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Grand Canonical Distribution for Multicomponent System in the Collective Variables Method

I. R. Yukhnovskii[1] **and O. V. Patsahan**[1]

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The collective variables method with a reference system is developed for the case of the grand canonical ensemble for a multicomponent continuous system. The method is used to investigate phase transitions in a binary system. For a binary symmetrical system the relations between microscopic parameters determining the alternation of gas–liquid and separation phase transitions are found. The functional of the grand partition function of the symmetrical mixture is examined in the framework of parameters containing the separation point. The system is described with two sets of collective variables: $\rho_{\mathbf{k}}$, a set connected with the gas–liquid critical point, and $c_{\mathbf{k}}$, a set connected with the separation phenomenon. The fourfold basic density measure is constructed in $c_{\mathbf{k}}$-variable phase space which contains the variable c_0 connected with the order parameter of the system. It is shown that the problem can be reduced to the 3D Ising model in an external field.

KEY WORDS: Multicomponent system; collective variable; symmetrical system; gas–liquid and separation phase transitions; fourfold basic density measure.

1. INTRODUCTION

In the last few decades much theoretical research has been devoted to the problem of phase transitions, and powerful new methods have been developed.(1–4) However, the problem remains of constructing a theory which allows within a unified approach a complete description of the phase behavior of ulticomponent continuous systems beginning with the Hamiltonian and ending with the thermodynamic functions in the neighborhood of the phase transition point.

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[1] Institute for Condensed Matter Physics, 290011 Lviv, Ukraine. E-mail: oksana@sigma.icmp.Lviv.ua.

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In this paper we propose a new approach to the study of phase instability in multicomponent fluids depending on the microscopic interaction between particles. It enables us to obtain both universal and nonuniversal quantities. This approach is based on the method of collective variables (CV) with a distinguished reference system (RS). Using this method, we study the thermodynamic properties of a binary fluid in the vicinity of the separation critical point. The present paper is devoted to the first part of the investigation, namely, the derivation of the functional of the grand partition function for an m-component continuous system, its investigation in the Gaussian approximation for $m=2$, and the construction of the fourfold basic density measure for a binary symmetrical mixture in the vicinity of a gas–gas separation critical point.

The method of collective variables was developed in ref. 5 and it appears to be useful for the consideration of problems connected with phase transitions. The point is that the statistical description of the phase transition process is to be performed in the appropriate phase space specific for a certain physical model. Among the independent variables of this space there must be the ones connected with order parameters. This phase space forms a set of CV. Each of them is a mode of density fluctuations corresponding to the specifics of the model under consideration. In particular, for a magnetic system the CV are variables connected with spin density fluctuation modes, for a one-component fluid, with particle density fluctuation modes. What is the content of the CV for a multicomponent system? We answer this question below.

The CV method allows us to determine the explicit form of Ginsburg–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.(6)

The use of the CV method for the solution of certain physical tasks in refs. 5 and 6 and other work was limited to the canonical ensemble (CE). But for the description of processes relating to a phase separation in a multicomponent system in which composition fluctuations play the decisive part (for example, the gas–gas or liquid–liquid phase equilibria for the case of the binary system) the grand canonical ensemble (GCE) should be used. On the other hand, the task of the development of the CV method for the case of the GCE raises the problem of selecting the CV phase space which includes the variable connected with the order parameter. Therefore it is necessary to introduce the GCE in the CV method in the case of the gas–liquid critical point.(7)

The layout of this paper is as follows. The main aspects of the CV method with a reference system for a multicomponent system in the GCE are clarified in Section 2. In the process of calculation of the partition function integral it is an important task to find the Jacobian of the transition to CV, which is expressed as the cumulant (semiinvariant) expansion into a series. It is shown that the nth cumulant is expressed in terms of $S_{\gamma_1 \ldots \gamma_n}(k_1, \ldots, k_n)$, the nth structure factor of the RS. For the latter in the limit $k_i = 0$ one can obtain thermodynamic relations. As a result, the exponent of the functional integral of the grand partition function gives the free energy density of the system defined in the CV phase space. This energy has the form of an infinite series in powers of CV. The coefficients of this expansion are known. They are expressed in terms of the Fourier transforms of the initial attractive potentials and thermodynamic functions of the RS. As was already shown,(5) in the vicinity of the critical point a basic density measure exists which includes higher powers of CV, including the fourth. Our aim is to integrate the functional of the partition function of the binary continuous system with a basic fourfold density measure in the neighborhood of the separation critical point. In order to find the form of CV connected with the phase transition and to understand the mechanism of the phenomena which take place in the binary mixture we first consider simpler calculations based on the use of the Gaussian density measure in Section 3. In Section 4 we construct the fourfold density measure with respect to CV, which include a variable corresponding to the order parameter for the separation phase transition. A brief summary and conclusions paper follow in Section 5.

2. THE METHOD

Let us consider a classical multicomponent system of interacting particles consisting of N_{a_1} particles of species a_1, N_{a_2} particles of species $a_2, \ldots,$ and N_{a_m} particles of species a_m. The system is in a volume V at temperature T.

Let us assume that the interaction in the system has pairwise additive character. The interaction potential between a γ particle at $\mathbf{r}_i$ and a δ particle at $\mathbf{r}_j$ 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, which is chosen as the interaction between two hard spheres $\sigma_{\gamma\gamma}$ and $\sigma_{\delta\delta}$:

$$\psi_{\gamma\delta}(r) = \begin{cases} \infty, & r < \sigma_{\gamma\delta} \\ 0, & r \geqslant \sigma_{\gamma\delta} \end{cases} \tag{2.1}$$

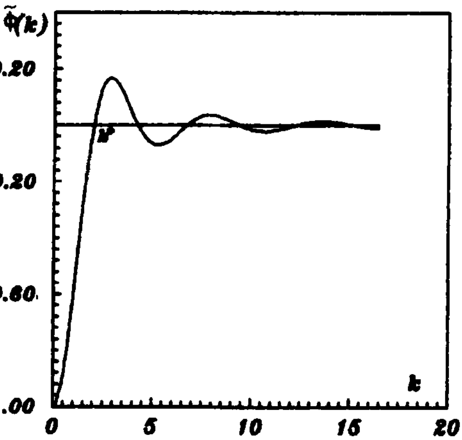

Fig. 1. The Fourier transform $\tilde{\Phi}(k)/|\tilde{\Phi}(0)|$ of the attractive potential $\Phi_{\gamma\delta}(r)$, where $\Phi_{\gamma\delta}(r)=0$ if $r<\sigma_{\gamma\delta}$ and $\Phi_{\gamma\delta}(r)=-\varepsilon_{\gamma\delta}\{\exp[-2(r-R_{\gamma\delta})/\alpha_{\gamma\delta}]-2\exp[-(r-R_{\gamma\delta})/\alpha_{\gamma\delta}]\}$ if $r\geqslant\sigma_{\gamma\delta}$.

$\phi_{\gamma\delta}(r)$ is the potential describing an attraction at long distances. $\phi_{\gamma\delta}(r)$ has the form of a potential well and is negative at large distances r. The behavior of $\phi_{\gamma\delta}(r)$ in the region of the core $r<\sigma_{\gamma\delta}$ must be determined from the conditions of optimal separation of the interaction. The Fourier transform $\tilde{\Phi}_{\gamma\delta}(k)$ is negative for small values of k, $\min\tilde{\Phi}_{\gamma\delta}(k)=\tilde{\Phi}_{\gamma\delta}(k=0)<0$ and $\lim_{k\to\infty}\Phi(k)=0$. For a very broad class of potentials the general form of $\tilde{\Phi}_{\gamma\delta}(k)$ is presented in Fig. 1.

We shall consider the grand partition function of an m-component system

$$\Xi=\sum_{\{N\}\geqslant 0}\prod_{\gamma}\left[\frac{z_{\gamma}^{N_{\gamma}}}{N_{\gamma}!}\right]\int e^{-\beta U_{\{N\}}}\,(d\Gamma),\qquad \gamma=a_1,a_2,\ldots,a_m \tag{2.2}$$

The following notations are introduced here:

$$\sum_{\{N\}\geqslant 0}=\sum_{N_{a_1}\geqslant 0}\cdots\sum_{N_{a_m}\geqslant 0};\qquad (d\Gamma)=\prod_{\gamma}d\Gamma_{N_{\gamma}}$$

$d\Gamma_{N_{\gamma}}$ is an element of configurational space of the γth species: $d\Gamma_{N_{\gamma}}=d\mathbf{r}_1\,d\mathbf{r}_2\cdots d\mathbf{r}_{N_{\gamma}}$; z_{γ} is the activity of the γth species: $z_{\gamma}=\exp(\beta\mu'_{\gamma})$, $\mu'_{\gamma}=\mu_{\gamma}+\beta^{-1}\ln[(2\pi m_{\gamma}\beta^{-1})^{3/2}/h^3]$; β is the reciprocal temperature, $\beta=(kT)^{-1}$; m_{γ} is the mass of the γth species; h is the Planck constant; and

$$U_{\{N\}}=U_{N_{a_1}\cdots N_{a_m}}$$

is the potential energy of an m-component system of N interacting particles with N_1 particles of the a_1th species, N_{a_2} particles of the a_2th species, etc.:

$$U_{\{N\}} = \Psi_{\{N\}} + \Phi_{\{N\}} \tag{2.3a}$$

$$\Psi_{\{N\}} = \frac{1}{2}\sum_{\gamma,\delta} \sum_{ij} \psi_{\gamma\delta}(r_{ij}) \tag{2.3b}$$

$$\Phi_{\{N\}} = \frac{1}{2}\sum_{\gamma,\delta} \sum_{ij} \phi_{\gamma\delta}(r_{ij}) \tag{2.3c}$$

The phase transition is an equilibrium process. Therefore we obtain detailed information by calculating the grand partition function $\Xi(T, V, \mu_{a_1},..., \mu_{a_m})$, (2.2). The chemical potentials are determined from

$$\frac{d \ln \Xi}{d\beta\mu'_\gamma} = \langle N_\gamma \rangle \tag{2.4}$$

where $\langle N_\gamma \rangle$ is the average number of the γ-species, which may be equal to the given number of N_γ particles from the experimental conditions.

