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INVESTIGATION OF PHASE TRANSITIONS IN BINARY SYSTEMS BY COLLECTIVE VARIABLES METHOD

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The collective variables method with a reference system is used for the investigation of phase transitions in the binary mixture. The explicit expressions for critical temperatures of a two-component system of different size particles interacting via different attractive potentials are obtained in the Gaussian approximation. The phase space of collective variables connected with order parameters is found. The case of the symmetrical mixture is considered in detail. The results are compared with the already known ones obtained for hard-core Yukawa mixture by the integral equation methods. The main difference is a presence of the second branch of critical temperatures. Numerical results are in a good agreement with those obtained in the mean-spherical approximation.

1. Introduction

It is known that gas-liquid and mixing-demixing phase transitions can occur in a binary fluid mixture [1,2]. The possibility of the realization of these phenomena and their priority depends both on external conditions (pressure, temperature, concentration) and on microscopic properties of components of the mixture (relations between interactions of a-a, b-b and a-b particles). The study of the influence of interparticle interaction potentials $U_{aa}(r)$, $U_{bb}(r)$ and $U_{ab}(r)$ on phase diagram topology of a binary mixture is an intresting and actual problem. In recent years this problem has been studied intensively by integral equation methods. But the pioneering work in this field was Waisman's one [3]. Waisman considered a symmetrical mixture with the same number densities in which particles interact via the two-body hard core plus a Yukawa tail potential:

$$U_{ij}(r) = \begin{cases} \infty & \text{if} \quad r \leq 1 \\ \frac{K_{ij}}{r} e^{-z(r-1)} & \text{if} \quad r > 1 \end{cases} . \tag{1.1}$$

In Waisman's model the same species particles (like particles) outside the core attract each other, and the different species particles (unlike particles) repulse (or vice versa) with the same magnitude ($K_{11} = K_{22} = K_{12}$). Waisman solved the mean-spherical-approximation (MSA) integral equation for this model and showed that for the repulsion between the unlike particles

(and attraction between the like ones) there was a region in the density-temperature plane where no real solution existed. He interpreted this fact as an evidence of the separation phase transition. In the more recent work [4] the authors considered the extended Waisman's model: ($K_{11} = K_{22} \neq K_{12}$) (the symmetrical model). Having solved analytically MSA for this model they showed that two types of phase transition can occur in the mixture depending on K_{11} and K_{12} relation: liquid-gas and mixing-demixing phase transitions.The latest works [5–9] were devoted to numerical solutions of integral equations. There were considered on the one hand more complicated mixtures of hard spheres of different sizes interacting via different Yukawa tails ($K_{11} \neq K_{22} \neq K_{12}$) [5,6] and on the other hand – mixtures of particles interacting via Lennard-Jones potentials [7–9]. It is also necessary to note Ref. [10] in which the authors related the second order expansion of the grand canonical potential to direct correlation functions. For a binary mixture of hard spheres with attractive Yukawa potentials direct correlation functions were calculated making use of the reference hypernetted chain integral equation. All the works have shown a considerable progress in the study of the properties of phase transitions in binary mixtures as a function of the microscopic interaction between particles. However, there exist some problems in the studies based on integral equation methods, namely: a) an analytical solution of the Ornstein–Zernike equation exists only in case of the simplest closure : the MSA for several pair potentials (e.q. eq.(1.1)); b) both the Percus–Yevick (PY) equation and the hypernetted chain equation show the existence of a limit of stability $T_s(\rho)$ for the given mixture at fixed concentration and density. As the temperature is lowering towards this limit, the osmotic or the isothermal compressibility increases and it becomes more and more difficult to get the numerical convergence. The failure of the numerical algorithm to converge is not always associated with the true divergence, thus the interpretation of $T_s(\rho)$ as the spinodal line of the mixture is not straightforward [11].

In this paper we propose a new approach to the study of phase transition properties in binary fluid mixtures depending on microscopical interactions between particles. It is based on the method of collective variables (CV) with a distinguished reference system (RS) [12].The CV method is a functional method which allows: a) to determine the explicit form of Ginsburg–Landau–Wilson Hamiltonian; b) to perform an integration of the partition function using the fixed point method proposed in [13] for 3-d Ising model and as a result 3) to obtain thermodynamic functions in the neighbourhood of the phase transition point as functions of microscopical parameters of the Hamiltonian. Recently [14,15] we extended the CV method for the case of the grand canonical ensemble. The use of the CV method for the phase instability study in binary mixtures permits to avoid the difficulties which have been noted above.

The layout of this paper is as follows. The main aspects of the CV method with the RS for a binary system are clarified briefly in Sec.2. The phase space of CV which includes the variable corresponding to the order parameter is separated here. Sec.3 is devoted to the investigation of phase transitions in a binary fluid in the Gaussian approximation. The explicit expressions for critical temperatures of a two-component system of hard spheres of different sizes interacting via attractive potentials $\phi_{ij}(r)$ ($\phi_{ii} \neq \phi_{jj} \neq \phi_{ij}$) are obtained. The case of the symmetrical mixture is considered in detail. In Sec.4 we compare our results with previous investigations [4,10]. A brief summary with the main conclusions of this paper follows in Sec.5.

2. The method of collective variables with the reference system. Binary system

Let us consider the classical two-component system of interacting particles consisting of N_a particles of species a and N_b particles of species b. The system is in a volume V at temperature T.

Let us assume that the interaction in the system has the pairwise additive character. The interaction potential between a γ particle at $\vec{r}_i$ and a δ particle at $\vec{r}_j$ may be expressed as a sum of two terms:

$$U_{\gamma\delta}(r_{ij}) = \psi_{\gamma\delta}(r_{ij}) + \phi_{\gamma\delta}(r_{ij}),$$

where $\psi_{\gamma\delta}(r)$ is the potential of short-range repulsion that is chosen as the interaction between two hard spheres $\sigma_{\gamma\gamma}$ and $\sigma_{\delta\delta}$; $\phi_{\gamma\delta}(r)$ is the potential describing an attraction at long distances. An arbitrary positive function belonging to the L class can be chosen as the potential $\phi_{\gamma\delta}(r)$.

Further consideration of the problem is done in the extended phase space: in the phase space of Cartesian coordinates of the particles and in the CV phase space. The interaction connected with the repulsion (potential $\psi_{\gamma\delta}(r)$) is considered in the space of Cartesian coordinates of the particles. We call this two-component hard spheres system the reference system (RS). The interaction connected with the attraction (potential $\phi_{\gamma\delta}(r)$) is considered in the CV space. The phase space overflow is cancelled by introduction the transition Jacobian.

