
THE DISTRIBUTION OF COMPONENTS OF A BINARY SOLUTION IN THE SPATIALLY BOUNDED SYSTEM. I. A PLANAR PORE WITH ASYMMETRIC NEAR-WALL POTENTIAL

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A lattice model of liquid is applied to the calculation of the concentration of a binary mixture. The expansion of the potential of an external field in a functional series is constructed, and, as a result, the expansion in direct correlation functions of all orders is obtained. For a plane-parallel pore with asymmetric exponential near-wall potential, a solution of the deduced differential equation is constructed.

An important result of the development of statistical physics is the possibility to quantitatively describe a binary homogeneous liquid solution in a wide interval of variations of thermodynamical parameters, including the neighborhoods of possible critical points. The state of such a system can be completely set by both a collection of intensive parameters, each of which does not describe sizes of the system or a shape of the surface bounding the system, and the total number of particles $N = N_A + N_B$, where N_A and N_B are, respectively, the numbers of particles of kinds “A” and “B”. But it is clear that any real system is inhomogeneous in all the cases. One can distinguish two main reasons for the appearance of this inhomogeneity: the first reason is related to the presence of external fields $u(\mathbf{r})$ (gravitational, electric, etc.), and the second – to the presence of walls bounding the system.

The traditional methods of description of properties of an inhomogeneous system consist in the partition of it into sufficiently thin layers between two equipotential surfaces. In this case, the corresponding thermodynamical potentials of such a system are represented as the sum of thermodynamical potentials of these layers [1]. In the frame of this approach, the chemical potential of a one-component system $\mu(\mathbf{r})$ in

an external field is described by the well-known classical formula [2]

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

where μ_0 – the chemical potential of the system in the absence of an external field.

It is clear that the given approach is local in the sense that one considers the thermodynamical potentials of the system as functions of the number density instead of considering them as the corresponding functionals. This yields 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 phase transitions of the second kind.

In [3], it was shown that, in order to take the nonlocal (“collective”) properties of a one-component system into account, formula (1) should be written in the form

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

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

In order to develop a consistent thermodynamical theory which would describe the behavior of a one-component inhomogeneous system, we proposed earlier a fundamental approach based on the calculation of the contribution of each layer between equipotential surfaces

to the Hamiltonian of the system [5], rather than to the corresponding thermodynamical potentials. In this case, formula (1) looks as

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

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

The purpose of the present work is to generalize the formalism proposed in [5] to the case of a two-component system and to construct the spatial distribution of the concentration of a two-component solution which is placed into a plane-parallel pore with asymmetric near-wall potential. To describe the thermodynamical behavior of an inhomogeneous binary fluid in the bounded system, we use, following [6], the lattice model of fluid. According to this model, molecules of a solution are at sites of the lattice, and the total number of particles N coincides with 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 (i.e. the absence of the “third component of a solution”, i.e. sites of the lattice which are free from particles – holes) corresponds to the case of a sufficiently compressed fluid. The simple calculations indicate that just such a situation occurs in the case of the so-called random closest packing of particles of the system [7]. It is observed, in particular, in fluids in nanoobjects such as carbon nanotubes and fullerenes.

For convenience of the consideration, we divide the volume of the system into layers with thickness l which are perpendicular to the line of action of the external force. That is, their geometry is determined by the form of equipotential surfaces of an external field. We write the Hamiltonian of such a system as

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

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

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

where $N^i = \frac{N}{M}$ – the total number of particles in the i -th layer. We note that, due to the imposition of condition (4), N^i depends only on the external field, namely on the geometry of equipotential surfaces, and does not depend on the spatial distribution of the concentration. In this case, relation (5) can be presented in the form

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

where

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

To simplify the consideration, we will analyze the system possessing a cubic lattice, in which the external field $u(z)$ acts along the $0z$ axis. Moreover, the system is bounded in this direction, and, therefore, z can vary in the limits $[-L, L]$. Such a situation is realized in a homogeneous gravitational field or in the system with plane-parallel walls, at which the near-wall potential acts, in the absence of a gravitational field. In this case, relation (7) takes the form

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

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

For the further description of the system by analogy with the theory of fluids, we introduce a direct correlation s -order function “concentration–concentration”

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

for the relevant layers of a solution with regard for δ -like singularities, where $\beta = 1/kT$.

