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## SPATIAL DISTRIBUTION OF COMPONENTS OF A BINARY MIXTURE IN A BOUNDED SYSTEM

L.A. BULAVIN, D.A. GAVRYUSHENKO, V.M. SYSOEV

UDC 512  
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Taras Shevchenko Kyiv National University  
(6, Academician Glushkov Ave., Kyiv 03127, Ukraine; e-mail: dm\_g@univ.kiev.ua)

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In the lattice model of a liquid, we have calculated the spatial distribution of the concentrations of components of a binary mixture with the use of the expansion of the potential of an external field in a Taylor functional series, which is reduced to a series in direct correlation functions of all orders. As an example, a plane-parallel pore with the exponential near-wall potential is considered.

An important result of the development of statistical physics is the possibility to obtain the quantitative description of the binary solution of a homogeneous liquid in a wide interval of variation of thermodynamical parameters, including the vicinities of possible critical points. The state of such a system can be completely set by the collection of intensive parameters, such that none of them describes the size of the system or the shape of its bounding surface, and by the total number of particles  $N = N_A + N_B$ , where  $N_A$  and  $N_B$  are the numbers of particles of the sort "A" and "B", respectively. But it is obvious that any real system is always inhomogeneous. One may separate two main reasons for the appearance of this inhomogeneity: they are related, respectively, to the presence of external fields  $u(\vec{r})$  (gravitational, electric, etc. ones) and the walls which bound the system.

The traditional methods describe properties of an inhomogeneous system by dividing it into sufficiently thin layers, each being positioned between two equipotential surfaces, and by representing the relevant thermodynamical potentials (in particular, the internal energy  $U$ ) of such a system as a sum of thermodynamical potentials of these layers [1]. In this case, the volumes of these layers are considered as physically infinitely small, i.e. they are sufficiently small in order that a substance in their limits remains homogeneous, but,

on the other hand, they are sufficiently great in order that their properties can be considered in the scope of thermodynamics and statistical physics. In the frame of this approach, the chemical potential of a one-component system  $\mu(\vec{r})$  in an external field is described by the well-known classical formula [2]

$$u(\vec{r}) = \mu_0 - \mu(\vec{r}), \quad (1)$$

where  $\mu_0$  is the chemical potential of the system without external field.

It is clear that the given approach is local in the following sense. We consider the thermodynamical potentials of the system as functions of the number density rather than as the corresponding functionals. This leads to the loss of the information about the "collective" behavior of the system, which is extremely important for the description of properties of the system in the vicinity of the points of second-order phase transitions.

In [3], it was shown that, with regard for nonlocal "collective" properties of a one-component system, expression (1) should be written as

$$u(\vec{r}) = \mu_0 - \mu(\vec{r}) + a\nabla^2 n(\vec{r}), \quad (2)$$

where the constant  $a$  is determined in terms of the second spatial moment of the so-called direct second-order correlation function. Relation (2) allows one to calculate, in a certain approximation, the spatial distribution of the density of the liquid in wide intervals of variation of thermodynamical parameters, including the critical point [4, 5].

In order to construct a consistent thermodynamic theory which would describe the behavior of a one-component inhomogeneous system, we have proposed

a fundamental approach [6] based on the calculation of contributions from each layer positioned between equipotential surfaces to the Hamiltonian of a system, rather than to the corresponding thermodynamical potentials. In this case, relations (1) and (2) can be written as

$$u(\vec{r}) = \mu_0 - \mu(\vec{r}) + \Delta\mu_{\text{cor}}(\vec{r}), \quad (3)$$

where  $\Delta\mu_{\text{cor}}$  is the contribution from the correlation effects which is represented in the form of an infinite series.

The goal of our work is to generalize the formalism proposed in [6] to the case of two-component systems.