Then the grand partition function in the CV representation with the RS has the form

$$\Xi = \Xi_0 \Xi_1, \tag{2.1}$$

where Ξ_0 is the grand partition function of the RS:

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

Here $(d\Gamma)$ is an element of phase space of Cartesian coordinates of particles; $\beta = \frac{1}{kT}$ is the reciprocal temperature; μ_0 is the 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:

$$\Xi_1 = \int (d\rho) exp[\beta \sum_{\gamma} \mu_1^\gamma \rho_{0,\gamma} - \frac{1}{2} \sum_{\gamma\delta} \sum_{\vec{k}} \alpha_{\gamma\delta}(k) \rho_{\vec{k},\gamma} \rho_{-\vec{k},\delta}] J(\rho), \tag{2.2}$$

where $\alpha_{\gamma\delta}(k) = \frac{\beta}{V} \tilde{\phi}_{\gamma\delta}(k)$, $\tilde{\phi}_{\gamma\delta}(k)$ is the Fourier transform of $\phi_{\gamma\delta}(r)$; μ_1^γ is the part of the chemical potential of the γ-th species which equals to

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

(μ_γ is the full chemical potential of the γ-th species). μ_1^γ is determined from the equation

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

The CV $\rho_{\vec{k},\gamma}$ has the form

$$\rho_{\vec{k},\gamma} = \rho^{c}_{\vec{k},\gamma} - i\rho^{s}_{\vec{k},\gamma},$$

where c and s are used to denote real and coefficient at imaginary part of $\rho_{\vec{k},\gamma}$; $\rho^{c}_{\vec{k},\gamma}$ and $\rho^{s}_{\vec{k},\gamma}$ describe the value of $\vec{k}$-th fluctuation mode of number of γ-th species particles. Each of $\rho^{c}_{\vec{k},\gamma}$ and $\rho^{s}_{\vec{k},\gamma}$ takes all real values from $-\infty$ to $+\infty$.

$(d\rho)$ is the volume element of the CV phase space:

$$(d\rho) = \prod_{\gamma} d\rho_{0,\gamma} \prod_{\vec{k}\neq 0}{}' d\rho^{c}_{\vec{k},\gamma} d\rho^{s}_{\vec{k},\gamma}.$$

The prime means that the product over $\vec{k}$ is performed for the positive values of k.

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

$$J(\rho) = \int (d\nu) \prod_{\gamma=a}^{b} \exp\left[i2\pi \sum_{\vec{k}} \nu_{\vec{k},\gamma}\rho_{\vec{k},\gamma}\right] \exp\left[\sum_{n\geq 1} \frac{(-i2\pi)^n}{n!} \sum_{\gamma_1\ldots\gamma_n} \sum_{\vec{k}_1\ldots\vec{k}_n} \times M_{\gamma_1\ldots\gamma_n}(\vec{k}_1,\ldots,\vec{k}_n)\nu_{\vec{k}_1,\gamma_1}\ldots\nu_{\vec{k}_n,\gamma_n}\right], \quad (2.3)$$

where variable $\nu_{\vec{k},\gamma}$ is conjugated to the CV $\rho_{\vec{k},\gamma}$. $M_{\gamma_1\ldots\gamma_n}(\vec{k}_1,\ldots,\vec{k}_n)$ 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 the relation

$$M_{\gamma_1\ldots\gamma_n}(\vec{k}_1,\ldots,\vec{k}_n) = \sqrt[n]{N_{\gamma_1}\ldots N_{\gamma_n}} S_{\gamma_1\ldots\gamma_n}(k_1,\ldots,k_n)\delta_{\vec{k}_1+\ldots+\vec{k}_n}, \quad (2.4)$$

where $\delta_{\vec{k}_1+\ldots+\vec{k}_n}$ is Kroneker symbol.

It is known that near the critical point the density fluctuations increase and the correlation radius becomes infinite. From this point of view the limit $k_i \to 0$ in the cumulants is especially important. Relations which connect $M_{\gamma_1\ldots\gamma_n}(0,\ldots,0)$ with thermodynamic functions of the RS are obtained in [14] (see Appendix A).

In order to understand the mechanism of realization of gas- liquid and mixing - demixing phase instabilities in the binary fluid we shall consider the Gaussian approximation of the functional (2.1) -(2.3). For this aim we shall let $n = 2$ in (2.3). As a result of the integration in eq.(2.3) over variables $\nu_{\vec{k},a}$ and $\nu_{\vec{k},b}$ Ξ_1 may be written as

$$\Xi_1 = \Xi_1^G = \frac{1}{2}\prod_{\vec{k}} \frac{1}{\sqrt{\pi \det \mathbf{M}(k)}} \int (d\rho) exp[-H(0) + \sum_{\gamma=a,b} F_\gamma \rho_{0,\gamma} - \frac{1}{2}\sum_{\vec{k}} \sum_{\gamma,\delta} a_{\gamma\delta}(k)\rho_{\vec{k},\gamma}\rho_{-\vec{k},\delta}]. \quad (2.5)$$

Here we introduced the following notations: $\mathbf{M}(k)$ is 2×2 symmetrical matrix, elements of which are cumulants $M_{\gamma\delta}(k)$:

$$M_{\gamma\delta}(k) = \langle N_\gamma \rangle (\delta_{\gamma\delta} + \frac{\langle N_\delta \rangle}{V} \tilde{h}_{\gamma\delta}(k)) = \\ = \sqrt{\langle N_\gamma \rangle \langle N_\delta \rangle} S_{\gamma\delta}(k), \tag{2.6}$$

$$H(0) = \frac{1}{2} \sum_{\gamma\delta} \langle N_\gamma \rangle \langle N_\delta \rangle [\mathbf{M}^{-1}(0)]_{\gamma\delta}, \tag{2.7}$$

$$F_\gamma = \beta\mu_1^\gamma + \sum_{\delta=a,b} \langle N_\delta \rangle [\mathbf{M}^{-1}(0)]_{\gamma\delta}, \tag{2.8}$$

$$a_{\gamma\delta}(k) = \alpha_{\gamma\delta}(k) + [\mathbf{M}^{-1}(k)]_{\gamma\delta}. \tag{2.9}$$

$\tilde{h}_{\gamma\delta}(k)$ is the Fourier transform of the pair correlation function; $[\mathbf{M}^{-1}(k)]_{\gamma\delta}$ is an element of an inverse matrix. As it is already proposed in Ref.[16] we separate the CV phase space, which includes the variable, connected with the order parameter by diagonalization the square form under the integral in eq.(2.5). As a result of the orthogonal transformation

$$\rho_{\vec{k},\gamma} = \sum_{i=1,2} \Delta_{\gamma i} \xi_{\vec{k},i} \qquad \gamma = a, b \tag{2.10}$$

for the square form we have

$$-\frac{1}{2} \sum_{\vec{k},i} \varepsilon_i(k) \xi_{\vec{k},i} \xi_{-\vec{k},i}, \tag{2.11}$$

where

$$\varepsilon_{1,2}(k) = \frac{1}{2}(a_{aa}(k) + a_{bb}(k) \mp \sqrt{(a_{aa}(k) - a_{bb}(k))^2 + 4a_{ab}^2(k)}), \tag{2.12}$$

(the signs '-' and '+' correspond to indices 1 and 2).The explicit forms for $\Delta_{\gamma i}$ are given in Appendix B.

