
DIFFUSION COEFFICIENT AND BARODIFFUSION RATIO OF MESOSCALE FLUIDS IN THEIR CRITICAL REGION

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The calculation results for the dependences of the diffusion coefficient and the barodiffusion ratio on the pressure and the density in vicinity of the critical point obtained for spatially confined fluid systems are presented. The critical behavior of those kinetic properties in small volumes of fluids has been analyzed in the fluctuation, dynamic crossover, and regular regions. Spatial dispersion effects have been taken into consideration to avoid the zero value of diffusion coefficient and the infinite value of barodiffusion ratio, when approaching the critical state. Numerical estimations that use experimental data have been made, and plots that illustrate our theoretical calculations have been built.

1. Introduction

This work is devoted to studying the features of barodiffusion phenomena in mesoscale (i.e. nano- and micro-sized) fluid systems which are in the critical region of their thermodynamic parameters. The solution of such a problem is not of only theoretical interest, but also has a substantial practical value due to the following factors.

1. The character of phase transitions and critical phenomenon running in systems of various origins drastically changes, when their linear dimensions, L , diminish to the ξ_{\max} -value, the maximum of the correlation length for a characteristic order parameter. Thin films, near-surface layers, fluids in small pores, biological membranes, and synaptic gaps are typical mesoscale objects, where the behavior features of physical parameters have no analogs in ordinary bulk phases. In works [1–3], the modified hypothesis of scale invariance for spatially confined systems was formulated. The basic result of its application to particular fluids (see, e.g., work [4]) is the fact that the fluctuation part of the thermodynamic potential turns out dependent not only on the temperature variable $\tau = (T - T_c)/T_c$ (T_c is the critical temperature), the order parameter $\Delta\rho = (\rho - \rho_c)/\rho_c$ (ρ_c

is the critical density), and the conjugate external field $h = \Delta p + (\partial p/\partial T)_\rho \tau$ introduced in work [5] (here, the quantity $\Delta p = (p - p_c)/p_c$ is a deviation of the pressure p from its critical value p_c), as is valid for spatially infinite systems, but also on the system dimensions L in the spatial confinement direction and on the shape of bounding surfaces.

2. The features of physical properties of condensed media are not localized in asymptotically narrow regions around the points (curves) of phase transitions and critical phenomena, but manifest themselves in rather wide ranges of thermodynamic parameters. For instance, for fluids with a relatively large Ginzburg number $Gi \leq 1$, the phase coexistence curve (binodal) is described by Guggenheim's law with the critical index $\beta \approx 1/3$ in a very wide (to 100 K and higher temperatures) vicinity of the critical point [6, 7].

3. Since the ultrasonic wave (its application range in modern medicine has not been studied at length) is one of the barodiffusion-stimulating factors, the research of barodiffusion processes is rather interesting and useful for working out new diagnostic and medical procedures [8, 9].

In contrast to work [10], where barodiffusion phenomena were studied in large enough volumes of fluid ($L \gg \xi_{\max}$), the main attention in this research is concentrated on such parameters of barodiffusion phenomena in spatially confined fluids with nano- and micro-sized linear dimensions $L \leq \xi_{\max}$ as the diffusion coefficient and the barodiffusion ratio.

2. Barodiffusion Processes in a Two-Phase Fluid System with Confined Geometry

Let us consider barodiffusion phenomena in a two-phase one-component fluid system, provided that only the temperatures in both phases are equal, whereas the pressures

and the chemical potentials are different: $T_1 = T_2$, $p_1 \neq p_2$, $\mu_1 \neq \mu_2$. The intracellular (the first phase) and extracellular (the second phase) media which are separated from each other by a plasmatic membrane, can be regarded as an example of such a system. In addition, we assume that the spatially confined fluid system is at a constant temperature which is rather close to the critical one in the sense of the inequality $\Delta p \gg (\partial p / \partial T)_\rho \tau$. Under such conditions, the external field is mainly governed by the pressure difference: $h \approx \Delta p = (p - p_c) / p_c$. Then, the diffusion flux \mathbf{J}_n in the linear approximation with respect to the gradients of chemical potential, $\nabla \mu$, and pressure, ∇p , and in the absence of other thermodynamic forces, which could give a contribution to \mathbf{J}_n in accordance with the Curie principle (see, e.g., works [11–13]), should be written down in the form

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

where a and b are the Onsager kinetic coefficients. Changing from the variables μ and p to new independent variables, the density ρ and the pressure p , we obtain

$$\nabla \mu = (\partial \mu / \partial p)_\rho \nabla p + (\partial \mu / \partial \rho)_p \nabla \rho, \tag{2}$$

which brings about

$$\mathbf{J}_n = -a(\partial \mu / \partial \rho)_p \nabla \rho - [b + a(\partial \mu / \partial p)_\rho] \nabla p \tag{3}$$

for the diffusion flux.