We find the equation of state of the system from the relation $PV = kT \ln \Xi$ and from Eq. (2.4). Having solved Eq. (2.4), it is possible to find the free energy of a multicomponent system with the help of the standard expression

$$F = -\beta^{-1} \ln \Xi + \sum_\gamma \mu'_\gamma \langle N_\gamma \rangle$$

The correlation effects of different scales are connected with the potentials $\psi_{\gamma\delta}(r)$ and $\phi_{\gamma\delta}(r)$: the potential $\psi_{\gamma\delta}(r)$ describes the behavior of the particles at very short distances and provides their mutual impenetrability. The potential $\phi_{\gamma\delta}(r)$, on the contrary, describes mainly an attraction between particles which takes place at long distances. These effects are proportional to different parameters. In order to investigate them simultaneously, it is necessary to perform the considerations successively in two phase spaces. First we write the grand partition function and the correlation functions of the RS in the phase space of Cartesian coordinates. A model m-component system of additive hard spheres will be taken as the RS. Here the pair interaction will be described by the potential $\psi_{\gamma\delta}(r)$. Then the grand partition function of the initial system will be constructed in the collective variables space by means of the RS functions. The phase space overflow will be canceled by introduction of the transition Jacobian.

Let us introduce in (1.2) the RS and the grand partition function Ξ_0 corresponding to it:

$$\Xi_0 = \sum_{\{N\} \geqslant 0} \prod_{\gamma} \left[\frac{\exp(\beta \mu_0^{\gamma} N_{\gamma})}{N_{\gamma}!} \right] \int (d\Gamma) \exp(-\beta \psi_{\{N\}}) \tag{2.5}$$

Here $z_{0,\gamma}$ is the activity of the γth species of the RS; for chemical potentials $\mu_{0,\gamma}$ we have the condition

$$\frac{d \ln \Xi_0}{d\beta\mu_0^{\gamma}} = \langle N_{\gamma} \rangle_0 \tag{2.6}$$

where $\langle N_{\gamma} \rangle_0$ are the given values.

Now we rewrite the attractive potential (2.3c) in Fourier space

$$\tilde{\Phi}_{\{N\}} = \frac{1}{2} \sum_{\gamma,\delta} \sum_{\mathbf{k}} \frac{1}{V} \tilde{\Phi}_{\gamma\delta}(\mathbf{k}) [\hat{\rho}_{N_{\gamma}}(\mathbf{k})\, \hat{\rho}_{N_{\delta}}(-\mathbf{k}) - N_{\gamma} \delta_{\gamma\delta}] \tag{2.7}$$

where $\tilde{\Phi}_{\gamma\delta}(\mathbf{k})$ is the Fourier transform of $\phi_{\gamma\delta}(r)$, namely

$$\tilde{\Phi}_{\gamma\delta}(\mathbf{k}) = \int d\mathbf{r}_{\gamma\delta}\, \phi_{\gamma\delta}(r_{\gamma\delta}) \exp(i\mathbf{k}\mathbf{r}_{\gamma\delta}), \qquad \mathbf{r}_{\gamma\delta} = \mathbf{r}_1^{\gamma} - \mathbf{r}_2^{\delta}$$

$\delta_{\gamma\delta}$ is the Kronecker symbol;

$$\hat{\rho}_{N_{\gamma}}(\mathbf{k}) = \sum_{i=1}^{N_{\gamma}} \exp(-i\mathbf{k}\mathbf{r}_i^{\gamma}) \tag{2.8}$$

Let us introduce CV $\rho^{\mathrm{c}}_{\mathbf{k},\gamma}$, $\rho^{\mathrm{s}}_{\mathbf{k},\gamma}$, and $\rho_{o,\gamma}$ by means of the relations

$$\hat{\rho}^{\mathrm{c}}_{N_{\gamma}}(\mathbf{k}) = \int \rho^{\mathrm{c}}_{\mathbf{k},\gamma} \delta(\rho^{\mathrm{c}}_{\mathbf{k},\gamma} - \hat{\rho}^{\mathrm{c}}_{N_{\gamma}}(\mathbf{k}))\, d\rho^{\mathrm{c}}_{\mathbf{k},\gamma} \tag{2.9a}$$

$$\hat{\rho}^{\mathrm{s}}_{N_{\gamma}}(\mathbf{k}) = \int \rho^{\mathrm{s}}_{\mathbf{k},\gamma} \delta(\rho^{\mathrm{s}}_{\mathbf{k},\gamma} - \hat{\rho}^{\mathrm{s}}_{N_{\gamma}}(\mathbf{k}))\, d\rho^{\mathrm{s}}_{\mathbf{k},\gamma} \tag{2.9b}$$

$$N_{\gamma} = \int \rho_o \delta(\rho_o - N_{\gamma})\, d\rho_o \tag{2.9c}$$

where

$$\hat{\rho}^{\mathrm{c}}_{N_{\gamma}}(\mathbf{k}) = \sum_{i=1}^{N_{\gamma}} \cos(\mathbf{k}\mathbf{r}_i^{\gamma}), \qquad \hat{\rho}^{\mathrm{s}}_{N_{\gamma}}(\mathbf{k}) = \sum_{i=1}^{N_{\gamma}} \sin(\mathbf{k}\mathbf{r}_i^{\gamma}) \tag{2.10}$$

$\delta(\cdots)$ is the Dirac delta function.

In contrast to the CE, we have introduced the CV $\rho_{o,\gamma}$, connected with the number of particles of the γth species.

According to (2.10), let us assume also that

$$\rho^{c}_{\mathbf{k},\gamma}=\rho^{c}_{-\mathbf{k},\gamma}, \qquad \rho^{s}_{\mathbf{k},\gamma}=-\rho^{s}_{-\mathbf{k},\gamma}$$

Let us distinguish in (2.2) the grand partition function of the RS Ξ_0 and represent Ξ in the form $\Xi=\Xi_0\Xi_1$. Then, taking into account (2.7)–(2.9), one can write Ξ_1 in the form of the functional integral

$$\Xi_1=\int \exp\left\{\beta\sum_{\gamma}\mu_1^{\gamma}\rho_{o,\gamma}-\tfrac{1}{2}\sum_{\gamma,\delta}\sum_{\mathbf{k}}\alpha_{\gamma\delta}(k)\,\rho_{\mathbf{k},\gamma}\rho_{-\mathbf{k},\delta}\right\}J(\rho)\,(d\rho) \qquad (2.11)$$

The following notations are introduced here: $\alpha_{\gamma\delta}(k)=\beta/V\tilde{\Phi}_{\gamma\delta}(k)$, and $(d\rho)$ is the volume element of the CV phase space

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

The prime means that the product over $\mathbf{k}$ is performed in the upper semispace (it follows from $\rho_{\mathbf{k},\gamma}=\rho^{c}_{\mathbf{k},\gamma}-i\rho^{s}_{\mathbf{k},\gamma}$ and $\rho_{-\mathbf{k},\gamma}=\rho^{c}_{\mathbf{k},\gamma}+i\rho^{s}_{\mathbf{k},\gamma}$ that $\rho^{c}_{\mathbf{k},\gamma}$ and $\rho^{s}_{\mathbf{k},\gamma}$ for positive values of $\mathbf{k}$ are independent variables). μ_1^{γ} is the additional chemical potential of the γth species:

$$\mu_1^{\gamma}=\mu'_{\gamma}-\mu_0^{\gamma}+\tfrac{1}{2}\sum_{\mathbf{k}}\alpha_{\gamma\gamma}(k)$$

As chemical potentials μ_0^{γ} in (1.11) are considered to be known, then the additional chemical potentials μ_1^{γ} are determined from

$$\frac{d\ln\Xi_1}{d\beta\mu_1^{\gamma}}=\langle N_{\gamma}\rangle \qquad (2.12)$$

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

$$\begin{aligned}J(\rho)=\Xi_0^{-1}&\sum_{\{N\}\geqslant 0}\prod_{\gamma}\left[\frac{z_{\gamma,0}^{N_{\gamma}}}{N_{\gamma}!}\right]\int(d\Gamma)\exp(-\beta\Psi_{\{N\}})\\&\times\prod_{\gamma}\delta(\rho_{o,\gamma}-N_{\gamma})\\&\times\prod_{\mathbf{k}}{}'\delta(\rho_{\mathbf{k},\gamma}-\hat{\rho}_{N_{\gamma}}(\mathbf{k}))\end{aligned} \qquad (2.13)$$

The determination of the transition Jacobian $J(\rho)$ is a very important task in the calculation of the functional integral Ξ_1. Here we calculate it for the GCE for the first time.

