

THERMODYNAMIC CHARACTERISTICS OF BINARY SYMMETRIC MIXTURE IN THE VICINITY OF THE VAPOR–LIQUID CRITICAL POINT

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Explicit expressions for the thermodynamic functions (grand thermodynamic potential, Helmholtz free energy, entropy, constant volume heat capacity, and isothermal compressibility) of a binary symmetric mixture (BSM) in the vicinity of the vapor–liquid (VL) critical point are derived. In the study, the method of collective variables (CV) with a reference system and step-by-step integration of the grand partition function were used. For the binary mixture of hard spheres interacting through a potential of the square-well, the dependences of thermodynamic characteristics on temperature and on macroscopic parameters of the system are calculated in the critical region.

partition function in the vicinity of the VL critical point is accomplished by a step-by-step integration proposed within the frame of the CV method [3] (with taking into account the non-Gaussian measure density relative to the essential CV connected with the order parameter [4]).

A binary symmetric mixture (BSM) is taken as an investigation object. This system comprises two identical pure components “*a*” and “*b*” in which an interaction between the particles of different types differs from that occurring between the particles of the same type. Although BSM is a simplified model of the real binary system, it demonstrates all the three types of a two-phase equilibrium which may be observed experimentally in such systems as “gas–gas”, “gas–liquid”, and “liquid–liquid” [5].

Recently, the BSM model has been studied both theoretically [6–8] and with using a computer simulation [6, 10–12]. However, the theoretical investigations of BSM’s were limited, in general, to the framework of the mean field approximation.

We consider a BSM in which the interaction is simulated by a one-component system of hard spheres interacting with each other through a potential of the square-well:

$$U_{ij}(r) = \begin{cases} \infty, & r < \sigma \\ -\epsilon_{ij}, & \sigma \leq r < \lambda\sigma \\ 0, & r \geq \lambda\sigma \end{cases}, \quad (1.1)$$

where σ is the hard spheres diameter; ϵ_{ij} and λ — depth and width of the square-well, respectively; and $i, j = a, b$ — species indices. For the BSM case, the following condition is met:

$$\epsilon_{aa} = \epsilon_{bb} = \epsilon, \quad \epsilon_{ab} = \delta\epsilon,$$

where the parameter $\delta = \epsilon_{ab}/\epsilon$ is introduced, and the case of $\delta = 1$ is a particular case of our consideration.

The interaction potential (1.1), in spite of its relative simplicity, allows the comprehension and description of a number of real fluids, as well as the testing of the

1. Introduction

Investigation of phase transitions and critical phenomena in multicomponent continuous systems still remains to be a topical problem. This, first of all, touches upon a calculation of nonuniversal values (such as the parameters of critical points, or amplitudes of thermodynamic functions in the vicinity of the phase transition points) depending on microscopic properties of the system. On the other hand, the multicomponent mixtures differ appreciably from the one-component ones in their phase behavior, thus demonstrating a wide variety. A topology of phase diagrams of such systems is largely dependent on the relationship between the interaction potentials of particles of different kinds. And so, the development of a theory that may serve as a basis for the prediction of the phase behavior of a multicomponent mixture in the vicinity of its critical points is of importance for a practical use of these systems.

This work is devoted to the theoretical description of the thermodynamic behavior of a binary fluid mixture in the vicinity of the VL critical point. The investigations are conducted within the frame of the CV-based macroscopic approach with the reference system [1], and extended to the case of multicomponent system in a large canonical ensemble [2]. Integration of the grand

theory by comparing the obtained results with computer simulation data (various values of λ).

In this work, the behavior of thermodynamic functions (entropy, specific heat, and isothermal compressibility) is investigated for the above-mentioned system in the vicinity of the VL critical point, as well as their dependence on the microscopic parameters λ and δ of the model.

2. Method

Let us represent the interaction potential (1.1) as a sum of short-ranging repulsion $\Psi_{ij}(r)$ and long-ranging attraction $\Phi_{ij}(r)$:

$$U_{ij}(r) = \Psi_{ij}(r) + \Phi_{ij}(r),$$

where, in accordance with Weeks–Chandler–Andersen's partition [13], we have:

$$\Psi_{ij}(r) = \begin{cases} \infty, & r \leq \sigma \\ 0, & r > \sigma \end{cases},$$

$$\Phi_{ij}(r) = \begin{cases} -\epsilon_{ij}, & 0 \leq r \leq \lambda\sigma \\ 0, & r > \lambda\sigma \end{cases}.$$

Then a functional of the grand partition function of BSM in the vicinity of the VL critical point may be represented as a product [9]:

$$\Xi = \Xi_0 \Xi_1,$$

where Ξ_0 is a grand partition function of the reference system in which an interaction is described with using potential $\Psi_{ij}(r)$. It is supposed that the thermodynamic and structural functions of the reference system are known. Ξ_1 is a functional written in the CV phase space $\rho_{\mathbf{k}}$ [9]:

$$\Xi_1 = \Xi_G^c \int (d\rho) \exp \left\{ \beta \mu_1^+ \rho_0 - \frac{\beta}{2} \sum_{\mathbf{k}} \tilde{V}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right\} J(\rho), \quad (2.1)$$

where

$$\Xi_G^c = \prod_{\mathbf{k}} \frac{1}{\sqrt{1 + \beta \tilde{W}(k) \mathcal{M}_2^{(2)}(0)/2}},$$

is a multiplier factor arising as a result of integration over non-essential CV's (i.e., those non-connected with

the order parameter) corresponding to concentration fluctuations .

$$\mu_1^+ = \sqrt{2} \mu_1, \quad \mu_1 = \mu_1^a = \mu_1^b, \quad (2.2)$$

μ_1^i is a part of the chemical potential of an i -type particle:

$$\mu_1^i = \mu_i - \mu_0^i + \frac{1}{2\beta} \sum_{\mathbf{k}} \alpha_{ii}(k), \quad (2.3)$$

μ_1^+ should be determined from the condition

$$\frac{d \ln \Xi_1}{d \beta \mu_1^+} = \frac{\langle N \rangle}{\sqrt{2}}, \quad (2.4)$$

$\langle N \rangle$ is the average number of particles in the system, $\alpha_{ij}(k) = (\beta/V) \Phi_{ij}(k)$, $\tilde{\Phi}_{ij}(k)$ is the Fourier transform of attraction potential $\Phi_{ij}(r)$, $\beta = 1/k_B T$, and k_B is the Boltzmann constant. Variables $\rho_{\mathbf{k}}$ are a combination of the species-relating CV's $\rho_{\mathbf{k},i}$ ($i = a, b$) [4]: $\rho_{\mathbf{k}} = \frac{\sqrt{2}}{2} (\rho_{\mathbf{k},a} + \rho_{\mathbf{k},b})$, $\rho_{\mathbf{k}} = \rho_{\mathbf{k}}^c - i \rho_{\mathbf{k}}^s$, where indices c and s define the real and imaginary parts of $\rho_{\mathbf{k}}$; $\rho_{\mathbf{k}}^c$ and $\rho_{\mathbf{k}}^s$ run through all real values from $-\infty$ to $+\infty$; $\rho_{\mathbf{k}}$ describes the \mathbf{k} -th mode of fluctuations of the overall density in the system, and variable $\rho_{\mathbf{k}=0}$ is connected with the order variable; $(d\rho)$ is a volume element of the CV's' phase space:

$$(d\rho) = d\rho_0 \prod_{\mathbf{k} \neq 0} d\rho_{\mathbf{k}}^c d\rho_{\mathbf{k}}^s.$$

