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Ab initio study of the vapour-liquid critical point of a symmetrical binary fluid mixture

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Вивчення з перших принципів критичної точки рідина-пара бінарної симетричної флюїдної суміші

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Анотація. Запропоновано мікроскопічний підхід до опису поведінки бінарної симетричної флюїдної суміші в околі критичної точки рідина-пара. Показано, що задачу можна звести до розрахунку статистичної суми $3D$ моделі Ізінга в зовнішньому полі. Для бінарної симетричної суміші, частинки якої взаємодіють з потенціалом прямокутної ями ми розраховуєм параметри критичної точки як функції мікроскопічного параметра r, який є мірою відносної сили взаємодії між частинками одинакових і різних сортів. Розрахунки проведені для двох різних областей дії потенціалу притягання: проміжної ($\lambda = 1.5$) і помірно далекодіючої ($\lambda = 2$). Результати добре узгоджуються з результатами, що отримані методом машинного моделювання.

Ab initio study of the vapour-liquid critical point of a symmetrical binary fluid mixture

O.V.Patsahan, M.P.Kozlovskii, R.S.Melnyk

Abstract. A microscopic approach to the investigation of the behaviour of a symmetrical binary fluid mixture in the vicinity of the vapour-liquid critical point is proposed. It is shown that the problem can be reduced to the calculation of the partition function of a 3D Ising model in an external field. For a square-well symmetrical binary mixture we calculate the parameters of the critical point (critical temperature and critical density) as functions of the microscopic parameters: the parameter r measuring the relative strength of interactions between the particles of dissimilar and similar species and the parameter λ measuring the width of the potential well. The obtained results agree well with the ones of computer simulations.

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1. Introduction

Binary mixtures in contrast to their constituent components can exhibit three different types of two-phase equilibria: vapour-liquid, liquid-liquid and gas-gas [1,2]. The possibility of the realization of these phenomena and their priority depend both on the external conditions and microscopic parameters of a mixture. The study of the influence of interparticle interactions on the critical properties of a binary mixture is an interesting and actual problem. During the last decade this problem has been intensively studied by integral equation theories (IETs). The advantages and limitations of these approaches were recently given by C. Caccamo in his extensive review [3]. Here we briefly point out some key features of IETs concerning phase equilibrium and critical properties of classical fluids.

The well-known IETs, such as the mean spherical approximation (MSA), the Percus-Yevick (PY) equation and the hypernetted chain (HNC) equation do not have a solution inside a certain region. In the case of the MSA, the boundary line of this forbidden region coincides with a spinodal line [4]-[6]. The MSA predictions for the existence of the critical points and the spinodal turn out to be qualitatively correct, although the thermodynamic inconsistency of the theory forbids a quantitative estimate of the location of these features. The PY equation and the HNC equation either do not predict the correct diverging trend of the compressibility when the spinodal is approached or do not predict any divergence at all [5], [7]-[8], [9]. The modified hypernetted chain (MHNC) theory is able to predict quite satisfactorily the liquid and the vapour branches of the binodal of a simple fluid at low enough temperature, but it fails to converge close to the critical point and the position of the critical point is not given directly by the theory but is to be determined by extrapolation [10]-[11]. Therefore, the IETs, although play an important role in the understanding of the properties of the liquid state, are not able to give a correct description of the fluid behaviour close to the critical point.

Of special interest is the hierarchical reference theory (HRT) concerned with the study of both universal and nonuniversal properties [12]-[17]. In this theory the long-wavelength part of the interaction is turning on gradually and the corresponding evolution of thermodynamic quantities and correlation functions is expressed by an infinite hierarchy of exact integro-differential equations. A simple closure of the hierarchy (the Ornstein-Zernike ansatz) yields nonclassical critical exponents with the correct scaling regime. The HRT was applied to one- and two-

component fluids. The results were found to be in a good agreement with both numerical simulations and experiments. However, as far as this method is computationally intensive, its application is limited.

On the other hand, the critical properties of simple fluids and binary mixtures have recently been studied using Monte Carlo (MC) simulations [18]-[24]. In [24] the vapour-liquid critical temperature was calculated for the symmetrical mixture of hard spheres interacting via the square-well potentials. Thus, it is interesting to test a theory using such a simple binary fluid model.

In the present paper we propose a microscopic approach to the study of the vapour-liquid critical point of a symmetrical binary mixture. This approach is based on the method of collective variables (CV) [25]. Its characteristic feature, in comparing with the above-mentioned theories, is that it allows one to determine, on the microscopic grounds, the explicit form of an effective Ginsburg-Landau-Wilson (GLW) Hamiltonian and then to integrate the partition function in the neighbourhood of the phase transition point taking into account the renormalization group (RG) symmetry. This method appears to be successful in describing the second order phase transition of the 3D Ising model [26] and the vapour-liquid critical point of a one-component fluid [27]. On the basis of this approach both universal and non-universal quantities were obtained.

In [28] the CV method with a reference system (RS) was generalized for the case of a grand canonical ensemble for a multicomponent continuous system. Using this approach the phase diagram of the symmetrical mixture was examined within the framework of the Gaussian approximation [29]-[31].

In this paper we determine an explicit form of the effective GLW Hamiltonian of the symmetrical binary mixture in the vicinity of the vapour-liquid critical point. Then we integrate the functional of the grand partition function by the use of the layer-by-layer integration method proposed in [26] for the 3D Ising model. As a result of this integration one obtains recursion relations for the coefficients of the GLW Hamiltonian. The analysis of these relations yields an equation for T_c. Here we avoid extensive consideration of the results pertaining to the Ising model and call the readers' attention to [26] where this problem was studied in detail. The method which we describe here yields the same critical exponents as in [32] (see table 1).

The paper is organized as follows. We give a functional representation of the grand partition function of a two-component continuous system in section 2 and appendix A. In section 3 we construct the basic density measure (GLW Hamiltonian) with respect to the CV which include a

Table 1. Values of the critical exponents and the ratios of the critical amplitudes for the 3D Ising model obtained within the framework of the CV method

ν	α	β	γ	A^+/A^-	Γ^+/Γ^-
0.637	0.088	0.319	1.275	0.435	6.967

variable corresponding to the order parameter. In this section we also present the basic ideas of the method of the partition function integration in the vicinity of the critical point. In section 4 we apply our formalism to calculating the critical characteristics (temperature and density) of the binary square-well symmetrical mixture. The obtained results are discussed and compared with the MC simulation data reported recently by N.B.Wilding [24] and E.de Miquel [23].

2. Functional representation of the grand partition function of a binary mixture

Let us consider a binary fluid mixture consisting of N_a particles of species "a" and N_b particles of species "b". The system is in volume V at temperature T. Let us assume that an interaction in the system has a pairwise additive character. The interaction potential between γ particle at $\mathbf{r}_i$ and δ particle at $\mathbf{r}_j$ can be expressed as a sum of two terms:

$$U_{\gamma\delta}(|\mathbf{r}_i-\mathbf{r}_j|)=\Psi_{\gamma\delta}(|\mathbf{r}_i-\mathbf{r}_j|)+\Phi_{\gamma\delta}(|\mathbf{r}_i-\mathbf{r}_j|), \tag{1}$$

where $\Psi_{\gamma\delta}(r)$ is a potential of a short-range repulsion and $\Phi_{\gamma\delta}(r)$ is an attractive part of the potential which dominates at large distances.