Substituting into (2.13) the explicit terms for delta functions, we get

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

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

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

$$(d\nu)=\prod_{\gamma}\left(d\nu_{o,\gamma}\prod_{\mathbf{k}\neq 0}{}' d\nu^{\mathrm{c}}_{\mathbf{k},\gamma}\,d\nu^{\mathrm{s}}_{\mathbf{k},\gamma}\right)$$

$J(\nu)$ is the Fourier transform of the transition Jacobian $J(\rho)$, which is analogous to the transition function appearing in the Hubbard–Stratonovich representation$^{(8)}$

$$J(\nu)=\Xi_0^{-1}\sum_{\{N\}\geqslant 0}\prod_{\gamma}\left[\frac{z_{\gamma,0}^{N_\gamma}}{N_\gamma!}\right]\int(d\Gamma)\exp(-\beta\Psi_{\{N\}})$$
$$\times\prod_{\gamma}\exp\left[-i2\pi\sum_{\mathbf{k}}\nu_{\mathbf{k},\gamma}\hat{\rho}_{N_\gamma}(k)\right]\qquad(2.14)$$

Performing in (2.14) integration over the phase space of Cartesian coordinates of the particles and summing over $\{N\}$, we may represent $J(\rho)$ in the form

$$J(\rho)=\int(d\nu)\exp\left[i2\pi\sum_{\gamma}\sum_{\mathbf{k}}\nu_{\mathbf{k},\gamma}\rho_{\mathbf{k},\gamma}+\sum_{n\geqslant 1}D_n(\nu)\right]\qquad(2.15)$$

where

$$D_n(\nu)=\frac{(-i2\pi)^n}{n!}\sum_{\gamma_1,\dots,\gamma_n}\sum_{\mathbf{k}_1,\dots,\mathbf{k}_n}\mathcal{M}_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)$$
$$\times\,\nu_{\mathbf{k}_1,\gamma_1}\nu_{\mathbf{k}_2,\gamma_2}\cdots\nu_{\mathbf{k}_n,\gamma_n};\qquad \gamma_i=a_1,a_2,\dots,a_m\qquad(2.16)$$

Here $\mathcal{M}_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)$ is the nth cumulant, which is determined from the relation

$$\mathcal{M}_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)$$
$$=\left.\frac{d^n\ln J(\nu)}{d\nu_{\mathbf{k}_1,\gamma_1}\,d\nu_{\mathbf{k}_2,\gamma_2}\cdots d\nu_{\mathbf{k}_n,\gamma_n}}\right|_{\nu_{\mathbf{k}_i,\gamma_i}=0}\qquad(2.17)$$

The cumulants $\mathcal{M}_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)$ are expressed as the sum of Fourier transforms of correlation functions $\tilde{h}_{\gamma_1\gamma_2}(\mathbf{k}_1,\mathbf{k}_2)$ and $\tilde{h}_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)$ and with the help of

$$\begin{aligned}\mathcal{M}_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n) &= (\langle N_{\gamma_1}\rangle\cdots\langle N_{\gamma_n}\rangle)^{1/n}\, S_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)\\ &\quad\times\delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n}\end{aligned}$$

are connected with the n-particle partial structure factors $S_{\gamma_1\cdots\gamma_n}(\mathbf{k}_1,\dots,\mathbf{k}_n)$. In particular, in the case of a one-component system of N particles the first four cumulants have the form

$$\begin{aligned}\mathcal{M}_1(\mathbf{k}_1) &= \langle N\rangle\,\delta_{\mathbf{k}_1}\\ \mathcal{M}_2(\mathbf{k}_1,\mathbf{k}_2) &= \delta_{\mathbf{k}_1+\mathbf{k}_2}\langle N\rangle[1+(\langle N\rangle/V)\,\tilde{h}_2(\mathbf{k}_2)]\\ \mathcal{M}_3(\mathbf{k}_1,\dots,\mathbf{k}_3) &= \delta_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3}\langle N\rangle[1+3(\langle N\rangle/V)\,\tilde{h}_2(\mathbf{k}_3)\\ &\quad+(\langle N\rangle^2/V^2)\,\tilde{h}_3(\mathbf{k}_2,\mathbf{k}_3)]\\ \mathcal{M}_4(\mathbf{k}_1,\dots,\mathbf{k}_4) &= \delta_{\mathbf{k}_1+\cdots+\mathbf{k}_4}\langle N\rangle[1+4(\langle N\rangle/V)\,\tilde{h}_2(\mathbf{k}_4)\\ &\quad+3(\langle N\rangle/V)\,\tilde{h}_2(\mathbf{k}_1+\mathbf{k}_2)+6(\langle N\rangle^2/V^2)\,\tilde{h}_3(\mathbf{k}_3,\mathbf{k}_4)\\ &\quad+(\langle N\rangle^3/V^3)\,\tilde{h}_4(\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)]\end{aligned}$$

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 $\mathbf{k}_i\to 0$ in the cumulants is especially important. From (2.17), taking into account (2.8), we obtain for the first four cumulants

$$\begin{aligned}\mathcal{M}_{\gamma_1}(0) &= \langle N_{\gamma_1}\rangle\\ \mathcal{M}_{\gamma_1\gamma_2}(0,0) &= \langle(N_{\gamma_1}-\langle N_{\gamma_1}\rangle)(N_{\gamma_2}-\langle N_{\gamma_2}\rangle)\rangle\\ \mathcal{M}_{\gamma_1\gamma_2\gamma_3}(0,0,0) &= \langle(N_{\gamma_1}-\langle N_{\gamma_1}\rangle)(N_{\gamma_2}-\langle N_{\gamma_2}\rangle)(N_{\gamma_3}-\langle N_{\gamma_3}\rangle)\rangle\\ \mathcal{M}_{\gamma_1\gamma_2\gamma_3\gamma_4}(0,0,0,0) &= \langle(N_{\gamma_1}-\langle N_{\gamma_1}\rangle)(N_{\gamma_2}-\langle N_{\gamma_2}\rangle)(N_{\gamma_3}-\langle N_{\gamma_3}\rangle)\\ &\quad\times(N_{\gamma_4}-\langle N_{\gamma_4}\rangle)-\sum_{i,j,l,p=\left\{\begin{smallmatrix}1,2,3,4\\1,3,2,4\\1,4,2,3\end{smallmatrix}\right\}}\langle(N_{\gamma_i}-\langle N_{\gamma_i}\rangle)\\ &\quad\times(N_{\gamma_j}-\langle N_{\gamma_j}\rangle)\rangle\langle(N_{\gamma_l}-\langle N_{\gamma_l}\rangle)(N_{\gamma_p}-\langle N_{\gamma_p}\rangle)\rangle\end{aligned}\tag{2.18}$$

Formulas (2.18) are useful from the point of view of possible numerical experiments. However, there also exists another way of calculating $\mathcal{M}_{\gamma_1\cdots\gamma_n}(0,\dots,0)$.

It follows from (2.13) and (2.17) that the Nth cumulant at $\mathbf{k}=0$ can be found from

$$\mathcal{M}_{\gamma_1 \cdots \gamma_n}(0,\dots,0)=\left.\frac{d^n \ln J(\nu)}{d\nu_{0,\gamma_1}\, d\nu_{0,\gamma_2} \cdots d\nu_{0,\gamma_n}}\right|_{\nu_{\mathbf{k}_i,\gamma_i}=0}$$

$$=\left[\frac{d^{n-1}\langle N_{\gamma_1}\rangle}{d\beta\mu_0^{\gamma_2}\, d\beta\mu_0^{\gamma_3} \cdots d\beta\mu_0^{\gamma_n}}\right]_{V,T,\mu_0^{\gamma'_n}}$$

Then the second cumulant has the form

$$\mathcal{M}_{\gamma_1\gamma_2}(0,0)=\left[\frac{d\langle N_{\gamma_1}\rangle}{d\beta\mu_0^{\gamma_2}}\right]_{V,T,\mu_0^{\gamma_k}} \tag{2.19}$$

Using the algebra of matrices, for $\mathcal{M}_{\gamma_1\gamma_2}(0,0)$ we obtain

$$\mathcal{M}_{\gamma_1\gamma_2}(0,0)=\beta^{-1}B_{\gamma_1\gamma_2}/\det B$$

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

$$b_{\gamma_1\gamma_2}=(d\mu_0^{\gamma_1}/d\langle N_{\gamma_2}\rangle)_{V,T,N_{\gamma_k}}$$

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

$$\mathcal{M}_{\gamma_1 \cdots \gamma_n}(0,\dots,0)=\left[\frac{d\mathcal{M}_{\gamma_1 \cdots \gamma_{n-1}}(0,\dots,0)}{d\beta\mu_0^{\gamma_n}}\right]_{V,T,\{\mu_0^{\gamma'_n}\}} \tag{2.20}$$

The relations (2.19)–(2.20) allow us to express cumulants at $\mathbf{k}_1=\mathbf{k}_2=\cdots=\mathbf{k}_n=0$ through the thermodynamic functions of the RS.

Let us consider now the determination of cumulants $\mathcal{M}_{\gamma_1 \cdots \gamma_n}$ in formulas (2.11) and (2.14)–(2.15). In general the cumulants $\mathcal{M}_{\gamma_1 \cdots \gamma_n}$ depend in a complicated way on $\mathbf{k}_i$. The essential contribution to the partition function comes from cumulants with wave vectors $\mathbf{k}_i$ corresponding to the attraction range of the potential $\Phi_{\gamma\delta}(r)$. For one-component system this is the range $|\mathbf{k}^*| \in [0, k]$, where for all $|\mathbf{k}_i| > \mathbf{k}^*$ the inequality $1/\mathcal{M}_2(k) > |\tilde{\Phi}(k)|$ holds $[\mathcal{M}_2(k)=NS(k)$, where $S(k)$ is the structure factor, $\tilde{\Phi}(k)$ is the Fourier transform of the attractive potential]; for an m-component system the range $[0, k^*]$ is determined separately for each particular m from the condition of negativity of the coefficient at a second power of CV (connected with an order parameter) in the functional Hamiltonian. As was already shown(9) for a one-component system in the range $k \in [0, k^*]$ the dependence of cumulants on k_i is very weak and it can be approximated by a parabola. The same conclusion follows from results obtained by Ashcroft and Langreth$^{(10)}$ for two-particle structure factors of the binary additive hard-sphere system. Hence in zeroth approximation constant values $\mathcal{M}_{\gamma_1 \cdots \gamma_n}(0,..., 0)$ can be substituted for $\mathcal{M}_{\gamma_1 \cdots \gamma_n}(\mathbf{k}_1,..., \mathbf{k}_n)$ and in the first approximation the dependence on $\mathbf{k}$ of cumulants on the binary correlation functions $\tilde{h}_{\gamma_1\gamma_2}(\mathbf{k}_1, \mathbf{k}_2)$ can be taken into account. As a result the functional of the grand partition function can be written as