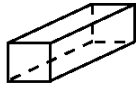
Let us compare formula (3) with the linear relation for the flux \mathbf{J}_n in the case of two thermodynamic forces caused by the density and pressure gradients ($\nabla \rho$ and ∇p , respectively), which looks, under isothermal conditions, like

$$\mathbf{J}_n = -D(\nabla \rho + k_p \nabla \ln p). \tag{4}$$

Whence, on the basis of expressions (3) and (4), we obtain formulas for the diffusion coefficient,

$$D = a(\partial \mu / \partial \rho)_p, \tag{5}$$

Table 1. Geometrical parameters χ and L

Parameter	Shape		
			
χ	π	μ_1^*	$2\sqrt{2\pi}$
L	gap thickness	cylinder diameter	side length of square cross-section

and the barodiffusion ratio,

$$k_p = p[b + a(\partial \mu / \partial p)_\rho] / a(\partial \mu / \partial \rho)_p. \tag{6}$$

In connection with obtained formulas (5) and (6), the following remarks are to be made. First, in the general case, fluxes and thermodynamic forces are coupled with one another in vicinities of the critical points and the points of phase transitions of the second kind by means of integral relations which are nonlocal in space and time. Just such relations, in which kinetic coefficients like the diffusion coefficient D and the barodiffusion ratio k_p are not local parameters, but are the kernels related to the transfer processes that are governed by the space–time correlation functions of the corresponding fluxes, allow the effects of spatial and time dispersions [12, 14] to be taken into consideration consistently. Below, we examine the issue concerning an influence of the spatial dispersion on a singular behavior of D and k_p in a close vicinity of the critical points for bulk fluids and certain analogs of critical points for spatially confined fluid systems.

Second, the Onsager coefficients a and b contain singular (a_S and b_S) and regular (a_R and b_R) components: $a = a_S + a_R$ and $b = b_S + b_R$. When the system is in a close vicinity of the critical points or the points of phase transitions of the second kind, the singular contributions to kinetic coefficients turn out to be proportional to the correlation length of order parameter fluctuations ξ ($a_S, b_S \propto \xi$) owing to the anomalous growth of fluctuation effects [6, 7, 15]. By analogy with the expression for a temperature dependence of the correlation length ξ obtained in work [4] for spatially confined systems, the relevant formulas for the dependences of ξ on the pressure Δp and the density $\Delta \rho$ are as follows:

$$\begin{aligned} \xi &= \xi_0 [\Delta p + (\chi / S_G)^{\beta \delta / \nu} (1 + \Delta p)]^{-\nu / \beta \delta}, \\ \xi &= \xi_0 [\Delta \rho + (\chi / S_G)^{\beta / \nu} (1 + \Delta \rho)]^{-\nu / \beta}. \end{aligned} \tag{7}$$

In expressions (7), the following notations are used: ξ_0 is the correlation length amplitude which has an order of the intermolecular interaction radius; χ is a constant that is determined by the system geometry; $S_G = L / \xi_0$ is a multiplier which characterizes the number of monomolecular layers along the spatial confinement direction for short-range intermolecular potentials; L is a quantity dependent on the system shape (see the corresponding values for χ and S_G in Table 1, where $\mu_1^* \approx 2.4048$ is the first zero of the Bessel function); $\beta \approx 1/3$, $\delta \approx 5$, and $\nu \approx 0.63$ are critical indices.

For the further consideration on the basis of formulas (7), it is expedient to introduce the notations

$$\Omega_{\Delta p, G} = \Delta p + (\chi / S_G)^{\beta \delta / \nu} (1 + \Delta p),$$

$$\Omega_{\Delta\rho,G} = \Delta\rho + (\chi/S_G)^{\beta/\nu}(1 + \Delta\rho) \quad (8)$$

for the functions $\Omega_{\Delta p,G}$ and $\Omega_{\Delta\rho,G}$ which determine the dependences of physical properties of fluids with confined geometry on the pressure and the density, respectively, as well as on the size and the shape of the system.

Below, the critical behavior of the diffusion coefficient D and the barodiffusion ratio k_p will be analyzed in detail for various approaches to the critical point in “strong” ($\Delta p \gg \Delta\rho^\delta$) and “weak” ($\Delta\rho \gg \Delta p^{1/\delta}$) external fields.

3. Fluctuation Region

In this region, the singular contributions to the Onsager kinetic coefficients substantially exceed their regular counterparts ($a_S \gg a_R$ and $b_S \gg b_R$). For an isothermal two-phase one-component spatially confined system, the diffusion coefficient can be presented by the formula

$$D = L^{1-\frac{\gamma}{\nu}} f_D(\Delta\rho L^{\frac{\beta}{\nu}}, \Delta p L^{\frac{\beta\delta}{\nu}}), \quad (9)$$

whereas the barodiffusion ratio is determined by the expression

$$k_p = L^{\frac{\gamma}{\nu}} f_k(\Delta\rho L^{\frac{\beta}{\nu}}, \Delta p L^{\frac{\beta\delta}{\nu}}). \quad (10)$$