A functional of the grand partition function (GPF) of the binary homogeneous system in the CV method with a RS can be represented as a product of two factors (see Appendix A):

$$\Xi=\Xi_0\Xi_1, \tag{2}$$

where Ξ_0 is the GPF of the RS which we suppose to be known. Ξ_1 is the part of the GPF which is written in the CV space:

$$\begin{aligned}\Xi_1 &= \int(d\rho)(dc)\exp\left\{\beta\mu_1^+\rho_0+\beta\mu_1^-c_0-\frac{\beta}{2}\sum_{\mathbf{k}}\left[\tilde V(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}+\right.\right.\\ &+ \left.\left.2\tilde U(k)\rho_{\mathbf{k}}c_{\mathbf{k}}+\tilde W(k)c_{\mathbf{k}}c_{-\mathbf{k}}\right]\right\}J(\rho,c).\end{aligned} \tag{3}$$

Chemical potentials $\mu_1^+=\frac{1}{\sqrt{2}}(\mu_1^a+\mu_1^b)$ and $\mu_1^-=\frac{1}{\sqrt{2}}(\mu_1^a-\mu_1^b)$ are determined from the conditions:

$$\frac{dln\Xi_1}{d\beta\mu_1^+} = <N_a>+<N_b>=<N> \tag{4}$$

$$\frac{dln\Xi_1}{d\beta\mu_1^-} = <N_a>-<N_b>. \tag{5}$$

Functions $\tilde V(k),\tilde W(k)$ and $\tilde U(k)$ are combinations of Fourier transforms of the initial interaction potentials $\tilde\Phi_{\gamma\delta}(k)$:

$$\begin{aligned}\tilde V(k) &= (\frac{\beta^{-1}}{2})\left[\alpha_{aa}(k)+\alpha_{bb}(k)+2\alpha_{ab}(k)\right],\\ \tilde U(k) &= (\frac{\beta^{-1}}{2})\left[\alpha_{aa}(k)-\alpha_{bb}(k)\right],\\ \tilde W(k) &= (\frac{\beta^{-1}}{2})\left[\alpha_{aa}(k)+\alpha_{bb}(k)-2\alpha_{ab}(k)\right].\end{aligned} \tag{6}$$

$$\begin{aligned}J(\rho,c) &= \int(d\nu)(d\omega)\exp\left\{i2\pi\sum_{\mathbf{k}}(\omega_{\mathbf{k}}\rho_{\mathbf{k}}+\nu_{\mathbf{k}}c_{\mathbf{k}})+\right.\\ &+ \left.\sum_{n\geq1}\sum_{i_n\geq0}D_n^{(i_n)}(\omega,\nu)\right\}\end{aligned} \tag{7}$$

is a transition Jacobian to the CV $\rho_{\mathbf{k}},c_{\mathbf{k}}$ averaged on the RS, variables $\omega_{\mathbf{k}},\nu_{\mathbf{k}}$ are conjugated to variables $\rho_{\mathbf{k}},c_{\mathbf{k}}$, respectively.

$$\begin{aligned}D_n^{(i_n)}(\omega,\nu) &= \frac{(-i2\pi)^n}{n!}\left(\frac{1}{2}\right)^{n/2}\sum_{\mathbf{k}_1\ldots\mathbf{k}_n}\mathcal{M}_n^{(i_n)}(\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_n)\times\\ &\times \nu_{\mathbf{k}_1}\ldots\nu_{\mathbf{k}_{i_n}}\omega_{\mathbf{k}_{i_n+1}}\ldots\omega_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_n}.\end{aligned} \tag{8}$$

Index i_n indicates the number of variables $\nu_{\mathbf{k}}$ in the cumulant expansion (8). Cumulants $\mathcal{M}_n^{(i_n)}(\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_n)$ are linear combinations of the initial cumulants $\mathcal{M}_{\gamma_1\ldots\gamma_n}(\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_n)$ $(\gamma_i=a,b)$ (see Appendix B). In general, the dependence of $\mathcal{M}_{\gamma_1\ldots\gamma_n}(\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_n)$ on wave vectors $\mathbf{k}_1,\mathbf{k}_2,...,\mathbf{k}_n$ is complicated [28]. Since we are interested in the critical properties, the small-$\mathbf{k}$ expansion of the cumulants can be considered.

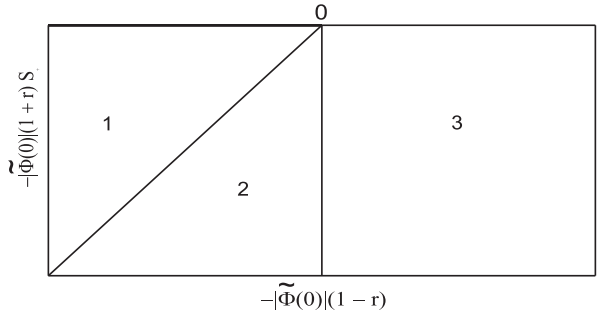

Figure 1. Three phase regions of the symmetrical mixture depending on the microscopic parameters: (1) gas-gas and vapour-liquid phase transitions ($T_c^{g-g} > T_c^{v-l}$); (2) vapour-liquid and liquid-liquid phase transitions ($T_c^{v-l} > T_c^{l-l}$); (3) vapour-liquid phase transition only. S_2 is the two-particle structure factor of the reference system

Hereafter we shall replace $\mathcal{M}_{\gamma_1\ldots\gamma_n}(\mathbf{k}_1, \mathbf{k}_2, ..., \mathbf{k}_n)$ by their values in the long-wave limit and we shall discuss this approximation in Sec. 4.

We consider a symmetrical binary fluid mixture (SBFM), i.e. a system in which the two pure components "a" and "b" are identical and only interactions between the particles of dissimilar species differ. Notwithstanding its simplicity, the SBFM exhibits all the three types of two-phase equilibria which are observed in real binary fluids, namely: vapour-liquid, liquid-liquid and gas-gas equilibria. For the SBFM $\tilde{U}(k) = 0$ in (3) and there are only terms with even indices i_n in the cumulant expansion (8) [30].

3. The method

As it was already shown [30], the phase diagram of the SBFM consists of three ranges (see figure 1): (1) gas-gas separation and vapour-liquid phase transitions; (2) vapour-liquid and liquid-liquid phase transitions; (3) vapour-liquid phase transition only.

The order of priority of the vapour-liquid and separation phase transitions depends on both the external conditions and the microscopic properties of the system. There exist two critical temperature branches in such a system: branch (T_c^{v-l}) connected with the variable ρ_0 and branch (T_c^{sep}) connected with the variable c_0 [30]. All the thermodynamic functions of the SBFM are symmetrical with respect to the concentration x=0.5 and have an extremum at this point [1,29]. The concentration

x=0.5 is a critical one for this model mixture.

We consider a symmetrical fluid mixture whose parameters satisfy the following condition:

$$r > \mathcal{L}, \qquad \mathcal{L} = \frac{1 - S_2(0)}{1 + S_2(0)}.$$

It corresponds to ranges 2 ($\mathcal{L} < r < 1$) and 3 ($r > 1$) on the phase diagram (see Fig. 1). In this paper we study the vapour-liquid critical point.

In the case of the SBFM the variables ρ_0 and c_0 are connected with the order parameters for the vapour-liquid and separation phase transitions, respectively [30]. This fact allows us to separate CV $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ into essential and non-essential ones depending on the phase transition considered. Since we are interested in the vapour-liquid critical point, we can consider CV $c_{\mathbf{k}}$ (and $\nu_{\mathbf{k}}$) to be non-essential (CV $c_{\mathbf{k}}$ do not contain a variable connected with the order parameter, the coefficients standing at the second power of $c_{\mathbf{k}}$ (and $\nu_{\mathbf{k}}$) are negative) and we can integrate over $c_{\mathbf{k}}$ (and $\nu_{\mathbf{k}}$) with the Gaussian density measure. In respect to CV $\rho_{\mathbf{k}}$ it is necessary to construct the basic density measure taking into account higher powers of $\rho_{\mathbf{k}}$ (we shall consider a ρ^4 model).