$$\begin{aligned}\Xi = \Xi_0 \int (d\rho)\,(d\nu) \exp \Bigg\{ & \beta \sum_{\gamma} \mu_1^{\gamma} \rho_{0,\gamma} - \frac{1}{2} \sum_{\gamma_1,\gamma_2}\sum \sum_{\mathbf{k}} \alpha_{\gamma_1\gamma_2}(k) \\ & \times \rho_{\mathbf{k},\gamma_1} \rho_{-\mathbf{k},\gamma_2} + i2\pi \sum_{\gamma} \sum_{\mathbf{k}} \nu_{\mathbf{k},\gamma} \rho_{\mathbf{k},\gamma} \\ & + \sum_{n \geqslant 1} \frac{(-i2\pi)^n}{n!} \sum_{\gamma_1 \cdots \gamma_n} \sum_{\mathbf{k}_1 \cdots \mathbf{k}_n} [\mathcal{M}_{\gamma_1 \cdots \gamma_n}(0,..., 0) \\ & + O(k^2)]\, \nu_{\mathbf{k}_1,\gamma_1} \cdots \nu_{\mathbf{k}_n,\gamma_n} \delta_{\mathbf{k}_1 + \cdots + \mathbf{k}_n} \Bigg\} \end{aligned} \tag{2.21}$$

where in the exponent the coefficients of the $\nu_{\mathbf{k},\gamma}$ and $\rho_{\mathbf{k},\gamma}$ variables are known.

We propose the following program of investigation: (1) to separate under the integral in (2.21) the phase space of CV $\rho^*_{\mathbf{k},\gamma}$ (and correspondingly $\nu^*_{\mathbf{k},\gamma}$), which includes the order parameter; (2) to integrate over CV $\rho_{\mathbf{k},\gamma}$ (and $\nu_{\mathbf{k},\gamma}$) which remain, using the Gaussian density measure as the basic one; (3) as a result of the integration performed in 2, to obtain the fourfold density measure with respect to the variables $\rho^*_{\mathbf{k},\gamma}$ and $\nu^*_{\mathbf{k},\gamma}$. Having performed this program, the problem of the phase transition in a multicomponent system can lead to an Ising-like problem for which a method of solution was proposed in ref. 6.

3. PHASE TRANSITIONS IN BINARY SYSTEMS. THE PHASE SPACE CHOICE

Let us consider a two-component continuous system of particles among which there exist N_a particles of species a and N_b particles of species b. A gas–liquid phase transition and a separation phase transition in both gas and liquid phases can occur in such a system. In order to understand the mechanism of realization of these phase instabilities in the binary fluid we shall perform first the simpler calculations based on the Gaussian density measure. This truncation generates the well-known random-phase-approximation (RPA) contribution to the free energy. We let $n = 2$ and

$\gamma_1, \gamma_2, \ldots, \gamma_n = a, b$ in formulas (2.5), (2.11), and (2.15)–(2.16). As a result of the integration in (2.15) over variables $\nu_{\mathbf{k},a}$ and $\nu_{\mathbf{k},b}$, Ξ_1 may be written as

$$\Xi_1 = \Xi_1^{\mathrm{G}} = \tfrac{1}{2} \prod_{\mathbf{k}} [\pi \det \mathcal{M}(k)]^{-1/2} \int (d\rho) \exp\Bigg[-H(0) + \sum_{\gamma=a,b} M_\gamma \rho_{0,\gamma} - \tfrac{1}{2} \sum_{\mathbf{k}} \sum_{\gamma,\delta} a_{\gamma,\delta}(k)\, \rho_{\mathbf{k},\gamma} \rho_{-\mathbf{k},\delta} \Bigg] \tag{3.1}$$

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

$$\begin{aligned} \mathcal{M}_{\gamma\delta}(k) &= \langle N_\gamma \rangle [\delta_{\gamma\delta} + \langle N_\delta \rangle / V\tilde{h}_{\gamma\delta}(k)] \\ &= (\langle N_\gamma \rangle \langle N_\delta \rangle)^{1/2}\, S_{\gamma\delta}(k) \end{aligned} \tag{3.2}$$

$$H(0) = \tfrac{1}{2} \sum_{\gamma,\delta} \langle N_\gamma \rangle \langle N_\delta \rangle [\mathcal{M}^{-1}(0)]_{\gamma\delta} \tag{3.3}$$

$$M_\gamma = \beta\mu_1^\gamma + \sum_{\delta=a,b} \langle N_\delta \rangle [\mathcal{M}^{-1}(0)]_{\gamma\delta} \tag{3.4}$$

$$a_{\gamma\delta} = \alpha_{\gamma\delta}(k) + [\mathcal{M}^{-1}(k)]_{\gamma\delta} \tag{3.5}$$

$[\mathcal{M}^{-1}(k)]_{\gamma\delta}$ is an element of an inverse matrix.

As proposed in ref. 11, we separate the CV phase space which includes the variable connected with the order parameter by diagonalizing the square form under the integral in (3.1). As a result of the orthogonal transformation

$$\rho_{\mathbf{k},\gamma} = \sum_{i=1,2} \Delta_{\gamma i} \xi_{\mathbf{k},i}, \qquad \gamma = a, b \tag{3.6}$$

for the square form we have

$$-\tfrac{1}{2} \sum_{i,\mathbf{k}} \varepsilon_i(k)\, \xi_{\mathbf{k},i} \xi_{-\mathbf{k},i} \tag{3.7}$$

where

$$\varepsilon_{1,2} = \tfrac{1}{2} \{ a_{aa} + a_{bb} \pm [(a_{aa} - a_{bb})^2 + 4a_{ab}^2)]^{1/2} \} \tag{3.8}$$

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

In the case of a binary mixture of particles of different sizes $(\alpha = \sigma_{aa}/\sigma_{bb} \neq 1)$ interacting through different attractive potentials $[\phi_{aa}(r) \neq \phi_{bb}(r) \neq \phi_{ab}(r)]$ the dependences of values $\Delta_{\gamma i}(k)$, $\varepsilon_1(k)$, and $\varepsilon_2(k)$

on RS characteristics and on the Fourier transforms $\tilde{\Phi}_{ij}(k)$ are complicated. Therefore to study the possibility of the realization of gas–liquid and separation phase transitions and their order of priority we shall consider the simplest case, namely a symmetrical mixture. A symmetrical mixture is a model system of equal-size particles ($\alpha = 1$) interacting via the same attractive potentials between "like" particles $[\phi_{aa}(r) = \phi_{bb}(r) = \phi(r)]$ and via different attractive potentials between "unlike" particles $[\phi(r) \neq \phi_{ab}(r)]$. Although the symmetrical mixture represents a simple model of a real binary fluid, it exhibits all three types of two-phase equilibrium which are observed in such a system. The critical curves of this mixture are symmetrical with respect to the concentration $x = 1/2$ and exhibit an extreme at this point. The concentration $x = 1/2$ is a critical one for the symmetrical mixture. At $x_0 = 1/2$, $\alpha = 1$, $\tilde{\Phi}_{aa} = \tilde{\Phi}_{bb} = \tilde{\Phi}$; from the equations $\varepsilon_1(0) = 0$ and $\varepsilon_2(0) = 0$ we get the critical temperatures in the RPA (or mean-field approximation):

$$\theta = \theta_1^c(x_c) = \begin{cases} \theta_c^{\text{sep}}, & \mathscr{L}(0) < 0 \\ \theta_c^{g\text{-}l}, & \mathscr{L}(0) > 0 \end{cases} \tag{3.9a}$$

$$\theta = \theta_1^c(x_c) = \begin{cases} \theta_c^{g\text{-}l}, & \mathscr{L}(0) < 0 \\ \theta_c^{\text{sep}}, & \mathscr{L}(0) > 0 \end{cases} \tag{3.9b}$$

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

where

$$\theta_c^{g\text{-}l} = -(\rho/2)[\tilde{\Phi}(0) + \tilde{\Phi}_{ab}(0)]\, S_+(0) \tag{3.10a}$$

$$\theta_c^{\text{sep}} = -(\rho/2)[\tilde{\Phi}(0) - \tilde{\Phi}_{ab}(0)]\, S_-(0) \tag{3.10b}$$

$$\mathscr{L}(0) = \tilde{\Phi}_{ab}(0)\, S(0) + \tilde{\Phi}(0)\, S_{ab}(0) \tag{3.11}$$

Here ρ is the density of the full system, and $S_+(0)$ and $S_-(0)$ are the density–density and concentration–concentration structure factors, respectively, of an equal-diameter hard-sphere mixture at $k = 0$. At $x = 1/2$, $S_+(0)$ and $S_-(0)$ have the form

$$S_+(0) = S(0) + S_{ab}(0)$$

$$S_-(0) = S(0) - S_{ab}(0) = 1$$

where $S(0) = S_{aa}(0) = S_{bb}(0)$; $S_+(0)$ is the structure factor of the one-component RS.

