$$C_2 = \frac{B_{BA1} - B_{BA2}}{m_{0BA}gL}$$

Properties of liquid systems within nano-structure in the vicinity of critical point

Gavryushenko D.A. (1), Atamas N.A.(1), Taranyk G.P.(2)

(1) Taras Shevchenko National University of Kyiv, Acad. Glushkov Ave.6, Kyiv-03034, Ukraine.
e-mail: dg@univ.kiev.ua
(2) International European University, Akad. Glushkov Ave, 42B, Kyiv- 03187, Ukraine

Introduction

Quantitative description of a binary solution of a homogeneous fluid in a wide range of changes in thermodynamic parameters, including the range of possible critical points, can be carried out by methods of statistical physics and thermodynamics. The state of such a system can be fully determined by a set of intensive parameters, none of which describes the size of the system or the shape of the surface that limits it, and the total number of particles, where and is the number of particles of the variety and, accordingly. But it is obvious that any real system is always heterogeneous [1]. Traditional methods of describing the properties of an inhomogeneous system are to divide it into sufficiently thin layers between two equipotential surfaces and to represent the corresponding thermodynamic potentials (in particular, internal energy). This leads to the loss of information about the "collective" behavior of the system, which is extremely important in describing the properties of the system in the vicinity of the points of phase transformations of the second kind. To build a consistent thermodynamic theory that described the behavior of a one-component inhomogeneous system, a fundamental approach was previously proposed based on calculating the contribution from each layer between equipotential surfaces not to the corresponding thermodynamic potentials but to the Hamiltonian of the system. In this case can write:

$$u(\vec{r}) = \mu_0 - \mu(\vec{r}) + \Delta\mu_{cor}(\vec{r}) \tag{1}$$

where μ_{cor} is the contribution from the correlation effects for which the expression in the form of an infinite series was obtained.

The aim of this work is to generalize the formalism proposed in [2] in the case of a two-component solution under the action of an external field in nano-systems in a wide range of changes in thermodynamic parameters, including around the critical point of stratification.

Methods and Results

Chemical potential of inhomogeneous binary system

To describe the thermodynamic behavior of an inhomogeneous binary fluid in a bounded system, we use a lattice model of a liquid in which the molecules of the solution are in the lattice nodes, and the total number of particles coincides with the number of lattice nodes:

$$N = N' = N_A + N_B. \tag{2}$$

It is obvious that the absence of unoccupied lattice nodes (i.e. the absence of the "third component of the solution" - unoccupied by the particles of the lattice nodes - "holes") corresponds to the case of sufficiently compressed fluid. For convenience, we will further consider the external fields of such symmetry, the equipotential surfaces of which allow the introduction of an orthogonal coordinate system, and the layers of solution between the equipotential surfaces have the same thickness. The Hamiltonian of such a system is written in the form:

$$H = H'_0 + \sum_{i=1}^{M}\left(N_A^i u_A^i + N_B^i u_B^i\right) \tag{3}$$

where H'_0 is the part of the Hamiltonian that describes the interparticle interaction, N_A^i- the number of layers, and N_B^i- the number of particles of the variety "A" and "B", accordingly, in the layer with the number, u_A^i and u_B^i - the potential energy of the particles of the variety and in the external field in this layer.

Distribution of concentration in a non-ideal pore in the gravitational field near the critical point of stratification