$\tilde{V}(k), \tilde{W}(k)$ are combinations of Fourier images of the initial interaction potentials $\tilde{\Phi}(k)$ and $\tilde{\Phi}_{ab}(k)$ ($\tilde{\Phi}_{aa}(k) = \tilde{\Phi}_{bb}(k) = \tilde{\Phi}(k)$):

$$\begin{aligned} \tilde{V}(k) &= \beta^{-1} [\alpha(k) + \alpha_{ab}(k)], \\ \tilde{W}(k) &= \beta^{-1} [\alpha(k) - \alpha_{ab}(k)]. \end{aligned} \quad (2.5)$$

$J(\rho)$ – Jacobian of transition to CV's:

$$\begin{aligned} J(\rho) &= \int (d\omega) \exp \left\{ i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}} \rho_{\mathbf{k}} + \sum_{n \geq 1}^4 \frac{(-i2\pi)^n}{n!} \times \right. \\ &\times \left. \left(\frac{1}{2} \right)^{n/2} \sum_{\mathbf{k}_1 \dots \mathbf{k}_n} \mathcal{M}_n(0) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_n} \right\}, \end{aligned} \quad (2.6)$$

where $\omega_{\mathbf{k}}$ are variables conjugate to $\rho_{\mathbf{k}}$; $\mathcal{M}_n(0) = \mathcal{M}_n^{(0)}(0) + \Delta \mathcal{M}_n$. Expressions for $\mathcal{M}_n^{(i_n)}(0)$ and $\Delta \mathcal{M}_n$ ($i_n = 0, \dots, 4$, $n = 1, \dots, 4$) for the case of $\mu_0^a = \mu_0^b$ are presented in [9].

In Fig. 1, the behavior of the Fourier transform of the attraction potential $\tilde{V}(k)/|\tilde{V}(0)|$ is shown by a solid line. Hereinafter, we consider $\tilde{V}(k) = 0$ under $|\mathbf{k}| > B$. Then the integration in (2.1) over variables $\rho_{\mathbf{k}}$ under

$|\mathbf{k}| > B$ gives δ function, and all the sums over \mathbf{k} in the expressions for Ξ will contain $|\mathbf{k}| \leq B$ only.

We consider the set of \mathbf{k} vectors of $|\mathbf{k}| \leq B$ as that which corresponds to the sites of a reciprocal lattice conjugated to a certain block lattice $\{r_i\}$ containing N_B block sites in volume V [9, 14]:

$$N_B = \frac{V}{C^3} = \frac{V}{(\pi/B)^3} = \frac{(B\sigma)^3 \langle N \rangle}{6\pi^2 \eta},$$

$\eta = \frac{\pi}{6} \rho \sigma^3$ is the reduced density. Henceforth, we will consider the B value to be a semi-zone of the first Brillouin zone of this block lattice.

To calculate the grand partition function, we use the following approximation of potential $\tilde{V}(k)$:

$$\tilde{V}(k) = \begin{cases} \tilde{V}(0)(1 - pk^2), & \text{for } k \leq B' \\ \tilde{V}(0)\bar{V}, & \text{for } B' < k \leq B \end{cases}, \quad (2.7)$$

$$p = \frac{1}{\tilde{V}(0)} \frac{1}{2} \frac{\partial^2 \tilde{V}(k)}{\partial k^2} \Big|_{k=0}$$

and the value of \bar{V} is defined as

$$\bar{V} = \langle \tilde{V} \rangle + \tilde{V}_\infty.$$

Here, $\langle \tilde{V} \rangle$ is some constant that may be found from condition:

$$\langle \tilde{V} \rangle = \frac{\int_0^B \tilde{V}(k) d\mathbf{k} - \int_0^{B'} \tilde{V}(0)(1 - pk^2) d\mathbf{k}}{\int_{B'}^B d\mathbf{k}},$$

\tilde{V}_∞ is a correction that provides a proper asymptotic behavior of the system in the limit of $\lambda \rightarrow \infty$:

$$\lim_{\lambda \rightarrow \infty} \beta_c \tilde{V}(0) = \beta_c^G \tilde{V}(0),$$

β_c^G is the inverse critical temperature defined within the frame of the Gaussian approximation.

Approximation (2.7) allows the employment of the step-by-step integration method [3, 15, 16] in the grand partition function calculation; it also has not affect essentially the critical behavior of the system in a close neighbourhood of T_c because of the good matching of curves in the vicinity of $\mathbf{k} = 0$ (see Fig.1).

Applying the standard integration procedure [3] to the grand partition function over variables $\rho_{\mathbf{k}}$, $\omega_{\mathbf{k}}$ belonging to $|\mathbf{k}| \in (B', B]$, we obtain an expression similar to (2.1) – (2.6) but involving renormalized cumulants $\mathcal{M}_n^r(0)$ and additional multiplier factor e^{a_0} going before the integration sign, where:

$$a_0 = -\frac{\mathcal{M}_2(0)}{4} b, \quad (2.8)$$

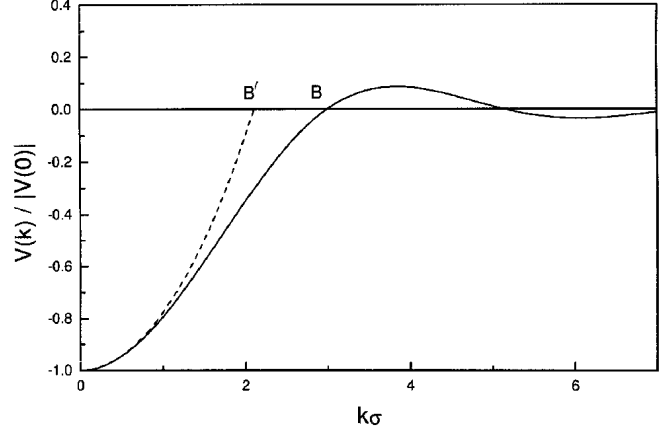


Fig. 1. Behavior of the Fourier transform of attraction potential $\tilde{V}(k)/|\tilde{V}(0)|$. Dashed curve shows the parabolic approximation

$$\mathcal{M}_1^r(0) = \mathcal{M}_1 - \frac{\mathcal{M}_3(0)}{4} b,$$

$$\mathcal{M}_2^r(0) = \mathcal{M}_2 + \frac{|\mathcal{M}_4(0)|}{4} b,$$

$$b = \sum_{\mathbf{k} \in (B', B]} \beta \tilde{V}(k)$$

(hereinafter, we omit the r indices for simplification).