As a result of integrating in (3)-(8) over variables $c_{\mathbf{k}}$ (and $\nu_{\mathbf{k}}$) we obtain for the GPF:

$$\Xi = \Xi_0 \Xi_G^c \int (d\rho) \exp\left\{\beta\mu_1^+ \rho_0 - \frac{\beta}{2}\sum_{\mathbf{k}} \tilde{V}(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\right\} J(\rho), \tag{9}$$

where

$$\Xi_G^c = \prod_{\mathbf{k}} \frac{1}{\sqrt{1 + \beta\tilde{W}(k)\mathcal{M}_2^{(2)}(0)/2}}, \tag{10}$$

$$\begin{aligned} J(\rho) \quad &= \quad \int (d\omega) \exp\left\{ i2\pi \sum_{\mathbf{k}} \omega_{\mathbf{k}}\rho_{\mathbf{k}} + \sum_{n\geq 1}^{4} \frac{(-i2\pi)^n}{n!} \left(\frac{1}{2}\right)^{n/2} \times \right. \\ &\times \quad \left. \sum_{\mathbf{k}_1\ldots\mathbf{k}_n} \mathcal{M}_n(0)\omega_{\mathbf{k}_1}\ldots\omega_{\mathbf{k}_n}\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_n} \right\}, \end{aligned} \tag{11}$$

$$\mathcal{M}_n(0) = \mathcal{M}_n^{(0)}(0) + \Delta\mathcal{M}_n. \tag{12}$$

$\Delta\mathcal{M}_n$ are the corrections obtained as the result of integration over variables $c_{\mathbf{k}}$:

$$\begin{aligned}
\Delta\mathcal{M}_1 &= \frac{\mathcal{M}_3^{(2)}(0)}{12}\frac{1}{<N>}\sum_{\mathbf{k}}\tilde{g}(|\mathbf{k}|),\\
\Delta\mathcal{M}_2 &= \frac{\mathcal{M}_4^{(2)}(0)}{12}\frac{1}{<N>}\sum_{\mathbf{k}}\tilde{g}(|\mathbf{k}|)+\\
&+ \frac{(\mathcal{M}_3^{(2)}(0))^2}{72}\frac{1}{<N>^2}\sum_{\mathbf{k}}\tilde{g}(|\mathbf{k}|)\tilde{g}(|\mathbf{k}_1-\mathbf{k}|),\\
\Delta\mathcal{M}_3 &= \frac{\mathcal{M}_3^{(2)}(0)\mathcal{M}_4^{(2)}(0)}{48}\frac{1}{<N>^2}\sum_{\mathbf{k}}\tilde{g}(|\mathbf{k}|)\tilde{g}(|\mathbf{k}_1-\mathbf{k}|)+\\
&+ \frac{(\mathcal{M}_3^{(2)}(0))^3}{6}\frac{1}{<N>^3}\sum_{\mathbf{k}}\tilde{g}(|\mathbf{k}|)\tilde{g}(|\mathbf{k}_1+\mathbf{k}|)\tilde{g}(|\mathbf{k}_2-\mathbf{k}|),\\
\Delta\mathcal{M}_4 &= \frac{(\mathcal{M}_4^{(2)}(0))^2}{96}\frac{1}{<N>^2}\sum_{\mathbf{k}}\tilde{g}(|\mathbf{k}|)\tilde{g}(|\mathbf{k}_1-\mathbf{k}|)+\\
&+ (\frac{\mathcal{M}_3^{(2)}(0)}{3!})^4\frac{1}{<N>^4}\sum_{\mathbf{k}}\tilde{g}(|\mathbf{k}|)\tilde{g}(|\mathbf{k}_1+\mathbf{k}|)\times\\
&\times \tilde{g}(|\mathbf{k}_2-\mathbf{k}|)\tilde{g}(|\mathbf{k}_3+\mathbf{k}_1+\mathbf{k}|), \qquad (13)
\end{aligned}$$

where

$$\tilde{g}(k) = -\frac{\beta<N>\tilde{W}(k)}{\frac{1}{2}\beta\tilde{W}(k)\mathcal{M}_2^{(2)}(0)+1}. \qquad (14)$$

In figure 2 the typical behaviour of the potential $\tilde{V}(k)/|\tilde{V}(0)|$ is shown.

Let us further assume that $\tilde{V}(k)=0$ at $|\mathbf{k}|>B$. Then, integration in (9) over $\rho_{\mathbf{k}}$ with $|\mathbf{k}|>B$ leads to δ - functions and the expression for Ξ contains only the sums over $\mathbf{k}$ with $|\mathbf{k}|\le B$.

We consider a set of $\mathbf{k}$ vectors, $|\mathbf{k}|\le B$, as corresponding to the sites of a reciprocal lattice conjugated to a certain block lattice $\{r_l\}$ with N_B block sites in the periodicity volume V:

$$<N_B>=\frac{V}{C^3}=\frac{V}{(\pi/B)^3}=\frac{(B\sigma)^3<N>}{6\pi^2\eta}, \qquad (15)$$

$\eta=\frac{\pi}{6}\rho\sigma^3$ is fraction density. Therefore, one may consider quantity B as the size of the first Brillouin zone of this block lattice.

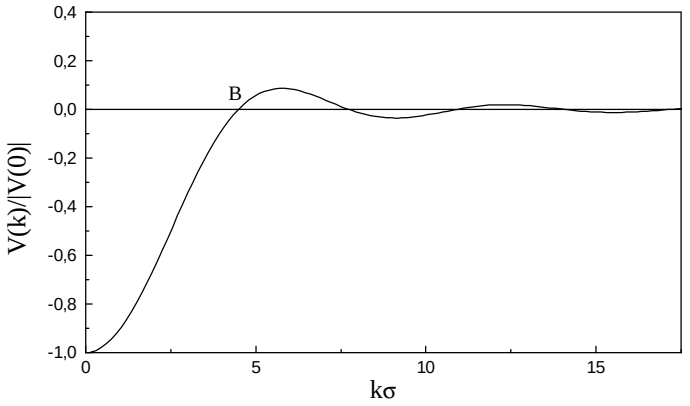

Figure 2. The behaviour of the Fourier transform $\tilde{V}(k)/|\tilde{V}(0)|$ of the attractive part of the interaction potential V(r)

The shift

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

where

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

$\left(\bar{\mathcal{M}}_n(0)=\frac{\mathcal{M}_n(0)}{(\sqrt{2})^n},\ n=1,...,4\right)$, transforms Ξ into a form containing terms $\tilde{\mathcal{M}}_1(0)$, $\tilde{\mathcal{M}}_2(0)$ and $\tilde{\mathcal{M}}_4(0)$ only (the primes on $\rho_{\mathbf{k}}$ and $\omega_{\mathbf{k}}$ are omitted for clarity):

$$\begin{aligned}
\Xi &= \Xi_0\Xi_G^{(1)}\int\exp\left\{\mu^*\rho_0-\frac{\beta}{2}\sum_{\mathbf{k}<B}\tilde{V}(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}}\right.\\
&+ i2\pi\sum_{\mathbf{k}<B}\omega_{\mathbf{k}}\rho_{\mathbf{k}}-\frac{(2\pi)^2}{2}\tilde{\mathcal{M}}_2(0)\sum_{\mathbf{k}<B}\omega_{\mathbf{k}}\omega_{-\mathbf{k}}-\frac{(2\pi)^4}{4!<N_B>}|\tilde{\mathcal{M}}_4(0)|\\
&\times\left.\sum_{\mathbf{k}_1...\mathbf{k}_4<B}\omega_{\mathbf{k}_1}\omega_{\mathbf{k}_2}\omega_{\mathbf{k}_3}\omega_{\mathbf{k}_4}\delta_{\mathbf{k}_1+...+\mathbf{k}_4}\right\}(d\omega)^{N_B}(d\rho)^{N_B}, \qquad (16)
\end{aligned}$$

