BARODIFFUSION PHENOMENA IN THE CRITICAL REGION OF NANOSCALE LIQUID MIXTURES

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The critical behavior of isobaric-isothermal compressibility, the diffusion and barodiffusion coefficients, and the barodiffusion ratio for two-component liquid mixtures with a confined geometry has been studied. To analyze the specific features of barodiffusion phenomena, the scaling hypothesis for spatially confined systems and the hypothesis of "complete scaling" have been applied. The influence of the lower crossover dimension and spatial dispersion effects on the characteristics of barodiffusion processes in nanoscale liquid mixtures in their critical region has been studied.

1. Introduction

This work is aimed at describing the barodiffusion processes in nano- and meso-sized (at the border between the nano- and microscales) liquid systems in their critical region, by using the general ideas of thermodynamics and statistical physics of nonequilibrium processes [1–3], as well as the scaling theory for spatially confined systems (finite-size scaling) [4–6]. It is well known that the barodiffusion phenomena are governed by density gradients in simple liquids or concentration gradients in liquid mixtures and, in addition, by pressure gradients. The latter become important, in particular, in high-frequency ultrasonic fields which find a more and more application in applied medicine due to a wide introduction of novel precision methods of diagnostics and therapy [7, 8].

Earlier, we studied such characteristics of barodiffusion phenomena as the diffusion coefficient and the barodiffusion ratio for a one-component two-phase system in its critical region [9], as well as the influence of a pressure gradient on equilibrium membrane electrical potentials (the Nernst concentration potential and the Goldman–Hodgkin–Katz stationary potential) [10] and the $\mathrm{Na}^+ - \mathrm{K}^+$ activity of ATPhase. In this paper, the main attention is focused on the features of such quantities as the isobaric-isothermal compressibility, the diffusion and barodiffusion coefficients, and the barodiffusion ratio for nanoscale liquid mixtures. For this purpose, the corresponding scaling hypothesis [1–3, 11] and the hypothesis of "complete scaling" [12, 13] were applied to two-component liquids which are confined in small volumes characterized by different geometrical shapes, i.e. which differ from one another by the value of lower crossover dimension (LCD) d_{LCD}. The very concept of LCD arose in connection with the introduction of universality classes which turn out necessary for a regular study of critical phenomena and phase transitions of the second kind in spatially confined systems of different origin. As is known (see, e.g., work [14]), the class of universality includes objects which are characterized by identical (i) spatial dimensionality, (ii) order parameter dimensionality, (iii) type of intermolecular interaction (short- or long-range), and (iv) Hamiltonian symmetry. In the case of mesoscale systems, those four attributes should be appended by the similar geometrical shape or, in other words, the identical LCD which determines the spatial dimensionality of the system, in which its linear sizes along spatial confinement directions tend to monomolecular ones. Under such conditions, a sphere or a cube confined from all sides shrinks into a molecule, i.e. into a zero-dimensional object with $d_{\mathrm{LCD}} = 0$; a cylindrical pore into a monomolecular thread, i.e. a one-dimensional object with $d_{\mathrm{LCD}} = 1$; and a gap-like pore into a monomolecular plane, i.e. a two-dimensional object with $d_{\mathrm{LCD}} = 2$ [15, 16].

2. Barodiffusion Phenomena in Two-component Liquid Mixtures

Barodiffusion phenomena in binary mixtures are classed as vector transport processes. In accordance with the

Curie principle, the linear relation for a diffusion flux $\mathbf{J}_n$, which determines the number of particles that cross a unit area per unit time, has to contain the gradients of the chemical potential, $\boldsymbol{\nabla}\mu$, pressure, $\boldsymbol{\nabla}p$, and the temperature, $\boldsymbol{\nabla}T$ (here, we do not consider the gradient of the electric field potential and other thermodynamic forces), and looks like

$$\mathbf{J}_n = -a\boldsymbol{\nabla}\mu - b\boldsymbol{\nabla}p - c\boldsymbol{\nabla}T, \tag{1}$$

where a, b, and c are the Onsager kinetic coefficients. In such an approximation, the equation of state, $\mu = f(p,T,x)$, where x is the mixture concentration, allows the chemical potential gradient to be written in the form

$$\boldsymbol{\nabla}\mu = (\partial\mu/\partial x)_{p,T}\boldsymbol{\nabla}x + (\partial\mu/\partial p)_{T,x}\boldsymbol{\nabla}p + (\partial\mu/\partial T)_{p,x}\boldsymbol{\nabla}T. \tag{2}$$

Substituting Eq. (2) into Eq. (1), we obtain the following expression for the diffusion flux:

$$\mathbf{J}_n = -a(\partial\mu/\partial x)_{p,T}\boldsymbol{\nabla}x - [b + a(\partial\mu/\partial p)_{T,x}]\boldsymbol{\nabla}p -$$

$$-[c + a(\partial\mu/\partial T)_{p,x}]\boldsymbol{\nabla}T. \tag{3}$$

On the other hand, the same diffusion flux can be presented in terms of such kinetic properties of mixtures as the diffusion, D, barodiffusion, D_p, and thermal diffusion, D_T, coefficients and the barodiffusion, k_p, and thermodiffusion, k_T, ratios:

$$\mathbf{J}_n = -D\boldsymbol{\nabla}x - \frac{D_p}{p}\boldsymbol{\nabla}p - \frac{D_T}{T}\boldsymbol{\nabla}T =$$

$$= -D(\boldsymbol{\nabla}x + \frac{k_p}{p}\boldsymbol{\nabla}p + \frac{k_T}{T}\boldsymbol{\nabla}T). \tag{4}$$

A comparison between formulas (3) and (4) brings about the following relation between the kinetic properties of two-component liquid mixtures, on the one hand, and the Onsager coefficients and thermodynamic derivatives, on the other hand:

$$D = a(\partial\mu/\partial x)_{p,T}, \tag{5}$$

$$D_p = Dk_p = p[b + a(\partial\mu/\partial p)_{T,x}], \tag{6}$$

$$D_T = Dk_T = T[c + a(\partial\mu/\partial T)_{p,x}], \tag{7}$$

$$k_p = p\frac{b + a(\partial\mu/\partial p)_{T,x}}{a(\partial\mu/\partial x)_{p,T}}, \tag{8}$$

$$k_T = T\frac{c + a(\partial\mu/\partial T)_{p,x}}{a(\partial\mu/\partial x)_{p,T}}. \tag{9}$$

Below, we are interested only in barodiffusion phenomena supposing – additionally to the previous approximations – that the temperature of liquid mixture is constant, i.e. $\boldsymbol{\nabla}T = 0$. The features of thermodiffusion phenomena in systems with membranes and in external fields have been considered earlier (see, e.g., work [17]).

Another principal remark concerns the necessity to consider the relations nonlocal in space and time between the diffusion flux and the concentration and pressure gradients in binary liquid mixtures for the study of barodiffusion phenomena in the critical region to be consistent. In this work, the effects of spatial non-locality (spatial dispersion) were studied only in a close vicinity to the curve of liquid-vapor critical points – namely, in the fluctuation region – in order to get rid of non-physical results (the vanishing of the diffusion coefficient and the infinite growth of the barodiffusion ratio).

