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**BARODIFFUSION PHENOMENA IN LIQUID SYSTEMS  
NEAR THEIR CRITICAL POINT**

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Results of theoretical researches of barodiffusion phenomena in one-component liquids are presented for various regions of approach to the critical point, namely, 1) for the dynamic fluctuation region, where the singular contributions to Onsager kinetic coefficients prevail over the corresponding regular ones ( $a_s \gg a_r$  and  $b_s \gg b_r$ ); 2) for the dynamic crossover (transition) region, where  $a_s \approx a_r$  and  $b_s \approx b_r$ ; and 3) for the dynamic regular region, where  $a_s \ll a_r$  and  $b_s \ll b_r$ . In addition to the dynamic crossover temperature  $\tau_D$ , the dynamic crossover pressure  $\Delta p_D$  and density  $\Delta \rho_D$  have been introduced, and the corresponding numerical estimations have been made. The peculiarities of critical behaviors of the self-diffusion coefficient  $D$  and the barodiffusion ratio  $k_p$  have been analyzed.

**1. Introduction**

A reliable theoretical basis for studying the peculiarities in the critical behavior of equilibrium and nonequilibrium liquid systems consists in the application of universal methods of physics of phase transitions and critical phenomena to the objects under investigation. These methods are based on scale invariance (scaling) and renormalization group ideas which have been formulated by A.Z. Patashinski, V.L. Pokrovski, M.E. Fisher, K.G. Wilson, L.P. Kadanoff, and other researchers (see, e.g., works [1–5]).

In this work, the main attention will be given to studying barodiffusion phenomena for liquid systems in their critical region, i.e. the diffusion processes that occur not only under the influence of a chemical potential gradient, but also a pressure gradient. For this purpose, let us use the general basic points of thermodynamics of nonequilibrium processes and nonequilibrium statisti-

cal mechanics [6–10], by applying them to the study of barodiffusion processes in one-component biphasic liquid systems, in particular, the behaviors of the self-diffusion coefficient and the barodiffusion ratio.

**2. Barodiffusion Phenomena in a  
One-component Biphasic System**

As an example of the first object to study, let us consider the diffusion motion of particles of a certain kind through a membrane which separates the internal (the first phase) and the external (the second phase) medium. As is known (see, e.g., works [6, 9]), the condition of thermodynamic equilibrium in such a system is the equalities between temperatures, pressures, and chemical potentials in both phases. Let only the first of those equalities be fulfilled:

$$T_1 = T_2, \quad p_1 \neq p_2, \quad \mu_1 \neq \mu_2.$$

Then, in the absence of velocity gradients and chemical reactions, the diffusion flux of particles  $\mathbf{I}_n$  can be written down as follows:

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

where  $a$  and  $b$  are kinetic coefficients (the Onsager coefficients presented as sums of singular and regular contributions:  $a = a_s + a_r$  and  $b = b_s + b_r$ ),  $\nabla \mu$  is the chemical potential gradient, and  $\nabla p$  is the pressure gradient.

The self-diffusion coefficient  $D$  for such an isothermal one-component system appears as a proportionality factor between the diffusion flux of particles  $\mathbf{I}_n$  and the

gradient of particle concentration  $\nabla\rho$  in the linear relation between the fluxes of physical quantities and thermodynamic forces, whereas the barodiffusion ratio  $k_p$  is included into the proportionality factor of the linear, in the pressure gradient  $\nabla p$ , term in the relation for  $\mathbf{I}_n$ . To obtain the corresponding expressions for those coefficients, let us pass from the independent variables  $(\mu, p)$  to a new set of independent variables  $(\rho, p)$ . For this purpose, let us write down the chemical potential gradient in terms of variables  $(\rho, p)$ :

$$\nabla\mu = (\partial\mu/\partial p)_\rho \nabla p + (\partial\mu/\partial\rho)_p \nabla\rho. \quad (2)$$