where

$$\begin{aligned}
\Xi_G^{(1)} &= \Xi_G^c \exp\left\{\mu^*\tilde{\mathcal{M}}_1 + \frac{\beta\tilde{V}^*(0)}{2}\tilde{\mathcal{M}}_1^2\right. \\
&- \left.\frac{\bar{\mathcal{M}}_1(0)\bar{\mathcal{M}}_3(0)}{\bar{\mathcal{M}}_4(0)} - \frac{\bar{\mathcal{M}}_2(0)\bar{\mathcal{M}}_3^2(0)}{2\bar{\mathcal{M}}_4^2(0)} - \frac{\bar{\mathcal{M}}_3^4(0)}{8\bar{\mathcal{M}}_4^3(0)}\right\}, \\
\mu^* &= h - a_1, \quad a_1 = \frac{\bar{\mathcal{M}}_3(0)}{|\bar{\mathcal{M}}_4(0)|} + \beta\tilde{V}^*(0)\tilde{\mathcal{M}}_1, \quad h = \beta\mu_1^+, \\
\tilde{\mathcal{M}}_2(0) &= \bar{\mathcal{M}}_2(0) - \frac{\bar{\mathcal{M}}_3^2(0)}{2\bar{\mathcal{M}}_4(0)}, \\
\tilde{\mathcal{M}}_4(0) &= < N_B > \bar{\mathcal{M}}_4(0). \qquad (17)
\end{aligned}$$

$(d\ldots)^{N_B}$ implies that the vector $\mathbf{k}$ takes the $< N_B >$ values inside the first Brillouin zone:

$$(d\rho)^{N_B} = d\rho_0 \prod_{\mathbf{k}<B}{}' d\rho_{\mathbf{k}}^c d\rho_{\mathbf{k}}^s,$$

$$(d\omega)^{N_B} = d\omega_0 \prod_{\mathbf{k}<B}{}' d\omega_{\mathbf{k}}^c d\omega_{\mathbf{k}}^s.$$

Expression (16) for Ξ corresponds to the Ising model in the external field $(a_1 - \beta\mu_1^+)$ with the only difference: cumulants $\tilde{\mathcal{M}}_2(0)$, $\tilde{\mathcal{M}}_4(0)$ are functions of the fraction density η, temperature T and parameters of the attractive interaction $\tilde{\Phi}_{\gamma\delta}(k)$.

After integration over $\omega_{\mathbf{k}}$ we obtain the following form for the GPF:

$$\begin{aligned}
\Xi &= \Xi_0\Xi_G^{(1)}\left[Z(\tilde{\mathcal{M}}_2, \tilde{\mathcal{M}}_4)\right]^{<N_B>}(\sqrt{2})^{<N_B>-1} \times \\
&\times \int \exp[E_4(\rho)](d\rho)^{N_B}. \qquad (18)
\end{aligned}$$

Here

$$\begin{aligned}
E_4(\rho) &= \mu^*\rho_0 - \frac{1}{2}\sum_{\mathbf{k}<B} d_2(k)\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - \frac{a_4}{4! < N_B >} \times \\
&\times \sum_{\mathbf{k}_1\ldots\mathbf{k}_4<B} \rho_{\mathbf{k}_1}\cdots\rho_{\mathbf{k}_4}\delta_{\mathbf{k}_1+\ldots+\mathbf{k}_4} + \cdots \quad , \qquad (19)
\end{aligned}$$

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

$$\begin{aligned}
d_2(k) = a_2 + \beta\tilde{V}(k), \quad a_2 &= \sqrt{\frac{3}{|\tilde{\mathcal{M}}_4(0)|}}K(x), \\
a_4 &= \frac{3}{|\tilde{\mathcal{M}}_4(0)|}L(x), \qquad (20)
\end{aligned}$$

where

$$\begin{aligned}
K(x) &= U(1,x)/U(0,x), \\
L(x) &= 3K^2(x) + 2xK(x) - 2, \\
x &= \sqrt{\frac{3}{|\tilde{\mathcal{M}}_4(0)|}}\tilde{\mathcal{M}}_2(0). \qquad (21)
\end{aligned}$$

$U(a,x)$ is a parabolic cylinder function [33]. Expressions (18)-(21) have the same forms as similar expressions for a one-component system obtained in [27]. This coincidence is achieved due to the symmetry of the model under consideration. $E_4(\rho)$ is the Ginzburg-Landau-Wilson Hamiltonian for the SBFM in the vicinity of the vapour-liquid critical point.

In order to integrate the GPF (18)-(21) over $\rho_{\mathbf{k}}$ and determine the critical temperature we use the method developed in [26,34] for the Ising model. The essence of the method consists in subsequent integration over the layers of the CV space, beginning from $\rho_{\mathbf{k}}$ which correspond to short-wave fluctuations. Variations of the coefficients of $E_4(\rho)$ as the result of integration over $\rho_{\mathbf{k}}$ in n subsequent layers of CV phase space are described by the recursion formulae derived in [26]. For the case $T > T_c$ in the interval $[0, B]$ there exist three characteristic regions [26]. The first region $B_{m_\tau} < k \leq B$ corresponds to the strongly correlated fluctuations $\rho_{\mathbf{k}}$, their density measure is non-Gaussian. The procedure based on the renormalization group symmetry is valid here. This is the region of the critical regime (CR). The second region $0 < k \leq B_{m_\tau}$ is related to the fluctuation distributed according to the Gaussian density measure. This is the limiting Gaussian regime (LGR).

The third region consists of the point $k = 0$. The variable ρ_0 is a macroscopic one and corresponds to the fluctuations of the particle density in the "external field" μ^*.

We integrate (18) according to the following scheme [26]. The region $(0, B)$ is divided into the intervals $(B_1, B), ..., (B_{i+1}, B_i), ...$, where $B_n = B/S^n$ (S is a division parameter). Each interval corresponds to a layer of subscripts $\mathbf{k}$ in the Brillouin zone and each layer of subscripts $\mathbf{k}$ - to a layer in the phase space $\rho_{\mathbf{k}}$. Integrating gradually over the layers we get a block lattice sequence with an appropriately growing block period

and with the Hamiltonian corresponding to each block. Each Hamiltonian is characterized by the coefficients $d_2, a_4; d_2^{(1)}, a_4^{(1)}; d_2^{(2)}, a_4^{(2)}$, etc.. For the sequence of the block Hamiltonians $\left\{d_2^{(n)}, a_4^{(n)}\right\}$ the renormalization group symmetry holds and the fixed point is of a saddle type. Because the explicit expressions for the initial values of coefficients $d(k)$ and a_4 are given (see (19)-(21)), the solutions of the renormalization group type are functions of microscopic parameters, density and temperature.

Generally, the division parameter $S > 1$ can take arbitrary values, but the highest precision of the results is achieved at some optimal value $S = S^*$ depending on the approximation considered. For example, if we have a ϕ^4 model approximation, the optimal value is $S^* = 3.4252$ providing the coefficient $d_2^{(n)}(0)$ to be equal to zero at the fixed point [26]-[27].