Consider the case when the system along the axis of the gravitational field, the potential of which is given by the obvious expression:

$$u_A(z) = -m_{0A}gz,$$
$$u_B(z) = -m_{0B}gz, \tag{4}$$

where g is the acceleration of free fall, and near the walls there are forces of attraction or repulsion (the so-called non-ideal time), the potential of which is modeled by the following expression [3]:

$$u_A(z) = B_{A1}e^{-k\,L+z} + B_{A2}e^{-k\,L-z} =$$
$$= B_{A1} + B_{A2}\ e^{-kL}\operatorname{ch}kz + B_{A1} - B_{A2}\ e^{-kL}\operatorname{sh}kz,$$
$$u_B(z) = B_{B1}e^{-k\,L+z} + B_{B2}e^{-k\,L-z} =$$
$$= B_{B1} + B_{B2}\ e^{-kL}\operatorname{ch}kz + B_{B1} - B_{B2}\ e^{-kL}\operatorname{sh}kz,$$

$$\tag{5}$$

where B_{A1} (B_{B1}) and B_{A2} (B_{B2}) are the amplitudes of the wall potentials at the left and right pore boundaries for substances and respectively.

The construction of the solution of the obtained equation for nano-systems has certain features. In particular, the solution of this equation must be subject to the conditions of trans-versality, which in this case have the following obvious form:

$$\Delta x(z) = -A\,m_{0BA}gL\left\{\left\{\frac{1}{\kappa L\operatorname{ch}\kappa L} - \frac{z}{L}\right\} -\right.$$
$$-C_1\,e^{-kL}\frac{k}{\kappa}\frac{1}{k^2-\kappa^2}\frac{\operatorname{sh}kL}{\operatorname{sh}kL}\operatorname{ch}\kappa z - C_2\,e^{-kL}\frac{k}{\kappa}\frac{1}{k^2-\kappa^2}\frac{\operatorname{ch}kL}{\operatorname{ch}kL}\operatorname{sh}\kappa z +$$
$$+C_1\,e^{-kL}\frac{1}{k^2-\kappa^2}\operatorname{ch}kz + C_2\,e^{-kL}\frac{1}{k^2-\kappa^2}\operatorname{sh}kz +$$
$$\left.+C_2\left(B_{BA1}+B_{BA2}\right)e^{-kL}\frac{1}{k\kappa^2 L}\operatorname{sh}kL\right\}.$$

$$\tag{6}$$

dimensionless parameters $C_1 = \dfrac{B_{BA1}+B_{BA2}}{m_{0BA}gL}$ and $C_2 = \dfrac{B_{BA1}-B_{BA2}}{m_{0BA}gL}$ which characterize the ratio of the characteristic energy of the fastening potentials to the change in the energy of the gravitational field at altitude .

The obtained results indicate that the classical formula can be used only to describe the concentration distribution of inhomogeneous binary systems only in the case of external fields with small spatial gradients far from the critical point. But as we approach the critical point, the role of correlation terms increases, and therefore it is necessary to use the obtained expression.

Conclusions

It is shown:
1. in the vicinity of the critical point of stratification the presence of non-ideal walls leads to a change in the concentration profile of the mixture in the volume determined by the correlation radius of the corresponding homogeneous system.
2. in systems bounded by non-ideal walls, the correlation contribution leads both to a decrease in the gravitational effect and to its increase depending on the symmetry of the near-wall potential and the orientation of the system relative to the gravitational field.
3. It is established that the presence of walls of different nature causes significant deviations of the concentration from that found in the local approximation, which affects the values of the critical amplitudes calculated from the results of experimental studies.

References

[1].Bulavin L.A., Gavryushenko D.A., Sysoev V.M. Spatial distribution of components of a binary mixture in a bounded System // Ukr. Journ. of Phys. – 2007. – Vol. 52, No 10. – P. 934-938.
[2] Bulavin L.A., Gavryushenko D.A., Sysoev V.M. Thermodynamic potential density of a nonuniform system // Ukr. Journ. of Phys. – 2002. – Vol. 47, No 11. – P.1085-1088.
[3]Gavryushenko D.A., Starovoitov O.O. Nonlocal fluid density distribution in the vicinity of the critical point // J. Molecular Liquids. 2005. – Vol. 120, Issues 1-3. – Vol. 123-125.

Acknowledgements

Contact information

Gavryushenko D.A. (*e-mail: dg@univ.kiev.ua*)