Then, following after [9], we change variables:

$$\omega_{\mathbf{k}} = \omega'_{\mathbf{k}} + \Delta' \delta_{\mathbf{k}}, \quad \rho_{\mathbf{k}} = \rho'_{\mathbf{k}} + \tilde{\mathcal{M}}_1 \delta_{\mathbf{k}},$$

where

$$\Delta' = -\frac{i \bar{\mathcal{M}}_3(0)}{2\pi \bar{\mathcal{M}}_4(0)},$$

$$\tilde{\mathcal{M}}_1 = \bar{\mathcal{M}}_1(0) - \frac{\bar{\mathcal{M}}_2(0)\bar{\mathcal{M}}_3(0)}{\bar{\mathcal{M}}_4(0)} + \frac{\bar{\mathcal{M}}_3^3(0)}{3\bar{\mathcal{M}}_4^2(0)}, \quad (2.9)$$

($\bar{\mathcal{M}}_n(0) = \mathcal{M}_n(0)/(\sqrt{2})^n$, $n = 1, \dots, 4$), thus eliminating the linear and cubic summands in (2.6). After the integration over $\omega_{\mathbf{k}}$ is done, for the BSM grand partition function in the vicinity of the VL critical point, we obtain the following expression [9]:

$$\Xi = \Xi_0 \Xi_G^{(1)} \left[Z(\tilde{\mathcal{M}}_2, \tilde{\mathcal{M}}_4) \right]^{N_{B'}} (\sqrt{2})^{N_{B'} - 1} \times e^{a_0} \int \exp[E_4(\rho)] (d\rho)^{N_{B'}}, \quad (2.10)$$

$$\Xi_G^{(1)} = \Xi_G^c \exp \left\{ \mu^* \tilde{\mathcal{M}}_1 + \frac{\beta \tilde{V}(0)}{2} \tilde{\mathcal{M}}_1^2 - \right.$$

$$- \left. \frac{\bar{\mathcal{M}}_1(0)\bar{\mathcal{M}}_3(0)}{\bar{\mathcal{M}}_4(0)} + \frac{\bar{\mathcal{M}}_2(0)\bar{\mathcal{M}}_3^2(0)}{2\bar{\mathcal{M}}_4^2(0)} - \frac{\bar{\mathcal{M}}_3^4(0)}{8\bar{\mathcal{M}}_4^3(0)} \right\}, \quad (2.11)$$

$$\mu^* = h - a_1, \quad h = \beta\mu_1^+, \quad (2.12)$$

$$a_1 = \frac{\bar{\mathcal{M}}_3(0)}{|\bar{\mathcal{M}}_4(0)|} + \beta\tilde{V}(0)\tilde{\mathcal{M}}_1, \quad (2.13)$$

$$\tilde{\mathcal{M}}_2(0) = \bar{\mathcal{M}}_2(0) - \frac{\bar{\mathcal{M}}_3^2(0)}{2\bar{\mathcal{M}}_4(0)},$$

$$\tilde{\mathcal{M}}_4(0) = \langle N_{B'} \rangle \bar{\mathcal{M}}_4(0);$$

$$Z(\tilde{\mathcal{M}}_2, \tilde{\mathcal{M}}_4) = \left(\frac{1}{2\pi} \right)^{1/2} \left(\frac{3}{|\tilde{\mathcal{M}}_4(0)|} \right)^{1/4} \times \\ \times e^{x^2/4} U(0, x), \quad (2.14)$$

where $U(0, x)$ is Weber's parabolic cylindrical function [19], $E_4(\rho)$ is Ginzburg–Landau–Wilson's effective Hamiltonian of a binary symmetric mixture in the vicinity of the VL critical point, which is defined by the formula:

$$E_4(\rho) = \mu^* \rho_0 - \frac{1}{2} \sum_{\mathbf{k} < B'} d_2(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{a_4}{4! \langle N_{B'} \rangle} \times \\ \times \sum_{\mathbf{k}_1 \dots \mathbf{k}_4 < B'} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \dots + \mathbf{k}_4} + \dots, \quad (2.15)$$

where

$$d_2(k) = a_2 + \beta\tilde{V}(k),$$

$$a_2 = \sqrt{\frac{3}{|\tilde{\mathcal{M}}_4(0)|}} K(x), \quad a_4 = \frac{3}{|\tilde{\mathcal{M}}_4(0)|} L(x) \quad (2.16)$$

and

$$K(x) = U(1, x)/U(0, x),$$

$$L(x) = 3K^2(x) + 2xK(x) - 2,$$

$$x = \sqrt{\frac{3}{|\tilde{\mathcal{M}}_4(0)|}} \tilde{\mathcal{M}}_2(0). \quad (2.17)$$

The Ξ functional representation (2.10)–(2.17) for BSM coincides by its form with expressions for a partition function of the Ising's model in external field ($a_1 - \beta\mu_1^+$) [3] except for one distinction: cumulants $\bar{\mathcal{M}}_2(0)$ and $\bar{\mathcal{M}}_4(0)$ are functions of reduced density η , temperature T , and potential parameters $\tilde{\Phi}_{ij}(k)$. That is why, to integrate functional (2.10)–(2.17) over $\rho_{\mathbf{k}}$

variables, we employ a method proposed in [3] for the Ising model.

The main idea of the method is a step-by-step integration of the partition function. The integration is carried out over the CVs' phase space layers, beginning from collective variables $\rho_{\mathbf{k}}$ with large values of wave vector \mathbf{k} , and ending by $\rho_{\mathbf{k}}$ with $\mathbf{k} \rightarrow 0$. This step-by-step integration results in the appearance of a certain regularity in changing the d_2 and a_4 coefficients belonging to the expression of $E_4(\rho)$. This regularity is described by recursive formulas.

In the case of $T \geq T_c$, within the interval $[0, B']$, there exist three characteristic domains, so-called "regimes." The first regime ($B_{m_\tau} < k \leq B'$) corresponds to the domain of strongly correlated fluctuations $\rho_{\mathbf{k}}$, and is named "critical regime" (CR). In the CR, the basic density of measure is non-Gaussian, and the coefficients in the recursive formulas are characterized by a renormalization-group symmetry. The second regime ($0 < k \leq B_{m_\tau}$) is named "limiting Gaussian regime" (LGR) and corresponds to CV's $\rho_{\mathbf{k}}$ whose fluctuations are described by a Gaussian measure density. The third domain contains the point $k = 0$ only. Variable ρ_0 is a macroscopic value connected with density fluctuations in "external field" μ^* .

In the case of $T \leq T_c$, the general scheme of calculation of the grand partition function in the critical temperature region is not differing fundamentally from that described above for the case of $T \geq T_c$. At first, we integrate over CV's $\rho_{\mathbf{k}}$ ($B_{m_\tau} < k \leq B'$) which belong to CR. General form of the recursive formulas remains the same as for the case of $T \geq T_c$. In the second regime, called "inverse Gaussian regime" (IGR), at first, we isolate the ordering energy occurring in the system at a given $\tau < 0$ ($\tau = \frac{T-T_c}{T_c}$), and then accomplish the integration over CV's $\rho_{\mathbf{k}}$ ($0 < k \leq B_{m_\tau}$) with Gaussian measure density. The latter integral over macroscopic variable $\rho_0 = \rho'_0 N$, connected with order parameter of the system, gives the main contribution to the grand partition function in the case of $T \leq T_c$.

Integration in (2.10) is conducted in accordance with the following scheme: domain $(0, B')$ is subdivided into intervals $(B_1, B'), \dots, (B_{i+1}, B_i), \dots$, where $B_n = B'/s^n$ (with s being a subdivision parameter); each of the intervals corresponds to a layer of \mathbf{k} wave vectors in the Brillouin zone and, correspondingly, to a $\rho_{\mathbf{k}}$ layer in the CV phase space; as a result of the stepwise level-by-level integration, we obtain a set of block lattices with continuous augmentation of the block period and with Hamiltonian coefficients corresponding to the levels. Each of the Hamiltonians is characterized by coefficients

$d_2, a_4; d_2^{(1)}, a_4^{(1)}; d_2^{(2)}, a_4^{(2)}$, etc. For the set $\{d_2^{(n)}, a_4^{(n)}\}$ of block Hamiltonians, a renormalization-group symmetry is characteristic, along with a saddle-type fixed point. Since the renormalization-group solutions are expressed through the coordinates of this point and eigenvalues and eigenvectors of the renormalization-group transformation matrix, these are dependent on the microscopic parameters, density, and temperature.