The CR takes place for all the variables $\rho_{\mathbf{k}}$ at the critical point. Therefore, the critical temperature can be determined from the solution of recurrent equations (see Appendix C). Combining (33) with (32) we derive the formula

$$A(\beta_c \tilde{V}(0))^2 + B(\beta_c \tilde{V}(0)) + D = 0, \tag{22}$$

where

$$A = 1 - f_0 - R^{(0)}\sqrt{\varphi_0},$$
$$B = -a_2,$$
$$D = a_4 R^{(0)}/\sqrt{\varphi_0}.$$

f_0, φ_0 are coordinates of the reduced fixed point, $R^{(0)}$ is a universal function of parameter S. The optimal value of S is 3.4252 and the values of $f_0, \varphi_0, R^{(0)}$ corresponding to it are taken from [34]. From the condition $\mu^* = 0$ we obtain the second equation [27]:

$$\mathcal{M}_3(0) = 0, \tag{23}$$

which allows us to determine the critical density of the system.

4. Results and discussions

In this section we present our results for the vapour-liquid critical point of symmetrical mixtures, using the method proposed above. These results are compared with those previously obtained by Monte-Carlo simulations [23,24].

The system under study is a symmetrical hard sphere square-well binary mixture. The interaction potential between the particles is given by:

$$U_{\gamma\delta}(r) = \begin{cases} \infty, & if \quad r < \sigma \\ -\epsilon_{\gamma\delta}, & if \quad \sigma \le r < \lambda\sigma \\ 0, & if \quad r \ge \lambda\sigma \end{cases},$$

where σ is a hard sphere diameter, λ is a range of the potential, and $\epsilon_{\gamma\delta}$ is a well-depth of the interaction between the particles of types γ and δ.

The square-well potential is the simplest model which includes the presence of attractive and repulsive forces. It is widely used to model an interaction of uncharged colloidal particles [37]-[39]. Moreover, this model is of substantial theoretical importance for the studies of systems with a varying potential range since it can represent three limiting cases, namely, a hard sphere fluid, a short-range sticky sphere fluid, and a long-range van der Waals fluid.

For a symmetrical mixture $\epsilon_{aa} = \epsilon_{bb} = \epsilon \neq \epsilon_{ab}$. In our formalism a completely analytical treatment for general λ is possible.

We split the potential $U_{\gamma\delta}(r)$ into short- and long-range parts using the Weeks-Chandler-Andersen partition [40]. As a result, we have:

$$\Psi_{\gamma\delta}(r) = \begin{cases} \infty, & r \le \sigma \\ 0, & r > \sigma \end{cases}, \tag{24}$$

$$\Phi_{\gamma\delta}(r) = \begin{cases} -\epsilon_{\gamma\delta}, & 0 \le r \le \lambda\sigma \\ 0, & r > \lambda\sigma \end{cases}. \tag{25}$$

For the WCA partition $\Phi_{\gamma\delta}(r)$ is perfectly smooth in the core region. As it was shown [41], this partition provides the best estimates for thermodynamic functions of the Lennard-Jones fluid.

In our case the RS is a one-component hard sphere system with the diameter σ (see (24)). In this case we can use the results for $\mathcal{M}_n(k_1, k_2, ..., k_n)$ obtained in [27]. As it was shown [27] the distinctive feature of $\mathcal{M}_2(k)$ is an almost horizontal "shoulder" at small k. Moreover, a weak dependence on k at small k is a common property of the cumulants of the higher order ($n = 3, 4$). This allows us to replace the functions $\mathcal{M}_n(k_1, k_2, ..., k_n)$ at $k_i < B$ by constant values $\mathcal{M}_n(0, 0, ..., 0)$.

The Fourier transform of function (25) has the form:

$$\tilde{\Phi}_{\gamma\delta}(k) = \tilde{\Phi}_{\gamma\delta}(0)\frac{3}{(\lambda x)^3}[-\lambda x\ cos(\lambda x) + sin(\lambda x)],$$

where

$$x = k\sigma,$$

$$\tilde{\Phi}_{\gamma\delta}(0) = -\epsilon_{\gamma\delta}\sigma^3\frac{4\pi}{3}\lambda^3.$$

Cumulants $\mathcal{M}_n^{(i_n)}(0,...,0)$ are calculated according to the formulae given in Appendix B. Both the Percus-Yevick (PY) approximation and the Carnahan-Starling (CS) approximation are used for $S_2(0)$.

The solutions of equations (22)-(23) are found numerically using a self-consistent procedure by means of which the dependencies of the coefficients a_2 and a_4 (as well as cumulants $\mathcal{M}_n(0)$) on β_c are taken into consideration.

The vapour-liquid critical temperatures T_c ($T_c = k_BT/\epsilon$) versus the microscopic parameter r ($r = \epsilon_{ab}/\epsilon$ is a dissimilar interaction strength) are shown for $\lambda = 1.5$ and $\lambda = 2.0$ in Fig 3. It is seen that the vapour-liquid critical temperature of the square-well binary mixture increases almost linearly with increasing r.

In Fig. 4 we demonstrate the dependence of the critical density η_c on r for $\lambda = 1.5$ and $\lambda = 2.0$. There is a region of r ($0.9 < r < 1.1$) on this plot where η_c remains almost constant and then ($r > 1.1$) it decreases with increasing r. Besides, in the region $r > 1.1$ the values of η_c for $\lambda = 2.0$ are higher than the ones for $\lambda = 1.5$. The curves depicted in Figs. 3-4 are obtained when the PY approximation for $S_2(0)$ is used.

Figures 5 and 6 demonstrate the results for T_c and η_c versus r when the both approximations (PY and CS) for $S_2(0)$ are used. As it can be seen, there is no significant discrepancy between the results, namely, the CS equation gives slightly higher values for T_c and η_c than the PY approximation.

In Fig. 7 the vapour-liquid critical temperature of the square-well binary mixture is plotted as a function of the width of the potential well λ for different r. Fig. 8 shows the λ dependence of the coefficients $a_2^c = a_2(T = T_c, \eta = \eta_c, r = 1)$ and $a_4^c = a_4(T = T_c, \eta = \eta_c, r = 1)$ of the effective GLW Hamiltonian (19). It is not surprising that for large values of λ the critical behaviour of the system becomes mean-field like.

We also compare our results with those obtained from MC simulations: for $\lambda = 1.5$ and r=0.72 we have $T_c = 1.055$, while the MC simulations give $T_c = 1.06(1)$ [24], for $\lambda = 2.0$ and r=1.0 (the case of r=1.0 corresponds to a one-component system) we obtain $T_c = 2.753$ and $\eta_c = 0.129$, while the simulations give $T_c = 2.684(51)$ and $\eta_c = 0.123(43)$ [23].

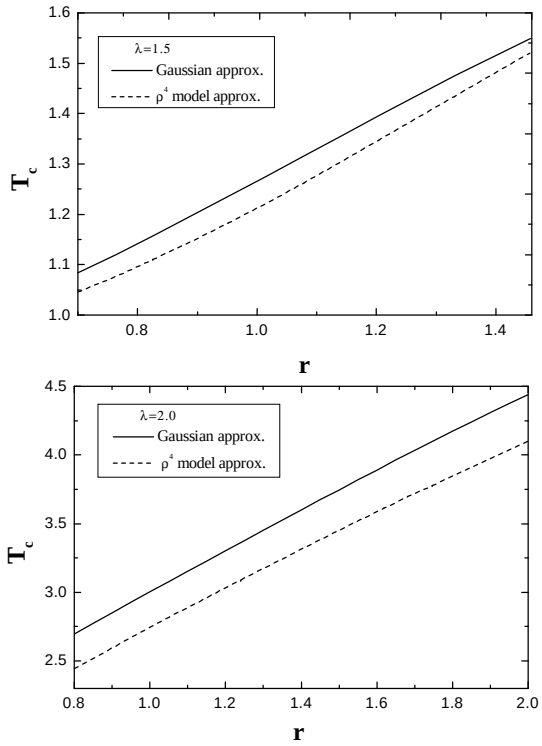

Figure 3. The vapour-liquid critical temperature as a function of the microscopic parameter r at $\lambda = 1.5$ (left) and $\lambda = 2.0$ (right)

