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Determination of the Order Parameter in Binary Fluid Mixtures

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We propose a microscopic approach to the study of phase transitions in fluid mixtures. It is based on the collective variables method with a reference system. The problem of definition of the order parameter in a two-component fluid system is considered in detail. This system is described with two sets of collective variables: $\eta_{\vec{k}}$ and $\xi_{\vec{k}}$. It is shown that the CV connected with the order parameter is $\eta_{\vec{k}=0}$ in the case of a gas–liquid critical point as well as in the case of a mixing–demixing phase transition. The relations between the microscopic parameters, temperature, density and concentration which determine the particular form of η_0 for each of these phenomena are obtained. Based on these results we will be able to construct an effective Ginsburg–Landau–Wilson Hamiltonian.

KEY WORDS: Phase transition; binary mixture; order parameter.

1. INTRODUCTION

Binary mixtures in contrast to their constituent components exhibit a variety of phase behaviour. In particular, such systems can demonstrate three different types of two-phase equilibrium: gas–liquid, liquid–liquid and gas–gas as well as continuous transitions between gas–liquid and mixing–demixing (liquid–liquid or gas–gas) critical phenomena.$^{(1, 2)}$ Revealing the microscopic mechanism of such intriguing behaviour is an actual and important task.

During the last decade this problem has been intensively studied by means of integral equation methods.$^{(3–11)}$ However, this approach, although reproduces different phase diagram types by varying the microscopic

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parameters, gives only a qualitative picture of the phenomenon under consideration.

Of special interest are refs. 12–16 devoted to the study of both the universal and non-universal properties of fluids. They are based on the previously proposed approach to the study of the gas–liquid critical point in a one-component fluid, namely, the hierarchical reference theory (HRT).(17) On the microscopic Hamiltonian grounds, the HRT develops the renormalization group (RG) structure near a critical point.

Another microscopic approach to the study of phase transitions was proposed in the late eighties. First it was applied to a 3D Ising model(18) and then was developed for a simple fluid near the gas–liquid critical point.(19–21) This theory has its origin in the approach based on a functional representation of a partition function in the collective variables (CV) space.(22, 23) Its particular feature is a choice of the phase space in which the system is considered. This phase space is formed by a set of CV and contains a variable connected with the order parameter. The proposed approach allows one to determine, on microscopic grounds, the explicit form of an effective Ginzburg–Landau–Wilson Hamiltonian and then to integrate the partition function in the neighborhood of the phase transition point taking into account the renormalization group symmetry. As a result, non-classical critical exponents and analytical expressions for thermodynamic functions are obtained.(18, 21) More recently this theory has been developed for a binary fluid mixture.(24–26).

In this paper, on the basis of the method of CV with a reference system (RS),(24, 25) we address an important task, namely, the definition of the order parameter of a binary fluid mixture. The next stage of our study will be constructing an effective Ginzburg–Landau–Wilson (GLW) Hamiltonian with respect to CV which include a variable corresponding to the order parameter. To this end we will follow the scenario proposed in ref. 25 for a symmetrical mixture. This task will be considered elsewhere.

The question of the physical nature of the order parameter in binary fluid mixtures has been discussed until recently from the point of view of both the phenomenological theory(27, 28) and the microscopic approach.(10, 13, 14, 25) Nowadays the commonly accepted idea is that both the gas–liquid and mixing–demixing phase transitions are accompanied by the total density fluctuations as well as by the relative density fluctuations. In the real mixtures the contribution from each type of the fluctuation processes changes along the critical curve. The evaluation of such contributions at each point of the critical curve is essential to determine the order parameter and to understand the phase transition character in the mixture. Below we show that within the framework of our approach this problem has a consistent and clear solution.

The layout of the paper is as follows. We give a functional representation of the grand partition function of a two-component continuous system in Section 2. Section 3 is devoted to the definition of the order parameter in a binary mixture. In this section we show that the order parameter can be found either on the basis of microscopic properties of the system or from thermodynamic relations. In the former case, we derive an explicit equation for the angle showing the direction of strong fluctuations and, in the latter one, the same formulas as in ref. 14 are obtained. We present our results in Figs. 1–8. Section 4 contains some concluding remarks.

2. FUNCTIONAL REPRESENTATION OF A GRAND PARTITION FUNCTION OF A MULTI-COMPONENT CONTINUOUS SYSTEM. A BINARY MIXTURE

Let us consider a classical multi-component continuous system of interacting particles consisting of N_{a_1} particles of species a_1, N_{a_2} particles of species a_2,... and N_{a_m} particles of species a_m. 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 particle γ at $\vec{r}_i$ and particle δ at $\vec{r}_j$ may be presented 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 a potential of a short-range repulsion that can be chosen as an interaction between the two hard spheres $\sigma_{\gamma\gamma}$ and $\sigma_{\delta\delta}$. $\phi_{\gamma\delta}(r)$ is an attractive part of the potential which dominates at large distances.

Let us start with a grand partition function

$$\Xi = \sum_{N_{a_1}=0}^{\infty} \sum_{N_{a_2}=0}^{\infty} \cdots \sum_{N_{a_m}=0}^{\infty} \prod_{\gamma=a_1}^{a_m} \frac{z_\gamma^{N_\gamma}}{N_\gamma!} \int (d\Gamma) \exp\left[-\frac{\beta}{2} \sum_{\gamma\delta} \sum_{ij} U_{\gamma\delta}(r_{ij}) \right], \qquad (2.1)$$

where $(d\Gamma) = \prod_\gamma d\Gamma_{N_\gamma}$, $d\Gamma_{N_\gamma} = d\vec{r}_1^{\,\gamma}\, d\vec{r}_2^{\,\gamma} \cdots d\vec{r}_{N_\gamma}^{\,\gamma}$ is an element of the configurational space of the γth species; z_γ is the fugacity of the γth species: $z_\gamma = \exp(\beta\mu'_\gamma)$, $\mu'_\gamma = \mu_\gamma + \beta^{-1} \ln[(2\pi m_\gamma \beta^{-1})^{3/2}/h^3]$; $\beta = \frac{1}{k_B T}$, k_B is the Boltzmann constant, T is temperature; m_γ is mass of the γth species, h is the Planck constant. μ'_γ is determined from

$$\frac{\partial \ln \Xi}{\partial \beta\mu'_\gamma} = \langle N_\gamma \rangle,$$

where $\langle N_\gamma \rangle$ is the average number of the γth species.

Further consideration of the problem is done in the extended phase space: in the phase space of the Cartesian coordinates of the particles and in the CV phase space. An interaction connected with the repulsion (potential $\psi_{\gamma\delta}(r)$) is considered in the space of the Cartesian coordinates of the particles. We call this multi-component hard-spheres system a reference system (RS). The thermodynamic and structural properties of the RS are assumed to be known. Although it is known that mixtures with only repulsive interactions might undergo a phase transition,$^{(29)}$ we assume that in the region of temperatures, concentrations and densities we are interested in, the thermodynamic functions of the RS remain analytic. The interaction connected with an attraction (potential $\phi_{\gamma\delta}(r)$) is considered in the CV space. The phase space overflow is cancelled by introduction of a Jacobian of the transition to CV. The contribution of the short-range forces to the long-range interaction screening is ensured by averaging this Jacobian over the RS.

Let us introduce the grand partition function of the RS

$$\Xi_0 = \sum_{N_{a_1}=0}^{\infty} \sum_{N_{a_2}=0}^{\infty} \cdots \sum_{N_{a_m}=0}^{\infty} \prod_{\gamma=a_1}^{a_m} \frac{\exp(\beta\mu_0^{\gamma} N_\gamma)}{N_\gamma!} \int (d\Gamma) \exp\left[-\frac{\beta}{2}\sum_{\gamma\delta}\sum_{ij}\psi_{\gamma\delta}(r_{ij})\right], \tag{2.2}$$

where μ_0^{γ} is the chemical potential of the γth species in the RS.