Now, let us substitute the chemical potential gradient (2) into formula (1). Then, the linear law for the diffusion flux of particles reads

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

Compare formula (3) with a linear relation for the flux  $\mathbf{I}_n$  in the case of two thermodynamic forces invoked by the gradients of particle concentration,  $\nabla\rho$ , and pressure,  $\nabla p$ . Under isothermal conditions, this relation looks like [8, 9]

$$\mathbf{I}_n = -D(\nabla\mu + k_p \nabla \ln p). \quad (4)$$

Whence, we obtain the following formulas for the self-diffusion coefficient  $D$ , the barodiffusion coefficient  $D_p = Dk_p$ , and the barodiffusion ratio  $k_p$  for a one-component biphasic liquid:

$$D = a(\partial\mu/\partial\rho)_p, \quad (5a)$$

$$D_p = p[b + a(\partial\mu/\partial p)_\rho], \quad (5b)$$

$$k_p = p[b + a(\partial\mu/\partial p)_\rho]/a(\partial\mu/\partial\rho)_p. \quad (5c)$$

Let us analyze the critical behavior of the quantities  $D$  and  $k_p$  which characterize barodiffusion phenomena in a one-component biphasic system at various approaches to critical points or phase transition points along the paths close to the critical isochore and isobar. The temperature, as was marked above, is fixed, i.e. the liquid system is isothermal. Moreover, for definiteness, let us assume this temperature to be critical:  $T_1 = T_2 = T_c = \text{const}$ .

### 3. Self-diffusion Coefficient

First of all, let us consider the behavior of self-diffusion coefficient  $D$ , which is determined by formula (5a), along three different paths of liquid system approach to the point of phase transition of the second kind, making no allowance for spatial dispersion effects.

#### 3.1. Fluctuation region

In this region, which corresponds to the asymptotic approach to phase transition points and the anomalous growth of fluctuation effects, the singular contributions  $a_s$  and  $b_s$  to the Onsager kinetic coefficients in formulas (1), (3), and (5) exceed their regular parts  $a_r$  and  $b_r$ . The inequalities  $a_s \gg a_r$  and  $b_s \gg b_r$  follow from the fact that, according to the conclusions of the dynamic scaling theory [11], the quantities  $a_s$  and  $b_s$  diverge in the fluctuation region, and this divergence is governed by the critical behavior of the correlation length  $\xi$ , i.e.  $a_s$  and  $b_s$  behave as follows, when approaching the critical point and the phase transition points of the second kind:

$$\begin{aligned} a_s = b_s &= \Delta\rho^{-\nu/\beta} f_1^{(a,b)}(\Delta p/\Delta\rho^\delta) = \\ &= \Delta p^{-\nu/\beta\delta} f_2^{(a,b)}(\Delta\rho/\Delta p^{1/\delta}), \end{aligned} \quad (6)$$

where  $\Delta\rho = (\rho - \rho_c)/\rho_c$  is the order parameter of a one-component liquid, i.e. a deviation of the density from the critical value  $\rho_c$ ;  $\Delta p = (p - p_c)/p_c$  is a deviation of the pressure  $p$  from its critical value  $p_c$ ;  $\beta$ ,  $\delta$ , and  $\nu$  are critical indices which are  $\beta \approx 1/3$ ,  $\delta \approx 5$ , and  $\nu \approx 0.63$  in the bulk liquid phase; and the scaling functions  $f_1(x)$  and  $f_2(y)$  have the asymptotics  $f_1(x \rightarrow 0) = \text{const}$  and  $f_2(y \rightarrow \infty) \sim y^{-\nu/\beta}$  in a close vicinity of the critical isobar, and  $f_1(x \rightarrow \infty) \sim x^{-\nu/\beta\delta}$  and  $f_2(y \rightarrow 0) = \text{const}$  in a close vicinity of the critical isochore.