3. Phase transitions in the binary system

Solving the equations

$$\varepsilon_1(k=0) = 0; \\ \varepsilon_2(k=0) = 0;$$

we obtain the expressions for critical temperatures of the binary mixture in the Gaussian approximation (RPA):

$$\theta_{1,2}^c = 2\rho x(1-x)[\tilde{\phi}_{aa}(0)\tilde{\phi}_{bb}(0) - \tilde{\phi}_{ab}^2(0)][S_{aa}(0)S_{bb}(0) - S_{ab}^2(0)] \times \\ \{-[(1-x)S_{aa}(0)\tilde{\phi}_{aa}(0) + xS_{bb}(0)\tilde{\phi}_{bb}(0) + 2\sqrt{x(1-x)}S_{ab}(0) \times \\ \tilde{\phi}_{ab}(0)] \pm [((1-x)S_{aa}(0)\tilde{\phi}_{aa}(0) - xS_{bb}(0)\tilde{\phi}_{bb}(0))^2 + \\ 4((1-x)S_{aa}(0)\tilde{\phi}_{ab}(0) + \sqrt{x(1-x)}S_{ab}(0)\tilde{\phi}_{bb}(0))(xS_{bb}(0)\tilde{\phi}_{ab}(0) + \\ \sqrt{x(1-x)}S_{ab}(0)\tilde{\phi}_{aa}(0))]^{\frac{1}{2}}\}^{-1}, \tag{3.1}$$

where sings '+' and '-' correspond to indices 1 and 2; $\theta_i^c = (\beta_i^c)^{-1}$, $\rho = \frac{N}{V}$ is the average density; x is the concentration of species b; $\tilde{\phi}_{ij}(0)$ and $S_{ij}(0)$ are the Fourier transforms of potentials $\phi_{ij}(r)$ and partial structure factors of the RS at $\vec{k} = 0$ accordingly.

As it is seen from the Gaussian approximation, dependence of the critical temperatures (3.1) on characteristics of the RS and on $\tilde{\phi}_{ij}(0)$ is complicated. Therefore to study the possibility of the realization of gas-liquid and mixing-demixing phase transitions and their priority first we shall consider the simplest case, namely, the symmetrical mixture.

a) The symmetrical mixture. The symmetrical mixture is the model system of equal size particles interacting via the same attractive potentials between like particles ($\phi_{aa}(r) = \phi_{bb}(r) = \phi(r)$) and via the different attractive potentials between unlike particles ($\phi(r) \neq \phi_{ab}(r)$). Although the symmetrical mixture represents the simple model of a real binary fluid, it exhibits all three types of two-phase equilibrium which are observed in such a system: gas-liquid, gas-gas and liquid-liquid. The critical curves $\theta_1^c(x)$ and $\theta_2^c(x)$ of this mixture are symmetrical with respect to the concentration $x = \frac{1}{2}$ and exhibit at this point an extremum. The concentration $x_c = \frac{1}{2}$ is a critical one for the symmetrical mixture. At $x_c = \frac{1}{2}$ the critical temperatures have the forms:

$$\theta_1^c(x_c) = \begin{cases} \theta_c^{\text{sep.}}, & L(0) < 0 \\ \theta_c^{\text{g.-l.}}, & L(0) > 0 \end{cases}; \tag{3.2}$$

$$\theta_2^c(x_c) = \begin{cases} \theta_c^{\text{g.-l.}}, & L(0) < 0 \\ \theta_c^{\text{sep.}}, & L(0) > 0 \end{cases}, \tag{3.3}$$

where

$$\theta_i^c = kT_i^c$$

$$\theta_c^{\text{g.-l.}} = -\frac{\rho}{2}(\tilde{\phi}(0) + \tilde{\phi}_{ab}(0))S_+(0); \tag{3.4}$$

$$\theta_c^{\text{sep.}} = -\frac{\rho}{2}(\tilde{\phi}(0) - \tilde{\phi}_{ab}(0))S_-(0); \tag{3.5}$$

$$L(0) = \tilde{\phi}_{ab}(0)S(0) + \tilde{\phi}(0)S_{ab}(0). \tag{3.6}$$

$S_+(0)$ and $S_-(0)$ are the density-density and concentration– concentration structure factors of equal-diameter hard sphere mixture at $\vec{k} = 0$. At $x_c = \frac{1}{2}$ quantities $S_+(0)$ and $S_-(0)$ reduce to the forms: $S_+(0) = S(0) + S_{ab}(0)$ – the structure factor of the one-component RS and $S_-(0) = S(0) - S_{ab}(0) = 1(S_{aa}(0) = S_{bb}(0) = S(0))$.

Quantities $\varepsilon_1(k)$, $\varepsilon_2(k)$, $\Delta_{a,i}$, $\Delta_{b,i}$ ((2.12), see appendix B) reduce and become equal to

$$\varepsilon_1(k) = \begin{cases} \alpha(k) - \alpha_{ab}(k) + \frac{2}{N}, & a_{12}(k) > 0 \\ \alpha(k) + \alpha_{ab}(k) + \frac{2}{NS_+(k)}, & a_{12}(k) < 0 \end{cases}; \tag{3.7}$$

$$\varepsilon_2(k) = \begin{cases} \alpha(k) + \alpha_{ab}(k) + \frac{2}{NS_+(k)}, & a_{12}(k) > 0 \\ \alpha(k) - \alpha_{ab}(k) + \frac{2}{N}, & a_{12}(k) < 0 \end{cases}, \tag{3.8}$$

where $\Delta_{a,1} = \frac{\sqrt{2}}{2}$, $\Delta_{a,2} = \frac{\sqrt{2}}{2}$

$$\Delta_{b,1} = \begin{cases} -\frac{\sqrt{2}}{2}, & a_{12} > 0 \\ \frac{\sqrt{2}}{2}, & a_{12} < 0 \end{cases}; \quad \Delta_{b,2} = \begin{cases} \frac{\sqrt{2}}{2}, & a_{12} > 0 \\ -\frac{\sqrt{2}}{2}, & a_{12} < 0 \end{cases}, \tag{3.9}$$

where

$$a_{12}(k) = \alpha_{ab}(k) - \frac{2}{N}\frac{S_{ab}(k)}{S_+(k)}.$$

Taking into account (3.9) for CV $\xi_{\vec{k},1}$ and $\xi_{\vec{k},2}$ we have

$$\xi_{\vec{k},1} = \begin{cases} c_{\vec{k}}, & a_{12}(k) > 0 \\ \rho_{\vec{k}}, & a_{12}(k) < 0 \end{cases}; \quad \xi_{\vec{k},2} = \begin{cases} \rho_{\vec{k}}, & a_{12}(k) > 0 \\ c_{\vec{k}}, & a_{12}(k) < 0 \end{cases}, \tag{3.10}$$

where

$$\rho_{\vec{k}} = \frac{1}{\sqrt{2}}(\rho_{\vec{k},a} + \rho_{\vec{k},b}), \quad c_{\vec{k}} = \frac{1}{\sqrt{2}}(\rho_{\vec{k},a} - \rho_{\vec{k},b}). \tag{3.11}$$

New variables $\rho_{\vec{k}}$ and $c_{\vec{k}}$ are connected with total density fluctuation modes and relative density (or concentration) fluctuation modes in the binary system. The diagonal square form (2.11) transforms as (independently on the sign of $a_{12}(k)$):

$$-\frac{1}{2}\sum_{\vec{k}}[(\alpha(k) - \alpha_{ab}(k) + 2/N)c_{\vec{k}}c_{-\vec{k}} +$$

$$+ (\alpha(k) + \alpha_{ab}(k) + 2/NS_+)\rho_{\vec{k}}\rho_{-\vec{k}}]. \tag{3.12}$$

As it follows from (3.7)-(3.8) and (3.10)-(3.11) in the case of symmetrical mixture there exist two critical branches $\varepsilon_1(0)$ and $\varepsilon_2(0)$ and according to them two subspaces of CV - $c_{\vec{k}}$ and $\rho_{\vec{k}}$, which include variables c_0 and ρ_0 connected with the order parameters.