3. Scaling Hypothesis for Barodiffusion Phenomena in Binary Mixtures with a Confined Geometry

Let us consider a binary liquid mixture that is confined in a small enough volume. We assume that the inequality $L \leq \xi$, where L is the characteristic linear dimension of the system, and ξ is the correlation length of order parameter fluctuations, holds. In what follows, for definiteness, we concentrate our attention on the critical liquid-liquid state. It is known (see, e.g., work [1]) that, in this case, the two-component liquid mixture behaves like a binary alloy, and it can be described using the collection of independent variables "temperature T–pressure p–concentration x". It is expedient to select the Gibbs free energy per mole of a mixture, $G(T,p,x) = \mu_1 + \mu x$ (its differential equals $dG = -SdT + Vdp + \mu dx$), as the thermodynamic potential; here, μ_1 is the chemical potential of a pure solvent, and $\mu = \mu_2 - \mu_1 = (\partial G/\partial x)_{p,T}$ is the difference between the chemical potentials of a dissolved substance and a solvent. The order parameter for the system under consideration is a deviation of the concentration from its critical value, $\Delta x = (x - x_c)/x_c$. Concerning the choice of an external field h, it is known that, on the basis of the fluctuation theory of critical points, $h = \Delta p + (\partial p/\partial T)_\rho \tau$ for one-component liquids, where $\Delta p = (p - p_c)/p_c$ and $\tau = (T - T_c)/T_c$ are deviations of the pressure and the temperature, respectively, from their corresponding critical values. For two-component mixtures, the external field has to receive an additional contribution proportional to $\Delta\mu = (\mu - \mu_c)/\mu_c$, which, in accordance with the hypothesis of the so-called "complete scaling" [12, 13], allows the following relation to be written for the external field:

$$h = c_1\Delta p + c_2\tau + c_3\Delta\mu. \tag{10}$$

The researches carried out in works [4–6, 11] testify that, for mesoscale liquids within the same class of universality, their properties demonstrate identical dependences on the characteristic dimension L of the system and the thermodynamic parameters in a vicinity of the critical state. Such a situation is predicted by the hypothesis of scale invariance which can be formulated for the singular part of the Gibbs free energy for spatially confined binary mixtures as follows:

$$G_{\text{sing}} = L^{-d} f_G(\Delta x L^{1/\nu}, h L^{\beta\delta/\nu}). \tag{11}$$

Here, the critical indices of a liquid mixture, which can be classed to the universality class of Ising-like systems with the spatial dimensionality $d = 3$, take the values $\beta = 0.325$, $\delta = 4.815$, and $\nu = 0.625$. The asymptotics of the scaling function $f_G(y, z)$, which satisfy the conditions $f_G(y \to \infty) \sim y^{\beta(\delta+1)}$ and $f_G(z \to \infty) \sim z^{1+1/\delta}$, ensure the passage to the limit from spatially confined binary mixtures to unconfined systems in the sense of the inequality $L \gg \xi$, because, on the basis of scaling hypothesis (11), we have $G_{\text{sing}} \sim \Delta x^{\delta+1} \sim h^{(\delta+1)/\delta}$ in this case.

Below, the external field h which is defined by formula (10) is associated, as a rule, with the pressure variation $h \approx \Delta p$, provided that the inequality $\triangle p \gg (c_2\tau + c_3\Delta\mu)/c_1$ is satisfied. In addition, in order to study the barodiffusion properties of liquid mixtures in more details, we use the following result obtained in work [16] for the temperature variable $\tau(S, \xi^*)$ in spatially confined systems,

$$\tau(S, \xi^*) = (G/S)^{1/\nu} + [1 + (G/S)^{1/\nu}](1/\xi^*)^{1/\nu}\text{sign}\tau.$$

We now write similar expressions for the pressure and order parameter variations (the latter are deviations of the concentration from its critical value) in a liquid mixture:

$$\Delta p(S, \xi^*) = (G/S)^{\beta\delta/\nu} +$$

$$+[1 + (G/S)^{\beta\delta/\nu}](1/\xi^*)^{\beta\delta/\nu}\text{sign}\Delta p, \tag{12}$$

$$\Delta x(S, \xi^*) = (G/S)^{\beta/\nu} +$$

$$+[1 + (G/S)^{\beta/\nu}](1/\xi^*)^{\beta/\nu}\text{sign}\Delta x. \tag{13}$$

In the formulas for $\tau(S, \xi^*)$, $\Delta p(S, \xi^*)$, and $\Delta x(S, \xi^*)$, the following notations are used: G is a factor that characterizes the geometrical shape of a studied liquid mixture ($G = \pi$ for a plane-parallel interlayer, and $G = \mu_1^*$ for a cylindrical specimen, where $\mu_1^* \approx 2.4048$ is the first zero of the Bessel function), $S = L/\xi_0$ is the number of monomolecular layers along the direction of spatial confinement ($L = H$ for a plane-parallel interlayer with the thickness H, and $L = d$ for a cylindrical pore with diameter d), $\xi^* = \xi/\xi_0$ is the dimensionless correlation length, and ξ_0 is its amplitude which is of the atomic (molecular) dimension for short-range intermolecular potentials in low-molecular liquids, namely, $\xi_0 \approx (0.1 \div 0.3)$ nm.

Expressions (12) and (13) allow various limiting cases to be analyzed, namely, (i) the case of mesoscale liquids where $S \leq \xi^*$, so that the first term, which depends on the linear dimensions of the system, plays the dominant role; and (ii) the case of macrosystems, when the inverse inequality $S \gg \xi^*$ takes place, and the dominating role belongs to the term which includes the correlation length ξ^* depending on the thermodynamic variables reckoned from the critical point. In particular, for large systems ($L \gg \xi$), formulas (12) and (13) yield the following known expressions for the correlation length [18]: $\xi \sim \Delta p^{-\nu/\beta\delta}$ and $\xi \sim \Delta x^{-\nu/\beta}$.

Now, let us consider the critical behavior of various multipliers and terms in formulas (5), (6), and (8) which describe the diffusion, D, and barodiffusion, D_p, coefficients and the barodiffusion ratio, respectively, for a binary mixture in three different regions, where a liquid-liquid system approaches the critical state, i.e. the fluctuation, dynamic crossover, and regular regions.