Then the grand partition function (2.1) can be written as:$^{(24, 25)}$

$$\Xi = \Xi_0 \Xi_1, \tag{2.3}$$

where Ξ_0 is given in (2.2).

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

$$\Xi_1 = \int (d\rho) \exp\left[\beta \sum_{\gamma} \mu_1^{\gamma} \rho_{0,\gamma} - \frac{\beta}{2V} \sum_{\gamma\delta} \sum_{\vec{k}} \tilde{\phi}_{\gamma\delta}(k)\, \rho_{\vec{k},\gamma} \rho_{-\vec{k},\delta}\right] \times J(\rho_{a_1}, \rho_{a_2}, \ldots, \rho_{a_m}). \tag{2.4}$$

Here,

(1) $\tilde{\phi}_{\gamma\delta}(k)$ is a Fourier transform of the attractive potential $\phi_{\gamma\delta}(r)$. $k_i = \frac{2\pi n_i}{L}$ with $L = V^{1/3}$, $k_i = k_x, k_y, k_z$, and $n_i = 0, \pm 1, \pm 2, \ldots$, the thermodynamic limit $L \to \infty$ is assumed. The function $\tilde{\phi}_{\gamma\delta}(k)$ satisfies the following requirements: $\tilde{\phi}_{\gamma\delta}(k)$ is negative for the small values of $\vec{k}$ and $\lim_{\vec{k}\to\infty} \tilde{\phi}_{\gamma\delta}(k) = 0$. The behaviour of $\phi_{\gamma\delta}(r)$ in the region of the core $r < \sigma_{\gamma\delta}$ should be determined from the conditions of optimal separation of the interaction.

(2) μ_1^γ is a part of the chemical potential of the γth species

$$\mu_1^\gamma = \mu_\gamma' - \mu_0^\gamma + \frac{\beta}{2V} \sum_{\vec{k}} \tilde{\phi}_{\gamma\gamma}(k)$$

and is determined from the equation

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

(3) $J(\rho) = J(\rho_{a_1}, \rho_{a_2}, \ldots, \rho_{a_m})$ is the Jacobian of the transition to CV averaged on the RS:

$$\begin{aligned} J(\rho) = \frac{1}{\Xi_0} \sum_{N_{a_1}=0}^{\infty} \sum_{N_{a_2}=0}^{\infty} \cdots \sum_{N_{a_m}=0}^{\infty} \prod_{\gamma=a_1}^{a_m} \frac{\exp(\beta\mu_0^\gamma N_\gamma)}{N_\gamma!} \int (d\Gamma) \\ \times \exp\left[-\frac{\beta}{2} \sum_{\gamma\delta} \sum_{ij} \psi_{\gamma\delta}(r_{ij}) \right] \prod_{\gamma=a_1}^{a_m} \delta(\rho_{0,\gamma} - \hat{\rho}_{N_\gamma}(0)) \\ \times \prod_{\vec{k}\neq 0}{}' \delta(\rho_{\vec{k},\gamma} - \hat{\rho}_{N_\gamma}(\vec{k})), \end{aligned} \tag{2.5}$$

where $\hat{\rho}_{N_\gamma}(\vec{k})$ is a Fourier transform of the particle number density operator

$$\hat{\rho}_{N_\gamma}(\vec{k}) = \sum_{j=1}^{N_\gamma} \exp(-i\vec{k}\vec{r}_j^{\,\gamma}),$$

$\delta(\cdots)$ is the Dirac delta function. The prime means that the product over $\vec{k}$ is performed in the upper semi-space.

$\rho_{\vec{k},\gamma} = \rho_{\vec{k},\gamma}^c - i\rho_{\vec{k},\gamma}^s$ are collective variables of the γth species, where the indices c and s denote the real part and the coefficient of the imaginary part of $\rho_{\vec{k},\gamma}$. Each $\rho_{\vec{k},\gamma}^c$ and $\rho_{\vec{k},\gamma}^s$ takes all the real values from $-\infty$ to $+\infty$. $(d\rho)$ is a volume element of the CV phase space:

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

$\rho_{\vec{k},\gamma}$ is related to $\hat{\rho}_{N_\gamma}(\vec{k})$ by means of the relations

$$\hat{\rho}_{N_\gamma}^c(\vec{k}) = \int \rho_{\vec{k},\gamma}^c \delta(\rho_{\vec{k},\gamma}^c - \hat{\rho}_{N_\gamma}^c(\vec{k})) \, d\rho_{\vec{k},\gamma}^c,$$

$$\hat{\rho}_{N_\gamma}^s(\vec{k}) = \int \rho_{\vec{k},\gamma}^s \delta(\rho_{\vec{k},\gamma}^s - \hat{\rho}_{N_\gamma}^s(\vec{k})) \, d\rho_{\vec{k},\gamma}^s.$$

First $J(\rho)$ was defined for the system of charged particles[(22)] and then discussed more extensively in ref. 23 (and also in ref. 18–21, 24, 25).

Substituting into (2.5) the explicit forms for delta functions, we obtain

$$J(\rho)=\int J(\nu)\prod_{\gamma}\exp\left(i2\pi\sum_{\vec{k}}\nu_{\vec{k},\gamma}\rho_{\vec{k},\gamma}\right)(d\nu),$$

where the variables $\nu_{\vec{k},\gamma}$ are conjugate to the CV $\rho_{\vec{k},\gamma}$:

$$\nu_{\vec{k},\gamma}=\tfrac{1}{2}(\nu^{c}_{\vec{k},\gamma}+i\nu^{s}_{\vec{k},\gamma}),\qquad \text{if}\quad \vec{k}\neq 0$$

and

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

$J(\nu)$ is a Fourier transform of the Jacobian of the transition $J(\rho)$

$$J(\nu)=\frac{1}{\Xi_0}\sum_{N_{a_1}=0}^{\infty}\sum_{N_{a_2}=0}^{\infty}\cdots\sum_{N_{a_m}=0}^{\infty}\prod_{\gamma=a_1}^{a_m}\frac{\exp(\beta\mu_0^{\gamma}N_{\gamma})}{N_{\gamma}!}\int(d\Gamma)$$
$$\times\exp\left[-\frac{\beta}{2}\sum_{\gamma\delta}\sum_{ij}\psi_{\gamma\delta}(r_{ij})\right]\prod_{\gamma,\vec{k}}\exp(-i2\pi\nu_{\vec{k},\gamma}\hat{\rho}_{N_{\gamma}}(\vec{k})).\tag{2.6}$$

Performing in (2.6) integration over the phase space of the Cartesian coordinates of the particles and summing over $N_{a_1},\ldots,N_{a_m}$, we can present $J(\rho)$ in the form:

$$J(\rho)=\int(d\nu)\prod_{\gamma=a_1}^{a_m}\exp\left[i2\pi\sum_{\vec{k}}\nu_{\vec{k},\gamma}\rho_{\vec{k},\gamma}\right]\exp\left[\sum_{n\geqslant 1}\frac{(-i2\pi)^n}{n!}\right.$$
$$\left.\times\sum_{\gamma_1\cdots\gamma_n}\sum_{\vec{k}_1\cdots\vec{k}_n}M_{\gamma_1\cdots\gamma_n}(\vec{k}_1,\ldots,\vec{k}_n)\,\nu_{\vec{k}_1,\gamma_1}\cdots\nu_{\vec{k}_n,\gamma_n}\right].\tag{2.7}$$

The nth cumulant $M_{\gamma_1\cdots\gamma_n}(\vec{k}_1,\ldots,\vec{k}_n)$ is determined from

$$M_{\gamma_1\cdots\gamma_n}(\vec{k}_1,\ldots,\vec{k}_n)=\left.\frac{\partial^n\ln J(\nu)}{\partial\nu_{\vec{k}_1,\gamma_1}\partial\nu_{\vec{k}_2,\gamma_2}\cdots\partial\nu_{\vec{k}_n,\gamma_n}}\right|_{\nu_{\vec{k}_i,\gamma_i}=0}$$

and is connected with $S_{\gamma_1\cdots\gamma_n}(k_1,\ldots,k_n)$, the n-particle partial structure factor of the RS, by means of the relation

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

where $\delta_{\vec{k}_1+\cdots+\vec{k}_n}$ is a Kronecker symbol.