Coefficients (3.6) are reduced and the CV $\xi_{\mathbf{k},i}$ become equal to

$$\xi_{\mathbf{k},1} = \begin{cases} c_{\mathbf{k}}, & a_{12}(k) > 0 \\ \rho_{\mathbf{k}}, & a_{12}(k) < 0 \end{cases}, \qquad \xi_{\mathbf{k},2} = \begin{cases} \rho_{\mathbf{k}}, & a_{12}(k) > 0 \\ c_{\mathbf{k}}, & a_{12}(k) < 0 \end{cases} \tag{3.12}$$

where

$$\rho_{\mathbf{k}} = (1/\sqrt{2})(\rho_{\mathbf{k},a} + \rho_{\mathbf{k},b}), \qquad c_{\mathbf{k}} = (1/\sqrt{2})(\rho_{\mathbf{k},a} - \rho_{\mathbf{k},b})$$
$$a_{12}(k) = \alpha_{ab}(k) - 2S_{ab}(k)/(NS_{+}(k)) \tag{3.13}$$

The new variables $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ are connected with total density fluctuation modes and relative density (or concentration) fluctuation modes in the binary system. The diagonal square form (3.7)–(3.8) transforms as [independent of the sign of $a_{12}(k)$]

$$-\tfrac{1}{2}\sum_{\mathbf{k}} \{[(\alpha(k) - \alpha_{ab}(k) + 1/N]\, c_{\mathbf{k}} c_{-\mathbf{k}}$$
$$+ [(\alpha(k) + \alpha_{ab}(k) + 1/NS_{+}(0)]\, \rho_{\mathbf{k}} \rho_{-\mathbf{k}}\}$$

It follows from (3.9)–(3.13) in the case of a symmetrical mixture that there exist two critical branches $\varepsilon_1(0)$ and $\varepsilon_2(0)$ and accordingly two subspaces of CV $c_{\mathbf{k}}$ and $\rho_{\mathbf{k}}$ which include variables c_o and ρ_o connected with the order parameters.

Let us consider the critical temperatures. Expressions (3.9)–(3.10) contain the quantities $\tilde{\Phi} - \tilde{\Phi}_{ab}$ 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 case (a) the attractive energy between "like" particles is stronger than that between "unlike" particles. Separation of components can occur in the system. In case (b) the attractive interaction between "unlike" particles is stronger than that between "like" particles and this is a condition of the existence of the mixture. In Fig. 2 critical temperatures $\tilde{\theta}_1^c(\eta)$ (curve 1) and $\tilde{\theta}_2^c(\eta)$ (curve 2) are plotted vs. packing fraction η at $r = 0.5$. Here $\tilde{\theta}_i^c(\eta) = \theta_i^c \eta/\rho\, |\tilde{\Phi}(0)|$ is the dimensionless temperature, $\eta = \pi/6\rho\sigma^3$, $\rho = N/V$, $N = N_a + N_b$, and 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. 2 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 $\eta^* = \eta_{\text{cross}}(r)$. The different slopes of the 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 formulas (3.9) that for $\eta < \eta^*$ the curve $\theta = \tilde{\theta}_1^c(\eta)$ is the line of the liquid–liquid phase equilibrium and for $\eta > \eta^*$ 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 $\eta < \eta^*$ and is the gas–gas phase equilibrium line for $\eta > \eta^*$. The curves $\tilde{\theta}_1^c(\eta)$ and $\tilde{\theta}_2^c(\eta)$ have one common point, for which the gas–liquid and the separation critical points coincide.

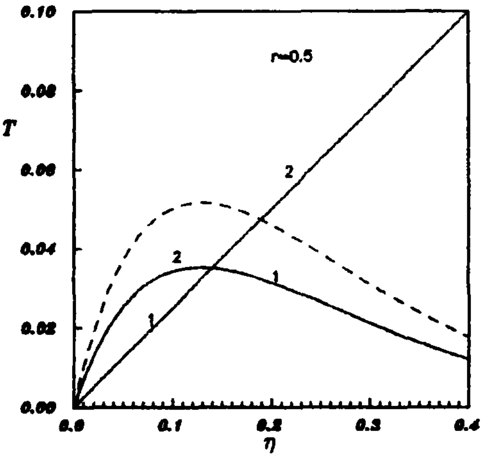

Fig. 2. Dependence of critical temperatures of the symmetrical mixture on the packing fraction; $r = 0.5$ (solid curves) and $r = 1.2$ (dashed curve).

The density η^* corresponding to this point is determined from the condition

$$\tilde{\theta}^c_1(\eta^*) = \tilde{\theta}^c_2(\eta^*) \tag{3.14}$$

or from the equation $\mathscr{L}(0) = 0$.

Now let us consider in Fig. 2 the line formed from the branch $\tilde{\theta}^c_2(\eta)$ for $\eta < \eta^*$ and from the branch $\tilde{\theta}^c_1(\eta)$ for $\eta > \eta^*$ and compare it with the dashed curve. These curves have the same form. The two remaining parts of $\tilde{\theta}^c_1(\eta)$ and $\tilde{\theta}^c_2(\eta)$ form a straight line. Hence for the symmetrical mixture one can separate exactly the gas–liquid and the separation (demixing) critical temperature lines. The existence of the point η^* for which (3.14) holds is connected with the simplicity of the model under consideration. On the other hand, the existence of a point on the critical curve at which the gas–liquid and the gas–gas separation critical temperatures coincide was confirmed experimentally. It is the so-called critical double point.(12)

The phase diagram of the symmetrical mixture is shown on Fig. 3. Depending on the relationships between microscopic values $\tilde{\Phi}(0)$, $\tilde{\Phi}_{ab}(0)$, and $S_+(0)$, three possible phase ranges can exist: (1) gas–gas separation and gas–liquid phase transitions; (2) gas–liquid and liquid–liquid phase transitions; (3) only gas–liquid phase transition.

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 (3.1) two CV subspaces were separated: the first with the order parameter

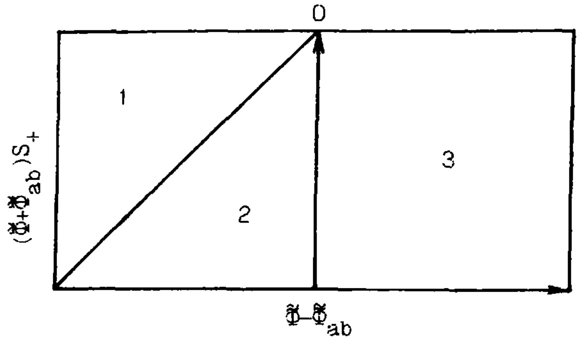

Fig. 3. Three phase regions of the symmetrical mixture depending on the microscopic parameters: (1) gas–gas and gas–liquid phase transitions; (2) gas–liquid and liquid–liquid phase transitions; (3) gas–liquid phase transition.

and with the critical temperature $\theta_c^{g\text{-}l}$, and the second with the other order parameter and with the critical temperature θ_c^{sep}; (2) since the CV describing phase transitions are the variables $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$, the variable ρ_0 describes the long-wavelength fluctuation mode of the total particle number $N=N_a+N_b$ (or total density) and connects with the order parameter whose nonzero value arises below the gas–liquid critical point, and 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 order of priority of the gas–liquid and the separation phase transitions depends on the microscopic properties of the system.

The purpose of our further study is the calculation of thermodynamic functions in the vicinity of the gas–gas separation phase transition point. We shall follow the program drawn in Section 2, namely: (1) having converted from CV $\rho_{\mathbf{k},a}$ and $\rho_{\mathbf{k},b}$ to CV $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ in (2.21), we shall integrate over variables $\rho_{\mathbf{k}}$ with the Gaussian density measure; (2) then we shall construct the fourfold basic density measure with respect to variables $c_{\mathbf{k}}$; (3) using a method proposed in ref. 6, we shall integrate the partition function in the vicinity of the gas–gas phase transition point (at $T \geqslant T_c$ and $T \leqslant T_c$). We perform the first two steps of this program in the next section.

4. BASIC DENSITY MEASURE IN THE VICINITY OF GAS–GAS SEPARATION CRITICAL POINT

We let $\gamma_1, \gamma_2, ..., \gamma_n = a, b$ in (2.21) and pass to CV $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ by means of formulas (3.11)–(3.12). Then we obtain

$$\Xi = \Xi_0 \int (d\rho)\,(dc) \exp\Big\{ \beta\mu_1^{+}\rho_0 + \beta\mu_1^{-} c_0 - (\beta/2) \sum_{\mathbf{k}} [\, \tilde{\mathscr{V}}(k)\, \rho_{\mathbf{k}}\rho_{-\mathbf{k}} + 2\tilde{\mathscr{U}}(k) \times \rho_{\mathbf{k}} c_{-\mathbf{k}} + \tilde{\mathscr{W}}(k)\, c_{\mathbf{k}} c_{-\mathbf{k}}] \Big\}\, J(\rho, c) \tag{4.1}$$

where the following notations are introduced:

$$\mu_1^{+} = 2^{-1/2}(\mu_1^{a} + \mu_1^{b}); \qquad \mu_1^{-} = 2^{-1/2}(\mu_1^{a} - \mu_1^{b}) \tag{4.2}$$

$$\begin{aligned} \tilde{\mathscr{V}}(k) &= (\beta^{-1}/2)[\alpha_{aa}(k) + \alpha_{bb}(k) + 2\alpha_{ab}(k)] \\ \tilde{\mathscr{U}}(k) &= (\beta^{-1}/2)[\alpha_{aa}(k) - \alpha_{bb}(k)] \\ \tilde{\mathscr{W}}(k) &= (\beta^{-1}/2)[\alpha_{aa}(k) + \alpha_{bb}(k) - 2\alpha_{ab}(k)] \end{aligned} \tag{4.3}$$

$$J(\rho, c) = \int (d\gamma)\,(d\omega) \Big\{ i2\pi \sum_{\mathbf{k}} (\omega_{\mathbf{k}}\rho_{\mathbf{k}} + \gamma_{\mathbf{k}} c_{\mathbf{k}}) + \sum_{n \geqslant 1} \sum_{i \geqslant 0} D_n^{(i_n)}(\gamma, \omega) \Big\} \tag{4.4}$$

$$\omega_{\mathbf{k}} = 2^{-1/2}(\nu_{\mathbf{k},a} + \nu_{\mathbf{k},b}), \qquad \gamma_{\mathbf{k}} = 2^{-1/2}(\nu_{\mathbf{k},a} - \nu_{\mathbf{k},b})$$

$$D_n^{(i_n)}(\gamma, \omega) = [(-i2\pi)^n/n!](2^{1/2}/2)^n \sum_{\mathbf{k}_1 \cdots \mathbf{k}_n} \mathscr{M}_n^{(i_n)}(0,\dots,0) \times \delta_{\mathbf{k}_1 + \cdots + \mathbf{k}_n} \gamma_{\mathbf{k}_1} \cdots \gamma_{\mathbf{k}_{i_n}} \omega_{\mathbf{k}_{i_n+1}} \cdots \omega_{\mathbf{k}_n} \tag{4.5}$$

The index i_n is used to indicate the number of variables $\gamma_{\mathbf{k}}$ in the cumulant expression (4.5). Cumulants $\mathscr{M}_n^{(i_n)}$ are expressed as linear combinations of initial cumulants $\mathscr{M}_{\gamma_1 \cdots \gamma_n}$ and for $\gamma_1, \dots, \gamma_n = a, b$ and $n \leqslant 4$ are represented in Appendix B.