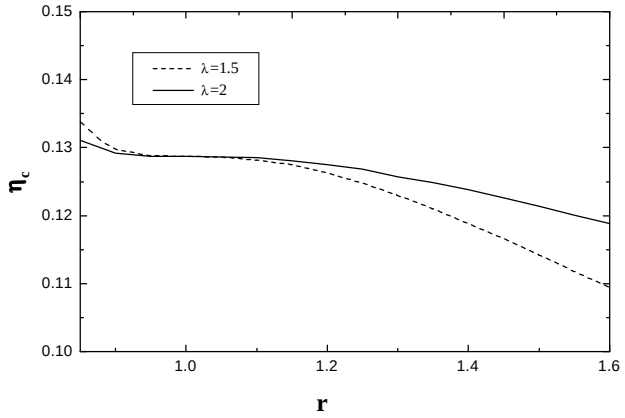

Figure 4. The critical density as a function of the microscopic parameter r

5. Conclusions

In this paper we propose a method for the study of the vapour-liquid critical point of a symmetrical binary mixture depending on its microscopic properties. We apply this method to the hard sphere square-well binary mixture. For this model we calculate the critical temperature and critical density versus the microscopic parameter r measuring the dissimilar interaction in the system as well as versus the width of the potential well. Our results agree well with those obtained by using MC simulations. We can improve our results in the following ways: 1) taking into consideration the region of $\mathbf{k}$ with $|\mathbf{k}| > B$ (see figure 2); 2) using a higher approximation than the ρ^4 one.

Having tested the theory by the results of MC simulations for such a simple model we can apply it to more realistic systems, for example, the hard sphere Yukawa mixtures and the Lennard-Jones mixtures. The relevant results will be given in a subsequent paper.

Appendix A

A grand partition function of a two-component fluid system in the CV representation with a RS can be written as in [28]:

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

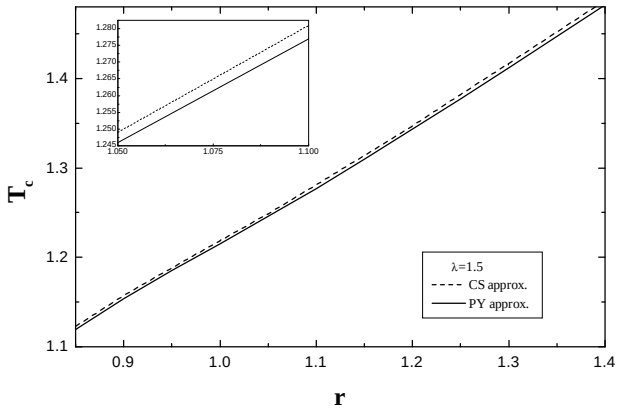

Figure 5. The vapour-liquid critical temperatures versus r when the PY approximation and the CS approximation for $S_2(0)$ are used

where

$$\Xi_0 = \sum_{N_a=0}^{\infty} \sum_{N_b=0}^{\infty} \prod_{\gamma=a}^{b} \exp\left[\frac{\beta\mu_0^\gamma N_\gamma}{N_\gamma!}\right] \int (d\Gamma) \exp\left[-\frac{\beta}{2} \sum_{\gamma,\delta=a,b} \sum_{i,j} \psi_{\gamma\delta}(r_{ij})\right]$$

is a grand partition function of the RS; $\beta = \frac{1}{k_B T}$, k_B- is the Boltzman constant, T is temperature; $(d\Gamma) = \prod_{a,b} d\Gamma_{N_\gamma}$, $d\Gamma_{N_\gamma} = d\vec{r}_1^{\gamma} d\vec{r}_2^{\gamma} \dots d\vec{r}_{N_\gamma}^{\gamma}$ is a volume element of the configurational space of the γ-th species; μ_0^γ is a chemical potential of the γ-th species in the RS.

The part of the grand partition function which is defined in the CV phase space has the form of a functional integral:

$$\Xi_1 = \int (d\rho) exp[\beta \sum_{\gamma} \mu_1^\gamma \rho_{0,\gamma} - \frac{1}{2\beta} \sum_{\gamma,\delta=a,b} \sum_{\mathbf{k}} \alpha_{\gamma\delta}(k) \rho_{\mathbf{k},\gamma} \rho_{-\mathbf{k},\delta}] J(\rho_a, \rho_b). \tag{26}$$

Here,

1) μ_1^γ is a part of the chemical potential of the γ-th species

$$\mu_1^\gamma = \mu_\gamma - \mu_0^\gamma + \frac{1}{2\beta} \sum_{\mathbf{k}} \alpha_{\gamma\gamma}(k),$$

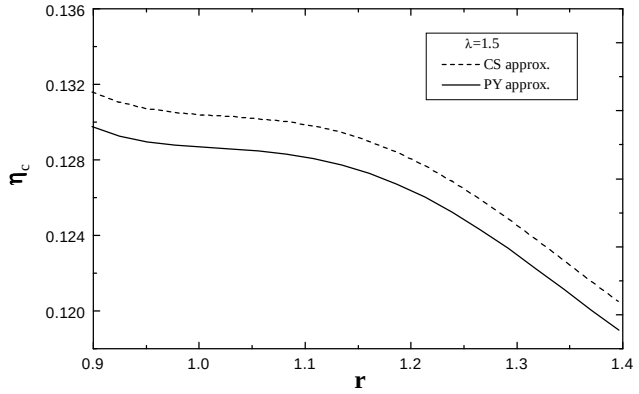

Figure 6. The critical density versus r when the PY approximation and the CS approximation for $S_2(0)$ are used

and is determined from the equation

$$\frac{\partial \ln \Xi_1}{\partial \beta \mu_1^\gamma} = \langle N_\gamma \rangle,$$

μ_γ is a full chemical potential of the γ-th species; $\alpha_{\gamma\delta}(k) = \frac{\beta}{V}\tilde{\phi}_{\gamma\delta}(k)$; $< N_\gamma >$ is an average number of the γ-th species particles.

2)$\rho_{\mathbf{k},\gamma} = \rho^c_{\mathbf{k},\gamma} - i\rho^s_{\mathbf{k},\gamma} (\gamma = a, b)$ are collective variables of the γ-th species, the indices c and s denote the real part and the coefficient at the imaginary part of $\rho_{\mathbf{k},\gamma}$; $\rho^c_{\mathbf{k},\gamma}$ and $\rho^s_{\mathbf{k},\gamma}$ describe the value of the $\mathbf{k}$-th fluctuation mode of the number of the γ-th species particles. Each $\rho^c_{\mathbf{k},\gamma}$ and $\rho^s_{\mathbf{k},\gamma}$ takes all the real values from $-\infty$ to $+\infty$. $(d\rho)$ is a volume element of the CV phase space:

$$(d\rho) = \prod_\gamma d\rho_{0,\gamma} \prod_{\mathbf{k}\neq 0}{}' d\rho^c_{\mathbf{k},\gamma} d\rho^s_{\mathbf{k},\gamma}.$$

The prime means that the product over $\mathbf{k}$ is performed in the upper semi-space;

3) $J(\rho_a, \rho_b)$ is a transition Jacobian to the CV averaged on the RS:

$$J(\rho_a, \rho_b) = \int (d\nu) \prod_{\gamma=a}^{b} \exp\left[i2\pi \sum_{\vec{k}} \nu_{\mathbf{k},\gamma}\rho_{\mathbf{k},\gamma}\right] \exp\left[\sum_{n\geq 1} \frac{(-i2\pi)^n}{n!} \times\right.$$