In the general case, the “layering” parameter $s > 1$ may take arbitrary values. In the following calculations, we shall use some optimal value $s = s^*$ allowing analytic calculations in the vicinity of the critical point. This value depends on the shape of the basic measure density [15,16]. In the case of the φ^4 approximation model, this optimal value that provides coefficient $d_2(0)$ to be equal to zero at the fixed point, is $s^* = 3.4252$ [15].

The CR takes place for all the $\rho_{\mathbf{k}}$ variables in the critical point. That is why the critical temperature may be found by resolving the recursive relations. An equation for determination of the critical temperature is [9]:

$$A(\beta_c \tilde{V}(0))^2 + B(\beta_c \tilde{V}(0)) + D = 0, \quad (2.18)$$

where

$$A = 1 - f_0 - R^{(0)} \sqrt{\varphi_0},$$

$$B = -a_2, \quad D = a_4 R^{(0)} / \sqrt{\varphi_0}.$$

f_0 and φ_0 are coordinates of the given fixed point, and $R^{(0)}$ is a universal function of subdivision parameter s . Specific values of $f_0, \varphi_0, R^{(0)}$ at $s^* = 3.4252$ are taken from [15]. The condition

$$\mu^* = 0 \quad (2.19)$$

gives us an equation for determination of the critical density. The study of critical parameters T_c and η_c of the VL critical point was carried out in [9].

3. Thermodynamic Functions under $T \geq T_c$ and $T \leq T_c$

In this work, we do not dwell on details of the step-by-step integration of the grand partition function, since a technique of the related calculations is similar to that proposed for the Ising model [3,16]. We will concentrate on the calculation of thermodynamic functions in the vicinity of VL critical point under $T \geq T_c$ and $T \leq T_c$.

3.1. Case of $T \geq T_c$

Grand thermodynamic potential. As a result of integration in (2.10)–(2.17) under $T \geq T_c$, for the grand partition function, we obtain [17]

$$\Xi = \exp(-\beta\Omega) = \exp\{-\beta\Omega_0 - \beta\Omega_1 - \beta\Omega_{\text{CR}} - \beta\Omega_{\text{LGR}} - \beta\Omega_{\mu^*}\}, \quad (3.1)$$

where Ω_0 is the grand thermodynamic potential of the reference system:

$$\Omega_0 = -k_B T \ln \Xi_0, \quad (3.2)$$

$$\Omega_1 = -k_B T \ln (\Xi_G^{(1)} e^{a_0}), \quad (3.3)$$

Ω_{CR} is a contribution into the grand thermodynamic potential, resulted from an integration with non-Gaussian measure density as a basic one (the contribution from CR):

$$\Omega_{\text{CR}} = -k_B T N s_0^{-3} [\gamma'_0 + \gamma_1 \tau + \gamma_2 \tau^2 + \gamma'_3 c_\nu^{3\nu} \tau^{3\nu} + \gamma'_4 c_\nu^{3\nu} c_\Delta \tau^{3\nu+\Delta}].$$

$$\Omega_{\text{LGR}} = -k_B T N s_0^{-3} [\gamma''_3 c_\nu^{3\nu} \tau^{3\nu} + \gamma''_4 c_\nu^{3\nu} c_\Delta \tau^{3\nu+\Delta}]$$

– contribution from LGR; $\Xi_G^{(1)}$ and a_0 are defined in (2.11) and (2.8), respectively; $s_0^3 = N_B/N_{B'}$. ν, Δ –critical exponents that take, within the frame of the given ρ^4 -model integration scheme, the values of $\nu = 0.608$ and $\Delta = 0.472$.

Explicit expressions of coefficients γ'_0, γ_1 , and γ_2 , and non-universal constants c_ν and c_Δ , and a manner of their calculation are similar to those stated in [15]. Numerical magnitudes of these values are presented in Table.

Ω_{μ^*} is a contribution from integration over CV ρ_0 , namely:

$$\exp(-\beta\Omega_{\mu^*}) = \int d\rho_0 \exp\left\{\mu^* \rho_0 - \frac{P}{2} \rho_0^2\right\}$$

Numerical Values of Coefficients $\gamma'_0, \gamma_1, \gamma_2, c_\nu$, and c_Δ under Various Values of λ and $\eta = \eta_c$

λ	γ'_0	γ_1	γ_2	c_ν	c_Δ
1.10	0.954	-0.632	-1.308	1.591	-0.564
1.15	1.062	-0.641	-1.328	1.609	-0.581
1.20	1.181	-0.650	-1.343	1.623	-0.596
1.25	1.313	-0.657	-1.352	1.635	-0.611
1.50	2.162	-0.687	-1.346	1.667	-0.672
1.75	3.364	-0.707	-1.299	1.673	-0.716
2.00	4.971	-0.720	-1.244	1.670	-0.747
2.50	9.619	-0.737	-1.144	1.656	-0.786
3.00	16.554	-0.745	-1.083	1.644	-0.807
4.00	39.103	-0.754	-1.015	1.632	-0.825
5.00	76.285	-0.757	-0.986	1.626	-0.833

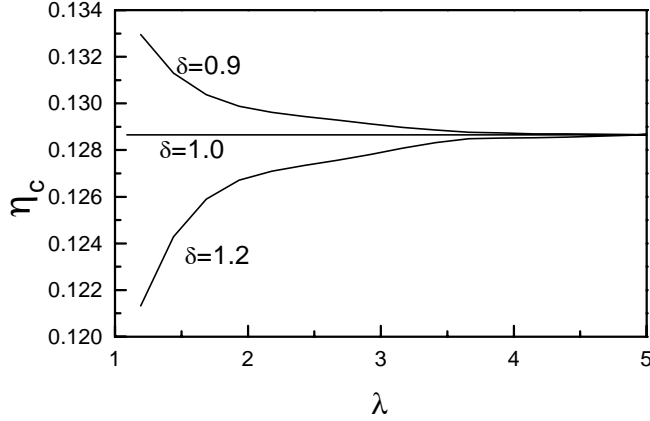


Fig. 2. Critical density of BSM with interaction potential (1.1) as a function of potential parameter λ

$$\begin{aligned}
& - \frac{1}{4!N_{m'_\tau}} a_4^{(m'_\tau)} \rho_0^4 \left. \right\} \simeq \exp\left(\frac{\mu^{*2}}{2P}\right) \times \\
& \times \left(1 - \frac{a_4^{m'_\tau}}{4!N_{m'_\tau}} \langle \rho_0^4 \rangle + \dots\right), \quad (3.4)
\end{aligned}$$