The arguments $x = \Delta\rho L^{\frac{\beta}{\nu}}$ and $y = \Delta p L^{\frac{\beta\delta}{\nu}}$ of the scaling functions in Eqs. (9) and (10) characterize the ratio between the linear size of a confined fluid system and the correlation length of density fluctuations which is equal to $\xi = \xi_0 \Delta\rho^{-\frac{\nu}{\beta}}$ in a vicinity of the critical isochore (or in a “weak” external field ($\Delta\rho \gg \Delta p^{1/\delta}$)) and to $\xi = \xi_0 h^{-\frac{\nu}{\beta\delta}} = x i_0 \Delta p^{-\frac{\nu}{\beta\delta}}$ in a vicinity of the critical isobar (or in a “strong” external field ($\Delta p \gg \Delta\rho^\delta$)). The asymptotics of the scaling functions $f_D(x, y)$ and $f_k(x, y)$ have the following representations:

$$f_D(x, y \rightarrow 0) \sim x^{\frac{\gamma-\nu}{\beta}}, \quad f_D(x \rightarrow 0, y) \sim y^{\frac{\gamma-\nu}{\beta\delta}}, \quad (11)$$

$$f_k(x, y \rightarrow 0) \sim x^{-\frac{\gamma}{\beta}}, \quad f_k(x \rightarrow 0, y) \sim y^{-\frac{\gamma}{\beta\delta}}. \quad (12)$$

From formulas (9) and (11), we obtain the following results for the diffusion coefficient:

$$D = D_0 \Delta\rho^{\frac{\gamma-\nu}{\beta}} \quad (13)$$

in “weak” ($\Delta\rho \gg \Delta p^{1/\delta}$) and

$$D = D_0 \Delta p^{\frac{\gamma-\nu}{\beta\delta}} \quad (14)$$

in “strong” ($\Delta p \gg \Delta\rho^\delta$) external fields, where $D_0 = a_R(\partial\mu/\partial\rho)_p^0$ is the diffusion coefficient amplitude.

By analogy with formulas (10) and (12), we obtain the corresponding expressions for the barodiffusion ratio in “weak” ($\Delta\rho \gg \Delta p^{1/\delta}$),

$$k_p = k_p^0 \Delta\rho^{-\frac{\gamma}{\beta}}, \quad (15)$$

and “strong” ($\Delta p \gg \Delta\rho^\delta$),

$$k_p = k_p^0 \Delta p^{-\frac{\gamma}{\beta\delta}}, \quad (16)$$

external fields, where the barodiffusion ratio amplitude is $k_p^0 = p[(\partial\mu/\partial\rho)_\rho^0 + a_R/b_R]/(\partial\mu/\partial\rho)_p^0$.

To take the geometrical shape of bounding surfaces into account, let us use expressions (8) and write down the diffusion coefficient for the fluid system in the form

$$D = D_0 \Omega_{\Delta p,G}^{\frac{\gamma-\nu}{\beta\delta}}. \quad (17)$$

On the basis of the identity $\gamma = \nu(2 - \eta)$, where η is the critical index of the anomalous dimension of the correlation function, formula (17) reads

$$D = D_0 \Omega_{\Delta p,G}^{\frac{\nu(1-\eta)}{\beta\delta}}. \quad (18)$$

In the Ornstein–Zernike approximation, where the critical index $\eta = 0$, we obtain

$$D = D_0 \Omega_{\Delta p,G}^{\frac{\nu}{\beta\delta}}. \quad (19)$$

The diffusion coefficient amplitude D_0 in formulas (17)–(19) is given by the Stokes–Einstein relation $D_0 = \frac{k_B T}{6\pi\eta_s \xi_0}$, where η_s is the shear viscosity coefficient which weakly diverges at the critical point according to the dynamic scaling theory [15],

$$\eta_s = \eta_{s0} (\xi/\xi_0)^{z_\eta} = \eta_{s0} \Omega_{\Delta p,G}^{-\frac{z_\eta \nu}{\beta\delta}}, \quad (20)$$

since the dynamic critical index $z_\eta \approx 0.06$. Then, formula (19), where the weak singularity of η_s is taken into account, looks like

$$D = \tilde{D}_0 \Omega_{\Delta p,G}^{\frac{(1+z_\eta)\nu}{\beta\delta}}, \quad (21)$$

where $(1 + z_\eta)\nu \approx 0.67$, $\tilde{D}_0 = \frac{k_B T}{6\pi\eta_{s0}\xi_0}$, and η_{s0} is the amplitude of the shear viscosity coefficient at a certain pressure p far from the critical value, i.e. in the regular region, where $\left| \frac{p-p_c}{p_c} \right| \approx 1$.

The formulas derived above for the diffusion coefficient in the fluctuation region have a basic shortcoming; namely, they result in unreal experimental consequences: the diffusion coefficient tends to zero at critical

points and points of phase transitions of the second kind ($D \rightarrow 0$). To avoid such unphysical features of the diffusion coefficient behavior at the critical point, effects of spatial dispersion (non-locality) must be taken into consideration.

In the Ornstein–Zernike approximation which describes a weak spatial dispersion ($\xi q \ll 1$), the diffusion coefficient at the critical point of a spatially confined fluid system is characterized by the formula

$$D = \tilde{D}_0 \left(\Omega_{\Delta p, G}^{\frac{(1+z\eta)\nu}{\beta\delta}} + bq^2 \right), \quad (22)$$

where q is the wave vector, and b is a constant. It should be noted that the microscopic meaning of b consists in that $b \approx r_0^2$, where r_0 is the intermolecular interaction radius. In addition, the minimum value of the wave vector is restricted by the linear dimension L , namely, $q_{\min} = 2\pi/L$. From expression (22), it follows that, at $\Omega_{\Delta p, G} \rightarrow 0$ (this condition corresponds to the pressure-governed approach to the critical point of a spatially confined system), the diffusion coefficient becomes nonzero, namely, $D = \tilde{D}_0 bq^2$.