Let us consider the critical temperatures . Expressions (3.2) - (3.3) contain the values $\tilde{\phi} - \tilde{\phi}_{ab}$ and $\tilde{\phi} + \tilde{\phi}_{ab}$. There are two possible cases: a) $|\tilde{\phi}| > |\tilde{\phi}_{ab}|$ and b) $|\tilde{\phi}| < |\tilde{\phi}_{ab}|$. In the case 'a' the attractive energy between like particles is stronger than between unlike particles. The separation of components can occur in the system. In the case 'b' the attractive interaction between unlike particles is stronger than between like particles and it is a condition of existence of the mixture. In Fig. 1 critical temperatures $\tilde{\theta}_1^c(\eta)$ (the curve 1) and $\tilde{\theta}_2^c(\eta)$ (the curve 2) are plotted vs packing fraction η at $r = 0.8$. Here $\tilde{\theta}_i^c(\eta) = \theta_i^c\eta/(\rho|\tilde{\phi}(0)|)$ is the dimensionless temperature, $\eta = \pi\rho\sigma^3/6$, $\rho = N/V$, $N = N_a + N_b$, r is the dimensionless unlike interaction strength: $r = -\tilde{\phi}_{ab}(0)/|\tilde{\phi}(0)|$ (the form of $\phi_{ij}(r)$ is not specified). The curve of the gas-liquid equilibrium ($r = 1.2$) is shown by the dashed line in Fig. 1 and has the same form as the corresponding curve in the one-component case. Both the curve $\theta = \theta_1^c(\eta)$ and the curve $\theta = \theta_2^c(\eta)$ are composed of two branches meeting at $\tilde{\eta} = \eta_{\mathrm{cros}}(r)$. The different slope of two branches can be interpreted as an indication of some difference in the physics of the transition undergone by the mixture. Indeed it is clear from Fig. 1 and formulae (3.2)-(3.3) that for $\eta < \tilde{\eta}$ the curve $\theta = \tilde{\theta}_1^c(\eta)$

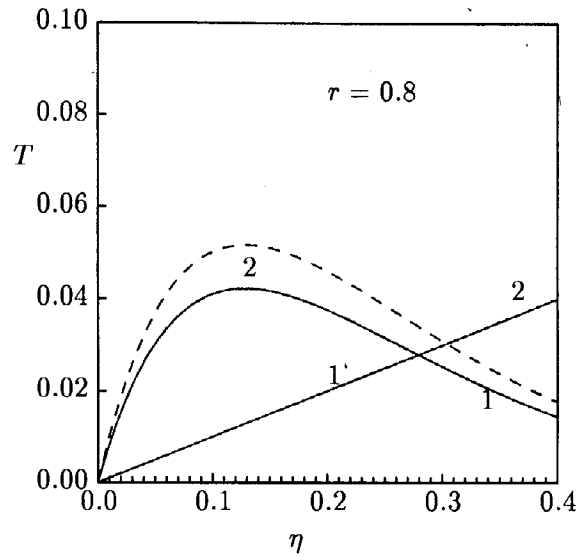

Figure 1. Dependence of critical temperatures of the symmetrical mixture on the packing fraction ($\alpha = 1$, $q = 1$, $x = 0.5$, $r = 0.8$ (solid curves) and $r = 1.2$ (dashed curve))

is the line of the liquid-liquid phase equilibrium and for $\eta > \tilde{\eta}$ is the line of the gas-liquid phase equilibrium. On the contrary the curve $\theta = \tilde{\theta}_2^c(\eta)$ is the gas-liquid phase equilibrium line for $\eta < \tilde{\eta}$ and is the gas-gas phase equilibrium line for $\eta > \tilde{\eta}$. The curves $\tilde{\theta}_1^c(\eta)$ and $\tilde{\theta}_2^c(\eta)$ have one common point, for which the gas-liquid and separation critical points coincide. The corresponding to this point density $\tilde{\eta}$ is determined from the condition

$$\tilde{\theta}_1^c(\tilde{\eta}) = \tilde{\theta}_2^c(\tilde{\eta}) \tag{3.13}$$

or from the equation $L(0) = 0$.

Now let us consider in Fig. 1 the line which is formed from the branch $\tilde{\theta}_2^c(\eta)$ for $\eta < \tilde{\eta}$ and from the branch $\tilde{\theta}_1^c(\eta)$ for $\eta > \tilde{\eta}$ and compare it with dashed curve, which is the line of gas-liquid critical temperatures. These curves have the same form. The two remaining parts of $\tilde{\theta}_1^c(\eta)$ and $\tilde{\theta}_2^c(\eta)$ form the straight line. Hence for the symmetrical mixture one can separate exactly the gas-liquid and the demixing-mixing critical temperature lines. An existence of the point $\tilde{\eta}$ for which (3.13) holds is connected with the simplicity of the model under consideration. On the other hand, an existence of a point on the critical curve in which the gas-liquid and the gas-gas separation critical temperatures coincide was confirmed experimentally. It is the so-called critical double point [16].

It can readily be shown that the gas-liquid critical temperatures $\theta_c^{g.-l.}$ satisfy the equation $\alpha(0) + \alpha_{ab}(0) + \frac{2}{NS_+(0)} = 0$ and the separation critical temperatures $\theta_c^{sep.}$ satisfy the equation $\alpha(0) - \alpha_{ab}(0) + \frac{2}{N} = 0$.

Hence in the case of the binary symmetrical mixture we can make the following conclusions: 1) as a result of the square form diagonalization in (2.5) two subspaces of CV were separated: the first with the order parameter

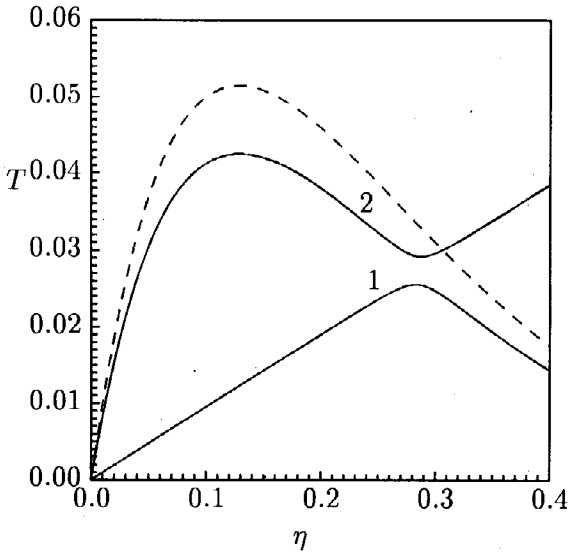

Figure 2. Dependence of critical temperatures of the binary mixture on the packing fraction ($\alpha = 1$, $q = 1$, $x = 0.6$, $r = 0.8$ (solid curves) and $r = 1.2$ (dashed curve))

and with the critical temperature $\theta_c^{\text{g-l}}$ and the second with the order parameter and with the critical temperature θ_c^{sep}; 2) the CV describing phase transitions being the variables $\rho_{\vec{k}}$ and $c_{\vec{k}}$, the variable ρ_0 describes the long-wavelength fluctuation mode of the total particle number $N = N_a + N_b$ (or total density) and is connected with the order parameter nonzero value of which arises below the gas-liquid critical point, the variable c_0 describes the long-wavelength fluctuation mode of the relative particle number $N_a - N_b$ (or relative density) and is connected with the order parameter for the separation phase transition. The priority of the gas-liquid and the separation phase transitions depends on microscopical properties of the system.