(the factor $(\frac{2\pi}{P})^{1/2}$ is taken into account in Ω_{LGR}).
 $m'_\tau = m_\tau + 1$,

$$P = \frac{\beta|\tilde{V}(0)|}{2D_0^+} c_\nu^{2\nu} \tau^{2\nu} (1 - D_1^+ c_\Delta \tau^\Delta),$$

$$D_0^+ = 1.913, \quad D_1^+ = 1.480.$$

Now, let us find the absolute minimum point for the expression written under the exponent sign in (3.4). From the equation

$$\mu^* - P\rho_0 - \frac{a_4^{(m'_\tau)}}{4!N_{m'_\tau}} \rho_0^3 = 0,$$

we determine that $\rho_0 = 0$ on the surface of $\mu^* = 0$, and we have a situation coinciding completely with that of the three-dimensional Ising model, and corresponding to a phase transition of the second kind. Near the surface of $\mu^* = 0$, this root is close to the value [14]:

$$\rho_0^{(1)} \simeq \frac{\mu^*}{P}. \quad (3.5)$$

As a result, for Ω_{μ^*} , we have

$$-\beta\Omega_{\mu^*} = \frac{\mu^{*2}}{2P}.$$

Thus, summarizing all the contributions, we obtain the following expression for the grand thermodynamic potential:

$$\begin{aligned}
\frac{(\Omega - \Omega_0)}{k_B T} = & - \left[a_0 + \ln \Xi_G^{(1)} + \frac{\mu^{*2}}{2P} + s_0^{-3} N (\gamma'_1 + \gamma_1 \tau + \right. \\
& \left. + \gamma_2 \tau^2 + \gamma_3 c_\nu^{3\nu} \tau^{3\nu} + \gamma_4 c_\nu^{3\nu} c_\Delta \tau^{3\nu+\Delta}) \right], \quad (3.6)
\end{aligned}$$

where $\gamma_3 = \gamma'_3 + \gamma''_3$, $\gamma_4 = \gamma'_4 + \gamma''_4$; γ_3 and γ_4 are universal values, i.e., such that they are independent of parameters of the system and, in the case of the ρ^4 model, are equal to $\gamma_3 = 0.708$; $\gamma_4 = -0.1001$.

From condition (2.4) for the chemical potential, we obtain

$$\frac{\mu^*}{P} = \phi, \quad (3.7)$$

where

$$\phi = \frac{N}{\sqrt{2}} - \tilde{M}_1 \quad (3.8)$$

(\tilde{M}_1 is defined in (2.9)).

As a result, Eq. (2.19) for determination of the critical density (with taking into account (3.5) and (3.7)) takes a form

$$\phi = \rho_0^{(1)} = 0, \quad (3.9)$$

or, accounting for (3.8),

$$-\frac{\Delta \bar{\mathcal{M}}_1}{\sqrt{2}} + \frac{\bar{\mathcal{M}}_2 \bar{\mathcal{M}}_3}{\bar{\mathcal{M}}_4} - \frac{\bar{\mathcal{M}}_3^3}{3\bar{\mathcal{M}}_4^2} = 0. \quad (3.10)$$

In Fig. 2, a behavior of critical density η_c as a function of microscopic parameter λ of the system is presented.

Chemical potential. Taking into account expressions (3.7), (3.8), (2.12), (2.13) and (2.2), (2.3), for the chemical potential $\mu (= \mu_a = \mu_b)$ under $T \geq T_c$, we obtain:

$$\begin{aligned}
\mu = & \mu_{\text{id}} + \mu_0 - \frac{1}{2V} \sum_k \tilde{\Phi}(k) + \frac{k_B T}{\sqrt{2}} \frac{\bar{\mathcal{M}}_3}{|\bar{\mathcal{M}}_4|} + \\
& + \frac{\tilde{V}(0)}{\sqrt{2}} \tilde{M}_1 + \frac{k_B T}{\sqrt{2}} \mu_{|\mu^*=P\phi}^* \quad (3.11)
\end{aligned}$$

where μ_{id} and μ_0 are the chemical potentials of the ideal gas and reference system, respectively.

Helmholtz free energy. By using the Legendre transformation $F = \Omega + \sum_{\gamma=a,b} \mu_\gamma N_\gamma$ and

formulas (3.6) and (3.11), we obtain for the free energy under $T \geq T_c$:

$$\begin{aligned}
 F &= F_{\text{id}} + F_0 - \frac{N}{2V} \sum_k \tilde{\Phi}(k) - k_B T a_0 - k_B T \ln \Xi_G^c - \\
 &- \frac{1}{2} \tilde{V}(0) \bar{\mathcal{M}}_1^2 + \frac{N}{\sqrt{2}} \tilde{V}(0) \tilde{\mathcal{M}}_1 + \\
 &+ k_B T \frac{\bar{\mathcal{M}}_3}{\mathcal{M}_4} \left(\frac{\Delta \bar{\mathcal{M}}_1}{\sqrt{2}} - \frac{\bar{\mathcal{M}}_2 \bar{\mathcal{M}}_3}{2|\mathcal{M}_4|} + \frac{\bar{\mathcal{M}}_3^3}{8\mathcal{M}_4^2} \right) - \\
 &- k_B T s_0^{-3} N (\gamma'_0 + \gamma_1 \tau + \gamma_2 \tau^2 + \gamma_3 c_\nu^{3\nu} \tau^{3\nu} + \\
 &+ \gamma_4 c_\nu^{3\nu} c_\Delta \tau^{3\nu+\Delta}) + \frac{k_B T}{2} P \phi^2, \quad (3.12)
 \end{aligned}$$

where F_{id} is a free energy of ideal gas, F_0 — free energy of a reference system to which we apply expression [20]

$$F_0 = k_B T N [-3 + 2(1 - \eta)^{-1} + (1 - \eta)^{-2}].$$

3.2 Case of $T \leq T_c$

Grand thermodynamic potential. As a result of integration in (2.10)–(2.17) under $T \leq T_c$, for the grand partition function, we obtain the following expression [17]:

$$\Xi = \exp \{ -\beta \Omega_0 - \beta \Omega_1 - \beta \Omega_{\text{CR}} - \beta \Omega_{\text{LGR}} - \beta \Omega_{\mu^*, \bar{\rho}} \}, \quad (3.13)$$

where Ω_0 and Ω_1 are the same as under $T \geq T_c$ (see (3.2) and (3.3)). Ω_{CR} and Ω_{LGR} are the contributions of CR and LGR, respectively:

$$\begin{aligned}
 \Omega_{\text{CR}} &= -k_B T N s_0^{-3} [\gamma'_0 + \gamma_1 \tau + \gamma_2 \tau^2 + \\
 &+ \gamma'_5 c_\nu^{3\nu} (-\tau)^{3\nu} + \gamma'_6 c_\nu^{3\nu} c_\Delta (-\tau)^{3\nu+\Delta}], \quad (3.14)
 \end{aligned}$$

$$\begin{aligned}
 \Omega_{\text{LGR}} &= -k_B T N s_0^{-3} [\gamma''_5 c_\nu^{3\nu} (-\tau)^{3\nu} + \\
 &+ \gamma''_6 c_\nu^{3\nu} c_\Delta (-\tau)^{3\nu+\Delta}]. \quad (3.15)
 \end{aligned}$$