Above, the finiteness of diffusion coefficient D at $\Omega_{\Delta p, G} \rightarrow 0$ was ensured in the Ornstein–Zernike approximation. A more consistent approach which takes not only weak but also arbitrary spatial dispersion effects into account was proposed in work [16]. It is based on the following formula for the diffusion coefficient:

$$D = \frac{k_B T K_0(q\xi)}{6\pi\eta_s q^2 \xi^3}. \quad (23)$$

Here, $K_0(x) = \frac{3}{4}[1 + x^2 + (x^3 - x^{-1}) \arctan x]$ is the Kawasaki function. Its asymptotics

$$K_0(x \rightarrow 0) = x^2, \quad K_0(x \rightarrow \infty) = \frac{3\pi x^3}{8} \quad (24)$$

give rise to both the well-known Stokes–Einstein formula $D = \frac{k_B T}{6\pi\eta_s \xi}$ at $x \rightarrow 0$ and the finite value of the diffusion coefficient $D = \frac{k_B T q_{\min}}{16\eta_s} = \frac{\pi k_B T}{8L\eta_s}$ at $x \rightarrow \infty$, i.e. a result that practically does not depend on the proximity to the critical state.

The barodiffusion ratio for mesoscale fluid systems looks like

$$k_p = k_p^0 \Omega_{\Delta p, G}^{-\frac{\gamma}{\beta\delta}} \quad (25)$$

and tends to infinity at $\Omega_{\Delta p, G} \rightarrow 0$, revealing itself as the growth of the isobaric compressibility of a fluid system. It is clear that, from the physical point of view, such a result is unreal. The account of spatial dispersion effects in the derivative $(\partial\mu/\partial\rho)_p$, which defines the

inverse isobaric compressibility [see formula (6)], results in the following expression for the barodiffusion ratio:

$$k_p = k_p^0 (\Omega_{\Delta p, G}^{-\frac{\gamma}{\beta\delta}} + bq^2), \quad (26)$$

which brings about the finiteness of the quantity $k_p = k_p^0 bq^2$ at $\Omega_{\Delta p, G} \rightarrow 0$.

4. Dynamic Crossover Region

We now consider the so-called dynamic (kinetic) crossover region, for which the regular and singular contributions to the Onsager kinetic coefficients are of the same order ($a_R \approx a_S$ and $b_R \approx b_S$). By analogy with the dynamic crossover temperature $\tau_D = \frac{T_D - T_c}{T_c}$ [17] which is estimated as $|\tau_D| \approx 10^{-4} \div 10^{-5}$ for fluids with a small enough Ginzburg number $Gi \leq 10^{-3}$, we introduce the dynamic crossover density $\Delta\rho_D = \frac{\rho_D - \rho_c}{\rho_c}$ and the dynamic crossover pressure $\Delta p_D = \frac{p_D - p_c}{p_c}$. The theory of dynamic scaling [15] gives the following result for the dependences of singular parts of the Onsager kinetic coefficients on the dynamic crossover density and pressure: $a_S = a_S^0 |\tau_D|^{-\nu}$, $a_S = a_S^0 |\Delta\rho_D|^{-\frac{\nu}{\beta}}$, and $a_S = a_S^0 |\Delta p_D|^{-\frac{\nu}{\beta\delta}}$, which enables one to estimate the density and the pressure of a dynamic crossover:

$$|\Delta\rho_D| \approx 10^{-1.3} \div 10^{-1.67}; \quad |\Delta p_D| \approx 10^{-6.67} \div 10^{-8.3}. \quad (27)$$

For fluids with a relatively large Ginzburg number (e.g., for H₂O, for which $Gi \approx 0.3$), the dynamic crossover temperature becomes $|\tau_D| \leq 10^{-1} \div 10^{-2}$, whereas the dynamic crossover density $|\Delta\rho_D| \approx 10^{-3} \div 10^{-6}$ and the dynamic crossover pressure $|\Delta p_D| \approx 10^{-1.67} \div 10^{-3.33}$. For water, with regard for the critical values for density, $\rho_c = 307 \text{ kg/m}^3$, and pressure, $p_c = 22 \text{ MPa}$, the dynamic crossover has to be realized in the range $|\rho_D - \rho_c| \approx 10^{-4.5} \rho_c \approx 0.01 \text{ kg/cm}^3$ and $|p_D - p_c| \approx 10^{-2.5} p_c \approx 70 \text{ kPa}$.

In the dynamic crossover region, the approximate equality $a_S \approx a_R$ is fulfilled. Therefore, the diffusion coefficient is determined by the formulas

a) in a “weak” external field ($\Delta\rho \gg \Delta p^{\frac{1}{\beta}}$),

$$D = D'_0 \Delta\rho^{\frac{\gamma}{\beta}} f_1(\Delta\rho L^{\frac{\beta}{\nu}}, \Delta p L^{\frac{\beta\delta}{\nu}}); \quad (28)$$

b) in a “strong” external field ($\Delta p \gg \Delta\rho^\delta$),

$$D = D'_0 \Delta p^{\frac{\gamma}{\beta\delta}} f_2(\Delta\rho L^{\frac{\beta}{\nu}}, \Delta p L^{\frac{\beta\delta}{\nu}}). \quad (29)$$

The diffusion coefficient amplitude $D'_0 \approx 2a_R(\partial\mu/\partial\rho)_p^0$ turns out to be approximately twice as large as its value D_0 in the fluctuation region.