The singular contributions to the self-diffusion coefficient  $D$  in the fluctuation region are determined, according to formula (5a), by two multipliers, namely, 1) the Onsager kinetic coefficient  $a \approx a_s$  and 2) the inverse isobaric compressibility of a one-component liquid

$$(\partial\mu/\partial\rho)_p = \Delta\rho^{\gamma/\beta} f_3(\Delta p/\Delta\rho^\delta) = \Delta p^{\gamma/\beta\delta} f_4(\Delta\rho/\Delta p^{1/\delta}), \quad (7)$$

where the critical index  $\gamma \approx 1.24$ . In accordance with the fluctuation theory of phase transitions [1, 12], the anomalous reduction of the quantity  $(\partial\mu/\partial\rho)_p$ , when approaching the critical point, is immediately associated with a “strong” divergence of the isobaric compressibility, which coincides with the known divergence of the isothermal compressibility  $(\partial\mu/\partial\rho)_T$ , since the same thermodynamic derivative is calculated at constant field variables—the pressure  $p$  or the temperature  $T$ . Note also that the asymptotics of the scaling functions  $f_3(x)$  and  $f_4(y)$  are identical, to an accuracy of nonuniversal constant coefficients, with those of the scaling functions  $f_1(x)$  and  $f_2(y)$  which enter formulas (6).

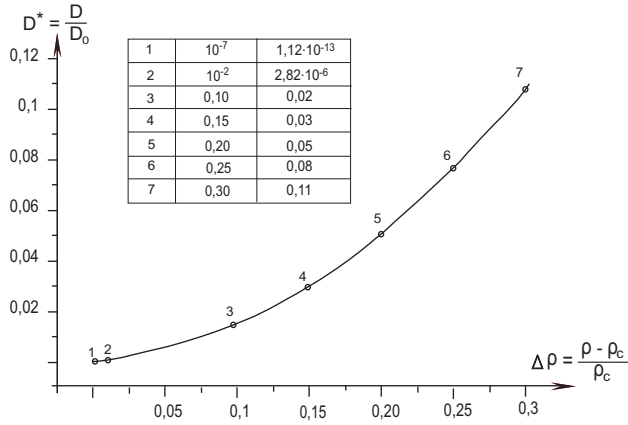


Fig. 1. Dependence of the normalized self-diffusion coefficient  $D^*$  on the order parameter  $\Delta\rho$  in a vicinity of the critical isobar

Hence, the self-diffusion coefficient is described by the following scaling dependence on the order parameter  $\Delta\rho$  and the pressure  $\Delta p$  in the fluctuation region that is asymptotically close to the critical point:

$$D = \Delta\rho^{(\gamma-\nu)/\beta} f_5(\Delta p/\Delta\rho^\delta) = \Delta p^{(\gamma-\nu)/\beta\delta} f_6(\Delta\rho/\Delta p^{1/\delta}), \quad (8)$$

where the scaling functions  $f_5(x) = f_1(x)f_3(x)$  and  $f_6(y) = f_2(y)f_4(y)$  are introduced.

For the specific numerical values of critical indices, formula (8) allows the following conclusions to be drawn concerning the critical behavior of the self-diffusion coefficient:

(i) in a vicinity of the critical isobar,

$$D \approx D_0 \Delta\rho^{1,85} (1 + A_1 \Delta p/\Delta\rho^5); \quad (9)$$

(ii) in a vicinity of the critical isochore,

$$D \approx D_0 \Delta p^{0,37} (1 + B_1 \Delta\rho/\Delta p^{0,2}). \quad (10)$$

The amplitude value  $D_0$  of the self-diffusion coefficient determines its value in the range  $\Delta\rho \approx 1$  and  $\Delta p \approx 1$ , where fluctuation effects cease to play the crucial role. The dependences of the normalized self-diffusion coefficient  $D^* = D/D_0$  on the order parameter  $\Delta\rho$  in a vicinity of the critical isobar ( $\Delta p/\Delta\rho^\delta \ll 1$ ) and on the pressure  $\Delta p$  in a vicinity of the critical isochore ( $\Delta\rho/\Delta p^{1/\delta} \gg 1$ ) are depicted in Figs. 1 and 2, respectively.