3.1. Fluctuation region

The term "fluctuation region" is used below in two senses: (i) as a dynamic fluctuation region, where singular contributions to the Onsager kinetic coefficients dominate over their regular parts ($a_s \gg a_0$, $b_s \gg b_0$), in accordance with the inequalities

$$0 \leq \tau < \tau_D, \quad 0 \leq \Delta p < \Delta p_D, \quad 0 \leq \Delta x < \Delta x_D, \tag{14}$$

where, $\tau_D = (T_D - T_c)/T_c$, $\Delta p_D = (p_D - p_c)/p_c$, $\Delta x_D = (x_D - x_c)/x_c$, and the quantities T_D, p_D, and x_D characterize the temperature, pressure, and concentration, respectively, of the dynamic crossover, at which $a_s \approx a_0$ and $b_s \approx b_0$ [10, 20]; and (ii) as a region in an immediate proximity to critical points or phase transitions of the second kind, where, in accordance with the Ginzburg–Levanyuk criterion [19], the role of fluctuation effects becomes crucial, if the following inequalities for the thermodynamic variables τ, Δp, Δx, and the Ginzburg number Gi are satisfied:

$$0 \le \tau \ll Gi, \quad 0 \le \Delta p \ll Gi^{1/\beta\delta}, \quad 0 \le \Delta x \ll Gi^{1/\beta}. \tag{15}$$

3.1.1. Onsager kinetic coefficients

The dynamic theory of scale invariance (dynamic scaling) [21] predicts that the singular parts of the Onsager kinetic coefficients a_s and b_s behave as the correlation length ξ of order parameter fluctuations in the system, so that

$$a_s/a_0 \approx b_s/b_0 \approx \xi/\xi_0 =$$

$$= \tau^{-\nu} \sim \Delta p(S,\xi^*)^{-\nu/\beta\delta} \sim \Delta x(S,\xi^*)^{-\nu/\beta} \tag{16}$$

with the power exponents $\nu = 0.625$, $\nu/\beta\delta = 0.399$, and $\nu/\beta = 1.923$. In formula (16), a_0 and b_0 stand for the amplitudes of the Onsager kinetic coefficients which coincide with the values of corresponding coefficients in the regular region, where $\tau \approx \Delta p \approx \Delta x \approx 1$.

3.1.2. Isobaric-isothermal compressibility

Formulas (5) and (8) include the derivative $(\partial\mu/\partial x)_{p,T}$ which determines the inverse isobaric-isothermal compressibility of two-component liquid mixture, $\chi_{p,T} \sim (\partial x/\partial\mu)_{p,T}$. As is known from the statistical theory of condensed systems [22], the fluctuation-dissipation theorems (in the equilibrium case, the term "fluctuation theorems" would be more precise), couple the liquid compressibility (in the general case, the system susceptibility) and the pair correlation functions for order parameter fluctuations. The "compressibility integral" $\rho kT\beta_T = \int G_2(r)d\vec{r}$, where $\beta_T = -V^{-1}(\partial V/\partial p)_T$ is the isothermal compressibility, and $G_2 = \langle\phi(\vec{r}_1)\phi(\vec{r}_2)\rangle$ is the pair correlation function of the order parameter, i.e. a deviation $\phi = \Delta\rho = (\rho-\rho_c)/\rho_c$ of the density from its critical value at two points $\vec{r}_1$ and $\vec{r}_2$ ($|\vec{r}_1-\vec{r}_2| = r$), can serve as an example of such relations for one-component liquids. Analogously, the derivative $(\partial x/\partial\mu)_{p,T}$ determines the features in a critical behavior of the pair correlation function $G_2 = \langle\Delta x(\vec{r}_1)\Delta x(\vec{r}_2)\rangle$ for concentration fluctuations, in accordance with the analog of the fluctuation theorem for a two-component liquid mixture near its critical liquid–liquid state:

$$(\partial x/\partial\mu)_{p,T} \sim \int\langle\Delta x(0)\Delta x(\mathbf{r})\rangle d\mathbf{r} =$$

$$= \Delta p^{-\gamma/\beta\delta} f_\chi(\Delta x L^{1/\nu}, hL^{\beta\delta/\nu}). \tag{17}$$

The pressure dependence of the susceptibility $\chi \sim (\partial x/\partial\mu)_{p,T}$ in expression (17) is a direct consequence of the scaling hypothesis (11), from which we have

$$\chi \sim (\partial^2 G_{\rm sing}/\partial z^2)_y(\partial z/\partial h)^2 \sim$$

$$\sim L^{-d+2\beta\delta/\nu} \sim L^{-\gamma/\nu} f_\chi(y,z) \sim \Delta p^{-\gamma/\beta\delta} f_\chi(y,z) \tag{18}$$

with regard for the identities $d\nu = 2-\alpha$, $\beta\delta = \beta+\gamma$, and $\alpha+2\beta+\gamma = 2$ (here, $\alpha = 0.110$) between the critical indices and the relation $f_\chi(y,z) \sim (\partial^2 f_G(y,z)/\partial z^2)_y$ between the scaling functions of the singular parts of the Gibbs free energy and the susceptibility.

In formula (18), we used the connection between the power-law dependence of an arbitrary physical quantity A on the system size L, $A(L) \sim L^n$, and the corresponding power-law dependence of the same quantity on the pressure, $A(\Delta p) \sim \Delta p^m$. Since the scale dimensionalities of the linear size L and the correlation length ξ coincide, we obtain $L \sim \xi \sim \Delta p^{-\nu/\beta\delta}$. Therefore, the following relation between the exponents n and m takes place:

$$m = (-\nu/\beta\delta)n. \tag{19}$$

It is worth to note that, owing to the Legendre transformation from the Gibbs free energy G to the Helmholtz free energy $F = G - pV$, whose differential equals $dF = -SdT - pdV + \mu dx$, the isochorical-isothermal susceptibility $(\partial x/\partial\mu)_{V,T}$ emerges instead of the isobaric-isothermal one $(\partial x/\partial\mu)_{p,T}$. The new susceptibility is characterized by a "weak" divergence $(\partial x/\partial\mu)_{p,T} \sim \tau^{-\gamma}$ rather than the "strong" one $(\partial x/\partial\mu)_{V,T} \sim \tau^{-\alpha}$ at $T \to T_c$, which must ultimately manifest itself in the critical behavior of the diffusion coefficient and the barodiffusion ratio.

3.1.3. Diffusion coefficient

In accordance with formulas (5), (16), (17), and (19), the diffusion coefficient for a binary liquid mixture in the fluctuation region equals

$$D = a_s(\partial\mu/\partial x)_{p,T} =$$

$$= L^{1-\gamma/\nu} f_D^{(1)}(y,z) \sim \Delta p(S,\xi^*)^{(\gamma-\nu)/\beta\delta} f_D^{(2)}(y,z). \tag{20}$$

Formula (20) predicts that the diffusion coefficient tends to zero following the power law $D \sim$

$\Delta p(S,\xi^*)^{0.393}$, when approaching the critical state of a binary mixture. An experimental confirmation of this result is a reduction of the central line width in the spectrum of the Rayleigh scattering of light. Of course, the vanishing of the diffusion coefficient and the narrowing of the Rayleigh central line width Γ_c down to zero are unphysical and require that the effects of spatial dispersion be taken into account (see, e.g., work [23]).