In order to describe the thermodynamic behavior of an inhomogeneous binary fluid in a bounded system, we use the lattice model of a liquid, in the frame of which the molecules of a solution are located in sites of the lattice, and the total number of particles  $N$  equal to the number of sites of the lattice  $N'$ :

$$N = N' = N_A + N_B. \quad (4)$$

It is obvious that the absence of unoccupied sites of the lattice (the absence of the “third component of the solution”, i.e., holes) corresponds to the case of a sufficiently compressed liquid. Simple calculations indicate that just such a situation occurs in the case of the so-called random dense packing of particles of a system [7], which is realized, in particular, for a liquid in nanoobjects such as carbon nanotubes and fullerenes.

For the sake of convenience, we divide the volume of the system into layers with thickness  $l$ , which are perpendicular to the line of action of an external force and whose geometry is defined by the form of equipotential surfaces of an external field. The Hamiltonian of such a system reads

$$H = H'_0 + \sum_{i=1}^M (N_A^i u_A^i + N_B^i u_B^i), \quad (5)$$

where  $H'_0$  – the part which describes the interparticle interaction,  $M$  – the number of layers,  $N_A^i$  and  $N_B^i$  – the numbers of particles of the sorts “A” and “B”, respectively, in the  $i$ -th layer, and  $u_A^i$  and  $u_B^i$  – the potential energies of particles of the sorts “A” and “B” in the external field in this layer. We introduce the concentration of the component “A” in the  $i$ -th layer as

$$x_i = \frac{N_A^i}{N^i}, \quad (6)$$

where  $N^i = \frac{N}{M}$  is the total number of particles in the  $i$ -th layer. We note that, due to condition (4),  $N^i$  depends only on an external field, namely on the geometry of equipotential surfaces, and is independent of the spatial distribution of the concentration. In this case, expression (5) can be presented as

$$H = H_0 + \sum_i u_{\text{BA}}^i x_i, \quad (7)$$

where  $H_0 = H'_0 + \sum_{i=1}^M N_i u_A^i$ ,  $u_{\text{BA}}^i = \frac{u_B^i - u_A^i}{N_i}$ .

For the sake of simplicity, we will consider a system with cubic lattice, in which the external field  $u(z)$  acts along the  $0z$  axis. Moreover, the system is bounded in this direction, therefore  $z$  can vary in the limits  $[-L, L]$ . Such a situation is realized in a uniform gravitational field or in a system with plane-parallel walls, at which the near-wall potential acts, in the absence of the gravitational field. In this case, expression (7) takes the form

$$H = H_0 + \sum_i u_{\text{BA}}^i x_i, \quad (8)$$

where, in the given case,  $u_{\text{BA}}^i = \frac{u_B^i - u_A^i}{N_l}$ ,  $N_l = N \frac{2L}{l} = \text{const}$  – is the number of particles (sites) in a layer with thickness  $l$ .

For the further description of the system, we introduce, by analogy with the theory of liquids, a correlation function “concentration-concentration” of the  $s$ -th order in the corresponding layers of the solution with regard for  $\delta$ -like singularities

$$\begin{aligned} \hat{F}_s(z, z_1 \dots z_{s-1}) &= \\ &= \frac{\delta^{s-1} x(z)}{\delta(\beta u_{\text{BA}}(z_1)) \dots \delta(\beta u_{\text{BA}}(z_{s-1}))} \Big|_{u_{\text{BA}}(z_1)=0, \dots, u_{\text{BA}}(z_{s-1})=0} \end{aligned} \quad (9)$$

and a direct correlation function “concentration-concentration” of the  $s$ -th order in the corresponding layers of the solution with regard for  $\delta$ -like singularities

$$\begin{aligned} C_s(z, z_1, \dots z_{s-1}) &= \\ &= \frac{\delta^{s-1} (\beta u_{\text{BA}}(z))}{\delta x(z_1) \dots \delta x(z_{s-1})} \Big|_{x(z_1)=x^0(z_1), \dots, x(z_{s-1})=x^0(z_{s-1})}, \end{aligned} \quad (10)$$

where  $\beta = 1/kT$ .