$\Omega_{\mu^*, \bar{\rho}}$ — contribution from the integration over CV ρ_0 :

$$\Omega_{\mu^*, \bar{\rho}} = -k_B T N s_0^{-3} [\mu^* \bar{\rho} + B \bar{\rho}^2 - G \bar{\rho}^4], \quad (3.16)$$

and the following notations are introduced:

$$B = \beta |\tilde{V}(0)| B_0^{(-)} c_\nu^{2\nu} (-\tau)^{2\nu} (1 + B_1^{(-)} c_\Delta (-\tau)^\Delta), \quad (3.17)$$

$$B_0^{(-)} = 0.406, \quad B_1^{(-)} = 0.769,$$

$$G = (\beta |\tilde{V}(0)|)^2 G_0^{(-)} c_\nu^{2\nu} (-\tau)^{2\nu} (1 + G_1^{(-)} c_\Delta (-\tau)^\Delta), \quad (3.18)$$

$$G_0^{(-)} = 0.406, \quad G_1^{(-)} = 0.769.$$

$\bar{\rho}$ is the order parameter that arises in the system under $T \leq T_c$. At $\mu^* = 0$, we have the following equation [14, 17] for $\bar{\rho}$:

$$\bar{\rho}^2 = \frac{B}{2G}. \quad (3.19)$$

Taking into account (3.17), (3.18), we can write for the order parameter $\bar{\rho}$:

$$\bar{\rho} = \bar{\rho}_0 (c_\nu)^{\nu/2} (-\tau)^{\nu/2} (1 + \bar{\rho}_1 c_\Delta (-\tau)^\Delta) \quad (3.20)$$

where $\bar{\rho}_0 = 0.5434$; $\bar{\rho}_1 = -0.6927$.

Condition for the chemical potential under $T \leq T_c$ leads to the following equation:

$$\bar{\rho} = \phi, \quad (3.21)$$

where ϕ is defined in (3.8). Expanding ϕ into a Taylor series in the vicinity of $\eta = \eta_c$, we can show that the order parameter is associated with the following value:

$$\bar{\rho} = \frac{\eta - \eta_c}{\eta_c}, \quad (3.22)$$

which appears in the phenomenological theory of phase transitions of the second kind [21].

Chemical potential. From the condition $\frac{\partial \Omega_{\mu^*, \bar{\rho}}}{\partial \bar{\rho}} = 0$ (see (3.16)), for μ^* at $T \leq T_c$, we have

$$\mu^* = -2B\bar{\rho} + 4G\bar{\rho}^3. \quad (3.23)$$

Taking into account (2.12), (2.13) and (2.2), (2.3), for the chemical potential $\mu (= \mu_a = \mu_b)$ at $T \leq T_c$, we obtain

$$\begin{aligned}
 \mu &= \mu_{\text{id}} + \mu_0 - \frac{1}{2V} \sum_k \tilde{\Phi}(k) + \frac{k_B T}{\sqrt{2}} \frac{\bar{\mathcal{M}}_3}{|\mathcal{M}_4|} + \\
 &+ \frac{\tilde{V}(0)}{\sqrt{2}} \tilde{\mathcal{M}}_1 + \frac{k_B T}{\sqrt{2}} \mu^* \quad (3.24)
 \end{aligned}$$

where μ^* is defined in (3.23).

Helmholtz free energy. Employing the Legendre transformations and formulas (3.13)–(3.16) and (3.23)–(3.24) for the free energy at $T \leq T_c$, we have

$$F = F_{\text{id}} + F_0 - \frac{N}{2V} \sum_k \tilde{\Phi}(k) - k_B T a_0 - k_B T \ln \Xi_G^c -$$

$$- \frac{1}{2} \tilde{V}(0) \bar{\mathcal{M}}_1^2 + \frac{N}{\sqrt{2}} \tilde{V}(0) \tilde{\mathcal{M}}_1 +$$

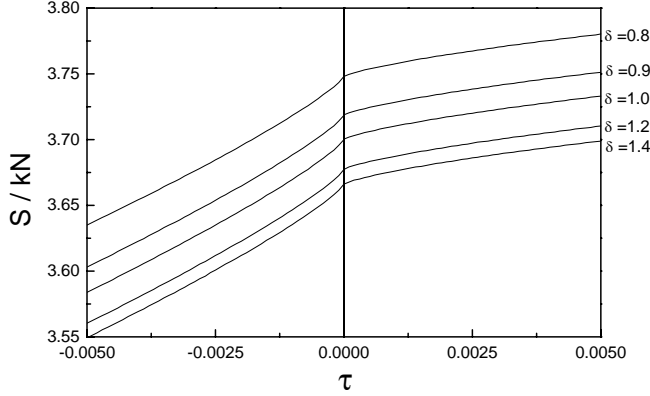


Fig. 3. Temperature dependence of the entropy of BSM with interaction potential (1.1) at $\lambda = 1.5$

$$\begin{aligned}
& +k_{\text{B}}T \frac{\bar{\mathcal{M}}_3}{\bar{\mathcal{M}}_4} \left(\frac{\Delta \bar{\mathcal{M}}_1}{\sqrt{2}} - \frac{\bar{\mathcal{M}}_2 \bar{\mathcal{M}}_3}{2|\bar{\mathcal{M}}_4|} + \frac{\bar{\mathcal{M}}_3^3}{8\bar{\mathcal{M}}_4^2} \right) - \\
& -k_{\text{B}}T s_0^{-3} N (\gamma'_0 + \gamma_1 \tau + \gamma_2 \tau^2 + \gamma_3 c_{\nu}^{3\nu} (-\tau)^{3\nu} + \\
& + \gamma_4 c_{\nu}^{3\nu} c_{\Delta} (-\tau)^{3\nu+\Delta}) - k_{\text{B}}T (B\bar{\rho}^2 - G\bar{\rho}^4), \quad (3.25)
\end{aligned}$$

where B and G are defined in (3.17) and (3.18), respectively.

3.3. Entropy

Using Eq. (3.12) and relation $S = -\left(\frac{\partial F}{\partial T}\right)_V$ for S at $T \geq T_c$ and $\eta = \eta_c$ (the critical isochor), we obtain:

$$(S - \tilde{S}) = k_{\text{B}}N [S_1 + S_2\tau + S_3\tau^{3\nu-1} + S_4\tau^{3\nu-1+\Delta}].$$

Here,

$$\tilde{S} = S_{\text{id}} + S_0,$$

where S_{id} is the entropy of ideal gas, S_0 – entropy of the reference system:

$$S_{\text{id}} = k_{\text{B}}N \left[\frac{5}{2} + \frac{3}{2} \ln(1 + \tau) - \ln \left(\frac{\rho}{2} \left(\frac{2\pi m k_{\text{B}} T}{h^2} \right)^{-3/2} \right) \right],$$

m – mass of a particle.

$$S_0 = -k_{\text{B}}N [-3 + 2(1 - \eta)^{-1} + (1 - \eta)^{-2}],$$

$$S_1 = \frac{1}{N} (\ln \Xi_G^{(1)} + a_0) + s_0^{-3} (\gamma'_0 + \gamma_1) +$$

$$+ \frac{1}{2N} \sum_{k=0} \frac{G(k)}{1 + G(k)},$$

$$S_2 = 2s_0^{-3} (\gamma_1 + \gamma_2), \quad S_3 = 3\nu c_{\nu}^{3\nu} \gamma_3 s_0^{-3},$$

$$S_4 = (3\nu + \Delta) c_{\Delta} c_{\nu}^{3\nu} \gamma_4 s_0^{-3},$$

and

$$G(k) = \beta W(k) \mathcal{M}_2^{(0)} / 2.$$

Under $T \leq T_c$, the expression for entropy takes a form (if temperature is lower than T_c , then the critical isochor for common fluids coincides with the coexistence curve):

$$\begin{aligned}
(S - \tilde{S}) = k_{\text{B}}N [S_1 - S_2^L(-\tau) - S_3^L(-\tau)^{3\nu-1} - \\
- S_4^L(-\tau)^{3\nu-1+\Delta}].
\end{aligned}$$

Here,

$$S_3^L = 3\nu c_{\nu}^{3\nu} \gamma_{30} s_0^{-3}, \quad S_4^L = (3\nu + \Delta) c_{\Delta} c_{\nu}^{3\nu} \gamma_{31} s_0^{-3}.$$

$$\gamma_{30} = 1.691, \quad \gamma_{31} = -2.539.$$

In Fig. 3, the dependence of entropy $(S - S')/kN$ on temperature is shown for $\lambda = 1.5$; $\delta = 0.9$. $S' = \ln \left(\frac{\rho}{2} \left(\frac{2\pi m k_{\text{B}} T}{h^2} \right)^{-3/2} \right)$.