Equations (1.12) can be rewritten in the form

$$d \ln \Xi_1 / d\beta\mu_1^{+} = \langle N_a \rangle + \langle N_b \rangle = \langle N \rangle \tag{4.6a}$$

$$d \ln \Xi_1 / d\beta\mu_1^{-} = \langle N_a \rangle - \langle N_b \rangle \tag{4.6b}$$

In the case of the binary symmetrical mixture

$$\tilde{\mathscr{U}}(k) = 0 \tag{4.7a}$$

$$\mathscr{M}_{aa}(k) = \mathscr{M}_{bb}(k) \tag{4.7b}$$

and the square form under the integral (4.1) is diagonal. In this case the index i_n takes only even values (see Appendix B). The nth cumulant $\mathscr{M}_n^{(i_n)}$ with $i_n = 0$ is connected with the nth structure factor of the one-component hard-sphere system: $\mathcal{M}_n^{(0)} = \langle N \rangle S_n$. Cumulants with $i_n \neq 0$ can be expressed in terms of $\mathcal{M}_n^{(0)}$ as follows:

$$\begin{aligned} \mathcal{M}_n^{(2)} &= [n!/2!\,(n-2)!]\,\mathcal{M}_{n-1}^{(0)} \\ \mathcal{M}_n^{(4)} &= [n!/4!\,(n-4)!](3\mathcal{M}_{n-2}^{(0)} - 2\mathcal{M}_{n-3}^{(0)}) \\ \mathcal{M}_n^{(6)} &= [n!/6!\,(n-6)!](15\mathcal{M}_{n-3}^{(0)} - 30\mathcal{M}_{n-4}^{(0)} + 16\mathcal{M}_{n-5}^{(0)}) \end{aligned} \tag{4.8}$$

For simplicity of calculation and without loss of completeness let us further assume that $\tilde{\Phi}_{\gamma\delta}(k) = 0$ at $|\mathbf{k}| > k^*$ (see Fig. 1). Then integrating in (4.1) over $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ with $|\mathbf{k}| > k^*$ leads to δ-functions. As a result for the transition Jacobian we obtain an expression which has only one difference in comparison with the old one, namely, all the sums over $\mathbf{k}$ are carried out in a sphere of radius $\mathbf{k}^*$. The quantity $\mathbf{k}^*$ determines the sizes of the Brillouin half-zones of a crystal lattice corresponding to the given system. Here a new periodic function should be introduced in place of $\tilde{\Phi}_{\gamma\delta}(k)$:

$$\tilde{\Phi}_{\gamma\delta}(k) = \sum_n \tilde{\Phi}'_{\gamma\delta}(\mathbf{k} + 2\mathbf{k}^*\mathbf{n})$$

We multiply both sides of this equality by $\exp(i\mathbf{kr})$ and sum over all $\mathbf{k}$ with $\mathbf{k} < \mathbf{k}^*$:

$$\begin{aligned} &(1/V) \sum_{\mathbf{k} < \mathbf{k}^*} \tilde{\Phi}_{\gamma\delta}(k) \exp(i\mathbf{kr}) \\ &\quad = \sum_{\mathbf{k} < \mathbf{k}^*} \sum_n (1/V)\, \tilde{\Phi}'_{\gamma\delta}(\mathbf{k} + 2\mathbf{k}^*\mathbf{n}) \exp(i\mathbf{kr}) \end{aligned}$$

Let it be required that the right-hand side is a complete Fourier transform, which is possible when $2\mathbf{nrk}^*$ is a multiple of 2π. Thus, $\mathbf{r} = \mathbf{m}c$, where $\mathbf{m} = m_x\mathbf{i} + m_y\mathbf{j} + m_z\mathbf{k}$; m_x, m_y, m_z are integers, $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are unit basic vectors, and c is the size of the period of the simple cubic lattice. The number N^* of collective variables is determined by

$$N^* = V/c^3 = V(k^*/\pi)^3 = \langle N \rangle (k^*)^3\, \sigma^3/6\pi^2\eta$$

In general, the quantity k^* depends both on the form of the attractive potential $\phi_{\gamma\delta}(r)$ and the diameter σ as well as on the average density and the temperature of the system. In the case when $\phi_{\gamma\delta}(r)$ is the Morse potential

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

we have that

$$k^* = \alpha_{\gamma\delta}^{-1}[4 - \exp(R_{\gamma\delta}/\alpha_{\gamma\delta})]^{1/2}\,[\exp(R_{\gamma\delta}/\alpha_{\gamma\delta}) - 1]^{-1/2}$$

Here $\exp(R_{\gamma\delta}/\alpha_{\gamma\delta}) < 4$.

After the integration over $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ with $|\mathbf{k}| > \mathbf{k}^*$ their number reduces to N^*. As a result, the partition function (4.1) can be rewritten as

$$\Xi = \Xi_0 \int (d\rho)^{N^*} (dc)^{N^*} \exp\Bigg\{\beta\mu_1^+ \rho_0 + \beta\mu_1^- c_0 - (\beta/2) \sum_{\mathbf{k}<\mathbf{k}^*} [\tilde{\mathscr{V}}(k)\,\rho_{\mathbf{k}}\rho_{-\mathbf{k}} + \tilde{\mathscr{W}}(k)\,c_{\mathbf{k}}c_{-\mathbf{k}}]\Bigg\} J(\rho, c) \qquad (4.9)$$

In (4.9) the new cumulants $\mathscr{M}_n^{(i_n)'}$ differ from the previous ones by multipliers

$$\mathscr{M}_n^{(i_n)'} = \mathscr{M}_n^{(i_n)} \langle N^* \rangle / \langle N \rangle$$

We shall calculate the partition function (4.9) in the vicinity of the gas–gas separation phase transition point. According to results of the previous section, the inequality $\theta_c^{\text{sep}} \gg \theta_c^{g\text{-}l}$ holds. It follows from (3.9)–(3.10) that we have the following relations between microscopic parameters of the binary system in this case:

$$\tilde{\mathscr{W}}(k) < 0, \qquad |\tilde{\mathscr{W}}(k)| > |\mathscr{M}_2^{(0)} \tilde{\mathscr{V}}(k)| \qquad (4.10)$$

The region 1 in Fig. 3 corresponds to these conditions. The CV $\rho_{\mathbf{k}}$ do not include the variable connected with the order parameter for the separation phase transition. Thus we integrate over $\rho_{\mathbf{k}}$ with the Gaussian density measure. Let us eliminate the linear term in the exponent in (4.4) by a shift $\rho'_{\mathbf{k}} = \rho_{\mathbf{k}} - \langle N \rangle\, \delta_{\mathbf{k}} 2^{1/2}/2$ and present $D_n^{(i_n)}$ in (4.4) as a sum of two terms

$$D_n^{(i_n)} = D_n^{(i_n)'} + D_n^{(i_n)''}$$

where

$$D_n^{(i_n)'} = D_n^{(0)}(\omega) + D_n^{(i_n)}(\omega, \gamma), \qquad D_n^{(i_n)''} = D_n^{(i_n)}(\gamma)$$