3.1.4. Barodiffusion ratio

On the basis of formula (8), one may assert that the barodiffusion ratio is characterized by the divergence

$$k_p = k_p^0 \Delta p(S,\xi^*)^{-\gamma/\beta\delta} f_k(y,z) \tag{21}$$

which coincides completely with the divergence of the isobaric-isothermal susceptibility $(\partial\mu/\partial x)_{p,T}$. As for other factors in formula (8), the singularities of the Onsager kinetic coefficients a_s and b_s are mutually compensated, so that the derivative $(\partial\mu/\partial p)_{T,x}$ has no divergence in the critical state of a binary mixture, because it is a derivative of one field variable, μ, with respect to the other field variable, p. In expression (21), the quantity $k_p^0 = p[b/a + (\partial\mu/\partial p)^0_{T,x}]/(\partial\mu/\partial x)^0_{T,p}$ stands for the barodiffusion ratio amplitude which remains almost constant, when approaching the critical state.

3.1.5. Barodiffusion coefficient

In view of all that was said above about the singular parts of the Onsager kinetic coefficients a_s and b_s and the absence of a divergence in the derivative $(\partial\mu/\partial p)_{T,x}$, it becomes clear that, according to formula (6), the barodiffusion coefficient D_p has the same singularity as the correlation length has, i.e.

$$D_p \sim \xi = \xi_o \Delta p(S,\xi^*)^{-\nu/\beta\delta} f_\xi(y,z), \tag{22}$$

and its maximal value, while approaching the critical state, cannot exceed the largest linear size of the geometrical volume occupied by a liquid mixture.

It should be noted that a reduction of the diffusion coefficient and the simultaneous growth of the barodiffusion coefficient, when approaching the critical state of a binary mixture, have obtained the indirect experimental confirmation in work [24], where the thermodiffusion phenomena of a similar nature in macroscopic liquid mixtures were studied [see formulas (6) and (7)].

3.2. Dynamic crossover region

In contrast to the fluctuation region, in the dynamic crossover one, where the inequalities

$$\tau_D < \tau < Gi, \quad \Delta p_D < \Delta p < Gi^{1/\beta\delta},$$

$$\Delta x_D < \Delta x < Gi^{1/\beta}, \tag{23}$$

are satisfied, the singular and regular contributions to the Onsager kinetic coefficients are of the same order of magnitude, i.e. $a_s \approx a_0$ and $b_s \approx b_0$. In this case, the features in the critical behavior of such barodiffusion properties of liquid mixtures as the diffusion coefficient D and the barodiffusion ratio k_p are determined by the derivative $(\partial\mu/\partial x)_{p,T}$ only, because the other quantities in formulas (5), (6), and (8) can be regarded as approximate constants: $a = a_s + a_0 \approx 2a_0$, $b = b_s + b_0 \approx 2b_0$, and $D_p \approx 2p[a_0 + b_0(\partial\mu/\partial p)^0_{T,x}]$. So, instead of formula (20), we now have the following expression for the diffusion coefficient:

$$D = 2a_0(\partial\mu/\partial x)_{p,T} =$$

$$= L^{-\gamma/\nu} f_D^{(3)}(y,z) \sim \Delta p(S,\xi^*)^{\gamma/\beta\delta} f_D^{(4)}(y,z), \tag{24}$$

whereas the barodiffusion ratio and the barodiffusion coefficient preserve the same power-law dependences on thermodynamic variables as in formulas (21) and (22), respectively.

3.3. Regular region

Fluctuation effects cease to play a substantial role in the regular region. Let the following conditions for the thermodynamic variables and the Ginzburg number be satisfied:

$$Gi \ll \tau \le 1, \quad Gi^{1/\beta\delta} \ll \Delta p \le 1,$$

$$Gi^{1/\beta} \ll \Delta x \le 1. \tag{25}$$

Then the corresponding critical indices in the formulas for the diffusion coefficient D and the barodiffusion ratio k_p must accept the values characteristic of the Landau mean-field theory, namely, $\beta = \nu = 1/2$, $\gamma = 1$, and $\delta = 3$. As a result, we obtain the expressions

$$D = D_0 L^{-2} f_D^{(5)}(y,z) \sim \Delta p^{2/3}(S,\xi^*) f_D^{(6)}(y,z), \tag{26}$$

$$k_p = k_p^0 L^2 f_k^{(1)}(y,z) \sim \Delta p^{-2/3}(S,\xi^*) f_k^{(2)}(y,z), \tag{27}$$

where the arguments of the scaling functions are $y = \Delta x L^2$ and $z = \Delta p L^3$.

4. Hypothesis of "complete scaling" and specificity of barodiffusion phenomena in liquid mixtures

Let us consider some consequences of the "complete scaling" hypothesis used to study the barodiffusion phenomena in nano- and mesoscale liquids.

First of all, it is necessary to emphasize the principal result of the use of the "complete scaling" hypothesis (see details in works [12,13]). Namely, for two-component liquid mixtures, there are three – generally speaking, different – susceptibilities χ_1, χ_2, and χ_3 characterized by "strong", "weak", and "intermediate"divergences, respectively, in the critical region, provided that $\Delta p \to 0$. We have

$$\chi_1 \sim \Delta p(S,\xi^*)^{-\gamma/\beta\delta}, \quad \chi_2 \sim \Delta p(S,\xi^*)^{-\alpha/\beta\delta},$$

$$\chi_3 \sim \Delta p(S,\xi^*)^{-(1-\beta)/\beta\delta}, \tag{28}$$

where the exponents are $\gamma/\beta\delta = 0.792$, $\alpha/\beta\delta = 0.070$, and $(1-\beta)/\beta\delta = 0.431$. Note that, since the critical indices satisfy the identity $\alpha + 2\beta + \gamma = 2$, the third index exactly equals half the sum of the first and second indices.

As was marked above in connection with formula (17), the "strong" divergence of the susceptibility χ_1 is associated with a specific critical behavior of the correlation function $\langle \Delta x(\mathbf{r}_1)\Delta x(\mathbf{r}_2)\rangle$ for fluctuations of the key order parameter for a liquid mixture, i.e. concentration fluctuations. Concerning the "weak" divergence of the susceptibility χ_2, it is connected with the correlator of thermal (or energy) fluctuations $\langle \Delta E(\mathbf{r}_1)\Delta E(\mathbf{r}_2)\rangle$, and the isochoric heat capacity of the system is responsible for the correlator critical behavior. At last, the intermediate divergence of the susceptibility χ_3 is caused by the pair correlation function $\langle \Delta x(r_1)\Delta E(\mathbf{r}_2)\rangle$ of fluctuations of both order parameters – the concentration and the energy. This function is not equal to zero for liquid systems, unlike that for magnets, for which, owing to a different symmetry nature, this correlator is absent [19].

According to formulas (28), the specific critical behavior of susceptibilities of a binary liquid mixture can manifest itself in the spectra of molecular light scattering, in particular, in experimental studies of the pressure effect on the width Γ_c of the Rayleigh central line.

