m_b(b_1 + \mu_b^{(W)}) +\\
&+ \frac{m_b^2}{2} d_b(0) + \frac{b_3^4}{8b_4^3},
\end{aligned} \tag{57}$$

moreover,

$$\begin{aligned}
&\mu_a^{(W)} = -a_1 - m_a d_a(0) + \frac{a_3^3}{a_4^2},\\
&\mu_b^{(W)} = -b_1 - m_b d_b(0) + \frac{b_3^3}{b_4^2}.
\end{aligned} \tag{58}$$

The temperature dependence hides in the quantities $d_\delta(0)$. It is easy to see from the above formulas that the pressure along the Widom line is a function of the relative temperature τ and the parameter x. The dependence on x eventuates from $d_\delta(0)$ containing the critical temperature $T_{\rm c}(x)$, which is a function of the mixing parameter:

$$\begin{aligned}
&d_a(0) = -\tau \tilde{a}_2 \frac{T_{\rm c}}{T_{\rm c}^{(a)}} \frac{1 - \omega_{0a}}{1 + \omega_{0a}\tau_a} -\\
&- \tilde{a}_2 \frac{T_{\rm c} - T_{\rm c}^{(a)}}{T_{\rm c}^{(a)}} \frac{1 - \omega_{0a}}{1 + \omega_{0a}\tau_a},\\
&d_b(0) = -\tau \tilde{b}_2 \frac{T_{\rm c}}{T_{\rm c}^{(b)}} \frac{1 - \omega_{0b}}{1 + \omega_{0b}\tau_b} -\\
&- \tilde{b}_2 \frac{T_{\rm c} - T_{\rm c}^{(b)}}{T_{\rm c}^{(b)}} \frac{1 - \omega_{0b}}{1 + \omega_{0b}\tau_b},
\end{aligned} \tag{59}$$

where τ_a and τ_b are given in (22). For ω_δ, we have

$$\omega_{0a} = 2\tilde{a}_2, \quad \omega_{0b} = 2\tilde{b}_2. \tag{60}$$

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

$$n_a = \frac{\langle N_a\rangle}{N_v}, \quad n_b = \frac{\langle N_b\rangle}{N_v}. \tag{61}$$

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

$$n_a = \frac{1}{N_v}\frac{\partial \ln \Xi}{\partial \beta \mu_a}, \quad n_b = \frac{1}{N_v}\frac{\partial \ln \Xi}{\partial \beta \mu_b}. \tag{62}$$

With regard for (28), we find

$$\begin{aligned} n_a &= -M_a + n_{\rm c}^{(a)} + \tilde{a}_2 \gamma \tau_a \rho_n, \\ n_b &= -M_b + n_{\rm c}^{(b)} + \tilde{b}_2 \gamma \tau_b \rho_n. \end{aligned} \tag{63}$$

The quantities M_a, M_b are given in (30), which means that they are functions of τ and ρ_+. Equalities (30) yield

$$x^3 \rho_n^3 + g_a x \rho_n + q_a = 0, \tag{64}$$

where

$$g_a = \frac{6\tilde{a}_2}{a_4}, \quad q_a = \frac{6(n_{\rm c}^{(a)} - n_a)}{a_4}. \tag{65}$$

From (63), we have

$$(1-x)^3 \rho_n^3 + g_b (1-x)\rho_n + q_b = 0, \tag{66}$$

where

$$g_b = \frac{6\tilde{b}_2}{b_4}, \quad q_b = \frac{6(n_{\rm c}^{(b)} - n_b)}{b_4}. \tag{67}$$

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

$$n_a = \eta n_+, \quad n_b = (1-\eta) n_+. \tag{68}$$

Then

$$n_+ = n_a + n_b, \quad \eta = \frac{n_a}{n_+}, \quad 1 - \eta = \frac{n_b}{n_+}. \tag{69}$$

From (64), we have

$$x\rho_n = -2\bar{a}\cos\left(\frac{\alpha_n + \pi}{3}\right), \tag{70}$$

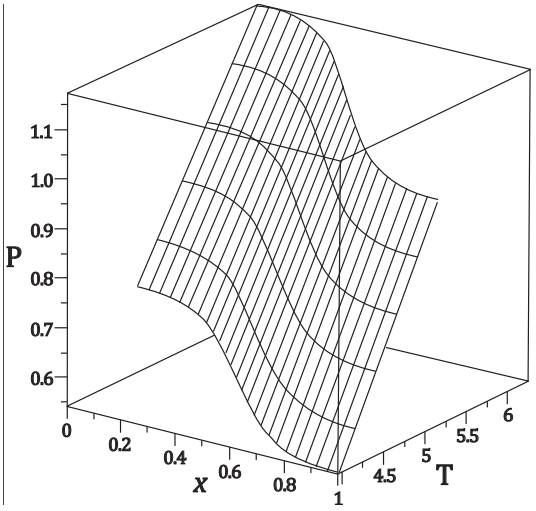

Fig. 3. Plot of the surface of the pressure extremum

where

$$\alpha_n = \arccos\left(\frac{n_{\rm c}^{(a)} - \eta n_+}{n_{\rm c}^{(a)}}\right), \quad \bar{a} = \left(-\frac{2\tilde{a}_2}{a_4}\right)^{1/2}. \tag{71}$$