Considering the physically infinitely thin layers as mathematically infinitely thin ones, as it is commonly made in the field theories of inhomogeneous systems, we expand the potential of an external field $u_{BA}(z)$ in a Taylor functional series [9] in deviations $\Delta x(z) = x(z) - x^0(z)$ of the concentration $x(z)$ from its value

$x^0(z)$ in the absence of an external field. With regard for relation (9), we obtain

$$\begin{aligned} \beta u_{BA}(z) = & \Delta x(z) \int_{-L}^L dz_1 C_2(z, z_1) + \int_{-L}^L dz_1 C_2(z, z_1) \times \\ & \times [\Delta x(z_1) - \Delta x(z)] + \frac{1}{2!} [\Delta x(z)]^2 \int_{-L}^L dz_1 \times \\ & \times \int_{-L}^L dz_2 C_3(z, z_1, z_2) + \Delta x(z) \int_{-L}^L dz_1 \times \\ & \times \int_{-L}^L dz_2 C_3(z, z_1, z_2) [\Delta x(z_1) - \Delta x(z)] + \\ & + \frac{1}{2!} \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) [\Delta x(z_1) - \Delta x(z)] \times \\ & \times [\Delta x(z_2) - \Delta x(z)] + \dots, \end{aligned} \quad (10)$$

where we used the following formal expression for deviations of the concentration:

$$\Delta x(z_1) = \Delta x(z) + [\Delta x(z_1) - \Delta x(z)]. \quad (11)$$

Series (10) converges due to the boundedness of the integral $\int_{-L}^L dz_1 (x(z_1) - x^0(z_1))$ [10]. It is worth noting that $C_s(z, z_1, \dots, z_{s-1})$ in relation (10) are the corresponding direct correlation functions of the homogeneous system without external field which are symmetric relative to the permutation of their arguments.

Thus, by using a procedure developed in [5] for the description of one-component systems, we obtain, analogously to relation (3),

$$u_{BA}(z) = \mu_0 - \mu(z) + \Delta\mu_{\text{cor}}(z), \quad (12)$$

where $\Delta\mu_{\text{cor}}$ – the contribution of the correlation effects to the difference of the chemical potentials. 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 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 $(z_1 - z)$. Then the formula for $\Delta\mu_{\text{cor}}$ can be presented in the form

$$\begin{aligned} \beta \Delta\mu_{\text{cor}}(z) = & \frac{1}{2} \frac{d^2 \Delta x(z)}{dz^2} \int_{-L}^L dz_1 C_2(z, z_1) (z_1 - z)^2 + \\ & + \frac{1}{2} \left(\frac{d \Delta x(z)}{dz} \right)^2 \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) (z_1 - z) \times \\ & \times (z_2 - z) + \frac{d \Delta x(z)}{dz} \left[\int_{-L}^L dz_1 C_2(z, z_1) (z_1 - z) + \right. \\ & \left. + \Delta x(z) \int_{-L}^L dz_1 \int_{-L}^L dz_2 C_3(z, z_1, z_2) (z_1 - z) \right] + \dots \end{aligned} \quad (13)$$

According to the theory of scale transformations [11], we have $(\mu - \mu_c) \sim |x - x_c|^\delta$ in the vicinity of the point of stratification into the critical isotherms, where δ is the corresponding critical index. Therefore, it is obvious that the zero moments of the direct correlation functions of the order of five and more diverge at the very critical point. Hence, series (13) diverges as well.

To evaluate the contribution of the correlation terms $\Delta\mu_{\text{cor}}(z)$, we consider the case where the forces of attraction (repulsion) act in the system near walls. We will model the potential of these forces by the following expression:

$$\begin{aligned} u_A(z) = & N_l (B_{A1} + B_{A2}) e^{-k(L-z)} \text{ch}kz + \\ & + N_l (B_{A1} - B_{A2}) e^{-k(L-z)} \text{sh}kz, \\ u_B(z) = & N_l (B_{B1} + B_{B2}) e^{-k(L-z)} \text{ch}kz + \\ & + N_l (B_{B1} - B_{B2}) e^{-k(L-z)} \text{sh}kz, \end{aligned} \quad (14)$$

where B_{A1} (B_{B1}) and B_{A2} (B_{B2}) – the amplitudes of the near-wall potentials on the left and right boundaries of the pore for substances A and B , respectively, and k^{-1} – the effective radius of action of these forces. It is obvious that the positive values of the amplitudes correspond to the forces of repulsion, and the negative ones do to the forces of attraction. It is worth noting that the values of these constants depend on the nature of a fluid (and on the presence of impurities), the material of the wall bounding the volume, and the state of the surface, i.e. the quality of its mechanical processing, clearness of the