Accordingly, the barodiffusion ratio in the crossover region is characterized by the following expressions:

a) in a “weak” external field ($\Delta\rho \gg \Delta\rho^{\frac{1}{\delta}}$),

$$k_p = \tilde{k}_p^0 \Delta\rho^{-\frac{\gamma}{\beta}} f_3(\Delta\rho L^{\frac{\beta}{\nu}}, \Delta p L^{\frac{\beta\delta}{\nu}}); \quad (30)$$

b) in a “strong” external field ($\Delta p \gg \Delta\rho^\delta$),

$$k_p = \tilde{k}_p^0 \Delta p^{-\frac{\gamma}{\beta\delta}} f_4(\Delta\rho L^{\frac{\beta}{\nu}}, \Delta p L^{\frac{\beta\delta}{\nu}}). \quad (31)$$

The barodiffusion ratio amplitude practically is not changed in comparison with the amplitude k_p^0 in the fluctuation region.

5. Regular Region

This region, being the most remote from the critical point, is defined by the relations $Gi^{\beta\delta} < \Delta p \leq 1$ and $Gi^\beta < \Delta\rho \leq 1$ for the pressure and the density and by the strong inequalities $a_R \gg a_S$ and $b_R \gg b_S$ for the regular and singular parts of the Onsager kinetic coefficients. It should be noted that the fluctuation effects can be neglected only when the Ginzburg number $Gi = \frac{\langle \Delta\varphi^2 \rangle}{\varphi_0^2}$, which is defined for a fluid system as the ratio between the root-mean-square density fluctuation $\langle \Delta\varphi^2 \rangle = \langle \Delta\rho^2 \rangle$ and the square of equilibrium density value $\varphi_0^2 = \Delta\rho_0^2$, is small enough ($Gi < 1$). In this case, on the basis of formula (5), the self-diffusion coefficient D is completely determined by the inverse isobaric compressibility, and the corresponding critical indices are characterized by their values $\gamma = 1$, $\nu = \beta = 1/2$, $\delta = 3$, typical of the Landau mean-field theory [5]:

$$D = L^{-2} f'_D(x, y). \quad (32)$$

Here, the scaling arguments are $x = \Delta\rho L$ and $y = \Delta p L^3$, and the scaling function $f_D(x, y)$ has the following asymptotics:

(a) $f_D(x, 0) \sim x^2$ in a “weak” external field ($\Delta\rho \gg \Delta p^{1/3}$);

(b) $f_D(0, y) \sim y^{2/3}$ in a “strong” external field ($\Delta p \gg \Delta\rho^3$).

In a vicinity of the critical isochore in “strong” external fields caused by deviations of the pressure p from the critical value p_c , we have

$$D = D_0 \Omega_{\Delta p, G}^{\frac{2}{3}}, \quad \Omega_{\Delta p, G} = \Delta p + \left(\frac{\chi}{S_G}\right)^3 (1 + \Delta p). \quad (33)$$

Accordingly, in “weak” external fields and in a vicinity of the critical isobar,

$$D = D_0 \Omega_{\Delta\rho, G}^2, \quad \Omega_{\Delta\rho, G} = \Delta\rho + \frac{\chi}{S_G} (1 + \Delta\rho). \quad (34)$$

For systems, the bounding surfaces of which form a cylinder, two parallel planes, or a parallelepiped with square cross-section, the values for parameters χ and S_G are quoted in Table 1.

Concerning the behavior of the barodiffusion ratio in the regular region, its dependence on the pressure and the density is determined by the following formulas: $k_p = k_p^0 \Omega_{\Delta p, G}^{-\frac{2}{3}}$ in “strong” and $k_p = k_p^0 \Omega_{\Delta\rho, G}^{-2}$ in “weak” external fields, where the functions $\Omega_{\Delta p, G}$ and $\Omega_{\Delta\rho, G}$ are given in Eqs. (33) and (34), respectively.

If the Ginzburg number $Gi < 1$, there must exist a region $Gi^{1.5} < \Delta p \leq 1$ and $Gi^{0.5} < \Delta\rho \leq 1$, where $|p - p_c|/p_c \approx 1$ and $|\rho - \rho_c|/\rho_c \approx 1$, in which the behavior of the diffusion coefficient and the barodiffusion ratio is determined by the expressions

$$D = \text{const}, \quad k_p = \text{const}. \quad (35)$$

In other words, this region is noncritical in the sense that both those characteristics of barodiffusion processes cease to depend on the proximity to the critical point with respect to the pressure and the density.

6. Discussion of Results

The results obtained above allow the following conclusions to be drawn.