From (66), we have

$$(1-x)\rho_n = -2\bar{b}\cos\left(\frac{\beta_n + \pi}{3}\right), \tag{72}$$

where

$$\beta_n = \arccos\left(\frac{n_{\rm c}^{(b)} - (1-\eta)n_+}{n_{\rm c}^{(b)}}\right), \quad \bar{b} = \left(-\frac{2\tilde{b}_2}{b_4}\right)^{1/2}. \tag{73}$$

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

$$\rho_n = -2\bar{a}\cos\left(\frac{\alpha_n + \pi}{3}\right) - 2\bar{b}\cos\left(\frac{\beta_n + \pi}{3}\right). \tag{74}$$

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

$$x = \frac{1}{2}\left[1 + \frac{\bar{a}\cos\left(\frac{\alpha_n+\pi}{3}\right) - \bar{b}\cos\left(\frac{\beta_n+\pi}{3}\right)}{\bar{a}\cos\left(\frac{\alpha_n+\pi}{3}\right) + \bar{b}\cos\left(\frac{\beta_n+\pi}{3}\right)}\right], \tag{75}$$

which allows us to find the relation between the mixing parameter x and the concentration η 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 $T > T_{\rm c}$. 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 $T_{\rm c}$ (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, $\alpha_a = \alpha_b = \alpha$, as well as $R_0^{(a)} = R_0^{(b)} = R_0$:

$$R_0 = 5.3678, \quad \alpha = 1.8167, \quad \alpha_R = 0.3385, \tag{A1}$$

which coincide with the parameters of the Morse potential for sodium [29, 30]. We choose the following values of the parameters γ_a and $n_0^{(a)}$ of the potential $U_a(r)$ (see (1)) corresponding to species a:

$$\gamma_a = 1.6500, \quad n_0^{(a)} = 1.7255. \tag{A2}$$

The values (A2) give

$$p_a = 1, \quad \alpha_a^* = 5, \tag{A3}$$

see (12). This set of parameters eventuates in the following values of the coefficients a_n (see (11) and (18)):

$$\begin{aligned} &a_0 = 1.1220, \quad a_1 = 0.7506, \quad a_2 = 0.3413,\\ &a_3 = 0.0265, \quad a_4 = -0.0407, \quad \tilde{a}_2 = 0.3500. \end{aligned} \tag{A4}$$

The values of the parameters γ_b and $n_0^{(b)}$ of the potential $U_b(r)$ differ from γ_a and $n_0^{(a)}$:

$$\gamma_b = 1.6000, \quad n_0^{(b)} = 1.7613. \tag{A5}$$

They give

$$p_b = 1, \quad \alpha_b^* = 5.5 \tag{A6}$$

and the following values of the coefficients b_n:

$$\begin{aligned} &b_0 = 1.1951, \quad b_1 = 0.7832, \quad b_2 = 0.3437,\\ &b_3 = 0.0231, \quad b_4 = -0.0302, \quad \tilde{b}_2 = 0.3526. \end{aligned} \tag{A7}$$

The normalization constants given in (2) equal

$$\begin{aligned} &C_H^{(a)} = 1.2544, \quad A_a = 0.2217,\\ &C_H^{(b)} = 1.2938, \quad A_b = 0.2742. \end{aligned} \tag{A8}$$

The values of the critical temperatures of separate single systems of species a and species b are

$$k_{\rm B}T_{\rm c}^{(a)} = 3.9502, \qquad k_{\rm B}T_{\rm c}^{(b)} = 4.8028. \tag{A9}$$

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ПОВЕДІНКА БІНАРНОЇ
АСИМЕТРИЧНОЇ СУМІШІ ВЗАЄМОДІЮЧИХ
ЧАСТИНОК В НАДКРИТИЧНІЙ ОБЛАСТІ

Р е з ю м е

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. Асиметричність 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 введений нами параметр змішування x із концентрацією системи. Знайдено явний вигляд виразу для тиску бінарної системи як функції відносної температури та параметра змішування x для побудови лінії Відома. Встановлено, що для граничних значень цього параметра ($x = 0$ та $x = 1$) рівняння стану суміші переходить у рівняння стану однієї з окремих компонент.