A direct consequence of the "complete scaling" hypothesis related to different types of susceptibilities in the two-component mixture is the emergence of three diffusion coefficients, each of which demonstrates a different critical behavior in the fluctuation region, namely,

$$D_1 = a_s\chi_1^{-1} \sim \Delta p(S,\xi^*)^{(\gamma-\nu)/\beta\delta} \sim \Delta p(S,\xi^*)^{0.393}, \tag{29}$$

$$D_2 = a_s\chi_2^{-1} \sim \Delta p(S,\xi^*)^{(\alpha-\nu)/\beta\delta} \sim \Delta p(S,\xi^*)^{-0.329}, \tag{30}$$

$$D_3 = a_s\chi_3^{-1} \sim \Delta p(S,\xi^*)^{(1-\beta-\nu)/\beta\delta} \sim \Delta p(S,\xi^*)^{0.032}. \tag{31}$$

The results obtained allow the following conclusions about the diffusion coefficients of a liquid mixture to be formulated.

According to formula (29) the diffusion coefficient D_1 decreases with the approach to the critical state of a mixture as approximately the reciprocal of the correlation length, because, on the basis of the identity $\gamma = (2-\eta)\nu$ and owing to the small numerical value $\eta \approx 0.037$ of the critical index for the anomalous dimensionality of the pair correlation function of order parameter fluctuations, we have $\gamma - \nu = (1-\eta)\nu \approx \nu$. In other words, the diffusion coefficient D_1 is isomorphic to the diffusion coefficient D, which is given by formula (20), according to the scaling hypothesis (11) for the singular part of the Gibbs free energy.

In contrast to D_1, the second diffusion coefficient D_2, according to formula (30), grows, rather than diminishes, while approaching the critical state, and its divergence $D_2 \sim \Delta p(S,\xi^*)^{-0.33}$ (the spatial dispersion effects are not taken into account) turns out almost the same as that of the correlation length, $\xi \sim \Delta p(S,\xi^*)^{-0.40}$. It can be stated that the diffusion coefficient D_2 is isomorphic to the diffusion coefficient $D = a_s(\partial\mu/\partial x)_{V,T}$, which corresponds to the scaling hypothesis for the singular part of the Helmholtz free energy.

The third diffusion coefficient D_3, which is connected with the reciprocal value of intermediate susceptibility, remains almost constant and behaves itself as a "weak zero" owing to a very small positive value of the power exponent in formula (31).

In the dynamic crossover region, the hypothesis of "complete scaling" gives rise to three different types of the diffusion coefficient, but the power exponents in formulas (29)–(31) change. Now, they do not, naturally, contain the critical index ν, because the Onsager kinetic coefficient can be considered as having no divergence in this region and being equal $a \approx 2a_0$, where a_0 is its regular part. As a consequence, all the three diffusion coefficients have to decrease with the approach to the critical state following the dependences

$$D_1 \sim \Delta p(S,\xi^*)^{\gamma/\beta\delta} \sim \Delta p(S,\xi^*)^{0.792}, \tag{32}$$

$$D_2 \sim \Delta p(S,\xi^*)^{\alpha/\beta\delta} \sim \Delta p(S,\xi^*)^{0.070}, \tag{33}$$

$$D_3 \sim \Delta p(S,\xi^*)^{(1-\beta)/\beta\delta} \sim \Delta p(S,\xi^*)^{0.431}. \qquad (34)$$

At last, in the regular region, where conditions (25) are satisfied, the application of the Landau mean-field theory brings about the following results for the diffusion coefficients:

$$D_1 \sim \Delta p(S,\xi^*)^{2/3}, \quad D_2 = \text{const},$$

$$D_3 \sim \sqrt{\Delta p(S,\xi^*)}. \qquad (35)$$

The constant value of D_2 stems from the fact that the critical index of heat capacity $\alpha = 0$ in the Landau theory.

A direct consequence of the hypothesis of "complete scaling" is also a modification of the critical behavior of the barodiffusion ratio k which is completely governed by the features of three different types of susceptibilities χ_1, χ_2, and χ_3, in accordance with those expressions that remain valid in both the fluctuation and dynamic crossover regions:

$$k_{p1} = k^0_{p1}\Delta p(S,\xi^*)^{-\gamma/\beta\delta} \sim \Delta p(S,\xi^*)^{-0.792} \sim \chi_1, \qquad (36)$$

$$k_{p2} = k^0_{p2}\Delta p(S,\xi^*)^{-\alpha/\beta\delta} \sim \Delta p(S,\xi^*)^{-0.070} \sim \chi_2, \qquad (37)$$

$$k_{p3} = k^0_{p3}\Delta p(S,\xi^*)^{-(1-\beta)/\beta\delta} \sim \Delta p(S,\xi^*)^{-0.431} \sim \chi_3. \qquad (38)$$

In the regular region, the first and third barodiffusion ratios grow with the approach to the critical state under conditions (25) according to the formulas $k_{p1} = k^0_{p1}\Delta p(S,\xi^*)^{-2/3}$ and $k_{p3} = k^0_{p3}\Delta p(S,\xi^*)^{-1/3}$, whereas the second barodiffusion ratio $k_{p2} = \text{const}$ owing to the zero value of the critical index α.

Comparing formulas (36)–(38) and (28), it is easy to see that the dimensionless values of barodiffusion ratios and susceptibilities are equal in pairs, namely, $k^*_{p1} = \chi^*_1$, $k^*_{p2} = \chi^*_2$, and $k^*_{p3} = \chi^*_3$, where $k^*_{pi} = k_{pi}/k^0_{pi}$ and $\chi^*_i = \chi_i/\chi^0_i$.

5. Influence of the low-crossover dimensionality on barodiffusion properties of binary mixtures

Let us consider an issue concerning the influence of the low crossover dimension on a shift of the critical parameters: the critical temperature T_c, the critical pressure p_c, and the critical concentration x_c. Of course, in the case of spatially confined systems, it is not a matter of those critical parameters, for which the singular behavior of physical properties – an unlimited growth (without taking spatial dispersion effects into account) of the correlation length or the susceptibility, the vanishing of the diffusion coefficients or the temperature conductivities, and so forth – takes place. Under the term "critical parameters of a system with confined geometry", we will understand the values of the temperature, $T_m(L)$, pressure, $p_m(L)$, and concentration, $x_m(L)$, at which the finite extrema (maxima or minima) of indicated physical properties are observed.

The critical parameters of confined and unconfined pure liquids are related to one another by the following formulas:

$$T_m(L) = T_c[1 + (G/S)^{1/\nu}]^{-1}, \qquad (39)$$

$$p_m(L) = p_c[1 + (G/S)^{\beta\delta/\nu}]^{-1}, \qquad (40)$$

$$x_m(L) = x_c[1 + (G/S)^{\beta/\nu}]^{-1}. \qquad (41)$$

Formulas (39)–(41) can be easily checked with respect to the passage to the limit of a bulk liquid mixture. Really, at $S \to \infty$, we obtain $T_m(L) \to T_c$, $p_m(L) \to p_c$, and $x_m(L) \to x_c$.