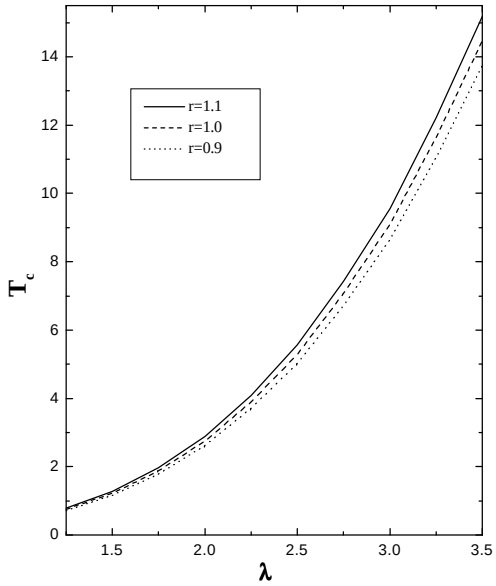

Figure 7. The vapour-liquid critical temperature as a function of the width of the potential well λ

$$\left. \sum_{\gamma_1 \ldots \gamma_n} \sum_{\mathbf{k}_1 \ldots \mathbf{k}_n} M_{\gamma_1 \ldots \gamma_n}(\mathbf{k}_1, \ldots, \mathbf{k}_n) \nu_{\mathbf{k}_1,\gamma_1} \ldots \nu_{\mathbf{k}_n,\gamma_n} \right],$$

where variables $\nu_{\mathbf{k},\gamma}$ are conjugated to CV $\rho_{\mathbf{k},\gamma}$. $M_{\gamma_1 \ldots \gamma_n}(\mathbf{k}_1, \ldots, \mathbf{k}_n)$ is the n-th cumulant connected with $S_{\gamma_1 \ldots \gamma_n}(k_1, \ldots, k_n)$, the n-particle partial structure factor of the RS, by means of the relation

$$M_{\gamma_1 \ldots \gamma_n}(\mathbf{k}_1, \ldots, \mathbf{k}_n) = \sqrt[n]{N_{\gamma_1} \ldots N_{\gamma_n}} S_{\gamma_1 \ldots \gamma_n}(k_1, \ldots, k_n) \delta_{\mathbf{k}_1 + \ldots + \mathbf{k}_n},$$

where $\delta_{\mathbf{k}_1 + \ldots + \mathbf{k}_n}$ is a Kronecker symbol.

4) $\tilde{\phi}_{\gamma\delta}(k)$ is a Fourier transform of the attractive potential $\phi_{\gamma\delta}(r)$. Function $\tilde{\phi}_{\gamma\delta}(k)$ satisfies the following requirements: $\tilde{\phi}_{\gamma\delta}(k)$ is negative for small values of $\mathbf{k}$ and $lim_{\mathbf{k}\to\infty}\tilde{\phi}_{\gamma\delta}(k) = 0$.

We pass in (26) to CV $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ (according to $\omega_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$) by means of the orthogonal linear transformation:

$$\rho_{\mathbf{k}} = \frac{\sqrt{2}}{2}(\rho_{\mathbf{k},a} + \rho_{\mathbf{k},b}), \quad c_{\mathbf{k}} = \frac{\sqrt{2}}{2}(\rho_{\mathbf{k},a} - \rho_{\mathbf{k},b}),$$

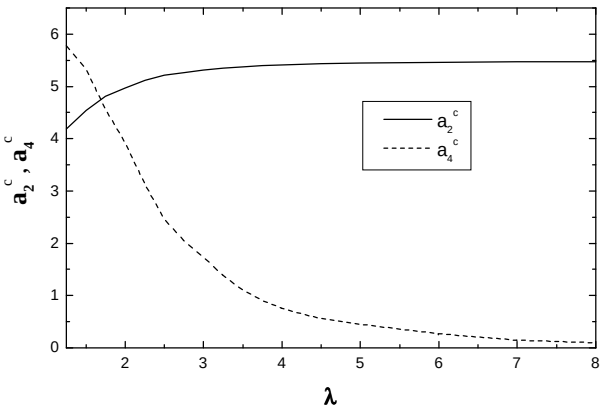

Figure 8. Coefficients a_2^c and a_4^c of the effective GLW Hamiltonian as functions of the width of the potential well λ

$$\omega_{\mathbf{k}} = \frac{\sqrt{2}}{2}(\nu_{\mathbf{k},a} + \nu_{\mathbf{k},b}), \quad \nu_{\mathbf{k}} = \frac{\sqrt{2}}{2}(\nu_{\mathbf{k},a} - \nu_{\mathbf{k},b}). \tag{27}$$

Now $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ are connected with the total density fluctuation modes and the relative density (or concentration) fluctuation modes, respectively.

As a result, for Ξ_1 we obtain formulae (3)-(8).

Appendix B

Cumulants $\mathcal{M}_n^{(i_n)}(0)$ with $n \leq 4$ are expressed in terms of the initial cumulants $\mathcal{M}_{\gamma_1 \ldots \gamma_n}(0, \ldots, 0)$ $(\gamma_1, \ldots, \gamma_n = a, b)$ as follows [30]:

$$\begin{aligned}
\mathcal{M}_1^{(0)}(0) &= \mathcal{M}_a(0) + \mathcal{M}_b(0) =< N > \\
\mathcal{M}_1^{(1)}(0) &= \mathcal{M}_a(0) - \mathcal{M}_b(0) =< N_a > - < N_b > \\
\mathcal{M}_2^{(0)}(0) &= \mathcal{M}_{aa}(0) + \mathcal{M}_{bb}(0) + 2\mathcal{M}_{ab}(0) \\
\mathcal{M}_2^{(1)}(0) &= \mathcal{M}_{aa}(0) - \mathcal{M}_{bb}(0) \\
\mathcal{M}_2^{(2)}(0) &= \mathcal{M}_{aa}(0) + \mathcal{M}_{bb}(0) - 2\mathcal{M}_{ab}(0) \\
\mathcal{M}_3^{(0)}(0) &= \mathcal{M}_{aaa}(0) + \mathcal{M}_{bbb}(0) + 3[\mathcal{M}_{aab}(0) + \mathcal{M}_{abb}(0)] \\
\mathcal{M}_3^{(1)}(0) &= \mathcal{M}_{aaa}(0) - \mathcal{M}_{bbb}(0) + \mathcal{M}_{aab}(0) - \mathcal{M}_{abb}(0)
\end{aligned}$$

$$\begin{aligned}
\mathcal{M}_3^{(2)}(0) &= \mathcal{M}_{aaa}(0) + \mathcal{M}_{bbb}(0) - \mathcal{M}_{aab}(0) - \mathcal{M}_{abb}(0) \\
\mathcal{M}_3^{(3)}(0) &= \mathcal{M}_{aaa}(0) - \mathcal{M}_{bbb}(0) - 3[\mathcal{M}_{aab}(0) - \mathcal{M}_{abb}(0)] \\
\mathcal{M}_4^{(0)}(0) &= \mathcal{M}_{aaaa}(0) + \mathcal{M}_{bbbb}(0) + \\
&+ 4[\mathcal{M}_{aaab}(0) + \mathcal{M}_{abbb}(0)] + 6\mathcal{M}_{aabb}(0) \\
\mathcal{M}_4^{(1)}(0) &= \mathcal{M}_{aaaa}(0) - \mathcal{M}_{bbbb}(0) + 2[\mathcal{M}_{aaab}(0) - \mathcal{M}_{abbb}(0)] \\
\mathcal{M}_4^{(2)}(0) &= \mathcal{M}_{aaaa}(0) + \mathcal{M}_{bbbb}(0) - 2\mathcal{M}_{aabb}(0) \\
\mathcal{M}_4^{(3)}(0) &= \mathcal{M}_{aaaa}(0) - \mathcal{M}_{bbbb}(0) - 2[\mathcal{M}_{aaab}(0) - \mathcal{M}_{abbb}(0)] \\
\mathcal{M}_4^{(4)}(0) &= \mathcal{M}_{aaaa}(0) + \mathcal{M}_{bbbb}(0) - \\
&- 4[\mathcal{M}_{aaab}(0) + \mathcal{M}_{abbb}(0)] + 6\mathcal{M}_{aabb}(0)
\end{aligned} \tag{28}$$

The same expressions hold at $\mathbf{k}_i \neq 0$.