In general, the dependence of $M_{\gamma_1 \cdots \gamma_n}(\vec{k}_1, \ldots, \vec{k}_n)$ on wave vectors $\vec{k}_1, \ldots, \vec{k}_n$ is complicated. Since we are interested in the critical properties, the small-$\vec{k}$ expansion of the cumulants can be considered. Hereafter we shall replace $M_{\gamma_1 \cdots \gamma_n}(\vec{k}_1, \ldots, \vec{k}_n)$ by their values in the long-wavelength limit $M_{\gamma_1 \cdots \gamma_n}(0, \ldots, 0)$. We have a recurrence formula for $M_{\gamma_1 \cdots \gamma_n}(0, \ldots, 0)$:$^{(30)}$

$$M_{\gamma_1 \cdots \gamma_n}(0, \ldots) = |\mathbf{B}|^{-1} \times \begin{vmatrix} \left(\dfrac{\partial M_{\gamma_1 \cdots \gamma_{n-1}}(0, \ldots)}{\partial N_{\gamma_n}} \right)_{V,T,\{N_{\gamma_{n'}}\}} & \left(\dfrac{\partial M_{\gamma_1 \cdots \gamma_{n-1}}(0, \ldots)}{\partial \{N_{\gamma_{n'}}\}} \right)_{V,T,N_{\gamma_n}} \\ \left(\dfrac{\partial \{\mu_{\gamma_{n'}}\}}{\partial N_{\gamma_n}} \right)_{V,T,\{N_{\gamma_{n'}}\}} & \left(\dfrac{\partial \{\mu_{\gamma_{n'}}\}}{\partial \{N_{\gamma_{n'}}\}} \right)_{V,T,N_{\gamma_n}} \end{vmatrix},$$

where $\{\mu_{\gamma_{n'}}\}$ denotes a column-vector

$$\begin{pmatrix} \mu_{\gamma_1} \\ \vdots \\ \mu_{\gamma_{n-1}} \end{pmatrix},$$

which does not include the element μ_{γ_n}, $\partial \cdots / \partial \{N_{\gamma_{n'}}\}$ denotes a row-vector

$$\left(\frac{\partial \cdots}{\partial N_{\gamma_1}} \cdots \frac{\partial \cdots}{\partial N_{\gamma_{n-1}}} \right),$$

which does not include $\frac{\partial \cdots}{\partial N_{\gamma_n}}$. **B** is a square $(m \times m)$ matrix, the elements of which are

$$B_{\gamma_1 \gamma_2} = \left(\frac{\partial \beta \mu_{\gamma_1}}{\partial \langle N_{\gamma_2} \rangle} \right)_{V,T,N_{\gamma_k}}.$$

Two-particle cumulants $M_{\gamma\delta}(k)$ can be found, for example, in the Percus–Yevick approximation using the analytic solution obtained for a hard sphere mixture.$^{(32)}$

Now let us consider a two-component system consisting of N_a particles of species a and N_b particles of species b ($\gamma_1, \gamma_2, \ldots, \gamma_n = a, b$ in (2.3)–(2.7)). Having passed in (2.4) to CV $\rho_{\vec{k}}$ and $c_{\vec{k}}$ by means of the orthogonal linear transformation

$$\rho_{\vec{k}} = \frac{\sqrt{2}}{2} (\rho_{\vec{k},a} + \rho_{\vec{k},b}), \qquad c_{\vec{k}} = \frac{\sqrt{2}}{2} (\rho_{\vec{k},a} - \rho_{\vec{k},b}), \tag{2.8}$$

we obtain for Ξ_1:

$$\Xi_1 = \int (d\rho)(dc) \exp\left[\beta\mu_1^+ \rho_0 + \beta\mu_1^- c_0 - \frac{\beta}{2V} \sum_{\vec{k}} [\tilde{V}(k)\, \rho_{\vec{k}} \rho_{-\vec{k}} \right.$$

$$\left. + \tilde{W}(k)\, c_{\vec{k}} c_{-\vec{k}} + 2\tilde{U}(k)\, \rho_{\vec{k}} c_{-\vec{k}}] \right] J(\rho, c). \tag{2.9}$$

Here the following notations are introduced:

$\rho_{\vec{k}}$ and $c_{\vec{k}}$ are CV connected with the total density fluctuation modes and the relative density (or concentration) fluctuation ones respectively.

Functions μ_1^+ and μ_1^- have the forms:

$$\mu_1^+ = \frac{\sqrt{2}}{2}(\mu_1^a + \mu_1^b), \qquad \mu_1^- = \frac{\sqrt{2}}{2}(\mu_1^a - \mu_1^b) \tag{2.10}$$

and are determined from the equations

$$\frac{\partial \ln \Xi_1}{\partial \beta\mu_1^+} = \langle N \rangle, \tag{2.11}$$

$$\frac{\partial \ln \Xi_1}{\partial \beta\mu_1^-} = \langle N_a \rangle - \langle N_b \rangle. \tag{2.12}$$

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

$$\begin{aligned} \tilde{V}(k) &= (\tilde{\phi}_{aa}(k) + \tilde{\phi}_{bb}(k) + 2\tilde{\phi}_{ab}(k))/2, \\ \tilde{W}(k) &= (\tilde{\phi}_{aa}(k) + \tilde{\phi}_{bb}(k) - 2\tilde{\phi}_{ab}(k))/2, \\ \tilde{U}(k) &= (\tilde{\phi}_{aa}(k) - \tilde{\phi}_{bb}(k))/2. \end{aligned} \tag{2.13}$$

$$J(\rho, c) = \int (d\omega)(d\gamma) \exp\left[i2\pi \sum_{\vec{k}} (\omega_k \rho_k + \gamma_k c_k) \right] J(\omega, \gamma), \tag{2.14}$$

$$J(\omega, \gamma) = \exp\left[\sum_{n \geqslant 1} \sum_{i_n \geqslant 0} \frac{(-i2\pi)^n}{n!} \sum_{\vec{k}_1 \cdots \vec{k}_n} M_n^{(i_n)}(0, \ldots, 0) \right.$$

$$\left. \times \gamma_{\vec{k}_1} \cdots \gamma_{\vec{k}_{i_n}} \omega_{\vec{k}_{i_{n+1}}} \cdots \omega_{\vec{k}_n} \right], \tag{2.15}$$

where

$$\omega_{\vec{k}} = \frac{\sqrt{2}}{2}(\nu_{\vec{k},a} + \nu_{\vec{k},b}),$$
$$\gamma_{\vec{k}} = \frac{\sqrt{2}}{2}(\nu_{\vec{k},a} - \nu_{\vec{k},b}).$$

Index i_n indicates the number of variables $\gamma_{\vec{k}}$ in the cumulant expansion (2.15). Cumulants $M_n^{(i_n)}$ are expressed as linear combinations of the partial cumulants $M_{\gamma_1\cdots\gamma_n}$ (see (2.7)) and are presented for $n \leqslant 4$ in Appendix A.