For the sake of definiteness, let us examine the liquid system "ethane C_2H_6–benzene C_6H_6" with 39.2 mol% of ethane. For large liquid volumes, the experimental data [25] give the following values for the critical pressures of pure components: $p_1 = 4.883$ Mpa for ethane and $p_2 = 4.893$ MPa for benzene, and the critical pressure $p_{\rm sum} = 8.489$ MPa for the given mixture with $x = 0.392$. The dependence $p_{\rm sum}(x)$ of the critical pressure for an ethane-benzene mixture on the concentration is essentially nonlinear. To approximate it, let us use the formula

$$p_{\rm sum}(x) = 4.883 + 15.144x - 15.134x^2 \ \ (10^6\ \text{Pa}) \qquad (42)$$

which satisfies all indicated experimental data. From this expression, it follows that the maximal pressure in the bulk phase of this mixture, $p_{\max} = 8.671$ MPa, is attained at the concentration $x = 0.5$. In Fig. 1, solid curve a represents the dependence of the critical pressure for the binary mixture ethane-benzene, which can be regarded as unconfined in the sense of the inequality $L \gg \xi$, on the ethane concentration.

To elucidate the dependence of physical properties of a nanoscale binary mixture ethane-benzene with a given concentration on the LCD, let us assume that the

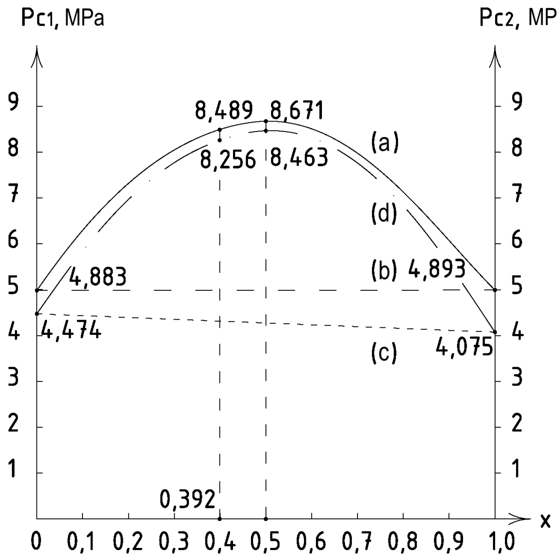

Fig. 1. Dependences of the critical pressure for a binary mixture ethane-benzene on the concentration

mixture occupies two volumes different by geometrical shape: 1) a plane-parallel gap (a gap-like pore) with $d_{\mathrm{LCD}} = 2$ and 2) a cylindrical pore with $d_{\mathrm{LCD}} = 1$. Let their maximal linear dimensions along the direction of spatial confinement – i.e. along the thickness H of the gap or the diameter d of the cylinder – be identical and equal to 4.75 nm. To calculate the geometrical factors S, let us estimate the amplitudes of the correlation lengths ξ_{0x} using the approximate formula

$$\xi_{0x} = \sqrt[3]{\frac{M_x}{M}}\xi_0, \tag{43}$$

where ξ_0 is the known amplitude of the correlation length for a substance with molar mass M (e.g., for water, $\xi_0 = 1.6 \times 10^{-10}$ m and $M = 18 \times 10^{-3}$ kg/mol). Then, on the basis of formula (43), the unknown amplitudes of the correlation length ξ_{0x} for C_2H_6 with the molar mass $M_x = 30 \times 10^{-3}$ kg/mol and for C_6H_6 with the molar mass $M_x = 78 \times 10^{-3}$ kg/mol equal $\xi_{01} = 1.9 \times 10^{-10}$ m and $\xi_{02} = 2.6 \times 10^{-10}$ m, respectively.

Let us calculate a variation of the critical pressure in nanoscale pores, using formula (40) and the values presented above. It should be noted that the geometrical factors S, which determine the number of monomolecular layers in the direction of spatial confinement of those objects, are different. Really, a gap with the width $H = 4.75$ nm contains $S_1 = H/2\xi_0$ such parallel monomolecular layers, whereas a cylindrical pore with the diameter $d = 4.75$ nm includes $S_2 = R/2\xi_0$ coaxial cylindrical layers, where R is the cylinder radius. With regard for these values of geometrical factors S_1 and S_2, as well as the values of constants $G_1 = \pi$ and $G_2 = \mu_1^* = 2.4048$, we obtain the critical pressures of pure components p_{m1} and p_{m2} on the basis of formula (40): $p_{m1} = 4.734$ MPa and $p_{m2} = 4.577$ MPa for a gap-like pore ($d_{\mathrm{LCD}} = 2$), and $p_{m1} = 4.474$ MPa and $p_{m2} = 4.075$ MPa for a cylindrical pore ($d_{\mathrm{LCD}} = 1$).

Therefore, the critical pressure in nanoscale liquids varies towards lower values, because, for ethane, $(p_m - p_c)_1 = -0.149$ MPa in the gap and $(p_m - p_c)_2 = -0.409$ MPa in the cylinder, and, for benzene, $(p_m - p_c)_1 = -0.316$ MPa in the gap and $(p_m - p_c)_2 = -0.818$ MPa in the cylinder. Moreover, with a reduction of the low crossover dimension d_{LCD}, the difference $|p_m - p_c|$ grows by absolute value, which is qualitatively confirmed by theoretical calculations of the temperature shifts $|T_m - T_c|$ which were executed for the heat capacity [15] and the diffusion coefficient [16] of water.

Now, let us calculate a variation of the critical pressure in the studied binary mixture, when it is located in nanoscale pores. In Fig. 1, line *b* depicts the result of the linear approximation

$$p_c(x) = xp_{c1} + (1 - x)p_{c2} \tag{44}$$

for the concentration dependence of the critical pressure in a mixture in the unconfined (bulk) phase, whereas line *c* characterizes the result of using the linear approximation

$$p_m(L) = xp_{c1}/[1 + (\mu_1^*\xi_{01}/R)^{\beta\delta/\nu}] +$$

$$+(1 - x)p_{c2}/[1 + (\mu_1^*\xi_{01}/R)^{\beta\delta/\nu}] \tag{45}$$

for a cylindrical pore with the diameter $d = 4.75$ nm. A comparison between the results obtained using formula (42), which is based on experimental data [25], and the linear approximation (44) shows that the non-linear effects in the dependence $p_c(x)$ cannot be neglected in any case (see curve *a* and straight line *b*). This means, in particular, that approximation (45) is not valid in the case of an ethane-benzene mixture with a confined geometry, but it might give quite good results only in the case of similar components in the mixture.

In order to obtain correct results for the concentration dependence of the critical pressure in nanoscale binary mixtures, let us apply the following technique. Using experimental data on $p_c(x)$ for a mixture in the bulk phase, let us determine the critical pressure shifts at the change to the confined geometry by using formula (40) and the linear approximation for the effective amplitude of the correlation length in the mixture,

$$\xi_{0\text{sum}} = x\xi_{01} + (1-x)\xi_{02}. \tag{46}$$

For the mixture 39.2% C_2H_2–60.8% C_6H_6, we obtain $\xi_{0\text{sum}} = 2.375 \times 10^{-10}$ m, which corresponds to 10 average diameters or 20 correlation length amplitudes $\xi_{0\text{sum}}$ along the direction of the spatial confinement of a cylindrical pore with a diameter of 4.75 nm. The calculation of the critical pressure in such a liquid system brings about the value $p_m = 8.256$ MPa, i.e. the critical pressure variation at the given concentration is $p_m - p_c = -0.233$ MPa. In Fig. 1, curve d illustrates the concentration dependence of the critical pressure for the binary ethane-benzene mixture in a nanoscale cylindrical pore 2.375 nm in radius.