3.4. Specific Heat Capacity

We determine the constant volume heat capacity C_V in the vicinity of the VL critical point from the relation $C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$. At $T \geq T_c$ and $\eta = \eta_c$ (the critical isochor), we obtain the following expression:

$$C_V = k_{\text{B}}N [C_1 + C_3^{(+)} \tau^{-\alpha} + C_4^{(+)} \tau^{\Delta-\alpha}], \quad (3.26)$$

in which the critical exponent $\alpha = 2 - 3\nu$ and the following notation is used:

$$C_1 = \frac{3}{2} + \frac{1}{2N} \sum_k \left(\frac{G(k)}{1 + G(k)} \right)^2 + 2s_0^{-3} (\gamma_1 + \gamma_2)$$

$$C_3^{(+)} = 3\nu(3\nu - 1) c_{\nu}^{3\nu} \gamma_3 s_0^{-3}$$

$$C_4^{(+)} = (3\nu + \Delta)(3\nu + \Delta - 1) c_{\Delta} c_{\nu}^{3\nu} \gamma_4 s_0^{-3}.$$

In the case of $T \leq T_c$, specific heat capacity C_V takes a form:

$$C_V = k_{\text{B}}N [C_1 + C_3^{(-)} (-\tau)^{3\nu-2} + C_4^{(-)} (-\tau)^{3\nu-2+\Delta}], \quad (3.27)$$

where we obtain the expressions of $C_3^{(-)}$ and $C_4^{(-)}$ from $C_3^{(+)}$ and $C_4^{(+)}$ by replacing the values of γ_3 and γ_4 with γ_{30} and γ_{31} , respectively.

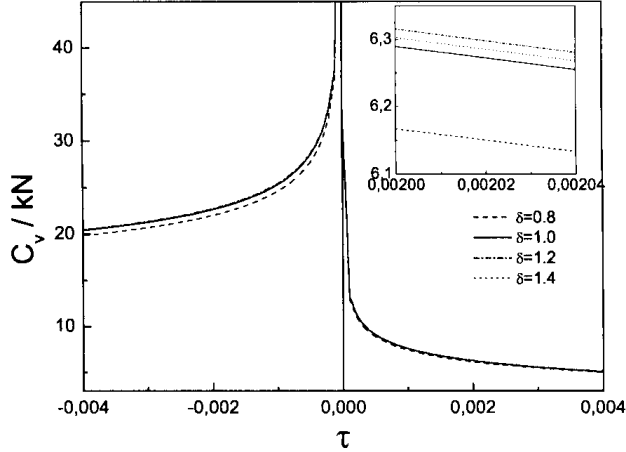


Fig. 4. Temperature dependence of the specific heat capacity of BSM with interaction potential (1.1) at various values of δ ($\lambda = 1.5$)

Figs. 4 and 5 show the dependence of specific heat capacity C_V on temperature in the vicinity of the VL critical point for various values of the microscopic parameters δ and λ .

By using expressions (3.26), (3.27) for specific heat capacity, we can find the relations for critical amplitudes of heat capacity under $T \geq T_c$ and $T \leq T_c$. For the main amplitudes in the limit of $\tau \rightarrow 0$, we have

$$\frac{C_3^{(+)}}{C_3^{(-)}} = \frac{\gamma_3}{\gamma_{30}} = 0.418. \quad (3.28)$$

For the critical amplitudes defining a correction to the scaling in the limit of $\tau \rightarrow 0$, we, correspondingly, find

$$\frac{C_4^{(+)}}{C_4^{(-)}} = \frac{\gamma_4}{\gamma_{31}} = -0.039. \quad (3.29)$$

Expressions (3.28) and (3.29) are universal values since these are independent of the microscopic parameters.

3.5. Isothermic Compressibility

To obtain an expression for isothermic compressibility of BSM in the vicinity of the VL critical point, we employ the Kirkwood–Buff relations written for an arbitrary multicomponent system [22]:

$$\chi_T k_B T = \frac{|\mathcal{B}|}{\sum_{\alpha, \beta}^{\nu} c_{\alpha} c_{\beta} |\mathcal{B}|_{\alpha\beta}}, \quad (3.30)$$

where χ_T is isothermic compressibility; $|\mathcal{B}|$ – determinant of a matrix with elements $\mathcal{B}_{\alpha\beta} = \frac{|A|_{\alpha\beta}}{V|A|}$, where $A_{\alpha\beta} = \frac{1}{k_B T} (\partial \mu_{\alpha} / \partial N_{\beta})_{V, T, N_{\gamma}}$; V – volume of the

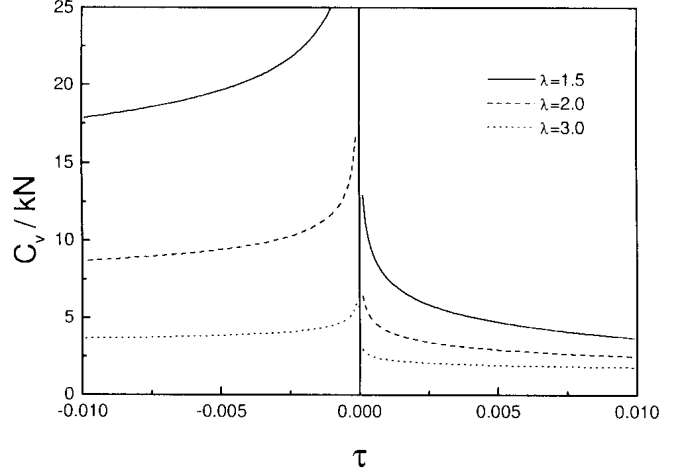


Fig. 5. Temperature dependence of the specific heat capacity of BSM with interaction potential (1.1) at various values of λ ($\delta = 0.9$)

system; $c_i = \frac{\langle N_i \rangle}{V}$; and α and β – species indices. In the case of a binary system with $\mu_a = \mu_b = \mu$, expression (3.30) takes the form

$$\rho k_B T \chi_T = \frac{1}{\eta \left(\frac{\partial \beta \mu}{\partial \eta} \right)_{V, T}}. \quad (3.31)$$