Formulas (2.9)–(2.15) are the initial formulas in our study of phase transitions in binary fluids.

3. THE ORDER PARAMETER IN A BINARY MIXTURE

In order to derive the effective GLW Hamiltonian we should first find the CV connected with the order parameter. To this end we restrict ourselves to the consideration of the Gaussian approximation of functional integral (2.9)–(2.15) by setting $n=2$ in (2.14)–(2.15). This truncation, also known as the random-phase approximation, assumes that fluctuation contributions to the free energy are small. While this approximation yields the classical critical behaviour, it provides the correct qualitative picture of the phenomenon under consideration. As we will see below, it is successful in defining the order parameter and, hence, in revealing the phase transition mechanism in binary fluids.

As a result of integrating over variables γ_k and ω_k in (2.14)–(2.15), Ξ_1 can be rewritten as

$$\Xi_1^G = \frac{1}{2\pi}\prod_{\vec{k}}{}' \frac{1}{\pi}\frac{1}{\sqrt{\Delta(k)}}\int (d\rho)(dc)\exp\Bigg[\rho_0(\beta\mu_1^+ + \aleph_1/\Delta) + c_0(\beta\mu_1^- + \aleph_2/\Delta) - (M_1^{(0)}\aleph_1 + M_1^{(1)}\aleph_2) - \frac{1}{2}\sum_{\vec{k}}[\rho_{\vec{k}}\rho_{-\vec{k}}A_{11}(k) + c_{\vec{k}}c_{-\vec{k}}A_{22}(k) + 2\rho_{\vec{k}}c_{-\vec{k}}A_{12}(k)]\Bigg], \tag{3.1}$$

where

$$\aleph_1 = M_2^{(2)}M_1^{(0)} - M_2^{(1)}M_1^{(1)}, \qquad \aleph_2 = M_2^{(0)}M_1^{(0)} - M_2^{(1)}M_1^{(0)}$$

$$
\begin{aligned}
A_{11}(k)&=\frac{1}{2}\left(\frac{\beta}{V}\tilde{V}(k)+\frac{M_2^{(2)}}{\Delta}\right)\\
A_{22}(k)&=\frac{1}{2}\left(\frac{\beta}{V}\tilde{W}(k)+\frac{M_2^{(0)}}{\Delta}\right)\\
A_{12}(k)&=\frac{1}{2}\left(\frac{\beta}{V}\tilde{U}(k)-\frac{M_2^{(1)}}{\Delta}\right)\\
\Delta&=M_2^{(0)}M_2^{(2)}-(M_2^{(1)})^2.
\end{aligned}
\tag{3.2}
$$

It is easily seen that the inverse of matrix **A** where

$$\mathbf{A}=\begin{pmatrix} A_{11}(k) & A_{12}(k)\\ A_{12}(k) & A_{22}(k)\end{pmatrix}$$

yields a matrix of structure factors **S** obtained in the Gaussian approximation[33]

$$\mathbf{S}=\begin{pmatrix} S_{\rho\rho}(k) & S_{\rho c}(k)\\ S_{\rho c}(k) & S_{cc}(k)\end{pmatrix}.$$

Here

$$
\begin{aligned}
S_{\rho\rho}(k)&=\langle\hat{\rho}_{\vec{k}}\hat{\rho}_{-\vec{k}}\rangle-\delta_{\vec{k}}\langle N_a+N_b\rangle^2,\\
S_{\rho c}(k)&=\langle\hat{\rho}_{\vec{k}}\hat{c}_{-\vec{k}}\rangle-\delta_{\vec{k}}\langle N_a+N_b\rangle\langle N_a-N_b\rangle,\\
S_{cc}(k)&=\langle\hat{c}_{\vec{k}}\hat{c}_{-\vec{k}}\rangle-\delta_{\vec{k}}\langle N_a-N_b\rangle^2
\end{aligned}
$$

and

$$
\begin{aligned}
\hat{\rho}_{\vec{k}}&=\sum_{i=1}^{N_a}\exp(-i\vec{k}\vec{r}_i^{\,a})+\sum_{i=1}^{N_b}\exp(-i\vec{k}\vec{r}_i^{\,b}),\\
\hat{c}_{\vec{k}}&=\sum_{i=1}^{N_a}\exp(-i\vec{k}\vec{r}_i^{\,a})-\sum_{i=1}^{N_b}\exp(-i\vec{k}\vec{r}_i^{\,b}).
\end{aligned}
$$

In order to determine the phase space of CV connected with the order parameters we introduce independent collective excitations by diagonalizing the square form in (3.1) by means of the orthogonal transformation:

$$
\begin{aligned}
\rho_{\vec{k}}&=A(k)\,\xi_{\vec{k}}+B(k)\,\eta_{\vec{k}}\\
c_{\vec{k}}&=C(k)\,\xi_{\vec{k}}+D(k)\,\eta_{\vec{k}}
\end{aligned}
\tag{3.3}
$$

The explicit forms for coefficients $A(k)$, $B(k)$, $C(k)$ and $D(k)$ are given in Appendix B.

As a result, we have

$$\begin{aligned}\Xi_1^G = \frac{1}{2\pi}\prod_{\vec{k}}{}' \frac{1}{\pi}\frac{1}{\sqrt{\Delta(k)}}\int (d\eta)(d\xi)\exp\Bigg[& \eta_0(AM_1+CM_2) \\ & +\xi_0(BM_1+DM_2)-(M_1^{(0)}\aleph_1+M_1^{(1)}\aleph_2)/(\Delta(0)) \\ & -\frac{1}{2}\sum_{\vec{k}}\,(\varepsilon_1(k)\,\eta_{\vec{k}}\eta_{-\vec{k}}+\varepsilon_2(k)\,\xi_{\vec{k}}\xi_{-\vec{k}})\Bigg],\end{aligned}$$

where

$$\varepsilon_{1,2}(k) = A_{11}(k)+A_{22}(k)\mp\sqrt{(A_{11}(k)-A_{22}(k))^2+4A_{12}^2(k)} \tag{3.4}$$

(the + and − signs correspond to indices 1 and 2).

One of the quantities (3.4) (or both) tends to zero as the critical temperature is approached at a certain wave vector $\vec{k}^*$. Thus, the CV $\eta_{\vec{k}^*}$ (or $\xi_{\vec{k}^*}$) can be identified as the order parameter where wave vector $\vec{k}^*$ must correspond to the minimum of one of the functions $\varepsilon_1(k)$ or $\varepsilon_2(k)$ (or both). These functions depend on temperature, attractive potentials $\tilde{\phi}_{\gamma\delta}(k)$ and characteristics of the RS. The RS enters into (3.4) by cumulants $M_{\gamma\delta}(k)$.