The diffusion coefficient D grows, and the barodiffusion ratio k_p diminishes in mesoscale fluid systems, if the pressure and the density move away from the corresponding values $p_c^*(L) = p_c [1 + (\chi/S_G)^{\beta\delta/\nu}]^{-1}$ and $\rho_c^*(L) = \rho_c [1 + (\chi/S_G)^{\beta/\nu}]^{-1}$ which correspond to the D -minimum and k_p -maximum values. The parameters $p_c^*(L)$ and $\rho_c^*(L)$ for a mesoscale fluid system with the linear dimension L in the spatial confinement direction are certain analogs of the critical parameters p_c and ρ_c for a fluid in the bulk (unconfined) phase. The differences of the pressures, $p_c^*(L) - p_c$, and the densities, $\rho_c^*(L) - \rho_c$, are negative, and their absolute values grow with a reduction of the linear dimension $L = \xi_0 S_G$ in accordance to the formulas

$$\begin{aligned} p_c^*(L) - p_c &= -p_c [1 + (\chi/S_G)^{\beta\delta/\nu}]^{-1}, \\ \rho_c^*(L) - \rho_c &= -\rho_c [1 + (\chi/S_G)^{\beta/\nu}]^{-1}. \end{aligned} \quad (36)$$

Table 2 presents the dependences of the reduced diffusion coefficient $D^* = D/D_0$ on the variables $\Omega_{\Delta p, G}$ and $\Omega_{\Delta\rho, G}$, which take variations of the pressure, Δp , and the density, $\Delta\rho$, and the geometrical bulk parameters χ and S_G of the mesoscale fluid system into account for fluctuation, dynamic crossover, and regular regions and for

Table 2. Dependences of the diffusion coefficient on the pressure Δp , density $\Delta\rho$, and geometrical parameters for unconfined and confined fluid systems

Regions for pressure, density, and kinetic coefficients	Unconfined fluid	Confined fluid
Critical point and its analog in confined fluid	$D_c^* = bq^2$ (OZ approximation) $D_c^* = \frac{k_B T q}{16\eta_s} = \text{const}$ (Kawasaki approximation)	$D_c^* = \frac{4\pi^2 b}{L^2}$ (OZ approximation) $D_c^* = \frac{\pi k_B T}{8L\eta_s} = \text{const}$ (Kawasaki approximation)
Fluctuation region	$D^* = \Delta p^{\frac{\gamma-\nu}{\beta\delta}} = \Delta p^{0.390}$ $D^* = \Delta\rho^{\frac{\gamma-\nu}{\beta}} = \Delta\rho^{1.877}$	$D^* = \Omega_{\Delta p, G}^{\frac{\gamma-\nu}{\beta\delta}} = \Omega_{\Delta p, G}^{0.390}$ $D^* = \Omega_{\Delta\rho, G}^{\frac{\gamma-\nu}{\beta}} = \Omega_{\Delta\rho, G}^{1.877}$
Dynamic crossover region	$D^* = \Delta p^{\frac{\gamma}{\beta\delta}} = \Delta p^{0.792}$ $D^* = \Delta\rho^{\frac{\gamma}{\beta}} = \Delta\rho^{3.815}$	$D^* = \Omega_{\Delta p, G}^{\frac{\gamma}{\beta\delta}} = \Omega_{\Delta p, G}^{0.792}$ $D^* = \Omega_{\Delta\rho, G}^{\frac{\gamma}{\beta}} = \Omega_{\Delta\rho, G}^{3.815}$
Regular region	$D = D_0 \Delta p^{2/3}, D = D_0 \Delta\rho^2$ $D^* \rightarrow 1 (D \rightarrow D_0)$	$D = D_0 \Omega_{\Delta p, G}^{2/3}, D = \Omega_{\Delta\rho, G}^2$ $D^* \rightarrow 1 (D \rightarrow D_0)$

Table 3. Dependences of the diffusion coefficient on the pressure, density, and geometrical parameters for unconfined and confined fluid systems

Regions for pressure, density, and kinetic coefficients	Unconfined fluid	Confined fluid
Critical point and its analog in confined fluid	$(k_p^*)_c = \frac{1}{bq^2} = \text{const}$	$(k_p^*)_c = \frac{L^2}{4\pi^2 b} = \text{const}$
Fluctuation region	$k_p^* = \Delta p^{-\frac{\gamma}{\beta\delta}} = \Delta p^{-0.792}$ $k_p^* = \Delta\rho^{-\frac{\gamma}{\beta}} = \Delta\rho^{-3.815}$	$k_p^* = \Omega_{\Delta p, G}^{-\frac{\gamma}{\beta\delta}} = \Omega_{\Delta p, G}^{-0.792}$ $k_p^* = \Omega_{\Delta\rho, G}^{-\frac{\gamma}{\beta}} = \Omega_{\Delta\rho, G}^{-3.815}$
Dynamic crossover region	$k_p^* = \Delta p^{-\frac{\gamma}{\beta\delta}} = \Delta p^{-0.792}$ $k_p^* = \Delta\rho^{-\frac{\gamma}{\beta}} = \Delta\rho^{-3.815}$	$k_p^* = \Omega_{\Delta p, G}^{-\frac{\gamma}{\beta\delta}} = \Omega_{\Delta p, G}^{-0.792}$ $k_p^* = \Omega_{\Delta\rho, G}^{-\frac{\gamma}{\beta}} = \Omega_{\Delta\rho, G}^{-3.815}$
Regular region	$k_p = k_p^0 \Delta p^{-2/3}, k_p = k_p^0 \Delta\rho^{-2}$ $(k_p^*)_R \rightarrow 1, (k_p^*)_R \rightarrow k_p^0$	$k_p = k_p^0 \Omega_{\Delta p, G}^{-2/3}, k_p = k_p^0 \Omega_{\Delta\rho, G}^{-2}$ $(k_p^*)_R \rightarrow 1, (k_p^*)_R \rightarrow k_p^0$

“strong” and “weak” external fields. Analogous dependences for the reduced barodiffusion ratio $k_p^* = k_p/k_p^0$ are exhibited in Table 3.