At last, consider the problem on the influence of LCD on the main properties of barodiffusion phenomena in binary mixtures: the diffusion coefficient and the barodiffusion ratio.

5.1.1. Diffusion coefficient

In Fig. 2, the dependences of the diffusion coefficient $D^* = D/D_0$ on the variable $\Delta p(S, \xi^*)$ are depicted. The solid curve corresponds to the diffusion coefficient in an unconfined (bulk) binary ethane-benzene mixture, for which the low crossover dimension coincides with the spatial one ($d_{\text{LCD}} = d = 3$). The dashed and dash-dotted curves illustrate the dependence D^* on the pressure $\Delta p(S, \xi^*)$ for a gap-like pore with $d_{\text{LCD}} = 2$ and a cylindrical pore with $d_{\text{LCD}} = 1$. While calculating D^*, we also took into account the asymmetry of the diffusion coefficient amplitude in the critical region and behind it, $D_0^- \neq D_0^+$, as was done in works [16, 28].

To evaluate the diffusion coefficient D^* at its minimum points $p_m(S, \xi^*)$ for various LCDs, let us determine, into which region – the fluctuation or dynamic crossover one – fall the values of $p_m(S, \xi^*)$ that correspond to the minimum of the diffusion coefficient D and the maxima of the barodiffusion coefficient D_p and the barodiffusion ratio k_p. It turns out that, for liquid mixtures with the Ginzburg number comparable with $Gi_{H_2O} \approx 0.3$ (see, e.g., work [26]), the relative changes of the critical pressure $|\Delta p_c| = |p_m - p_c| / p_c$, which equal 0.027 for cylindrical and 0.052 for gap-like pores, fall into the interval

$$|\Delta p_D| \ll |\Delta p_c| < Gi^{1/\beta\delta} \tag{47}$$

which characterizes the dynamic crossover region. In inequality (47), $Gi^{1/\beta\delta} \approx 0.46$, and the notation $|\Delta p_D| = |(p_D - p_c)| / p_c$ is used to designate the dynamic crossover pressure introduced in work [10], at which the singular and regular contributions to the Onsager kinetic coefficients become of the same order of magnitude. For liquids with a rather large Ginzburg number $Gi \approx 0.3$, the order of the dynamic crossover temperature is $|\Delta\tau_D| = |(T_D - T_c)| / T_c \approx 10^{-5}$; therefore, the dynamic crossover pressure is $|\Delta p|_D \approx |\tau|^{\beta\delta} \approx 10^{-7.8}$. This means that, for the examined liquid ethane-benzene mixture, the dynamic crossover occurs, provided that the pressure is $|p_D - p_c| \approx 10^{-7.8} p_c \approx 0.135$ Pa. This estimate confirms once more the conclusion of work [20] that the dynamic fluctuation region, where the inequalities $0 \le \tau < Gi$, $0 < \Delta p < Gi^{1/\beta\delta}$, and $0 \le \Delta x < Gi^{1/\beta}$ are satisfied and the singular parts of the Onsager kinetic coefficients considerably exceed their regular parts, is most likely inaccessible experimentally.

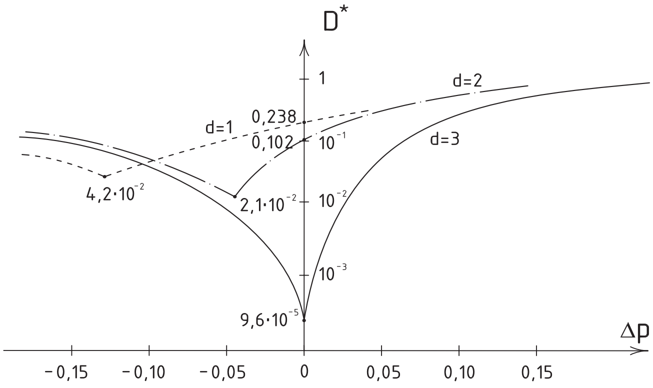

Fig. 2. Dependences of the diffusion coefficient $D^* = D/D_0$ on the pressure Δp taking the LCD and a spatial dispersion into account

That is why the calculations of the diffusion coefficient D^* were carried out by such a formula that is valid in the dynamic crossover region,

$$D^* = \{(G/S)^{\beta\delta/\nu} +$$

$$+[1 + (G/S)^{\beta\delta/\nu}](1/\xi^*)^{\beta\delta/\nu} \text{sign}\Delta p\}^{\gamma/\beta\delta} + D^*_{\min}, \tag{48}$$

where the diffusion coefficient at the critical point, $D^*_{\min} = D_{\min}/D_0$, is determined by a contribution of spatial dispersion effects. In the approximation that takes the relation between the order parameter and the viscous mode [27] into account, we obtain

$$D^*_{\min} = \frac{kTK_0(q\xi)}{6\pi\eta q^2 \xi^3 D_0}, \tag{49}$$

where η is the shear viscosity, and $K_0(u) = (3/4)[1 + u^2 + (u^3 - u^{-1}) \arctan u]$ is the Kawasaki function; in the hydrodynamic region ($u = q\xi \ll 1$), $K_0(u) = u^2$.

$d_{\rm LCD}$	p_c, p_m MPa	$p_m - p_c$, MPa	Δp_c	$\xi_{\max}$, nm	$D^*_{\min}$	D^* ($\xi^* \to \infty$)	$(k^*_p)_{\max}$	k^*_p ($\xi^* \to \infty$)
3	8.489	0	0	$\approx 10^3$	9.6×10^{-5}	9.6×10^{-5}	1.04×10^4	1.04×10^4
2	8.048	–0.443	–0.052	4.7	2.1×10^{-2}	0.102	47.6	9.8
1	7.318	–1.171	–0.138	2.375	4.2×10^{-2}	0.238	23.8	4.2

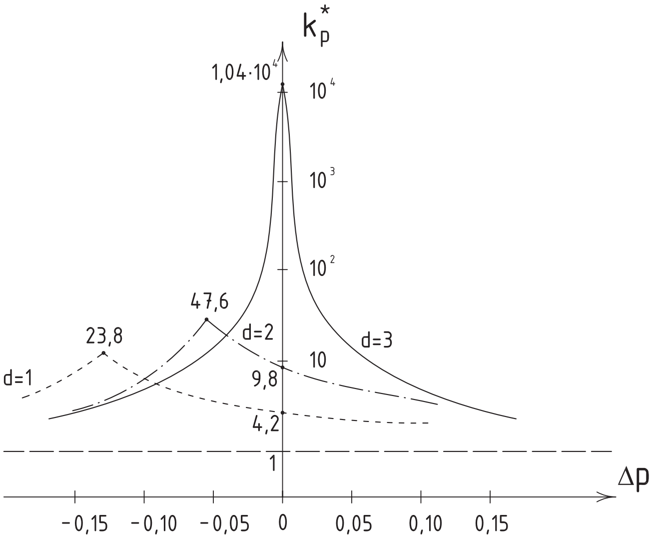

Fig. 3. Dependences of the barodiffusion ratio $k^*_p = k_p/k^0_p$ on the pressure Δp taking the LCD and a spatial dispersion into account

Substituting this asymptotics into expression (49), we obtain an analog of the known Stokes–Einstein formula for the diffusion coefficient of a two-component liquid mixture in the critical state:

$$D^*_{\min} = \frac{kT}{6\pi\eta\xi_{\max}D_0}. \tag{50}$$

The results of corresponding estimations for the mixture concerned and various LCD values are given in the sixth column of Table 1.