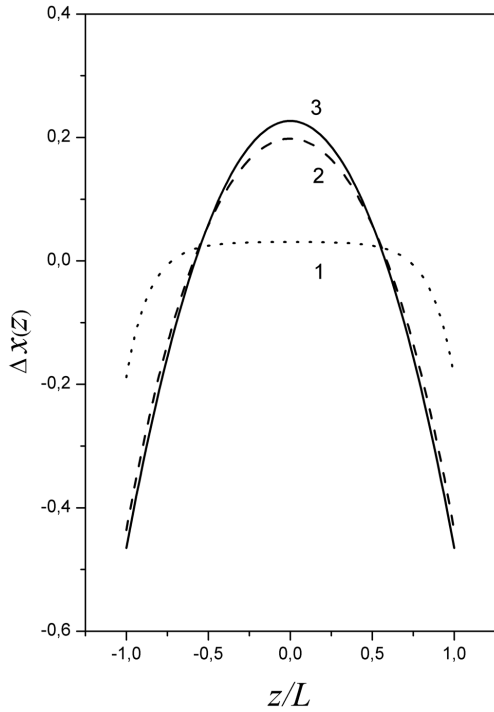


Fig. 1. Spatial dependence of the concentration $\Delta x(z)$ of a binary solution for various values of ξ : 1 - 10^{-6} , 2 - 5×10^{-6} , 3 - 10^{-5} m ($L = 10^{-5}$ m, $k^{-1} = 3 \times 10^{-10}$ m, $B_{BA1} = B_{BA2} = 10^{-24}$ J)

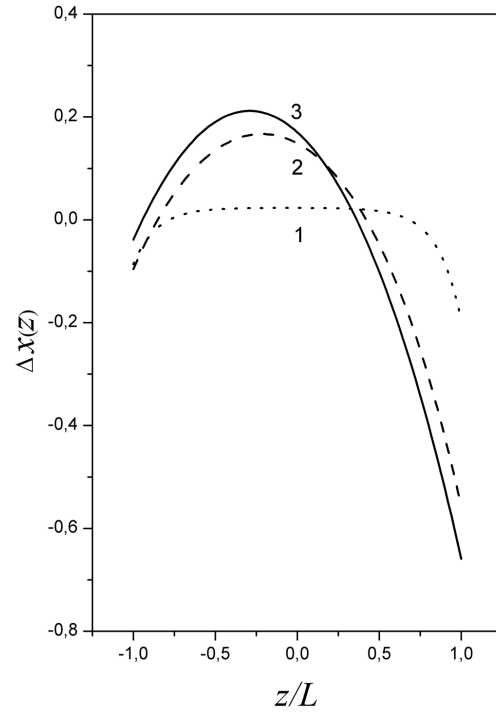


Fig. 2. Spatial dependence of the concentration $\Delta x(z)$ of a binary solution for various values of ξ : 1 - 10^{-6} , 2 - 5×10^{-6} , 3 - 10^{-5} m ($L = 10^{-5}$ m, $k^{-1} = 3 \times 10^{-10}$ m, $B_{BA1} = 10^{-24}$ J, $B_{BA2} = 0.5 \times 10^{-24}$)

surface, level of radiation-induced defects, etc. [12]. Due to the last factors, these constants can vary in wide limits even for the same fluid, and, therefore, there exist no exact values of these constants for a given substance.

In the approximation of smooth inhomogeneity [13], taking only the first term of series (13), one can obtain the differential equation for $\Delta x(z)$ [14]:

$$\frac{d^2 \Delta x}{dz^2} - \kappa^2 \Delta x = A(\lambda + (B_{BA1} + B_{BA2})e^{-k(L-z)} \operatorname{ch}kz + (B_{BA1} - B_{BA2})e^{-k(L-z)} \operatorname{sh}kz), \quad (15)$$

where $\kappa = \frac{1}{\sqrt{2\xi}}$, ξ - the correlation length, $B_{BA1} = \frac{B_{B1} - B_{A1}}{N_l}$, $B_{BA2} = \frac{B_{B2} - B_{A2}}{N_l}$, $A = A(\xi)$ - the constant depending on parameters of the critical point of the given solution, and λ - the constant, whose values are determined from the so-called condition of isoperimetrism - the constancy of the number of particles in the system. It is worth noting that the imposition of this additional condition on the solution of Eq. (15) is related to the necessity to set the chemical