The formulas for D^* and k_p^* in Tables 2 and 3 were written down with regard for numerical values of the critical indices α , β , γ , and ν . In the fluctuation and dynamic crossover regions for three-dimensional classical fluids with a short-range intermolecular potential, the critical indices have values typical of Ising-like systems: $\beta = 0.325$, $\delta = 4.815$, $\gamma = 1.240$, and $\nu = 0.625$. Accordingly, the functions $\Omega_{\Delta p, G}$ and $\Omega_{\Delta\rho, G}$ given by formulas (8) read $\Omega_{\Delta p, G} = \Delta p + (\chi/S_G)^{2.504}(1 + \Delta p)$ and $\Omega_{\Delta\rho, G} = \Delta\rho + (\chi/S_G)^{0.520}(1 + \Delta\rho)$, respectively.

In the regular region, where the singular contributions originating from the interaction between fluctuations can be neglected, a crossover takes place from the Ising-like critical behavior to that described by the Landau mean-

field theory with the critical indices $\beta = \nu = 0.5$, $\delta = 3$, and $\gamma = 1$. As a result, the functions $\Omega_{\Delta p, G}$ and $\Omega_{\Delta\rho, G}$ in the lower rows (for the regular region) of Tables 2 and 3 look like $\Omega_{\Delta p, G} = \Delta p + (\chi/S_G)^3(1 + \Delta p)$ and $\Omega_{\Delta\rho, G} = \Delta\rho + (\chi/S_G)(1 + \Delta\rho)$, respectively.

Figure 1 clearly illustrates the formulas given in Table 2 for the reduced diffusion coefficient $D^* = D/D_0$. Figure 2 depicts the reduced barodiffusion ratio $k_p^* = k_p/k_p^0$ (Table 3) in unconfined (solid curves) and confined (dotted curves) fluids. Panels *a* in the figures correspond to the pressure dependences, and panels *b* to the density ones for D^* and k_p^* ; p_c and ρ_c are the critical pressure and density, respectively; $p_c^*(L)$ and $\rho_c^*(L)$ are the pressure and the density, respectively, at which the minimum of D^* and the maximum of k_p^* in the confined fluid are observed; I, II, and III denote the fluctuation, dynamic crossover, and regular regions, respectively.

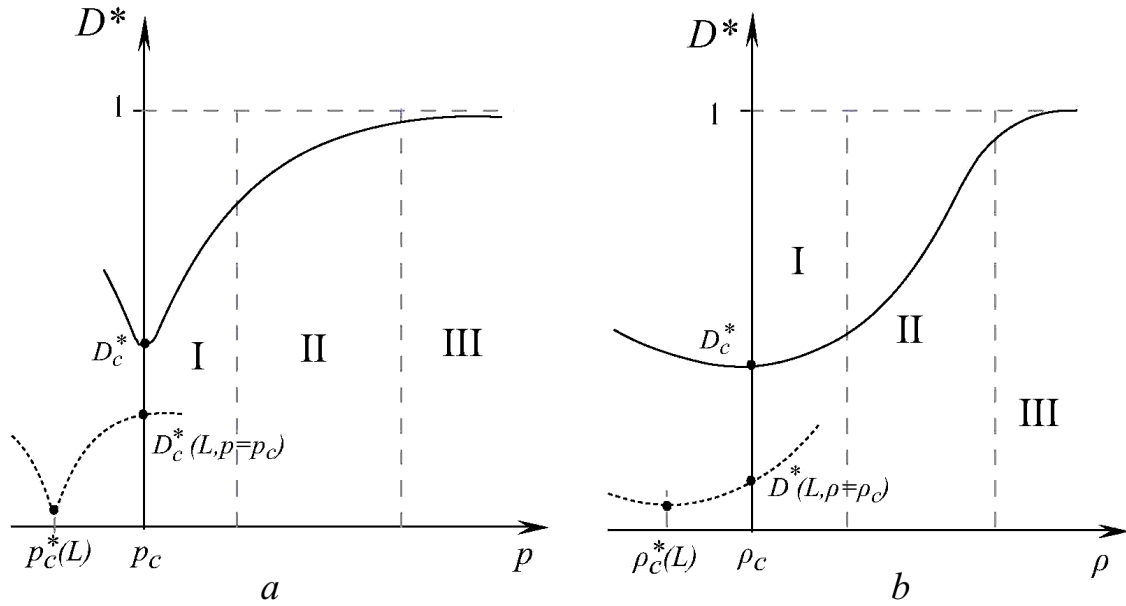


Fig. 1. Dependences of the reduced diffusion coefficient on the pressure (a) and the density (b)