Considering the physically infinitely thin layers as mathematically infinitely small ones like the field theories of inhomogeneous systems, we expand the potential of an external field  $u_{BA}(z)$  in a Taylor functional series [8] in variations  $\Delta x(z) = x(z) - x^0(z)$  of the concentration  $x(z)$  from its value  $x^0(z)$  without external field:

$$\begin{aligned} \beta u_{BA}(z) &= \int_{-L}^L dz_1 \frac{\delta(\beta u_{BA}(z))}{\delta x(z_1)} \Big|_{x(z_1)=x^0(z_1)} \Delta x(z_1) + \\ &+ \frac{1}{2!} \int_{-L}^L dz_1 \int_{-L}^L dz_2 \frac{\delta^2(\beta u_{BA}(z))}{\delta x(z_1) \delta x(z_2)} \Big|_{x(z_1)=x^0(z_1), x(z_2)=x^0(z_2)} \times \\ &\times \Delta x(z_1) \Delta x(z_2) + \dots \end{aligned} \tag{11}$$

Series (11) converges due to the boundedness of the integral  $\int_{-L}^L dz_1 (x(z_1) - x^0(z_1))$  [9]. With regard for relation (10), we obtain

$$\begin{aligned} \beta u_{BA}(z) &= \int_{-L}^L dz_1 C_2(z, z_1) \Delta x(z_1) + \\ &+ \frac{1}{2!} \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) \Delta x(z_1) \Delta x(z_2) + \dots \end{aligned} \tag{12}$$

We note that  $C_s(z, z_1, \dots, z_{s-1})$  in relation (12) are the corresponding correlation functions of a homogeneous system without external field.

For variations of the concentration, we write the formal expression

$$\Delta x(z_1) = \Delta x(z) + [\Delta x(z_1) - \Delta x(z)] \tag{13}$$

By substituting it in (12), we get

$$\begin{aligned} \beta u_{BA}(z) &= \Delta x(z) \int_{-L}^L dz_1 C_2(z, z_1) + \\ &+ \int_{-L}^L dz_1 C_2(z, z_1) [\Delta x(z_1) - \Delta x(z)] + \\ &+ \frac{1}{2!} [\Delta x(z)]^2 \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) + \end{aligned}$$

$$\begin{aligned} &+ \Delta x(z) \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) [\Delta x(z_1) - \Delta x(z)] + \\ &+ \frac{1}{2!} \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) [\Delta x(z_1) - \Delta x(z)] \times \\ &\times [\Delta x(z_2) - \Delta x(z)] + \dots, \end{aligned} \tag{14}$$

where we took the symmetry of the direct correlation functions of a homogeneous system relative to a permutation of their arguments into account.

Applying the procedure developed in [5] to the description of one-component systems, we obtain, analogously to (3),

$$u_{BA}(z) = \mu_0 - \mu(z) + \Delta\mu_{\text{cor}}(z), \tag{15}$$

where  $\Delta\mu_{\text{cor}}$  is the contribution of correlation effects to the difference of chemical potentials:

$$\begin{aligned} \beta \Delta\mu_{\text{cor}}(z) &= \int_{-L}^L dz_1 C_2(z, z_1) [\Delta x(z_1) - \Delta x(z)] + \\ &+ \Delta n(z) \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) [\Delta x(z_1) - \Delta x(z)] + \\ &+ \frac{1}{2!} \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) [\Delta x(z_1) - \Delta x(z)] \times \\ &\times [\Delta x(z_2) - \Delta x(z)] + \dots \end{aligned} \tag{16}$$

In the case of a sufficiently smooth spatial variation of the density,  $\Delta x(z)$ , at distances of the order of the radius of action of intermolecular forces, and far from the critical point (just in this case, the “radius of action” of the direct correlation functions is of the order of the radius of action of intermolecular forces),  $\Delta x(z_1) - \Delta x(z)$  can be expanded in a Taylor series in powers of  $(z_1 - z)$ . Relation (16) looks as

$$\begin{aligned} \beta \Delta\mu_{\text{cor}}(z) &= \frac{1}{2} \frac{d^2 \Delta x(z)}{dz^2} \int_{-L}^L dz_1 C_2(z, z_1) (z_1 - z)^2 + \\ &+ \frac{1}{2} \left( \frac{d \Delta x(z)}{dz} \right)^2 \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) \times \end{aligned}$$

$$\begin{aligned} & \times (z_1 - z)(z_2 - z) + \frac{d\Delta x(z)}{dz} \left[ \int_{-L}^L dz_1 C_2(z, z_1)(z_1 - z) + \right. \\ & \left. + \Delta x(z) \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2)(z_1 - z) \right] + \dots \quad (17) \end{aligned}$$