Coefficients $\varepsilon_1(k)$ and $\varepsilon_2(k)$ were studied both as wave vector functions at different values of temperature T, density η and concentration x including the gas–liquid and mixing–demixing critical points$^{(34)}$ and as temperature functions at $\vec{k}=0$.$^{(35)}$ The results showed that branch $\varepsilon_1(k)$ became a critical one, no matter whether the system approached the gas–liquid or gas–gas demixing critical point. Moreover, $\varepsilon_1(k)$ and $\varepsilon_2(k)$ had the minima at $\vec{k}=0$.$^{(34)}$

On the other hand, for $A_{ij}(k=0)$ by **AS=1** one can obtain the thermodynamic relations:$^{(31)}$

$$\begin{aligned} A_{11}(0) &= (\rho k_B T\kappa_T)^{-1}, \\ A_{12}(0) &= (\rho k_B T\kappa_T)^{-1}\,\hat{\delta}, \\ A_{22}(0) &= (\rho k_B T)^{-1}\left(\frac{\partial^2 G}{\partial x^2}\right)_{T,P}+(\rho k_B T\kappa_T)^{-1}\hat{\delta}^2, \end{aligned} \tag{3.5}$$

where κ_T is a compressibility, $\hat{\delta}=\rho(v_a-v_b)$, $v_i=(\frac{\partial V}{\partial N_i})_{T,P,N_{j\neq i}}$ is a partial volume, $x=\langle N_b\rangle/\langle N_a+N_b\rangle$ is a concentration, G is the Gibbs free energy.

At either the gas–liquid or mixing–demixing critical point the equality

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{T,P} = 0 \tag{3.6}$$

holds. Substituting (3.5) and (3.6) in (3.4) we also have

$$\varepsilon_1(k=0) \equiv 0, \qquad \varepsilon_2(k=0) = (\rho k_B T \kappa_T)^{-1}\,(1+\hat{\delta}^2).$$

Hence we can draw the following conclusions:

1. Branch $\varepsilon_1(k)$ is always critical, no matter whether the system approaches the gas–liquid or mixing–demixing phase transition point.

2. Because $\varepsilon_1(k)$ has the minimum at $\vec{k}=0$, the CV connected with the order parameter is η_0 in the case of the gas–liquid critical point as well as in the case of the mixing–demixing phase transition. The particular form of η_0 for each of these phenomena can be determined by means of the relations between the microscopic parameters, temperature, density and concentration of the system or by means of the thermodynamic relations.

3. In the plane (ρ_0, c_0) we have distinguished two directions: the direction of strong fluctuations η_0 and the direction of weak fluctuations ξ_0. As a result, we can write the conditions for the binary mixture critical point in the form:

$$\left[\frac{\partial^2 \Omega}{\partial \eta_0^2}\right]_c = 0,$$

$$\left[\frac{\partial^2 \Omega}{\partial \eta_0\,\partial \xi_0}\right]_c = 0,$$

$$\left[\frac{\partial^3 \Omega}{\partial \eta_0^3}\right]_c = 0,$$

where $\Omega = -kT \ln \Xi$ is a grand canonical potential.

Now let us consider the CV $\eta_{\vec{k}=0}$ which is connected with the direction of the strong fluctuations of the system in the vicinity of its critical line. From (3.3) it follows that

$$\begin{aligned} \xi_0 &= A(0)\,\rho_0 + C(0)\,c_0 \\ \eta_0 &= B(0)\,\rho_0 + D(0)\,c_0, \end{aligned} \tag{3.7}$$

On the other hand, (3.7) can be rewritten as

$$\begin{aligned}\xi_0 &= \rho_0 \cos\theta + c_0 \sin\theta \\ \eta_0 &= -\rho_0 \sin\theta + c_0 \cos\theta.\end{aligned} \tag{3.8}$$

Comparing (3.7) and (3.8) we can determine the rotation angle θ of axes η_0 and ξ_0 in the (ρ_0, c_0) plane from the equation

$$\tan\theta = \frac{C}{A}. \tag{3.9}$$

Hence, on the basis of (3.9) we can determine the direction of the order parameter either from the microscopic properties of the system (see (3.2))

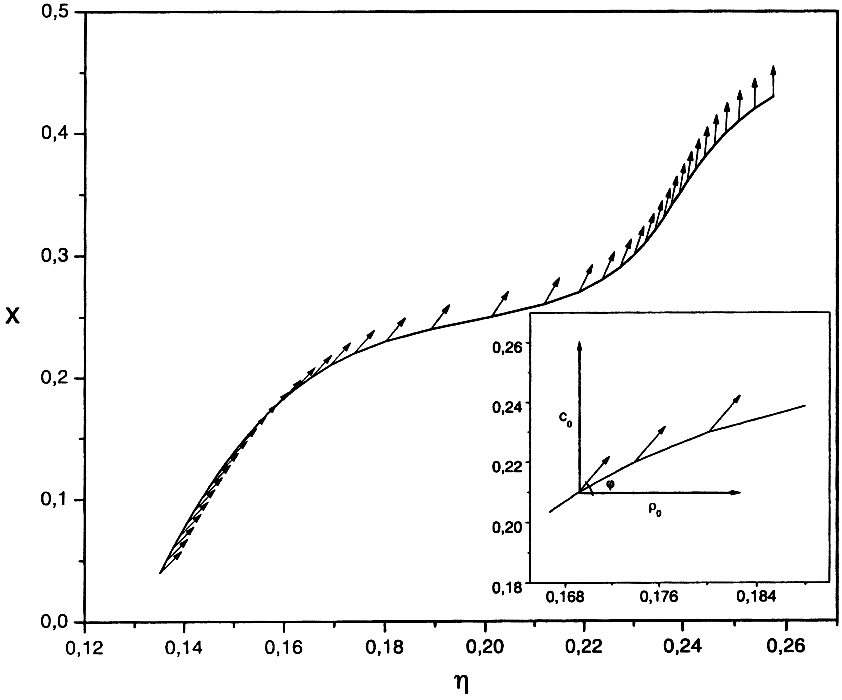

Fig. 1. Density-concentration projection of the critical line and direction of the order parameter of the model binary mixture at $\alpha = 1.0$, $q = 0.9$ and $r = 0.6$. The inset is provided to illustrate angle φ defined in the (ρ_0, c_0) plane (see explanation in the text).

or, by using (3.5), from the thermodynamic relations. In the latter case we find

$$\tan\theta = \hat{\delta} \qquad \text{or} \qquad \cot\theta = \frac{1}{\hat{\delta}}. \tag{3.10}$$

Having passed to the angle $\varphi = \theta - \pi/2$ we obtain the same formulas as in ref. 14:

$$x\cot\varphi = 1 - \rho v_a, \qquad \rho\tan\varphi = \frac{\partial x}{\partial(1/\rho)}.$$

We will illustrate below how the direction of the strong fluctuations calculated with (3.9) changes along the critical curve.

As was noted above, binary fluid mixtures can exhibit complex phase behaviour and different kinds of critical phenomena. It is convenient to

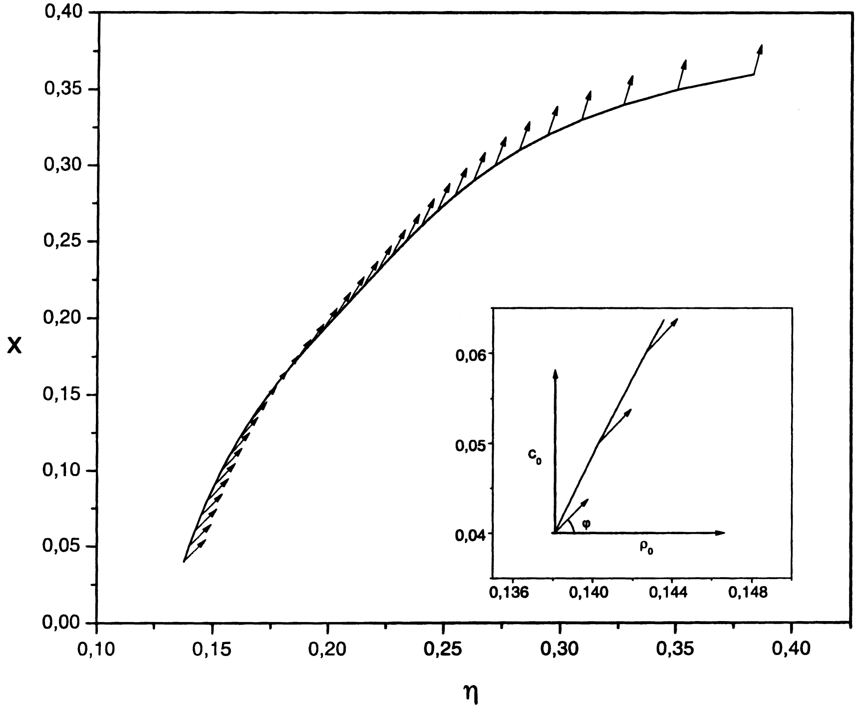

Fig. 2. Same as Fig. 1 at $\alpha = 0.9$, $q = 0.9$ and $r = 0.6$.