b) Asymmetrical mixture. In the case of an asymmetrical binary mixture the CV, connected with the order parameter are the variables $\xi_{0,i}$. We can present $\xi_{0,i}$ in the form of the linear combination of CV ρ_0 and c_0 with some coefficients dependent on the temperature, characteristics of the RS and $\tilde{\phi}_{\gamma\delta}(k)$. Therefore, both gas-liquid and separation phase instabilities in such a system are accompanied by fluctuations of the density as well as of the concentration. The study of a specific role of the density and the concentration fluctuations in gas-liquid and mixing-demixing phase transitions will be an purpose of the other paper. Now we consider a small deviation from the symmetry and its influence on a trend of critical temperature curves $\theta_1^c(\eta)$ and $\theta_2^c(\eta)$. In Fig. 2 it is shown $\tilde{\theta}_1^c(\eta)$ and $\tilde{\theta}_2^c(\eta)$ ($\tilde{\theta}_i^c(\eta) = \theta_i^c\eta/(|\tilde{\phi}_{bb}(0)|\rho)$) at $\alpha = \sigma_{aa}/\sigma_{bb} = 1$, $q = -\tilde{\phi}_{aa}(0)/|\tilde{\phi}_{bb}(0)| = 1$, $x = 0.6$ and $r = 0.8$ (solid curves) and $\tilde{\theta}_2^c(\eta)$ at $\alpha = 1$, $q = 1$, $x = 0.6$, $r = 1.2$ (the dashed curve). As it is seen the solid curves $\tilde{\theta}_1^c(\eta)$ and $\tilde{\theta}_2^c(\eta)$ do not have a contact point although one approaches the other. Also these curves have distinct extreme points.

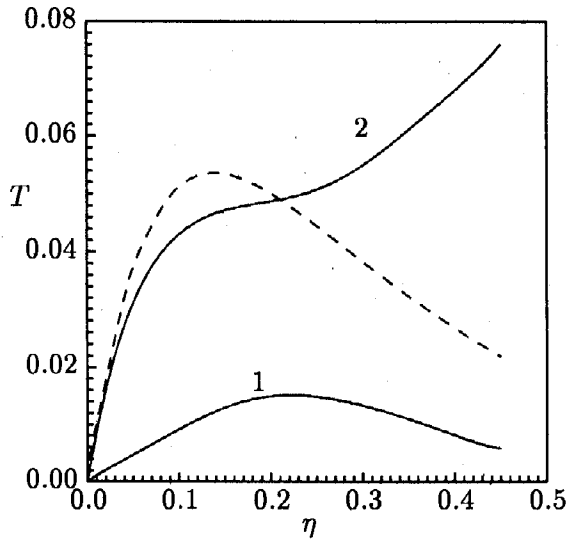

Figure 3. Dependence of critical temperatures of the binary asymmetrical mixture on the packing fraction ($\alpha = 0.8$, $q = 1$, $x = 0.4$, $r = 0.8$ (solid curves) and $r = 1.2$ (dashed curve))

Fig. 3 and 4 present the curves $\tilde{\theta}_1^c(\eta)$ and $\tilde{\theta}_2^c(\eta)$ for the binary fluid with larger deviations from the symmetry. The shape of curves $\tilde{\theta}_1^c(\eta)$ is similar in both figures. The behaviour of $\tilde{\theta}_2^c(\eta)$ on the contrary is very sensitive to changes of microscopical parameters: the curve $\tilde{\theta}_2^c(\eta)$ has a minimum (Fig. 3) or has not a minimum (Fig. 4). We can draw an analogy with experimental critical lines in the pressure temperature plot [16,17]. Two different kinds of gas-gas equilibria can be distinguished: the first type and the second type. In the first case the critical line starts at the critical point of the least volatile component and moves to higher temperatures and higher pressures. In the second case the curve first moves to lower temperature at increasing pressure and then, via a temperature minimum, again to higher temperatures. The point of a temperature minimum is the so-called critical double point: gas-liquid and gas-gas separation critical points coincide at this point.

4. An application: the binary hard-core Yukawa fluid

Now we shall consider the binary mixture of hard spheres interacting via Yukawa attractive potentials. The following division of interacting potential $U_{ij}(r)$ is associated with this model:

$$\psi_{ij}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ 0, & r \geq \sigma_{ij} \end{cases} ; \tag{4.1}$$

$$\phi_{ij}(r) = \begin{cases} 0, & r < \sigma_{ij} \\ -\frac{K_{ij}}{r} \exp[-z(r - \sigma_{ij})], & r \geq \sigma_{ij} \end{cases} \tag{4.2}$$

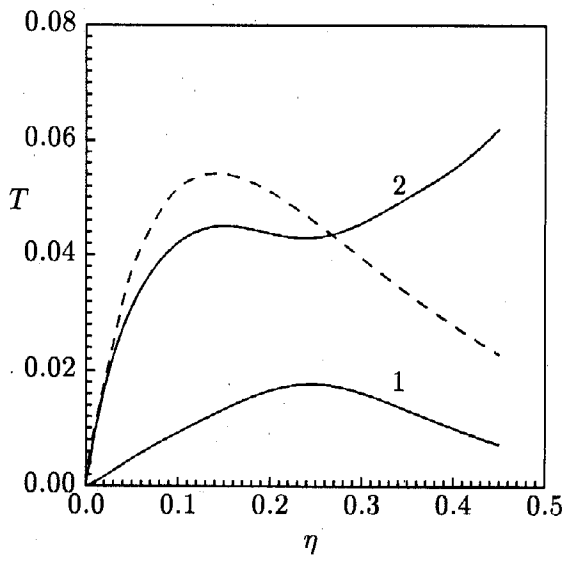

Figure 4. Dependence of critical temperatures of the binary asymmetrical mixture on the packing fraction ($\alpha = 0.8$, $q = 1$, $x = 0.6$, $r = 0.8$ (solid curves) and $r = 1.2$ (dashed curve))

Therefore, we shall use formulae from the Appendix C for $S_{ij}(0)$. Fourier transforms of interacting potentials (4.2) at $k = 0$ have the following form:

$$\tilde{\phi}_{ij}(0) = -K_{ij}\frac{4\pi}{z^2}(1 + z\sigma_{ij}).$$

a) Symmetrical Yukawa fluid ($K_{aa} = K_{bb} = K, \sigma_{aa} = \sigma_{bb} = \sigma$). In Fig. 5 curves θ_1^c and θ_2^c are shown ($\tilde{\theta}_i^c = \theta_i^c\sigma/K$). Parameters are chosen as in Ref.[4]: $K_{aa} = K_{bb} = -0,55$ ($q = 1$), $K_{ab} = -0,45$ ($r = 0,82$), $z\sigma = 1,8; 2,5$. Comparison of the curves derived in our approach with those derived in Ref.[4] exhibits the following: a) the maximum on the curve $\tilde{\theta}_2^c$ in Fig. 5 lies a bit lower than the maximum in Fig.4 [4]; b) the location of $\tilde{\eta}$ (see formula (3.13)) does not depend on z in Fig. 5 (in Ref.[4] the solution is depended on z).