The first row of Table 1 corresponds to the quasi-unconfined system ($L \gg \xi$) with $d_{\rm LCD} = 3$. The maximum of the correlation length obtained in modern experiments for classical liquids does not exceed $\xi_{\max} \approx 1\ \mu$m. To calculate $D^*_{\min}$ using formula (50), the following approximate technique was used. First, this quantity was found for water, for which reliable experimental data exist. We obtained $(D_{\min})_{\rm H_2O} \approx 2.2 \times 10^{-13}$ m/s^2. Since, the diffusion coefficient of water in the bulk phase equals $(D_0)_{\rm H_2O} \approx 2.3 \times 10^{-13}$ m/s^2, for the dimensionless value, we obtain $(D^*_{\min})_{\rm H_2O} \approx 10^{-4}$. Then, on the basis of the known formula for the diffusion coefficient in the elastic impact model (see, e.g., work [3]), the relation $(D_{\min})_{\rm sum} \approx (D_{\min})_{\rm H_2O}(\sqrt{T_{\rm sum}M_{\rm H_2O}}/\sqrt{T_{\rm H_2O}M_{\rm sum}}) \times [(\xi_0)_{\rm H_2O}/(\xi_0)_{\rm sum}]^2$ was derived. Ultimately, using the critical temperatures $T_{\rm H_2O} \approx 647$ K and $T_{\rm sum} \approx 462$ K, molar masses $M_{\rm H_2O} = 18 \times 10^{-3}$ kg/mol and $M_{\rm sum} \approx 59 \times 10^{-3}$ kg/mol, and correlation length amplitudes $(\xi_0)_{\rm H_2O} = 0.16$ nm and $(\xi_0)_{\rm sum} = 0.235$ nm, for the sought diffusion coefficients in the bulk phase of an ethane-benzene mixture, we obtain $(D_{\min})_{\rm sum} \approx 6.8 \times 10^{-14}$ m^2/s, $(D_0)_{\rm sum} \approx 7.1 \times 10^{-10}$ m^2/s, and $(D^*_{\min})_{\rm sum} \approx 10^{-4}$.

The second row corresponds to a gap-like pore with $d_{\rm LCD} = 2$ and the thickness $H = 4.7$ nm. In view of the values calculated above for a change of the critical pressure p_c (the pressure p_m at the extremum point) and assuming that $\xi_{\max} \approx H$, we obtain the estimate $D_{\min} \approx 1.5 \times 10^{-11}$ m^2/s. In the same way, for a cylindrical pore with $d_{\rm LCD} = 1$ and the radius $R = 2.375$ nm, we obtain $D_{\min} \approx 3.0 \times 10^{-11}$ m^2/s (see the third row).

The seventh column of Table 1 contains the calculation results by formula (48) for the diffusion coefficient D^* of the studied mixture, provided that the correlation length $\xi^* \to \infty$, i.e. at the critical point of the bulk phase. It should be noted that the dimensional dependence $D(S)$ of the diffusion coefficient is nonmonotonous [16]. Therefore, in the regular region, where the correlation length $\xi^* \to 1$, formula (48) gives a passage to the limit $D^* \to 1$, when changing to macroscopic volumes ($S \to \infty$), and the diffusion coefficient D of liquid systems approaches its bulk value D_0 from below, which is confirmed by independent calculations [29].

5.1.2. Barodiffusion ratio

The results of calculations for the dependence of the barodiffusion ratio k_p on the pressure $\Delta p(S, \xi^*)$ are illustrated in Fig. 3. As before, solid curve *1* corresponds to the unconfined (bulk) phase with $d_{\rm LCD} = 3$, dashed curve *2* to a gap-like pore with $d_{\rm LCD} = 2$, and dash-dotted curve *3* to a cylindrical pore with $d_{\rm LCD} = 1$.

The calculations of the barodiffusion ratio k^*_p in the dynamic crossover region with regard for the LCD and spatial dispersion effects were carried out by the formula

$$k^*_p = [\{(G/S)^{\beta\delta/\nu} + [1 + (G/S)^{\beta\delta/\nu}] \times$$

$$\times (1/\xi^*)^{\beta\delta/\nu} {\rm sign}\Delta p\}^{\gamma/\beta\delta} + Bq^2]^{-1}. \tag{51}$$

In the absence of spatial dispersion effects (the last term), the expression demonstrates an unphysical divergence which is characterized by the dependence $k_p^* \approx (\xi^*)^{-\gamma/\nu} \sim \Delta p^{-\gamma/\beta\delta}$ for a spatially unconfined system ($S \to \infty$). If spatial dispersion effects are considered in the critical point of a macroscopic liquid ($\Delta p \to 0$ and $\xi^* \to \infty$), the barodiffusion ratio remains finite and equals $k_p^* = L_{\max}^2/4\pi^2 B$, where $L_{\max}$ is the the maximal linear volume of a liquid system, and B is the parameter of non-locality that is proportional to the squared radius of the intermolecular interaction. In two last columns of Table 1, the calculation results for $k_{\max}^*$ at the extremal points and the values of $k_{\max}^*$ obtained from formula (51) in the limit $\xi^* \to \infty$ for the correlation length are presented.

Concerning the behavior peculiarities of the barodiffusion coefficient $D_p = Dk_p$ in the dynamic crossover region, its value must be almost independent of the proximity of the system to its critical state, because the singularities compensate each other in the product Dk_p and are absent from the Onsager kinetic coefficients ($a \approx 2a_0$ and $b \approx 2b_0$).

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БАРОДИФУЗІЙНІ ЯВИЩА В НАНОМАСШТАБНИХ РІДИННИХ СУМІШАХ У КРИТИЧНІЙ ОБЛАСТІ

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Резюме

Вивчено критичну поведінку ізобарно-ізотермічної стисливості, коефіцієнтів дифузії та бародифузії, а також бародифузійного відношення для 2-компонентних рідинних сумішей з обмеженою геометрією. Для розгляду специфіки бародифузійних явищ використано масштабну гіпотезу для просторово обмежених систем та гіпотезу “повного скейлінгу”. Досліджено вплив нижньої кросоверної розмірності та ефектів просторової дисперсії на характеристики бародифузійних процесів у наномасштабних рідинних сумішах в критичній області.