Here $D_n^{(0)}(\omega)$ includes only products of variables $\omega_{\mathbf{k}}$, $D_n^{(i_n)}(\omega, \gamma)$ includes mixed products of both variables $\omega_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$, and $D_n^{(i_n)}(\gamma)$ includes only products of variables $\gamma_{\mathbf{k}}$. Let us consider the integral

$$
\begin{aligned}
I = \int (d\rho)\,(d\omega) \exp[\beta\bar{\mu}_1^+ \langle N^* \rangle - \beta(\langle N^* \rangle^2/4)\, \tilde{\mathscr{V}}(0)] \\
\times \exp\left\{ -\frac{\beta}{2} \sum_{\mathbf{k} \leqslant \mathbf{k}^*} \tilde{\mathscr{V}}(k)\, \rho_{\mathbf{k}} \rho_{-\mathbf{k}} + R(0) + (-i2\pi)^2/2! \right. \\
\left. \times \sum_{\mathbf{k} < \mathbf{k}^*} \mathscr{M}_2^{(0)} \omega_{\mathbf{k}} \omega_{-\mathbf{k}} \right\} \left(1 + A_2 + \frac{1}{2!} A_2^2 + \cdots \right) \\
\times \exp\left(i2\pi \sum_{\mathbf{k} < \mathbf{k}^*} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right) \qquad (4.11)
\end{aligned}
$$

where the following notation is introduced

$$
\bar{\mu}_1^+ = 2^{-1/2} \mu_1^+, \qquad R(0) = \beta\bar{\mu}_1^+ - 2^{-1/2} \beta(\langle N^* \rangle / V)\, \tilde{\mathscr{V}}(0)
$$

$$
A_2 = \sum_{n \geqslant 3} D_n^{(i_n)'}
$$

[in (4.11) the prime on $\rho_{\mathbf{k}}$ and $\mathscr{M}_n^{(i_n)}$ is omitted for clarity]. If in A_2 the operator $d/d\rho_{\mathbf{k}}$ is substituted for $i2\pi\omega_{\mathbf{k}}$, (4.11) can be rewritten as

$$
I = \Xi_G^\rho (1 + \langle \hat{A}_2 \rangle + \tfrac{1}{2} \langle \hat{A}_2^2 \rangle + \cdots)
$$

where

$$
\begin{aligned}
\langle \cdots \rangle = (\Xi_G^\rho)^{-1} \exp\left[\beta\bar{\mu}_1^+ - \frac{\beta \langle N^* \rangle^2}{4V} \tilde{\mathscr{V}}(0) \right] \prod_{\mathbf{k} < \mathbf{k}^*} [\pi \mathscr{M}_2^{(0)}(k)]^{-1/2} \\
\times \int (d\rho)^{N^*} \exp\left[R(0) - \frac{\beta}{2} \sum_{\mathbf{k} < \mathbf{k}^*} \tilde{\mathscr{V}}(k)\, \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] \\
\times \cdots \exp\left(-\frac{1}{2} \sum_{\mathbf{k} < \mathbf{k}^*} \frac{\rho_{\mathbf{k}} \rho_{-\mathbf{k}}}{\mathscr{M}_2^{(0)}} \right) \qquad (4.12)
\end{aligned}
$$

$$
\begin{aligned}
\Xi_G^\rho = \exp\left[\beta\bar{\mu}_1^+ - \frac{\beta \langle N^* \rangle^2}{4V} \tilde{\mathscr{V}}(0) \right] \prod_{\mathbf{k} < \mathbf{k}^*} [\beta \tilde{\mathscr{V}}(k)\, \mathscr{M}_2^{(0)} + 1]^{-1/2} \\
\times \exp\left[\frac{R^2(0)}{2V_{11}(0)} \right] \qquad (4.13)
\end{aligned}
$$

$$
V_{11}(k) = \beta \tilde{\mathscr{V}}(k) + 1/\mathscr{M}_2^{(0)} \qquad (4.14)
$$

Finally after the integration over variables $\rho_{\mathbf{k}}$ we obtain

$$
\Xi = \Xi_0 \Xi_G^\rho \int (d\sigma)^{N^*} \exp\left[\beta\mu_1^- c_0 - (\beta/2) \sum_{\mathbf{k} < \mathbf{k}^*} \tilde{\mathscr{W}}(k)\, c_{\mathbf{k}} c_{-\mathbf{k}} \right] J(c) \qquad (4.15)
$$

where $J(c)$ has the form

$$J(c)=\int (dy)^{N^*} \exp\left\{ i2\pi \sum_{\mathbf{k}<\mathbf{k}^*} \gamma_{\mathbf{k}} c_{\mathbf{k}} + \sum_{n\geqslant 1} (-i2\pi)^{2n}/2n! \right.$$

$$\left. \times 2^{-n} \sum_{\mathbf{k}_i<\mathbf{k}^*} (\mathscr{M}_{2n}^{(2n)}+\varDelta\mathscr{M}_{2n})\, \gamma_{\mathbf{k}_1}\cdots\gamma_{\mathbf{k}_{2n}} \delta_{\mathbf{k}_1+\cdots+\mathbf{k}_{2n}} \right\} \tag{4.16}$$

Here the values $\mathscr{M}_{2n}^{(2n)}$ are determined from (4.9) and $\varDelta\mathscr{M}_{2n}$ are corrections obtained as a result of the integration over $\rho_{\mathbf{k}}$.

Let us now go through the assumptions that led us to the initial working formula. To investigate the qualitative picture of the events taking place at the critical point itself and in a small neighborhood of it we confine ourselves to fourth-degree polynomials in the expressions for ln $J(c)$,$^{(6)}$ setting $\mathscr{M}_{2n}^{(2n)}=0$ and $\varDelta\mathscr{M}_{2n}=0$ for $n\geqslant 3$ in (4.15).

It follows from (4.8) and (B.1) that

$$\mathscr{M}_2^{(2)}=\langle N^*\rangle \tag{4.17a}$$

$$\mathscr{M}_4^{(4)}=3\mathscr{M}_2^{(0)}-2\langle N^*\rangle \tag{4.17b}$$

Corrections $\varDelta\mathscr{M}_2$ and $\varDelta\mathscr{M}_4$ are determined from

$$\varDelta\mathscr{M}_2= -(1/12)\, \mathscr{M}_4^{(2)}/\mathscr{M}_2^{(0)}+(1/5!)\, \mathscr{M}_6^{(2)}/(\mathscr{M}_2^{(0)})^2+(1/3)\langle \rho_0\rangle$$

$$\times \mathscr{M}_3^{(2)}/\mathscr{M}_2^{(0)}+(1/12\langle N^*\rangle)\sum_{\mathbf{k}}\langle \rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle\, \mathscr{M}_4^{(2)}/(\mathscr{M}_2^{(0)})^2+\cdots \tag{4.18}$$

$$\varDelta\mathscr{M}_4= -(1/3)(\mathscr{M}_3^{(2)})^2/\mathscr{M}_2^{(0)}-(1/30)\, \mathscr{M}_6^{(4)}/\mathscr{M}_2^{(0)}+(1/4!)$$

$$\times(\mathscr{M}_4^{(2)}/\mathscr{M}_2^{(0)})^2-(1/200)(\mathscr{M}_5^{(2)})^2/(\mathscr{M}_2^{(0)})^3+(1/1800)$$

$$\times(\mathscr{M}_6^{(2)})^2/(\mathscr{M}_2^{(0)})^4+\cdots+\varepsilon \tag{4.19}$$

ε are terms of the form $\langle \rho_{\mathbf{k}_1}\cdots\rho_{\mathbf{k}_n}\rangle$, and $\langle\cdots\rangle$ means the average of the type (4.12). We shall evaluate contributions of $\varDelta\mathscr{M}_2$ and $\varDelta\mathscr{M}_4$ to (4.16). It can readily be shown that

$$\langle \rho_0\rangle = R(0)/V_{11}(0), \qquad \langle \rho_{\mathbf{k}}\rho_{-\mathbf{k}}\rangle=\begin{cases} V_{11}^{-1}, & k\neq 0\\ V_{11}^{-1}+[R(0)/V_{11}]^2, & k=0\end{cases}$$

We do not take into account terms $\langle \rho_{\mathbf{k}_1}\cdots\rho_{\mathbf{k}_n}\rangle$ because Eq. (4.6a) leads to $R(0)=0$ and V_{11}^{-1} is a small value $[\beta_c \tilde{\mathscr{V}}(k)\, \mathscr{M}_2^{(0)}\ll 1]$. Then using (4.8)–(4.9), $\varDelta\mathscr{M}_2$ and $\varDelta\mathscr{M}_4$ can be expressed in terms of structure factors of the one-component hard-sphere system $S_n(0)$ $[\mathscr{M}_n^{(0)}=N^*S_n(0)]$. The higher order structure factors can be obtained from $S_2(0)$ as done in ref. 9 by means of the familiar chain of equations for correlation functions.(13) As a result for $\Delta\mathcal{M}_2$ and $\Delta\mathcal{M}_4$ at $\eta = 0.15$ we get [values $S_n(0)$ have been taken from ref. 9]

$$\Delta\mathcal{M}_2 = 0.026 + \cdots + (1/\langle N^* \rangle)(0.035 + \cdots) + \cdots \tag{4.20}$$

$$\begin{aligned} \Delta\mathcal{M}_4 = {} & -3\mathcal{M}_2^{(0)} + (0.084 + 0.004 + \cdots) + (1/\langle N^* \rangle) \\ & \times(-0.013 - \cdots) + (1/\langle N^* \rangle)^2 (0.01 + \cdots) + \cdots \end{aligned} \tag{4.21}$$

It follows from comparison of formula (4.17a) with (4.20) that the contribution of $\Delta\mathcal{M}_2$ to the second cumulant is very insignificant. On the contrary, the first term of $\Delta\mathcal{M}_4$ in (4.21) has a significant influence on the value $\mathcal{M}_4$. It is clear from (4.17b) and (4.21) that for arbitrary η the following equality holds:

$$\mathcal{M}_4^{(4)} - 3\mathcal{M}_2^{(0)} = -2\langle N^* \rangle$$

As a result the partition function (4.15) transforms into the form

$$\begin{aligned} \Xi = \Xi_0 \Xi_G^\rho \int (d\gamma)^{N^*} (d\sigma)^{N^*} \exp \Bigg[& \beta\bar{\mu}_1 c_0 - (\beta/2) \sum_{\mathbf{k}<\mathbf{k}^*} \tilde{\mathcal{W}}(k)\, c_{\mathbf{k}} c_{-\mathbf{k}} \\ & + i2\pi \sum_{\mathbf{k}<\mathbf{k}^*} \gamma_{\mathbf{k}} c_{\mathbf{k}} + (-i2\pi)^2/2!\,(2)^{-1} \sum_{\mathbf{k}<\mathbf{k}^*} \mathcal{M}_2 \gamma_{\mathbf{k}} \gamma_{-\mathbf{k}} + (-i2\pi)^4/4!\,(2)^{-2} \\ & \times \sum_{\mathbf{k}_i<\mathbf{k}^*} \mathcal{M}_4 \gamma_{\mathbf{k}_1} \cdots \gamma_{\mathbf{k}_n} \delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n} \Bigg] \end{aligned} \tag{4.22}$$

where $\mathcal{M}_2 = \langle N^* \rangle + \delta$, $\mathcal{M}_4 = -2\langle N^* \rangle + \delta$, and δ is a small value.