It should be emphasized that, as was noted in work [13], the vanishing of the self-diffusion coefficient at the very critical point cannot be observed in experiments.

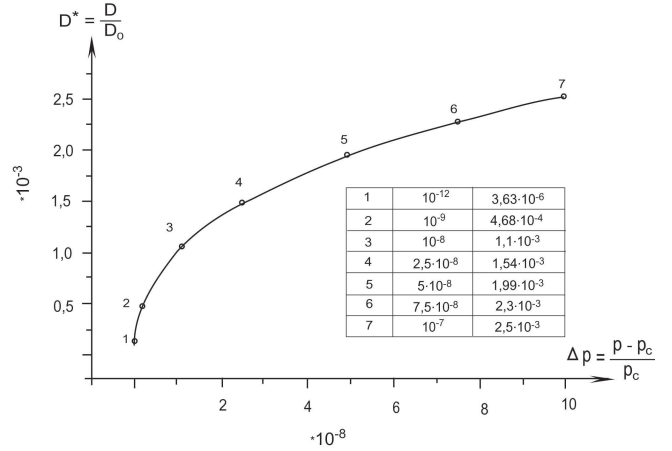


Fig. 2. Dependence of the normalized self-diffusion coefficient  $D^*$  on the order parameter  $\Delta p$  in a vicinity of the critical isochore

It is clear that, for the  $D$ -values obtained at the critical points and the points of phase transitions of the second kind to be minimal (nevertheless, nonzero), the contributions of the space-time dispersion, which make allowance for non-locality effects and memory effects with respect to physical properties (the Onsager coefficients, the isobaric compressibility, and so on) in the critical region, must be taken into account. In the Ornstein–Zernike approximation which corresponds to a relatively weak spatial dispersion (i.e.  $\xi k < 1$ , where  $\xi$  is the correlation length, and  $k$  is the wave vector), small terms of the  $\xi^2 k^2$ -order should be added to expressions (8)–(10) [14]. In the region of strong spatial dispersion ( $\xi k \geq 1$ ), an additional multiplier which includes the Kawasaki function (see, e.g., works [15, 16]) should be introduced into expressions for the self-diffusion coefficient.

### 3.2. Crossover region

In work [17], the temperature of the so-called dynamic crossover  $\tau_D$  was introduced for the critical phenomena and the phase transitions that depend only on the temperature variable  $\tau = (T - T_c)/T_c$ . At this temperature, the regular and singular contributions to Onsager kinetic coefficients are of the same order of magnitude. By analogy to  $\tau_D$ , in that case where critical phenomena and phase transitions occur only under the pressure action, it is useful to introduce the variable  $\Delta p_D$  which would determine the pressure, at which the dynamic crossover takes place, i.e. the approximate equalities  $a_s \approx a_r$  and  $b_s \approx b_r$  hold true. Evidently, such a situation takes place, when the critical points (the points

of phase transitions of the second kind) are approached along the three-dimensional phase surface and perpendicularly to the  $T - \rho$  plane. If the singular parts of Onsager kinetic coefficients are given by the formulas  $a_s = a_s^0 |\Delta p|^{-\nu/\beta\delta}$  and  $b_s = b_s^0 |\Delta \rho|^{-\nu/\beta\delta}$ , the dynamic crossover pressure  $\Delta p_D$  is characterized by the relations  $|\Delta p_D| \approx (a_r/a_s^0)^{-\beta\delta/\nu}$  and  $|\Delta \rho_D| \approx (b_r/b_s^0)^{-\beta\delta/\nu}$ . Provided that the dynamic crossover temperature is of the order of  $|\Delta \tau_D| \approx (a_r/a_s^0)^{-1/\nu} \approx 10^{-4} \div 10^{-5}$ , one should expect that  $|\Delta p_D| \approx |\tau_D|^{\beta\delta} \approx 10^{-6.5} \div 10^{-8}$ .