Dependence of critical temperatures $\tilde{\theta}_1^c$ and $\tilde{\theta}_2^c$ on the unlike interaction strength r is presented in Fig. 6. In contrast to results of Ref.[10], where only one curve with minimum has been obtained we have obtained two curves: one with minimum and the other with maximum at the same r. For the binary hard-core Yukawa fluid with parameters $q = 1$, $x = 0.5$, $z\sigma = 4$, $\eta = 0.26$ extremes are reached at $r = 0.774$ that is in perfect agreement with Ref.[10].

b) Asymmetrical mixture. In Fig. 7 curves $\tilde{\theta}_1^c(\eta)$ and $\tilde{\theta}_2^c(\eta)$ are shown ($\tilde{\theta}_i^c = \theta_i^c\sigma_{aa}/K_{aa}$). Parameters are chosen as in Ref.[5] for mixture M1: $\alpha = \sigma_{aa}/\sigma_{bb} = 0.67$, $q = \alpha K_{aa}/K_{bb} = 0.9$, $r = 2\alpha K_{ab}/((1+\alpha)K_{aa}) = 0.8$, $z\sigma_{aa} = 1.8$, $x = 0.35$ (solid line) and $x = 0.5$ (dashed line).In Fig. 7 the

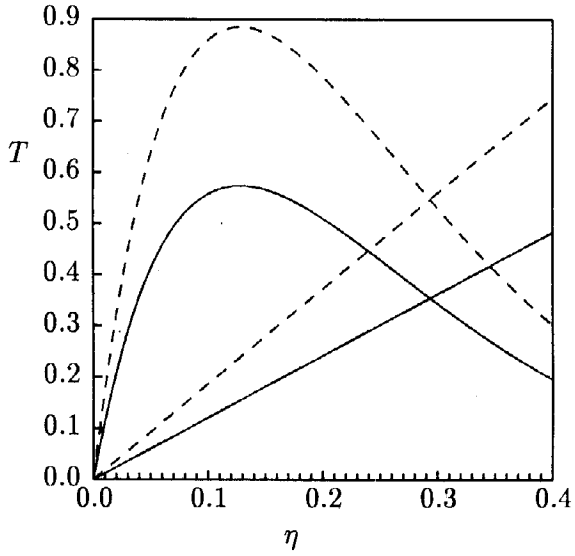

Figure 5. Dependence of critical temperatures of the symmetrical Yukawa fluid on the packing fraction ($r = 0.82$, $z\sigma = 1.8$ (dashed curves) and $z\sigma = 2.5$ (solid curves))

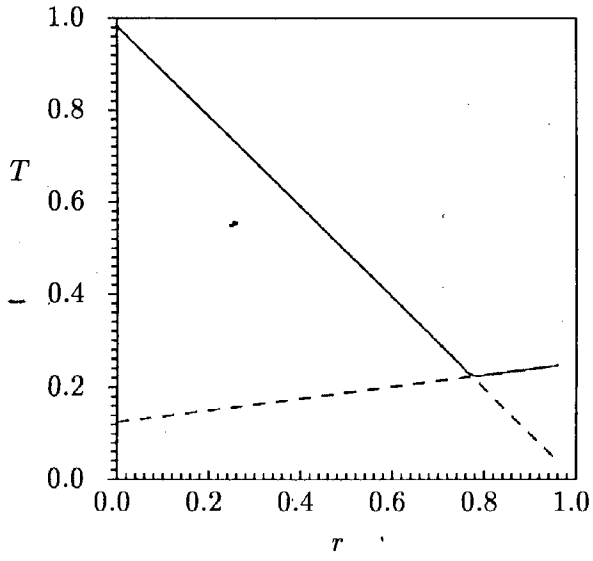

Figure 6. Dependence of critical temperatures of the symmetrical Yukawa fluid on the unlike interaction strength ($\eta = 0.26$, $z\sigma = 48$)

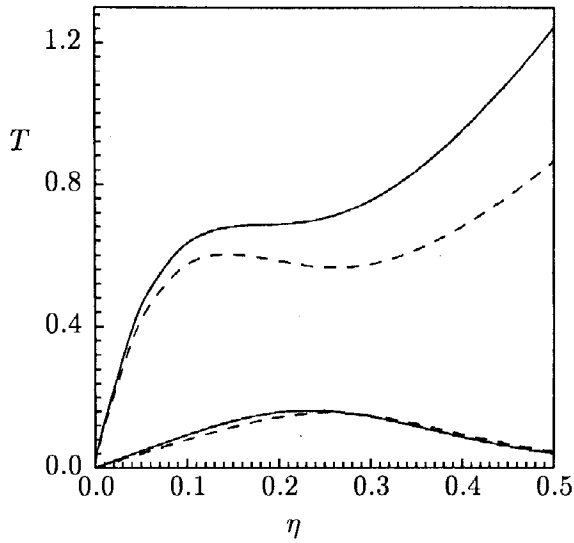

Figure 7. Dependence of critical temperatures of the asymmetrical Yukawa fluid on the packing fraction ($\alpha = 0.67$, $q = 0.9$, $r = 0.8$, $z\sigma_{aa} = 1.8$, $x = 0.35$ (solid line), $x = 0.5$ (dashed line))

behaviour $\tilde{\theta}_2^c$ with η is the same as in Ref. [5].The peak of θ_2^c lies a bit lower as it took place above for a symmetrical fluid. The location of η at which $\theta_2^c(\eta)$ has a minimum or a bend depends on z. The presence of curve θ_1^c in Fig. 7 is the main difference from results obtained in Ref.[5]. Fig. 8 shows the locus of critical temperatures for three different values of concentration x for the mixture with parameters corresponding to the mixture M2 from Ref. [5]: $\alpha = 0.86$, $q = 1.2$, $r = 1.39$, $z\sigma_{aa} = 1.8$, $x = 0.25, 0.5, 0.75$. In this case $r > 1$, so there exists only one curve $\theta_2^c(\eta)$ for each concentration (θ_1^c takes on negative values), and $\theta_2^c(\eta)$ is the curve of the gas-liquid phase equilibrium. The curves in Fig. 8 are in good agreement with corresponding curves from Ref.[5] (see Fig. 1 and 2 in [5]).