At first, let us consider expression (3.11) for chemical potential ($T \geq T_c$). Using (3.31), for χ_T , we have

$$\rho_c k_B T \chi_T = \frac{1}{\eta (A_1 + A_2 + A_3 + A_4 / D)} \Bigg|_{\eta = \eta_c}, \quad (3.32)$$

where $D = D_0^+ \tau^{-2\nu} (1 + D_1^+ c_{\Delta} \tau^{\Delta})$; for the case of potential (1.1) and Percus–Yevick approximation for the reference system, we have for A_1, \dots, A_4 :

$$A_1 = \frac{1}{\eta} \frac{(1 + 2\eta)^2}{(1 - \eta)^4},$$

$$A_2 = -\frac{1}{\sqrt{2}} \frac{\partial}{\partial \eta} \left(\frac{\bar{M}_3}{\bar{M}_4} \right),$$

$$A_3 = -\frac{4\lambda^3(1 + \delta) \sqrt{2}}{(k_B T / \epsilon) N} \left(\tilde{\mathcal{M}}_1 - \eta \frac{\partial \phi}{\partial \eta} \right),$$

$$A_4 = -\frac{2\lambda^3(1 + \delta) \sqrt{2}}{(k_B T / \epsilon) N} \left(\phi + \eta \frac{\partial \phi}{\partial \eta} \right).$$

Furthermore, we obtain for $\eta = \eta_c$:

$$A_1 + A_2 + A_3 = 0. \quad (3.33)$$

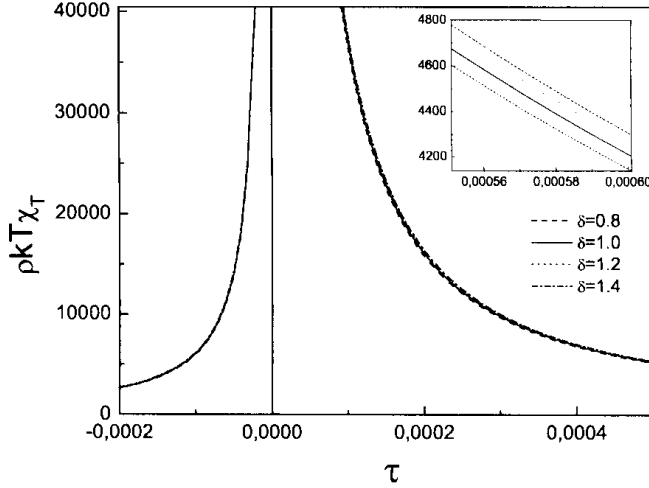


Fig. 6. Temperature dependence of the isothermal compressibility of BSM with interaction potential (1.1) ($\lambda = 1.5$)

Validity of (3.33) in the case of $\delta = 1$ (the monocomponent system) is proved analytically, and in the case of $\delta \neq 1$ – numerically.

As a result, we obtain for (3.32):

$$\rho_c k_B T_c \chi_T = \Gamma_0^{(+)} \tau^{-\gamma} (1 + \Gamma_1^{(+)} \tau^\Delta), \quad \tau \geq 0, \quad \eta = \eta_c,$$

where exponent $\gamma = 2\nu$ (the critical exponent of the correlation function equals zero in this approximation), and the following notation is introduced

$$\Gamma_0^{(+)} = \frac{2\sqrt{2}}{\beta_c |\tilde{V}(0)|} D_0^+ c_\nu^{-2\nu}, \quad \Gamma_1^{(+)} = c_\Delta D_1^+,$$

$$D_0^+ = 1.913, \quad D_1^+ = 1.480.$$

At $T \leq T_c$, from (3.24), and taking into account (3.19), we obtain

$$\left. \frac{\partial \mu^*}{\partial \eta} \right|_{\eta=\eta_c} = \frac{4B}{\eta_c}, \quad (3.34)$$

Taking into account Eqs. (3.31)–(3.33) and (3.34), for isothermic compressibility at $T \leq T_c$, we obtain the following expression:

$$\rho_c k_B T_c \chi_T = \Gamma_0^{(-)} (-\tau)^{-\gamma} (1 + \Gamma_1^{(-)} (-\tau)^\Delta),$$

where

$$\Gamma_0^{(-)} = (2\sqrt{2}\beta_c |\tilde{V}(0)| B_0^{(-)} c_\nu^{-2\nu})^{-1}, \quad \Gamma_1^{(-)} = -B_1^{(-)}.$$

The amplitudes' ratios equal, correspondingly,

$$\frac{\Gamma_0^{(+)}}{\Gamma_0^{(-)}} = 6.217, \quad \frac{\Gamma_1^{(+)}}{\Gamma_1^{(-)}} = -1.924.$$

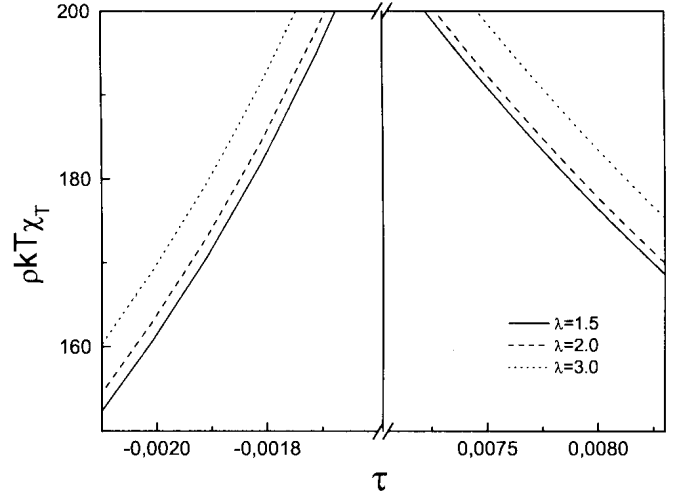


Fig. 7. The same as in Fig. 5, but for BSM isothermal compressibility

The behavior of isothermic compressibility vs temperature for various values of microscopic parameters δ and λ is shown in Figs. 6 and 7.

Conclusions

Using the step-by-step integration method [3] and basing upon the grand partition function functional derived in [9] for BSM in the vicinity of the VL critical point, we have obtained explicit expressions for the grand thermodynamic potential, chemical potential, Helmholtz free energy, entropy, constant volume specific heat capacity, and isothermic compressibility for both $T \geq T_c$ and $T \leq T_c$ temperature regions. The results show that the BSM critical behavior at $\mu_a = \mu_b$ (that corresponds to concentration $x = 0.5$) in the vicinity of the VL critical point is similar to that of a one-component fluid.

Entropy, specific heat capacity, and isothermic compressibility are calculated in the vicinity of the VL critical point for a binary symmetric mixture of hard spheres interacting through the potential of a square-well, and their behavior as a function of microscopic parameters δ and λ (δ is a force of “non-similar” interaction and λ – attraction range).

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ТЕРМОДИНАМІЧНІ ХАРАКТЕРИСТИКИ БІНАРНОЇ
СИМЕТРИЧНОЇ СУМІШІ В ОКОЛІ КРИТИЧНОЇ
ТОЧКИ ГАЗ—РІДИНА

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Резюме

Отримано явні вирази для термодинамічних функцій (великого термодинамічного потенціалу, вільної енергії, ентропії, питомої теплоємності, ізотермічної стисливості) бінарної симетричної суміші в околі критичної точки газ—рідина. В дослідженні використано метод колективних змінних з виділеною системою відліку і процедуру поетапного інтегрування великої статистичної суми. Для бінарної суміші твердих сфер, що взаємодіють через потенціал прямокутної ями, в критичній області розраховано температурну залежність термодинамічних характеристик та їхню залежність від мікроскопічних параметрів системи.