The nth cumulant $\mathcal{M}_n^{(i_n)}(0)$ with $i_n = 0$ is connected with the nth structure factor of the one-component system $S_n(0)$ [30]:

$$\mathcal{M}_n^{(0)}(0) =< N > S_n(0).$$

Structure factors $S_n(0) (n \geq 2)$ can be obtained from $S_2(0)$ by means of a chain of equations for correlation functions [36]. Cumulants with $i_n \neq 0$ can be expressed in terms of $\mathcal{M}_n^{(0)}(0)$ (see formulae (4.8) in [30]).

Appendix C

After the layer-by-layer integration of the partition function (18) one obtains [26]:

$$\begin{aligned}
\Xi &= \Xi_0 \Xi_G^{(1)} \left[Z(\tilde{\mathcal{M}}_2, \tilde{\mathcal{M}}_4) \right]^{<N_B>} (\sqrt{2})^{<N_B>-1} Q_0 Q_1 \ldots Q_n \\
&\times [Q(P_n)]^{N_{n+1}} \int \exp[E_4^{(n+1)}(\rho)] (d\rho)^{N_{n+1}},
\end{aligned}$$

$$\begin{aligned}
E_4^{(n+1)}(\rho) &= \mu^* \rho_0 - \frac{1}{2} \sum_{\mathbf{k} < B_{n+1}} d_2^{(n+1)}(k) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{a_4^{(n+1)}}{4! N_{n+1}} \\
&\times \sum_{\mathbf{k}_1 \ldots \mathbf{k}_4 < B_{n+1}} \rho_{\mathbf{k}_1} \ldots \rho_{\mathbf{k}_4} \delta_{\mathbf{k}_1 + \ldots + \mathbf{k}_4} + \ldots \quad .
\end{aligned}$$

Here $N_n =< N_B > S^{-3n}$, $B_n = BS^{-n}$. Q_n is a partial partition function of the n-th layer:

$$Q_n^{1/N_n} = Q(P_{n-1}) Q(d_2^{(n)}),$$

where

$$Q(P_n) = \int_{-\infty}^{+\infty} \varphi_n(\omega) d\omega,$$

$$\varphi_n(\omega) = exp\left\{-(2\pi)^2 P_2^{(n)}\omega^2 - \frac{(2\pi)^4}{4!} P_4^{(n)}\omega^4\right\},$$

$$Q(d_2^{(n)}) = \int_{-\infty}^{+\infty} f_n(\eta) d\eta,$$

$$f_n(\eta) = \exp\left\{-\frac{1}{2} d_2^{(n)}(B_{n+1}, B_n)\eta^2 - \frac{1}{4!} a_4^{(n)}\eta^4\right\},$$

$$P_2^{(n)} = \left[Q(d_2^{(n)})\right]^{-1} \int_{-\infty}^{+\infty} \eta^2 f_n(\eta) d\eta,$$

$$P_4^{(n)} = S^{-3}\left\{-\left[Q(d_2^{(n)})\right]^{-1} \int_{-\infty}^{+\infty} \eta^4 f_n(\eta) d\eta + 3(P_2^{(n)})^2\right\}.$$

Coefficients $d_2^{(n+1)}$, $a_4^{(n+1)}$ are linked to $d_2^{(n)}$, $a_4^{(n)}$ by the recursion relations. The recursion relations have the form [26]:

$$\begin{aligned} r_{n+1} &= S^2(-q + (r_n + q)N(x_n)), \\ u_{n+1} &= S^{4-d} U_n E(x_n), \end{aligned} \tag{29}$$

where the following notations are introduced:

$$r_n = d_2^{(n)}(0) S^{2n}, \quad u_n = a_4^{(n)} S^{4n},$$

$$d_2^{(n)}(0) = a_2^{(n)} + \beta\tilde{V}(0),$$

$$q = \bar{q}|\beta\tilde{V}(0)|, \quad \bar{q} = \frac{1}{2}(1 + S^{-2}),$$

$$N(x_n) = \left(\frac{y_n}{x_n}\right)^{1/2} \frac{K(y_n)}{K(x_n)},$$

$$E(x_n) = S^{2d} \frac{L(y_n)}{L(x_n)},$$

$$x_n = d_2^{(n)}(B_{n+1}, B_n)(3/a_4^{(n)})^{1/2},$$

$$y_n = S^{3/2} K(x_n)(3/L(x_n))^{1/2},$$

$$d_2^{(n)}(B_{n+1}, B_n) = d_2^{(n)}(0) + qS^{-2n}.$$

Equations (29) have the fixed-point type partial solution: $r_n = r^*$, $u_n = u^*$. The pair of numbers (r_n, u_n) can be considered as coordinates of a point in a parametric space. As a result of layer-by-layer integration we

obtain a trajectory. For the ρ^4 model there exists a unique temperature for which the trajectory reduces to a point

$$\begin{aligned} (r_n, u_n) \to (r^*, u^*) \quad n \to \infty; \\ r^*, u^* > 0. \end{aligned}$$

The (r^*, u^*) point is a fixed point of the renormalization group transformation.

In the vicinity of the critical point we can use linear approximations in (29). We obtain:

$$\begin{pmatrix} r_{n+1} - r^* \\ u_{n+1} - u^* \end{pmatrix} = R \begin{pmatrix} r_n - r^* \\ u_n - u^* \end{pmatrix}, \tag{30}$$

where R is a linearized renormalization group transformation matrix. In [26] a general solution of (30) was found in the form:

$$\begin{aligned} r_n &= r^* + c_1 E_1^{(n)} + c_2 E_2^{(n)} R, \\ u_n &= u^* + c_1 R_1 E_1^{(n)} + c_2 E_2^{(n)}, \end{aligned} \tag{31}$$

where $R = \frac{R_{12}}{E_2 - R_{11}}$, $R_1 = \frac{E_1 - R_{11}}{R_{12}}$, E_1 and E_2 are the eigenvalues of the matrix R; $E_1 > 1$, $E_2 < 1$. c_1 and c_2 are functions depending on temperature, density and interaction potential

$$\begin{aligned} c_1 &= \left(a_2 - \beta|\tilde{V}(0)| - r^* + (a_4 - u^*)R\right) w^{-1}, \\ c_2 &= \left[-\left(a_2 - \beta|\tilde{V}(0)| - r^*\right) R_1 + (a_4 - u^*)\right] w^{-1}, \end{aligned} \tag{32}$$

where $w = \frac{E_1 - E_2}{R_{11} - E_2}$.

The solutions (31) are valid in the vicinity of the critical point including the critical point itself. At the critical point the solutions r_n, u_n at $n \to \infty$ tend to the fixed-point values

$$lim_{n\to\infty} r_n = r^*, \quad lim_{n\to\infty} u_n = u^*.$$

This is possible only if $c_1 = 0$. So, from the equation

$$c_1(T_c) = 0, \tag{33}$$

using (32) we can find T_c.

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Вивчення з перших принципів критичної точки рідина-пара бінарної симетричної флюїдної суміші

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