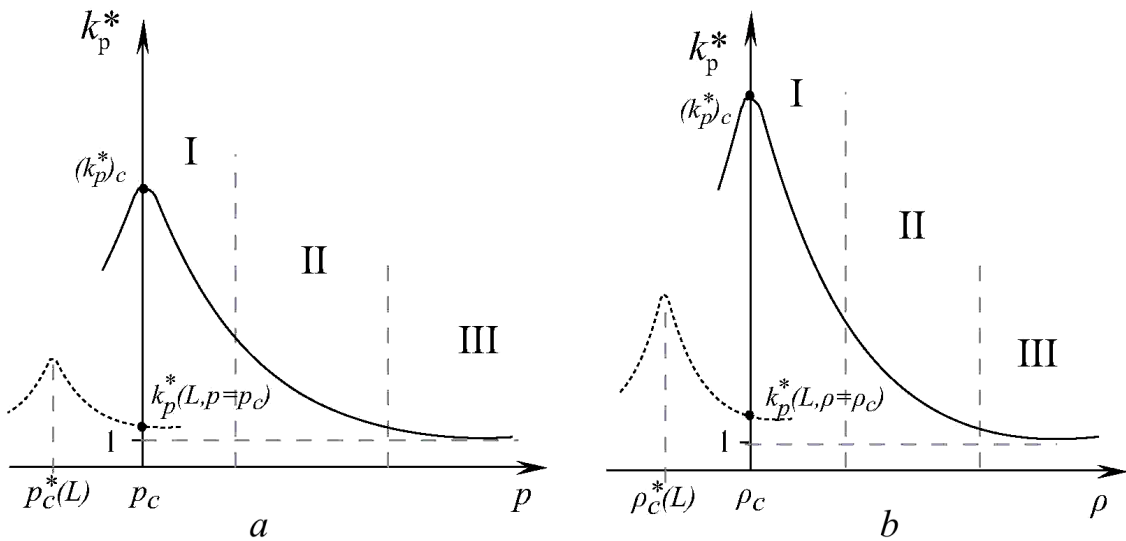


Fig. 2. Dependences of the reduced barodiffusion ratio on the pressure (a) and the density (b)

Let us numerically estimate the results obtained, using, as an example, a mesoscale aqueous system characterized by the cylindrical geometry with the radius $R = 3.2$ nm which is equal to approximately 10 diameters of a water molecule. In this case, on the basis of formula (36), where the values $\chi = \mu_1^* \approx 2.4$, $S_G = 10$, and $\beta\delta/\nu \approx 2.5$ are substituted to, we obtain that the pressure difference $p_c^* - p_c$, which equals the pressure change in a cylindrical pore, when the diffusion coefficient is minimal, with respect to the critical pres-

sure in the bulk phase (see Fig. 1,a), is $p_c^*(L) - p_c = -22[1 + (10/2.4)^{2.5}]^{-1} \approx -0.6$ MPa. Analogous estimations for the density difference $\rho_c^* - \rho_c$, i.e. the density change in a cylindrical pore at the point of the diffusion coefficient minimum with respect to the critical density in the bulk phase (see Fig. 1,b) bring about $\rho_c^*(L) - \rho_c = -307[1 + (10/2.4)^{0.52}]^{-1} \approx -99$ kg/m².

It is clear that taking spatial dispersion effects into account results in a nonzero value of the diffusion coef-

ficient both at the critical point of a bulk (unconfined) fluid and at its analog for a confined fluid system. In this connection, let us estimate the diffusion coefficient for water in the cylindrical geometry considered above at Δp , i.e. at the critical pressure of the bulk phase. Using the calculated estimate $|p_c^*(L) - p_c|/p_c \approx 0.027$ for the pressure change and formula (29) for the diffusion coefficient in the dynamic crossover region, we obtain $D^*(L, \Delta p = 0) = (\chi/S_G)^{\gamma/\nu} \approx 0.06$.

The results obtained provide a theoretical basis for the more profound study of unique properties of spatially confined fluid systems. The growing interest in this research direction is stimulated by relevant nanotechnology implementations in science, engineering, and applied medicine. In particular, as was shown in work [19], a detailed analysis of a dynamic state of water molecules in such mesoscale objects as the aqueous suspensions of plasmatic membranes of cancer cells is interesting and useful from the viewpoint of working out new techniques for the diagnostics and the treatment of oncological diseases.

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КОЕФІЦІЄНТ ДИФУЗІЇ ТА БАРОДИФУЗІЙНЕ ВІДНОШЕННЯ МЕЗОМАСШТАБНИХ РІДИН В КРИТИЧНІЙ ОБЛАСТІ

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Резюме

Наведено результати розрахунків коефіцієнта дифузії та бародифузійного відношення в залежності від тиску та густини в околі критичної точки рідинних систем з просторово обмеженою геометрією. Проаналізовано критичну поведінку цих кінетичних властивостей рідин у малих об'ємах у флуктуаційній, динамічній кросоверній та регулярній областях. Враховано ефекти просторової дисперсії з метою уникнення нульового значення коефіцієнта дифузії та нескінченного значення бародифузійного відношення з наближенням до критичного стану. Отримано числові оцінки з використанням наявних експериментальних даних та побудовано графіки, які ілюструють проведене теоретичні розрахунки.