In a similar way, for the critical phenomena and the phase transitions that depend only on the density, the variable  $\Delta \rho_D$  obeying  $|\Delta \rho_D| \approx (a_r/a_s^0)^{-\beta/\nu}$  and  $|\Delta \rho_D| \approx (b_r/b_s^0)^{-\beta/\nu}$ , which determines a density, at which the dynamic crossover takes place, should be introduced. The numerical estimation of the dynamic crossover density gives rise to the value  $|\Delta \rho_D| \approx |\Delta p_D|^{1/\delta} \approx |\tau_D|^\beta \approx 10^{-1.3} \div 10^{-1.65} \approx 0.5 \div 0.3$ .

Taking into account that  $a_s \approx a_r$  in the crossover region, we obtain the following relation for the Onsager kinetic coefficient:  $a = a_r + a_s \approx 2a_s$ . This result means that the amplitude of the self-diffusion coefficient in the dynamic crossover region is approximately twice as large as that in the dynamic fluctuation region, i.e.,

(i) in a vicinity of the critical isobar,

$$D \approx 2D_o \Delta \rho^{1.85} (1 + A_1 \Delta p / \Delta \rho^5); \tag{11}$$

(ii) in a vicinity of the critical isochore,

$$D \approx 2D_o \Delta p^{0.37} (1 + B_1 \Delta \rho / \Delta p^{0.2}). \tag{12}$$

### 3.3. Regular region

As was mentioned above, fluctuation effects can be neglected in this region, if the Ginzburg–Levanyuk number  $Gi = \langle \Delta \varphi^2 \rangle / \varphi_0^2$  – it is a ratio between the root-mean-square fluctuation of the order parameter,  $\langle \Delta \varphi^2 \rangle$ , and the squared equilibrium value of the order parameter,  $\varphi_0^2$  – is small enough ( $Gi < 1$ ). Then, for temperature-dependent critical phenomena and phase transitions in

the region, where  $Gi < \tau \leq 1$ , the Onsager kinetic coefficient,  $a \approx a_r$ , does not depend on the temperature variable  $\tau$ . In this case, every peculiarity in the critical behavior of the self-diffusion coefficient  $D$  is completely governed by the value of inverse compressibility:  $D = D_o \tau^\gamma$ .

However, if critical phenomena and phase transitions depend mainly only on the density, the expression for the diffusion coefficient in the regular region in a close vicinity to the critical isobar ( $\Delta p / \Delta \rho^\delta \ll 1$ ) looks like

$$D = D_o \Delta \rho^{\gamma/\beta} (1 + A_1 \Delta p / \Delta \rho^\delta), \tag{13}$$

or, for specific numerical values of critical indices,

$$D = D_o \Delta \rho^{3.76} (1 + A_1 \Delta p / \Delta \rho^5).$$

At last, for critical phenomena and phase transitions which are governed by a pressure variation, as it takes place in the case of barodiffusion phenomena, the diffusion coefficient in the regular region in a close vicinity to the critical isochore ( $\Delta \rho / \Delta p^{1/\delta} \gg 1$ ) is described by the formula

$$D = D_o \Delta p^{\gamma/\beta\delta} (1 + \Delta \rho / \Delta p^{1/\delta}), \tag{14}$$