potential of a homogeneous system. The solution of Eq. (15) is as follows:

$$\begin{aligned} \Delta x(z) = & -A(B_{BA1} + B_{BA2}) e^{-kL} \frac{k}{\kappa} \frac{1}{k^2 - \kappa^2} \frac{\operatorname{sh}kL}{\operatorname{sh}\kappa L} \operatorname{ch}\kappa z - \\ & -A(B_{BA1} - B_{BA2}) e^{-kL} \frac{k}{\kappa} \frac{1}{k^2 - \kappa^2} \frac{\operatorname{ch}kL}{\operatorname{ch}\kappa L} \operatorname{sh}\kappa z + \\ & +A(B_{BA1} + B_{BA2}) e^{-kL} \frac{1}{k^2 - \kappa^2} \operatorname{ch}kz + \\ & +A(B_{BA1} - B_{BA2}) e^{-kL} \frac{1}{k^2 - \kappa^2} \operatorname{sh}kz + \\ & +A(B_{BA1} + B_{BA2}) e^{-kL} \frac{1}{k\kappa^2 L} \operatorname{sh}kL. \end{aligned} \quad (16)$$

In Figs. 1-4, we give the spatial distribution of the concentration of a model binary solution, $\Delta x(z)$, for various values of the correlation length ξ and various values of B_{BA1} and B_{BA2} .

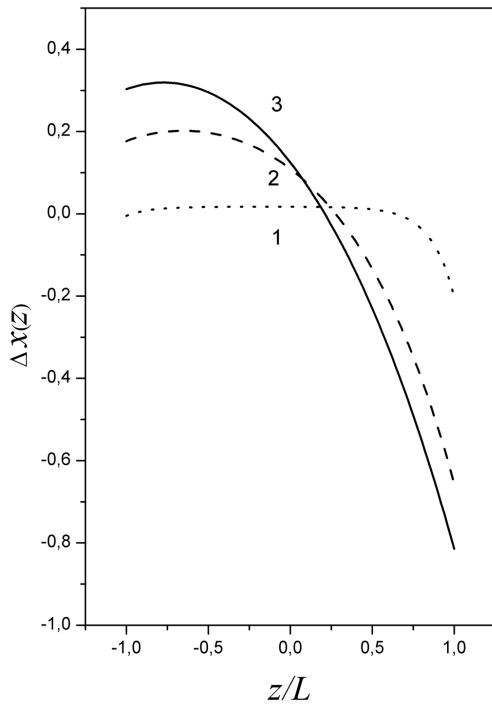


Fig. 3. Spatial dependence of the concentration $\Delta x(z)$ of a binary solution for various values of ξ : 1 - 10^{-6} , 2 - 5×10^{-6} , 3 - 10^{-5} m ($L = 10^{-5}$ m, $k^{-1} = 3 \times 10^{-10}$ m, $B_{BA1} = 10^{-24}$ J, $B_{BA2} = 0.1 \times 10^{-24}$)

It is seen from these figures that, far from the critical point, the profiles of the concentration of a fluid coincide with the internal solution of Eq. (1) which corresponds to the local approximation. That is, deviations of the concentration from the mean value occur only at distances of the order of the radius of action of surface forces. In the rest volume of the system, the concentration of a solution is equal to the mean value. But, while approaching the critical point, the singularly perturbed term plays the increasingly greater role, and a change of the concentration of a solution occurs in the greater part of the volume. That is, the characteristic distance, at which the significant changes of the density occur, is already the correlation length of the system ξ , rather than the radius of action of surface forces. In other words, in the consideration of specific features of the behavior of the system, the interaction of strongly developed fluctuations of the relevant parameter of order appears on the foreground, by leveling the details of the intermolecular interaction. Just this fact defines the universality of the behavior of systems of different nature near their critical points.