In Fig. 9 curves $\theta_1^c(r)$ and $\theta_2^c(r)$ are shown in comparison with corresponding curve from Ref.[10] (see Fig.8 in [10]). Again, the presence of two curves is the main difference here: one curve with the minimum (the curve $\theta_2^c(r)$) as it was obtained in [10] and the other curve with the maximum (the curve $\theta_1^c(r)$) and $\theta_1^c(r_{\max}) \neq \theta_2^c(r_{\min})$. It is evident that the more the mixture differs from the symmetrical one the less pronounced is the extreme on the curve $\theta_1^c(r)$ or $\theta_2^c(r)$ and the distance $r_{\max}$ from $r_{\min}$ extends. This fact confirms the conclusion made in Ref.[10] that the point r^* which is defined from the equation $\partial\theta^c/\partial r = 0$ is not a separation point of gas-liquid and mixing-demixing phase instabilities for the asymmetrical mixture.

5. Conclusions

The CV method with RS is used in the investigation of phase instabilities in the binary fluid system. The Gaussian approximation of the functional of the grand partition function is studied in detail. The explicit expressions for

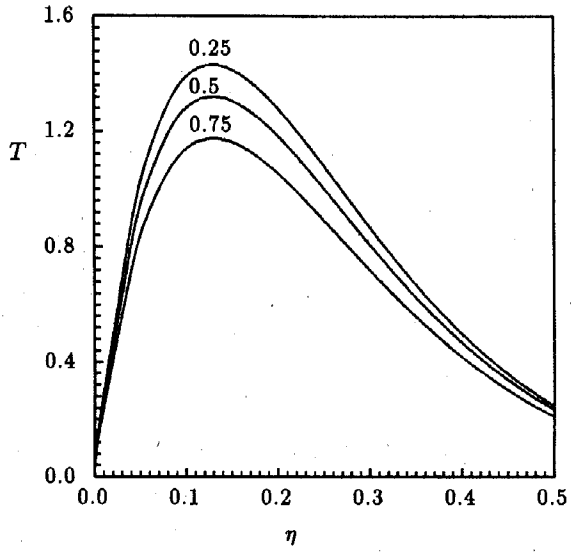

Figure 8. Dependence of gas-liquid critical temperatures of the asymmetrical Yukawa fluid on the packing fraction ($\alpha = 0.86$, $q = 1.2$, $r = 1.39$, $z\sigma_{aa} = 1.8$, $x = 0.25, 0.5, 0.75$)

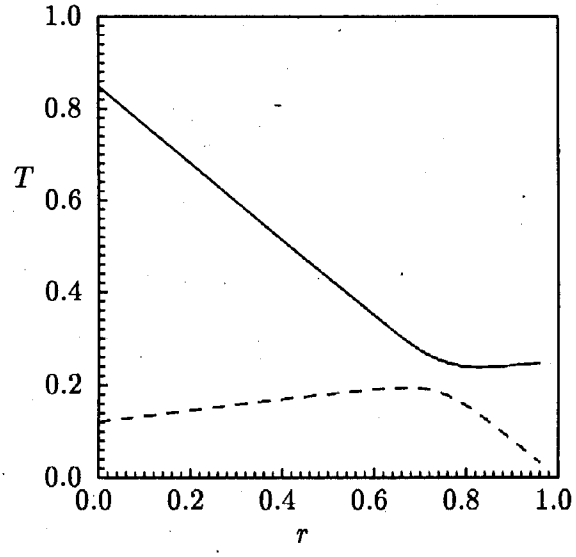

Figure 9. Dependence of critical temperatures of the asymmetrical Yukawa fluid on the unlike interaction strength ($\eta = 0.26$, $z\sigma = 4$, $\alpha = 1$, $q = 1$, $x = 0.7$)

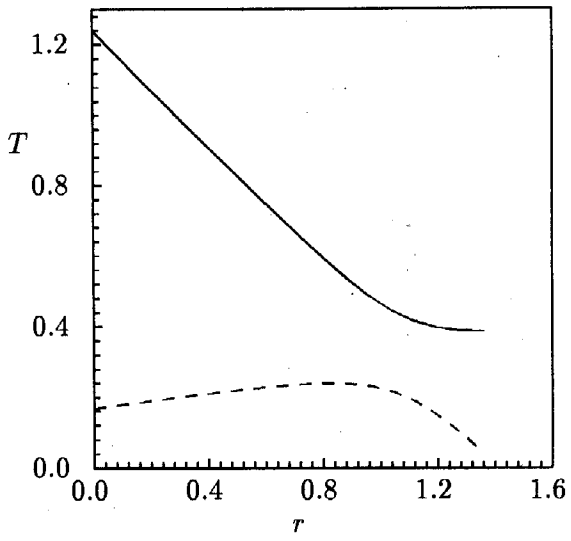

Figure 10. Dependence of critical temperatures of the asymmetrical Yukawa fluid on the unlike interaction strength ($\eta = 0.26$, $z\sigma = 4$, $\alpha = 1$, $q = 2$, $x = 0.7$)

critical temperatures of a two-component system of different size particles interacting via different attractive potentials are obtained. Two subspaces of CV, ($\xi_{1,\vec{k}}$ and $\xi_{2,\vec{k}}$) are distinguished by diagonalization the square form. It is shown that on the critical lines gas-liquid and separation critical points can be identified completely in the case of the symmetrical mixture. In this case when the gas-liquid critical point is approached, total density fluctuations grow and when the separation critical point is approached, fluctuations of relative density (or concentration) grow. For asymmetrical mixture the point identification on the critical line is not such a simple task and both gas-liquid and separation phase transitions are accompanied by total density fluctuations as well as by relative density fluctuations. For a binary symmetrical system the relationships between the microscopic parameters of Hamiltonian which determine alternation of gas-liquid and separation phase transitions are found.

In Sec.4 critical temperatures for binary hard sphere fluid with Yukawa attractive potentials are calculated by means of formula (3.1). The results are compared with the already known ones obtained by the integral equation method. The main difference of our results is the presence of the second branch of critical temperatures. Numerical results are in a good agreement with those obtained by the integral equation method.

Acknowledgments

I am very grateful to I.R.Yukhnovskii for helpful discussions.

Appendix A

In general all the cumulants $M_{\gamma_1 \ldots \gamma_n}(0, \ldots, 0)$ are the functions of chemical potentials of the RS (see Ref.[14]). For $M_{\gamma_1 \gamma_2}(0,0)$ we have

$$M_{\gamma_1 \gamma_2}(0.0) = \frac{1}{\beta} \frac{B_{\gamma_1 \gamma_2}}{\det \mathbf{B}},$$

where $\mathbf{B}$ is a square $(m \times m)$ matrix, elements of which are

$$b_{\gamma_1 \gamma_2} = \left(\frac{\partial \mu_0^{\gamma_1}}{\partial \langle N_{\gamma_2} \rangle} \right)_{V,T,N_{\gamma_k}}.$$

$B_{\gamma_1 \gamma_2}$ is an algebraic adjunct of an element $b_{\gamma_1 \gamma_2}$ of the matrix $\mathbf{B}$. Higher order cumulants can be obtained with the help of recurrent formula

$$M_{\gamma_1 \ldots \gamma_n}(0, \ldots, 0) = \left(\frac{\partial M_{\gamma_1 \ldots \gamma_{n-1}}(0, \ldots, 0)}{\partial \beta \mu_0^{\gamma_n}} \right)_{V,T,\mu_0^{\gamma_{n'}}}.$$