classify binary phase behaviour on the basis of the types of critical and three-phase lines present and on the way these intersect. For fluid phase equilibria, such a classification scheme was proposed by van Konynenburg and Scott.(36) Solely the mixtures showing critical behaviour according to class 1 are completely miscible and their critical curves appear to be continuous lines between the critical point of the pure components. The remaining five classes display mixing–demixing separation of various kinds. Except for classes 1 and 2 the phase diagrams do not demonstrate continuous lines between the critical points of the pure components.

In order to illustrate the behaviour of the order parameter we first consider the three model binary mixtures which consist of the hard spheres interacting via the attractive potentials $\phi_{ij}(r)$. We are not specifying the form of $\phi_{ij}(r)$ since we consider a mean-field approximation here. Each of these systems is characterized by a set of the parameters α, q and r, where $\alpha = \sigma_{aa}/\sigma_{bb}$ is the hard-sphere ratio, σ_{ii} is the hard-sphere diameter, $q = -\tilde{\phi}_{bb}(0)/|\tilde{\phi}_{aa}(0)|$ (provided that $|\tilde{\phi}_{aa}(0)| > |\tilde{\phi}_{bb}(0)|$) is the dimensionless

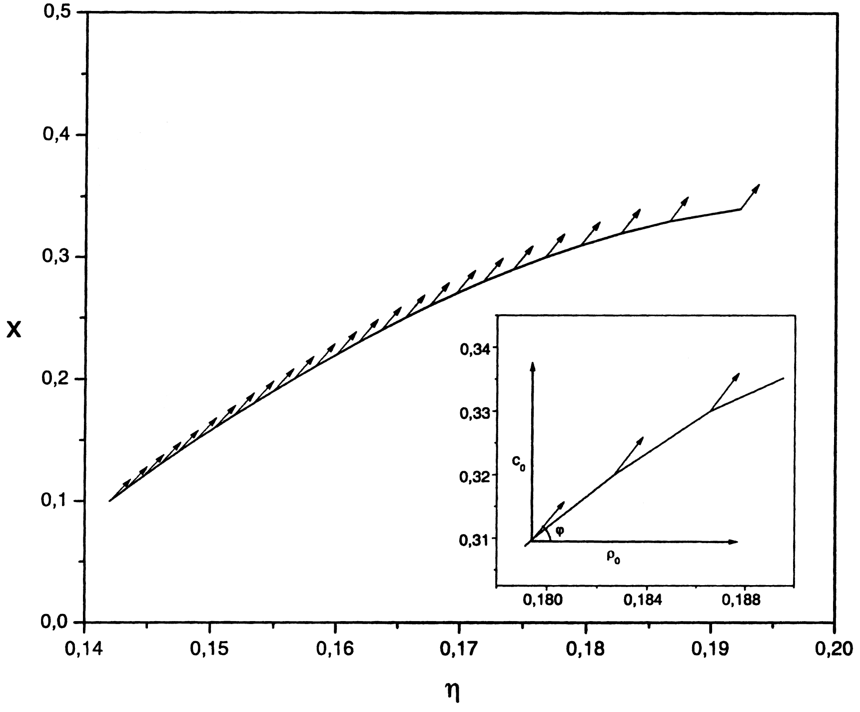

Fig. 3. Same as Fig. 1 at $\alpha = 0.9$, $q = 0.9$ and $r = 0.8$.

"like" interaction strength and $r = -\tilde{\phi}_{ab}(0)/|\tilde{\phi}_{aa}(0)|$ is the "unlike" interaction strength. As is known$^{(1,4,5,9,11,36)}$ the phase diagram of a mixture is sensitive to the relationship among these parameters. We also consider the argon–krypton mixture which exhibits phase behaviour of class 1.$^{(37)}$

We calculate critical curves of the binary fluid mixtures using thermodynamic criteria on the basis of the Helmholtz free energy f,$^{(1,36)}$

$$f_{2x} f_{2V} - f_{Vx}^2 = 0 \tag{3.11}$$

$$f_{3x} f_{2V}^2 - 3 f_{V2x} f_{Vx} f_{2V} + 3 f_{2Vx} f_{Vx}^2 - f_{3V} f_{2x} f_{Vx} = 0, \tag{3.12}$$

where

$$f_{nVmx} = \frac{\partial^{n+m} f}{\partial V^n \, \partial x^m}$$

and we restrict ourselves to the mean-field approximation for f (see Appendix C). Equations (3.11) and (3.12) are solved simultaneously by using (C.1)–(C.3).

First, for each mixture we calculate the critical curve in the (T^*, η, x) space (see notations for T^* and η in Appendix C). Then, for each set of the

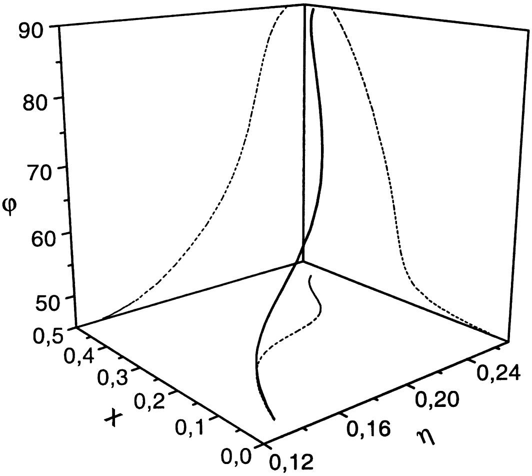

Fig. 4. The dependence of angle φ on packing density η and concentration x for the model binary mixture at $\alpha = 1.0$, $q = 0.9$ and $r = 0.6$. The full line is angle φ defined in the (ρ_0, c_0) plane, the dashed lines indicate its projections in planes (φ, η), (φ, x) and (η, x), respectively. φ is measured in degrees. The (η, x) projection coincides with the (η, x) projection of the critical line.

critical parameters T_c^*, η_c, x_c, we calculate angle θ showing the direction of strong fluctuations in the (ρ_0, c_0) plane. The results are presented in Figs. 1–8.

Figures 1–3 depict the (η, x) projections of the critical lines of the model binary mixture for the three sets of parameters α, q and r. The arrows show the direction of strong fluctuations (order parameter) along the critical curve. The direction corresponds to the angle $\varphi = \theta - \pi/2$ in the (ρ_0, c_0) plane. The figures are obtained by the superposition of the set of plots, namely, the plot displaying the (η, x) projection of the critical line and the plots displaying the directions of the order parameter (at the points of the critical curve) in the (ρ_0, c_0) plane. In fact, only parts of the full phase diagrams are shown in these figures. As one can see in Figs. 1–3, a change in the hard-sphere ratio α has a more pronounced effect on the trend of the critical line and, hence, on the behaviour of the order parameter than a slight change in the parameter r does. We also plot angle φ versus η and x in Figs. 4–6.