According to the theory of scale transformations [10],  $(\mu - \mu_c) \sim |x - x_c|^a$  in a vicinity of the stratification point on a critical isotherm, where the exponent  $a$  is a noninteger which is expressed via the critical indices. It is clear that the zero moments of direct correlation functions of the order of 5 and more diverge at the very critical point. Therefore, series (17) diverges as well.

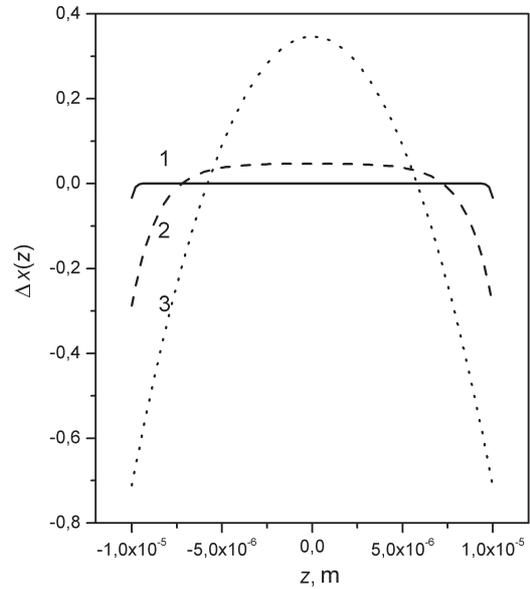
The results obtained testify that the classical formula (1) can be used exclusively for the description of the concentration distribution in inhomogeneous binary systems only in the case where the external fields with small spatial gradients are present and a system is far from the critical point. On approaching the critical point, the role of correlation terms increases, and therefore we must use relation (17), by taking the more and more correction terms into account. An analogous situation happens also far from the critical point in the presence of great variations of the concentration,  $\Delta x(z)$ .

In order to estimate the contribution of correlation terms  $\Delta\mu_{\text{cor}}(z)$ , we consider the case where the attractive (repulsive) forces act in the system near walls. We will simulate the potential of these forces as follows:

$$u_A(z) = 2B_A N_l e^{-kL} \text{ch}kz, \quad u_B(z) = 2B_B N_l e^{-kL} \text{ch}kz, \quad (18)$$

Here,  $B_A$  and  $B_B$  – the corresponding amplitudes ( $B > 0$  and  $B < 0$  correspond, respectively, to the attractive and repulsive forces), and  $k^{-1}$  is the effective radius of action of these forces. It is worth noting that the values of the constants  $B_A$  and  $B_B$  depend on the nature of a liquid (and on the presence of admixtures), a substance of the wall bounding the volume, and the state of the surface (the quality of its mechanical processing, the surface roughness, etc. [11]. Due to the last factors, these values can vary in a very wide range even for the same substance. Therefore, no exact values of these constants exist for a given substance.

Then, in the approximation of smooth inhomogeneity [12] and taking only the first term of series (17) into account, we obtain the differential equation for



Variations,  $\Delta x(z)$ , of the concentration of a binary solution for various  $\xi$ : 1- $10^{-7}$ , 2- $10^{-6}$ , 3- $0.999 \cdot 10^{-5}$  m ( $L = 10^{-5}$  m,  $k^{-1} = 3 \cdot 10^{-10}$  m, and  $B_{BA} = 10^{-24}$  J)

$$\Delta x(z) \quad [13]$$

$$\frac{d^2 \Delta x}{dz^2} - \kappa^2 \Delta x = A \kappa^2 (\lambda + 2B_{BA} e^{-kL} \text{ch}kz), \quad (19)$$