Appendix B

The quantities $\Delta_{\gamma,i}(k)$ have the forms:

$$\begin{aligned}
\Delta_{a,i} &= \sqrt{2}|-a_{ab}|[4a_{ab}^2 + (a_{aa}-a_{bb})^2 \pm (a_{aa}-a_{bb}) \times \\
&\quad \sqrt{(a_{aa}-a_{bb})^2 + 4a_{ab}^2}]^{-1}, \\
\Delta_{b,i} &= \frac{\sqrt{2}}{2} \frac{|-a_{ab}|}{(-a_{ab})} [a_{aa} - a_{bb} \pm \\
&\quad \sqrt{(a_{aa}-a_{bb})^2 + 4a_{ab}^2}][4a_{ab}^2 + (a_{aa}-a_{bb})^2 \pm (a_{aa}-a_{bb}) \times \\
&\quad \sqrt{(a_{aa}-a_{bb})^2 + 4a_{ab}^2}]^{-1},
\end{aligned}$$

where the signs '+' and '-' correspond to $i = 1$ and $i = 2$ respectively.

Appendix C

In Fourier space the Ornstein-Zernike equation may be written in matrix form as

$$\tilde{\mathbf{S}}(k)(\mathbf{I} - \tilde{\mathbf{C}}(k)) = \mathbf{I},$$

where

$$\tilde{\mathbf{S}}(k) = \begin{pmatrix} S_{11}(k) & S_{12}(k) \\ S_{12}(k) & S_{22}(k) \end{pmatrix}$$

and

$$\tilde{\mathbf{C}}(k) = \begin{pmatrix} \tilde{c}_{11}(k) & \tilde{c}_{12}(k) \\ \tilde{c}_{12}(k) & \tilde{c}_{22}(k) \end{pmatrix}.$$

I is the identity matrix. As a result for $S_{11}(k)$, $S_{22}(k)$ and $S_{12}(k)$ we have the following expressions:

$$S_{11}(k) = \left[1 - \rho_1\tilde{c}_{11}(k) - \frac{\rho_1\rho_2\tilde{c}_{12}^2(k)}{1-\rho_2\tilde{c}_{22}(k)}\right]^{-1},$$

$$S_{22}(k) = \left[1 - \rho_2\tilde{c}_{22}(k) - \frac{\rho_1\rho_2\tilde{c}_{12}^2(k)}{1-\rho_1\tilde{c}_{11}(k)}\right]^{-1},$$

$$S_{12}(k) = \frac{\sqrt{\rho_1\rho_2}\tilde{c}_{12}(k)}{(1-\rho_1\tilde{c}_{11}(k))(1-\rho_2\tilde{c}_{22}(k)) - \rho_1\rho_2\tilde{c}_{12}^2(k)}.$$

Using the results of Ref.[18] we have obtained the explicit forms for $\tilde{c}_{ij}(k=0)$ in PY approximation (see Ref.[19]):

$$\rho_1\tilde{c}_{11}(0) = -2\eta_1(4\alpha_1 + 3\beta_1 + 2\gamma_1),$$
$$\rho_2\tilde{c}_{22}(0) = -2\eta_2(4\alpha_2 + 3\beta_2 + 2\gamma_1\alpha_{-3}),$$
$$\sqrt{\rho_1\rho_2}\tilde{c}_{12}(0) = -\frac{1}{5!}\{40A + B[10\beta_{12}(4\tilde{a}+3) + 6\gamma_{12}(5\tilde{a}+4) + 4\gamma_1(6\tilde{a}+5)]\},$$

where

$$\eta_1 = \frac{(1-x)\alpha^3\eta}{x+(1-x)\alpha^3}, \qquad \eta_2 = \frac{x\eta}{x+(1-x)\alpha^3},$$
$$\eta = \eta_1 + \eta_2 \quad \alpha = \sigma_{11}/\sigma_{22}, \quad \tilde{a} = \frac{1-\alpha}{2\alpha},$$

$$\alpha_1 = \frac{1}{(1-\eta)^4}\{1-\eta^3 + (\eta_1+\alpha^3\eta_2)(\eta^2+4(1+\eta)) - 3\eta_2(1-\alpha)^2[(1+\eta_1+\alpha(1+\eta_2))(1-\eta+3\eta_1) + \eta_1(1-\eta)]\},$$

$$\alpha_2 = \frac{1}{\alpha^3(1-\eta)^4}\{\alpha^3(1-\eta^3) + (\eta_1+\alpha^3\eta_2)(\eta^2+4(1+\eta)) - 3\eta_1(1-\alpha)^2[(1+\eta_1+\alpha(1+\eta_2))(1-\eta+3\eta_2) + \alpha\eta_2(1-\eta)]\},$$

$$\beta_1 = -6[\eta_1 g_{11}^2 + \frac{1}{4}\eta_2(1+\alpha)^2\alpha g_{12}^2],$$
$$\beta_2 = -6[\eta_2 g_{22}^2 + \frac{1}{4}\eta_1\alpha^{-3}(1+\alpha)^2 g_{12}^2],$$
$$\beta_{12} = -3\alpha(1-\alpha)(\alpha^{-2}\eta_1 g_{11} + \eta_2 g_{22})g_{12},$$

$$\gamma_1 = \frac{1}{2}(\eta_1 a_1 + \alpha^3\eta_2 a_2),$$
$$\gamma_{12} = 2\gamma_1\frac{1-\alpha}{\alpha},$$

$$g_{11} = \frac{1}{(1-\eta)^2}[1 + \frac{\eta}{2} + 1\frac{1}{2}\eta_2(\alpha - 1)],$$

$$g_{22} = \frac{1}{(1-\eta)^2}[1 + \frac{\eta}{2} + 1\frac{1}{2}\eta_1(\alpha_{-1} - 1)],$$

$$g_{12} = \frac{1}{(1-\eta)^2}[1 + \frac{\eta}{2}\frac{3(1-\alpha)}{2(1+\alpha)}(\eta_1 - \eta_2)],$$

$$A = \frac{5\alpha_1(1+\alpha)^3 B}{\alpha^3}, \quad B = 4!\sqrt{\alpha^3\eta_1\eta_2}.$$

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ДОСЛІДЖЕННЯ ФАЗОВИХ ПЕРЕХОДІВ У БІНАРНИХ СИСТЕМАХ МЕТОДОМ КОЛЕКТИВНИХ ЗМІННИХ

О.В. Пацаган

Метод колективних змінних (КЗ) з виділеною системою відліку (СВ) застосовується до дослідження фазових переходів у бінарних сумішах. Для двокомпонентної системи частинок різних розмірів, які взаємодіють з різними потенціалами притягання отримано в гаусовому наближенні явні вирази для критичних температур. Визначено фазовий простір колективних змінних, зв"язаних з параметрами порядку. Детально розглянуто випадок симетричної суміші. Результати порівнюються з уже відомими, отриманими методами інтегральних рівнянь для суміші твердих сфер, взаємодіючих з потенціалами Юкави. Основною відмінністю є присутність на фазовій діаграмі другої гілки критичних температур. Числові результати добре узгоджуються з отриманими в середньосферичному наближенні (ССН).