Figure 7 depicts the (η, x) projection of the liquid–gas critical curve for the argon–krypton mixture. The calculations are performed for the model mixture of additive hard spheres attracting via the Morse potential

$$\phi_{\gamma\delta}(r) = \varepsilon_{\gamma\delta}\{\exp[-2\alpha_{\gamma\delta}(r - R_{\gamma\delta})] - 2\exp[\alpha_{\gamma\delta}(r - R_{\gamma\delta})]\}.$$

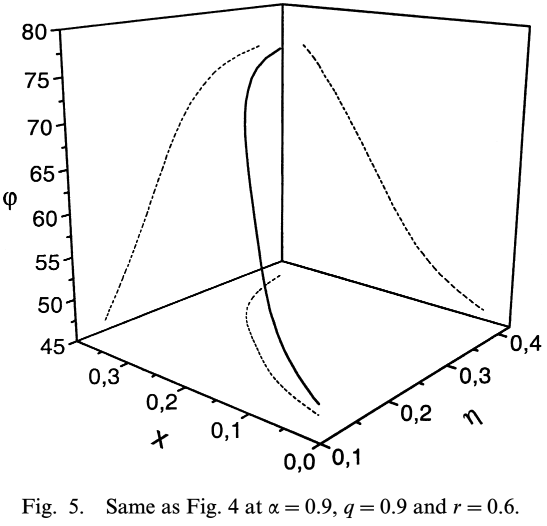

Fig. 5. Same as Fig. 4 at $\alpha = 0.9$, $q = 0.9$ and $r = 0.6$.

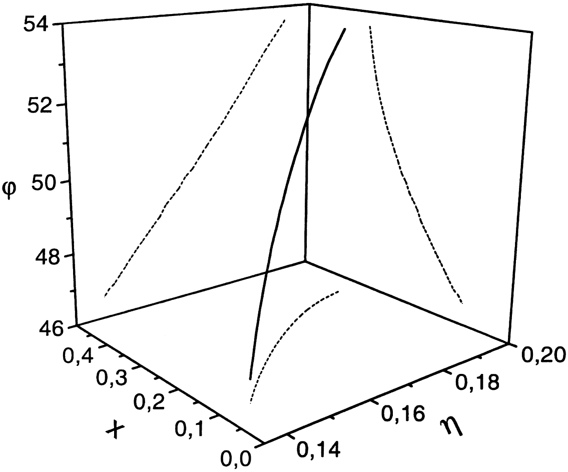

Fig. 6. Same as Fig. 4 at $\alpha = 0.9$, $q = 0.9$ and $r = 0.8$.

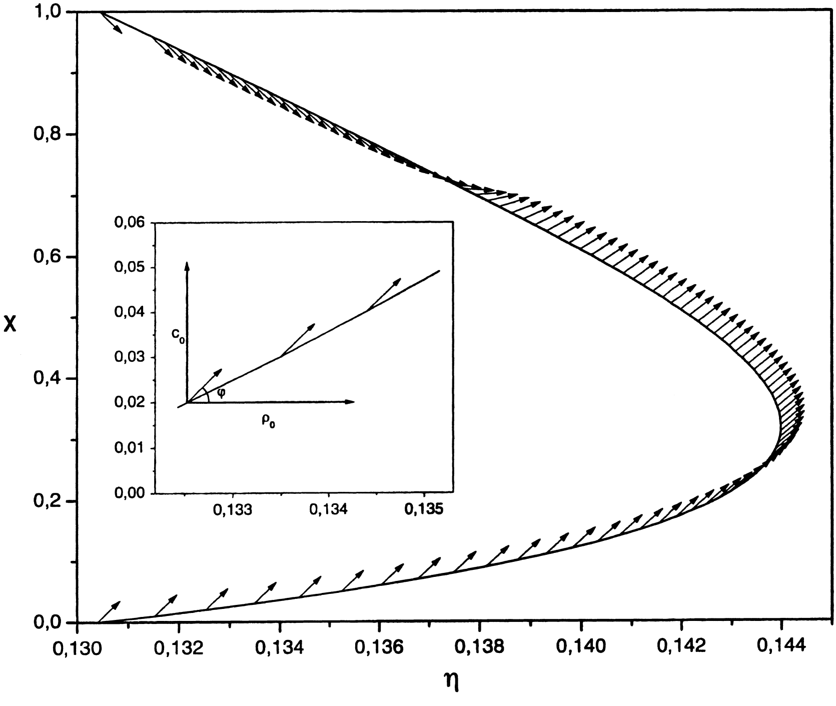

Fig. 7. Behaviour of the order parameter along the liquid–gas critical curve of the argon–krypton mixture (density-concentration projection). x is the concentration of argon.

Parameters of the interaction potentials are taken from ref. 38: $\varepsilon_{\mathrm{ArAr}}/k_B = 118.1$ K, $R_{\mathrm{ArAr}} = 4.13$ Å, $\alpha_{\mathrm{ArAr}} = 1.253$ Å^{-1}, $\varepsilon_{\mathrm{KrKr}}/k_B = 149.0$ K, $R_{\mathrm{KrKr}} = 4.49$ Å, $\alpha_{\mathrm{KrKr}} = 1.05$ Å^{-1}. The "unlike" interaction parameters $\varepsilon_{\mathrm{ArKr}}$, R_{ArKr}, α_{ArKr} and the hard sphere diameters σ_{ArAr}, σ_{KrKr} are chosen as: $\varepsilon_{\mathrm{ArKr}}/k_B = 132.7$ K, $R_{\mathrm{ArKr}} = 4.31$ Å, $\alpha_{\mathrm{ArKr}} = 1.162$ Å^{-1}, $\sigma_{\mathrm{ArAr}} = 3.58$ Å, $\sigma_{\mathrm{KrKr}} = 3.86$ Å. The arrows have the same meaning as above. The direction of the strong fluctuations changes continuously along the critical curve (from $\varphi = 45°$ (at $x = 0$) to $\varphi = -45°$ (at $x = 1.0$) around the axis $\rho_0$in the (ρ_0, c_0) plane). It follows from (2.8) that the equalities $\rho_0 = \pm c_0$ hold at the pure component critical points. The dependence of angle φ on η and x is plotted in Fig. 8. As is seen in Figs. 7 and 8, at the concentration of Ar about 0.7 the fluctuations have a pure density character.

Thus, the proposed approach enables us, on microscopic grounds, to determine the order parameter at each point along a critical curve and thus to understand the character of the phase transition in the binary mixture.

Based on the Gaussian distribution (3.1)–(3.2) we have determined the critical branch and, correspondingly, CV η_0 connected with the order parameter. The purpose of our further study will be calculating the binary mixture behaviour in the vicinity of its critical points.

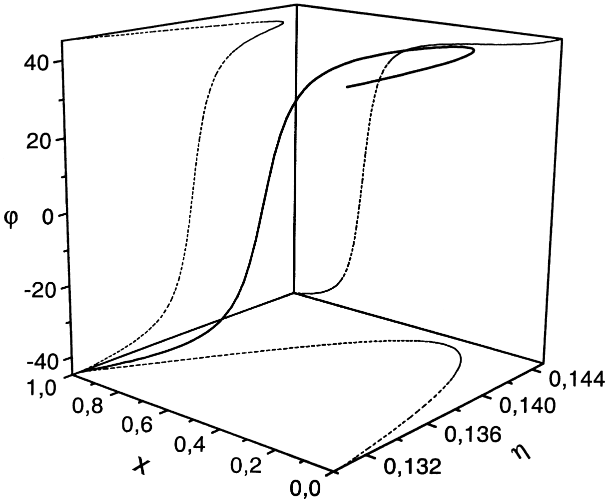

Fig. 8. Same as Fig. 4 but for the argon–krypton mixture.