where  $\kappa = \frac{1}{\sqrt{2}\xi}$ ,  $\xi$  – the correlation length,  $B_{BA} = \frac{B_B - B_A}{N_l}$ ,  $A$  – the constant which depends on parameters of the critical point of a given solution, and  $\lambda$  – the constant, whose value is determined from the so-called condition of isoperimetry, i.e. the invariability of the number of particles in the system. We note that the imposition of this additional condition on the solution of Eq. (19) is related to the necessity to set the chemical potential of a homogeneous system. The solution of Eq. (19) reads

$$\begin{aligned} \Delta x(z) &= 2B_{BA} e^{-kL} \times \\ & \times A \left[ -\frac{k\kappa}{k^2 - \kappa^2} \frac{\text{sh}kL}{\text{sh}\kappa L} \text{ch}\kappa z + \frac{\kappa^2}{k^2 - \kappa^2} \text{ch}kz + \frac{1}{kL} \text{sh}\kappa L \right]. \quad (20) \end{aligned}$$

In the figure, we present the spatial distribution of the concentration of a model binary solution,  $\Delta x(z)$ , for various values of the correlation length  $\xi$ .

As is seen from this figure, the profiles of the concentration of the liquid coincide with the internal solution of Eq. (1) far from the critical point. This

solution corresponds to the local approximation, i.e. the deviations of the concentration from the mean value occur only at distances of the order of the radius of action of the surface forces. In the whole remaining volume of the system, the concentration is equal to the mean one. But, on approaching the critical point, the singularly perturbed term begins to play the increasingly greater role, and the concentration of the liquid varies in a greater part of the volume. That is, the characteristic distance, at which the density varies significantly, is the correlation length of the system  $\xi$ , rather than the radius of action of the surface forces.

The obtained solution of the isoperimetric problem allows one to study a change of thermodynamical properties of a substance in the near-wall layer relative to the properties of a liquid in bulk. The essential change of the concentration (more than 30% in the mid-volume in a vicinity of the critical point) must lead to the corresponding phenomena which are observed in experiments, even on the molecular level. In particular, the results of experiments of the transmission of low-velocity neutrons [14] demonstrate the significant (at least 10%) dependence of the gravitational effect in a solution of ethane on the size of the system. The analysis of the results obtained in [14] indicates that the critical indices, which are calculated by experimental data, are not changed on the account of correlation effects. But the amplitudes of scale laws, which are calculated on the basis of experimental data, depend significantly on the size of a chamber. For example, the approximation of the dependence of the height on the concentration of ethane within the method of nonlinear regression indicates that the amplitude  $D$  is increased by more than 4 times on the decrease of the vessel's height by 4 times. Thus, it follows from the performed analysis that one should consider the correlation contribution to the density distribution in the calculations of critical indices by the data on the scattering of neutrons and light and only then take the other terms of the equation of state of a substance (asymmetric asymptotic terms, etc. [15]) into account.

As the other example, we mention the significant change in the viscosity of water and aqueous solutions near the surface of quartz [16] and a change of the mobility of an OH-group in water which is positioned in small volumes (pores of alumina) as compared with the mobility in the bulk of water, which is observed in experiments executed with the use of infrared spectroscopy [17]. It is worth noting that the above-considered behavior of binary mixtures coincides qualitatively with the behavior of individual liquids

in a vicinity of the critical point of the liquid-vapor system [18].

The obtained results can be used in experimental studies of the thermodynamical properties of multicomponent fluids near a critical point.

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Received 23.03.07.

Translated from Ukrainian by V.V. Kukhtin

#### ПРОСТОРОВИЙ РОЗПОДІЛ КОМПОНЕНТІВ БІНАРНОЇ СУМІШІ В ОБМЕЖЕНІЙ СИСТЕМІ

Л.А. Булавін, Д.А. Гаврюшенко, В.М. Сисоєв

#### Резюме

У моделі ґраткової рідини розраховано концентрацію бінарної суміші. З розкладу потенціалу зовнішнього поля у функціональний ряд Тейлора отримано розклад за прямими кореляційними функціями усіх порядків. Знайдено розв'язок одержаного диференціального рівняння для плоскопаралельної пори з експоненціальним пристінковим потенціалом.