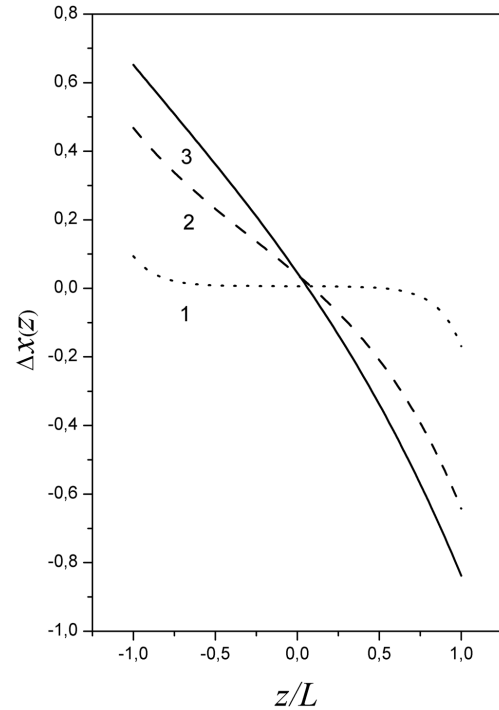


Fig. 4. Spatial dependence of the concentration $\Delta x(z)$ of a binary solution for various values of ξ : 1 - 10^{-6} , 2 - 5×10^{-6} , 3 - 10^{-5} m ($L = 10^{-5}$ m, $k^{-1} = 3 \times 10^{-10}$ m, $B_{BA1} = 10^{-24}$ J, $B_{BA2} = -0.5 \times 10^{-24}$)

While obtaining the above-presented results of calculations, we used a near-wall potential of the exponential form [see (14)]. But the usage of a near-wall potential of another type can only quantitatively change the result obtained without any qualitative effect on the presented conclusions.

As seen from these figures, depending on the ratio between the constants B_{A1} , B_{A2} , B_{B1} , and B_{B2} , the qualitatively different distributions of the concentration of a solution in the system are observed. In the case of a symmetric distribution of the near-wall potential, the distribution of the concentration also remains symmetric for any values of the correlation length. However, in the situation presented in Fig. 2, the distribution takes an essentially asymmetric shape, but only for sufficiently large values of the correlation length. In this case, the solution possesses the highest concentration (deviations reach 20%) at a distance of $\approx -0.3L$ from the center of the vessel, rather than at its middle. In the case presented in Fig. 2, the effective forces of repulsion (their amplitudes B_{BA1} and B_{BA2} differ from each other by one order) also act near both walls, but the concentration of the solution attains also the largest

value (the deviation is about 30%) near the wall with a less amplitude (at a distance of $\approx -0.9L$ from its center), rather than at the vessel center.

The obtained solution of the isoperimetric problem allows one to study a change of the thermodynamical properties of a substance in the near-wall layer as compared with the properties of a fluid in the bulk phase. The significant change of the concentration (by more than 30% inside the volume in the vicinity of the critical point) must lead to the corresponding phenomena which are observed experimentally even on the molecular level. In particular, the results of experiments on the transmission of slow neutrons [15] demonstrate a significant (more than 10%) dependence of the gravitational effect in a solution of ethane on the system sizes. The analysis of the results obtained in [15] indicates that the critical indices calculated by experimental data are not changed on the consideration of the correlation effects. But the amplitudes of scaling laws, which are calculated on the basis of experimental data, depend essentially on the chamber size. By using the method of nonlinear regression, we made approximation of the dependence of the ethane concentration on the vessel height and obtained that the decrease of the height by four times resulted in an increase in the amplitude D of the corresponding scaling law by more than four times.

Thus, the performed analysis implies that it is necessary to take the correlation contribution to the distribution of the density into account in the calculation of critical indices by the data on the scattering of neutrons and light and only then to consider the other terms of the equation of state of a substance.

As another example, we mention the essential change in the viscosities of water and aqueous solutions near the surface of quartz [16] and a change in the mobility of OH-groups in water in small volumes (pores of alumina) relative to the mobility in the bulk phase of water, which was observed by methods of infrared spectroscopy [17].

It is important to note that the above-considered behavior of a binary mixture coincides qualitatively with that of individual fluids in the vicinity of the “fluid–vapor” critical point [18].

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

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РОЗПОДІЛ КОМПОНЕНТІВ БІНАРНОГО РОЗЧИНУ
В ПРОСТОРОВО ОБМЕЖЕНІЙ СИСТЕМІ.
І. ПЛОСКА ПОРА З НЕСИМЕТРИЧНИМ
ПРИСТІНКОВИМ ПОТЕНЦІАЛОМ

Д.А. Гаврюшенко

Резюме

Для розрахунку концентрації бінарної суміші розглянуто ґратчасту модель рідини. Побудовано розклад потенціалу зовнішнього поля у функціональний ряд Тейлора, внаслідок чого було отримано розклад за прямими кореляційними функціями усіх порядків. Побудовано розв'язок одержаного диференціального рівняння для плоскопаралельної пори з несиметричним експоненціальним пристінковим потенціалом.