4. CONCLUSIONS

In this paper we propose a microscopic approach to the study of phase transitions and critical properties of binary fluid mixtures. The relevant problem, namely, the definition of the physical nature of the order parameter in such systems is considered in detail. We show that within the framework of our approach this question had a consistent and clear solution. As a result, we obtain an explicit equation for the determination of the order parameter direction at each point along a critical curve. We also confirm the result obtained in ref. 14 which reveals a connection between the order parameter direction and the thermodynamic characteristics.

Our approach as well as the HRT is based on two notions, namely, the notion of a reference fluid and the basic RG notion of the gradual inclusion of long-wavelength fluctuations. However, its characteristic feature in comparison with HRT, is that it allows one to determine, on the microscopic grounds, the explicit form of an effective GLW Hamiltonian and then to integrate the partition function in the vicinity of the phase transition point taking into account the RG symmetry.(18, 21)

Having solved the problem of the order parameter we can study the second important task, namely, the deriving of the effective GLW Hamiltonian. For this purpose we will follow the procedure:(25) (1) having passed from CV $\rho_{\vec{k}}$ and $c_{\vec{k}}$ to CV $\eta_{\vec{k}}$ and $\xi_{\vec{k}}$ in (2.9)–(2.15), we will integrate over variables $\xi_{\vec{k}}$ with the Gaussian density measure; (2) then we will construct the basic measure (the GLW Hamiltonian) with respect to variables $\eta_{\vec{k}}$ which includes higher powers of $\eta_{\vec{k}}$ than the second power. As a result, we will obtain the GLW Hamiltonian the coefficients of which are the known functions of the microscopic parameters, temperature, concentration and density.

APPENDIX A

Cumulants $M_n^{(i_n)}(0)$ with $n \leqslant 4$ are expressed in terms of the initial cumulants $M_{\gamma_1 \cdots \gamma_n}(0, \ldots, 0)$ $(\gamma_1, \ldots, \gamma_n = a, b)$ as follows:(25)

$$M_1^{(0)}(0) = M_a(0) + M_b(0) = \langle N \rangle$$

$$M_1^{(1)}(0) = M_a(0) - M_b(0) = \langle N_a \rangle - \langle N_b \rangle$$

$$M_2^{(0)}(0) = M_{aa}(0) + M_{bb}(0) + 2M_{ab}(0)$$

$$M_2^{(1)}(0) = M_{aa}(0) - M_{bb}(0)$$

$$M_2^{(2)}(0) = M_{aa}(0) + M_{bb}(0) - 2M_{ab}(0)$$

$$M_3^{(0)}(0) = M_{aaa}(0) + M_{bbb}(0) + 3[M_{aab}(0) + M_{abb}(0)]$$

$$M_3^{(1)}(0) = M_{aaa}(0) - M_{bbb}(0) + M_{aab}(0) - M_{abb}(0)$$

$$
\begin{aligned}
M_3^{(2)}(0) &= M_{aaa}(0)+M_{bbb}(0)-M_{aab}(0)-M_{abb}(0)\\
M_3^{(3)}(0) &= M_{aaa}(0)-M_{bbb}(0)-3[M_{aab}(0)-M_{abb}(0)]\\
M_4^{(0)}(0) &= M_{aaaa}(0)+M_{bbbb}(0)+4[M_{aaab}(0)+M_{abbb}(0)]+6M_{aabb}(0)\\
M_4^{(1)}(0) &= M_{aaaa}(0)-M_{bbbb}(0)+2[M_{aaab}(0)-M_{abbb}(0)]\\
M_4^{(2)}(0) &= M_{aaaa}(0)+M_{bbbb}(0)-2M_{aabb}(0)\\
M_4^{(3)}(0) &= M_{aaaa}(0)-M_{bbbb}(0)-2[M_{aaab}(0)-M_{abbb}(0)]\\
M_4^{(4)}(0) &= M_{aaaa}(0)+M_{bbbb}(0)-4[M_{aaab}(0)+M_{abbb}(0)]+6M_{aabb}(0).
\end{aligned}
$$

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

APPENDIX B

Coefficients $A(k)$, $B(k)$, $C(k)$ and $D(k)$ have the forms:

$$
A(k)=\frac{\alpha_1}{\sqrt{1+\alpha_1^2}}, \qquad B(k)=\frac{\alpha_2}{\sqrt{1+\alpha_2^2}},
$$

$$
C(k)=\frac{1}{\sqrt{1+\alpha_1^2}}, \qquad D(k)=\frac{1}{\sqrt{1+\alpha_2^2}},
$$

where

$$
\alpha_{1,2}=-\frac{A_{22}-A_{11}\mp\sqrt{(A_{11}-A_{22})^2+4A_{12}^2}}{2A_{12}}.
$$

APPENDIX C

The Helmholtz free energy of a binary mixture in the mean field approximation can be written as

$$
f=f_{\mathrm{id}}+f_{\mathrm{ref}}+f_{\mathrm{attr}}, \tag{C.1}
$$

where f_{id} is a free energy of a binary mixture of ideal gases, f_{ref} is a free energy of a binary mixture of hard spheres:(39)

$$\begin{aligned} f_{\mathrm{ref}} &= F_{\mathrm{ref}}/\langle N\rangle\, k_B T \\ &= -1.5(1-y_1+y_2+y_3)+(3y_2+2y_3)(1-\eta)^{-1} \\ &\quad +1.5(1-y_1-y_2-y_3/3)(1-\eta)^{-2}+(y_3-1)\ln(1-\eta), \end{aligned} \tag{C.2}$$

$$y_1 = \Delta_{12}\,\frac{1+\alpha}{\sqrt{\alpha}}, \qquad y_2 = \Delta_{12}\,\frac{\eta_a\alpha+\eta_b}{\sqrt{\alpha}\,\eta},$$

$$y_3 = \frac{1}{\eta^2}\,(\eta_a^{2/3}(1-x)^{1/3}+\eta_b^{2/3}x^{1/3})^3,$$

$$\Delta_{12} = \frac{\sqrt{\eta_a\eta_b}}{\eta}\,\frac{(\alpha-1)^2}{\alpha}\,\sqrt{x(1-x)},$$

$$\eta_a = \frac{(1-x)\,\alpha^3\eta}{x+(1-x)\,\alpha^3}, \qquad \eta_b = \frac{x\eta}{x+(1-x)\,\alpha^3}.$$

$f_{\mathrm{attr}} = F_{\mathrm{attr}}/\langle N\rangle\, k_B T$ is the contribution due to attraction between the particles:

$$f_{\mathrm{attr}} = -\frac{1}{2}\,\frac{\eta}{T^*(x+(1-x)\,\alpha^3)}\,((1-x)^2+2x(1-x)\,r+x^2q). \tag{C.3}$$

Here the following notations are introduced: η is packing density ($\eta = \eta_a+\eta_b$, $\eta_i = \pi\rho_i\sigma_{ii}^3/6$, $\rho_i = \langle N\rangle/V$ is the number density of species i), x is a concentration ($x = \langle N_b\rangle/\langle N\rangle$), $T^* = k_B T\sigma^3\,|\tilde{\phi}_{aa}(0)|^{-1}\,\pi/6$ is dimensionless temperature.

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