After the integration over $\gamma_{\mathbf{k}}$ in (4.22) we get

$$\Xi_1 = C \int \omega_4(c)\,(dc)^{N^*} \tag{4.23}$$

where

$$C = \Xi_0 \Xi_G^\rho [Z(\bar{\mathcal{M}}_2, \bar{\mathcal{M}}_4)]^{N^*}, \qquad \bar{\mathcal{M}}_{2n} = \mathcal{M}_{2n}/\langle N^* \rangle \tag{4.24}$$

$$\begin{aligned} \omega_4(c) = \exp \Bigg[& \beta\bar{\mu}_1 c_0 - (1/2) \sum_{\mathbf{k}} d(k)\, c_{\mathbf{k}} c_{-\mathbf{k}} \\ & - (a_4/4!) \sum_{\mathbf{k}_1 \cdots \mathbf{k}_n} c_{\mathbf{k}_1} \cdots c_{\mathbf{k}_n} \delta_{\mathbf{k}_1+\cdots+\mathbf{k}_n} \Bigg], \qquad \mathbf{k}_i < \mathbf{k}^* \end{aligned} \tag{4.25}$$

$$d(k) = a_2 - \beta\tilde{\mathcal{W}}(k) = a_2 - \beta(\langle N^* \rangle / V)[\tilde{\Phi}(k) - \tilde{\Phi}_{ab}(k)] \tag{4.26}$$

$[Z(\bar{\mathscr{M}}_2, \bar{\mathscr{M}}_4)]^{N^*}$ is the result of integration with respect to $\gamma_{\mathbf{k}}$ for $\mathbf{k} < \mathbf{k}^*$,

$$Z(\bar{\mathscr{M}}_2, \bar{\mathscr{M}}_4) = [(12)^{1/2}/(2\pi)]\, |\bar{\mathscr{M}}_4|^{-1/4}\, \xi^{1/4} \exp \xi K_{1/4}(\xi) \tag{4.27}$$

$\xi = (3/4)(\bar{\mathscr{M}}_2)^2/|\bar{\mathscr{M}}_4|$ and $K_{1/4}(\xi)$ is the Bessel function of an imaginary argument. The coefficients a_2 and a_4 are found from[6]

$$a_2 = (12)^{1/2}\, |\bar{\mathscr{M}}_4|^{-1/2}\, \mathscr{K}(\xi), \qquad a_4 = 6\, |\bar{\mathscr{M}}_4|^{-1}\, L(\xi) \tag{4.28}$$

$$\begin{aligned} \mathscr{K}(\xi) &= \xi^{1/2}\{[K_{3/4}(\xi)/K_{1/4}(\xi)] - 1\} \\ L(\xi) &= 6[\mathscr{K}(\xi)]^2 + 4\xi^{1/2}\mathscr{K}(\xi) - 1 \end{aligned} \tag{4.29}$$

The functions $\xi^{1/4}K_{1/4}(\xi)$, $\mathscr{K}(\xi)$, and $L(\xi)$ are analytic functions on the whole real ξ axis. The relationships (4.23)–(4.29) and equations in the chemical potentials (4.6b) are starting formulas in studies of the thermodynamic behavior of a binary system in the vicinity of the gas–gas separation critical point. It follows from (4.23)–(4.26) that the form of $\omega_4(c)$ is analogous to the basic density measure of the 3D Ising model obtained in ref. 6 [the only difference is the presence of the linear term $\beta\bar{\mu}_1 c_0$ in (4.25)]. If we set $\bar{\mathscr{M}}_2 = 1$ and $\bar{\mathscr{M}}_4 = -2$ in (4.22) we have $a_2 \simeq 0.645$ and $a_4 \simeq 0.183$ [see (4.28)]. Analogous values for corresponding coefficients were obtained in ref. 6. Having used the method of integration of the partition function of the 3D Ising model[6] in the vicinity of the critical point, we found the thermodynamic functions of the binary symmetrical mixture at $T \geqslant T_c$ and $T \leqslant T_c$ as functions of composition, temperature, and Hamiltonian initial parameters. The results of our study will be given in a subsequent paper.

5. CONCLUSIONS

The most important result of Section 2 is the explicit form of the cumulants. Of special note are formulas (2.19)–(2.20), which make it possible to find all the cumulants in the long-wavelength limit using thermodynamic relationships, from the matrix of derivatives $d\mu_0^i/dN_j$. Partial chemical potentials can be found in their turn from the familiar expression for the RS free energy.[14] The final result of that section is the expression for the functional of the grand partition function with explicit expressions for Hamiltonian coefficients. This expression can be used in studies of phase transitions in a multicomponent system.

The CV method with RS has been used in the investigation of phase transitions in a binary system. The Gaussian approximation of the functional of the grand partition function obtained in Section 2 has been studied in detail. It was shown that on the critical lines gas–liquid and separation critical points can be identified completely in the case of a symmetrical mixture. When the gas–liquid critical point is approached, total density fluctuations grow; and when the separation critical point is approached, fluctuations of relative density grow. For an asymmetrical mixture the identification of the point 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 the Hamiltonian which determine the alternation of gas–liquid and separation phase transitions have been found.

Upon integrating (4.1) over CV $\rho_{\mathbf{k}}$ and $c_{\mathbf{k}}$ with $\mathbf{k} > \mathbf{k}^*$ for which inequalities $(\beta/V)\,\tilde{\mathscr{V}}(k)\,\mathscr{M}_2^{(0)} < 1$ and $(\beta/V)\,\tilde{\mathscr{W}}(k)\,\mathscr{M}_2^{(2)} < 1$ hold there is a transition to a crystal lattice. It was shown in Section 3 that the CV $\rho_{\mathbf{k}}$ do not include the variable connected with the order parameter for the separation phase transition. Thus in the given considerations, the CV $\rho_{\mathbf{k}}$ are of secondary importance. After integration over all $\rho_{\mathbf{k}}$ the fourfold basic density measure with respect to $c_{\mathbf{k}}$ was constructed. It was shown that the task can be reduced to the 3D Ising model.

APPENDIX A

We have

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

where the + and − signs correspond to $i-1$ and $i-2$, respectively.

APPENDIX B

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

$$\mathscr{M}_1^{(0)}(0) = \mathscr{M}_a(0) + \mathscr{M}_b(0) = \langle N \rangle$$

$$\mathscr{M}_1^{(1)}(0) = \mathscr{M}_a(0) - \mathscr{M}_b(0) = \langle N_a \rangle - \langle N_b \rangle$$

$$\mathscr{M}_2^{(0)}(0) = \mathscr{M}_{aa}(0) + \mathscr{M}_{bb}(0) + 2\mathscr{M}_{ab}(0)$$

$$
\begin{aligned}
\mathscr{M}_2^{(1)}(0) &= \mathscr{M}_{aa}(0) - \mathscr{M}_{bb}(0)\\
\mathscr{M}_2^{(2)}(0) &= \mathscr{M}_{aa}(0) + \mathscr{M}_{bb}(0) - 2\mathscr{M}_{ab}(0)\\
\mathscr{M}_3^{(0)}(0) &= \mathscr{M}_{aaa}(0) + \mathscr{M}_{bbb}(0) + 3[\mathscr{M}_{aab}(0) + \mathscr{M}_{abb}(0)]\\
\mathscr{M}_3^{(1)}(0) &= \mathscr{M}_{aaa}(0) - \mathscr{M}_{bbb}(0) + \mathscr{M}_{aab}(0) - \mathscr{M}_{abb}(0)\\
\mathscr{M}_3^{(2)}(0) &= \mathscr{M}_{aaa}(0) + \mathscr{M}_{bbb}(0) - \mathscr{M}_{aab}(0) - \mathscr{M}_{abb}(0)\\
\mathscr{M}_3^{(3)}(0) &= \mathscr{M}_{aaa}(0) - \mathscr{M}_{bbb}(0) - 3[\mathscr{M}_{aab}(0) + \mathscr{M}_{abb}(0)]\\
\mathscr{M}_4^{(0)}(0) &= \mathscr{M}_{aaaa}(0) + \mathscr{M}_{bbbb}(0)\\
&\qquad + 4[\mathscr{M}_{aaab}(0) + \mathscr{M}_{abbb}(0)] + 6\mathscr{M}_{aabb}(0)\\
\mathscr{M}_4^{(1)}(0) &= \mathscr{M}_{aaaa}(0) - \mathscr{M}_{bbbb}(0) + 2[\mathscr{M}_{aab}(0) - \mathscr{M}_{abbb}(0)]\\
\mathscr{M}_4^{(2)}(0) &= \mathscr{M}_{aaaa}(0) + \mathscr{M}_{bbbb}(0) - 2\mathscr{M}_{aabb}(0)\\
\mathscr{M}_4^{(3)}(0) &= \mathscr{M}_{aaaa}(0) - \mathscr{M}_{bbbb}(0) - 2[\mathscr{M}_{aaab}(0) - \mathscr{M}_{abbb}(0)]\\
\mathscr{M}_4^{(4)}(0) &= \mathscr{M}_{aaaa}(0) + \mathscr{M}_{bbbb}(0)\\
&\qquad - 4[\mathscr{M}_{aaab}(0) + \mathscr{M}_{abbb}(0)] + 6\mathscr{M}_{aabb}(0) \qquad \text{(B.1)}
\end{aligned}
$$

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

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