which, after the substitution of numerical values of critical indices, reads

$$D = D_o \Delta p^{0.75} (1 + \Delta \rho / \Delta p^{0.2}).$$

Table 1 illustrates the dependences of the normalized self-diffusion coefficient  $D^* = D/D_o$  on pressure deviations within the interval  $\Delta p = 10^{-12} \div 1$  on the critical isochore (left side) and on density deviations within the interval  $\Delta \rho = 10^{-7} \div 1$  on the critical isobar (right side). Hence, an important conclusion follows: if a numerical value of the self-diffusion coefficient amplitude  $D_o$ , which is determined by the regular part of the Onsager kinetic coefficient amplitude  $a_r$  and the amplitude of the inverse isobaric compressibility  $(\partial \mu / \partial \rho)_p^0$  according to the formula  $D_o = a_r (\partial \mu / \partial \rho)_p^0$ , is known, this enables the absolute value of the self-diffusion coefficient of an arbitrary one-component liquid to be calculated. For instance, using the known value  $D_o = 2.3 \times 10^{-9}$  m<sup>2</sup>/s for water [13, 18], we obtain numerical values of self-diffusion coefficient  $D$  in wide intervals of pressure and density (see Table 2).

### 4. Barodiffusion Ratio

Let us now analyze the critical behavior of the barodiffusion ratio  $k_p$  for a one-component liquid. In accordance

**Table 1**

$\Delta p$	$D^* = D/D_o$	$\Delta \rho$	$D^* = D/D_o$
$10^{-12}$	$3.63 \times 10^{-5}$	$10^{-7}$	$1.12 \times 10^{-13}$
$10^{-10}$	$1.99 \times 10^{-4}$	$10^{-5}$	$5.26 \times 10^{-10}$
$10^{-8}$	$1.11 \times 10^{-3}$	$10^{-3}$	$2.82 \times 10^{-6}$
$10^{-6}$	$6.03 \times 10^{-3}$	0.1	$1.41 \times 10^{-2}$
$10^{-4}$	0.001	0.5	$7.38 \times 10^{-2}$
$10^{-2}$	0.18	0.75	0.34
1	1	1	1

with formula (5c), it can be rewritten as follows:

$$k_p = p[(b/a) + (\partial\mu/\partial p)_\rho]/(\partial\mu/\partial\rho)_p. \quad (15)$$

This expression demonstrates that  $k_p$  depends not only on the Onsager kinetic coefficient  $a$  and the inverse isobaric compressibility  $(\partial\mu/\partial\rho)_p$  (those two determine the self-diffusion coefficient  $D$ ), but also on the Onsager kinetic coefficient  $b$  in the cross term that corresponds to a contribution of the pressure gradient  $\nabla p$  to the diffusion flux  $\mathbf{I}_n$ , as well as on the thermodynamic derivative  $(\partial\mu/\partial p)_\rho$ . The latter quantity has no features at the critical point, because the derivative of one field variable (in this case, it is the chemical potential  $\mu$ ) with respect to another field variable (in this case, it is the pressure  $p$ ), provided that any field quantity ( $T$ ,  $p$ ,  $\nu$ , and so on) or the density one (the entropy  $S$ , volume  $V$ , density  $\rho$ , concentration  $x$ , and so on) is fixed, remains constant at the critical point [12].

The Onsager kinetic coefficient  $b$  has the same features at the critical point as the kinetic coefficient  $a$  which has already been considered, i.e. its singular behavior in the case of a one-component liquid is completely governed by the divergence of the density fluctuation correlation length  $\xi$  according to formula (6).

#### 4.1. Fluctuation region

Taking the conditions  $a_s \gg a_r$  and  $b_s \gg b_r$  into account and cancelling the identical divergences of singular contributions to the kinetic coefficients in formula (15), we obtain the following expression for the barodiffusion ratio  $k_p$ :

$$k_p = \Delta\rho^{-\gamma/\beta} \varphi_1(\Delta p/\Delta\rho^\delta) = \Delta p^{-\gamma/\beta\delta} \varphi_2(\Delta\rho/\Delta p^{1/\delta}). \quad (16)$$

Here, the scaling functions  $\varphi_1(x)$  and  $\varphi_2(y)$ , which depend on the arguments  $x = \Delta p/\Delta\rho^\delta$  and  $y = x^{-1/\delta} = \Delta\rho/\Delta p^{1/\delta}$ , can be written down as follows:

$$\begin{aligned} \varphi_1(x) &= p_c \left[ \frac{f_1^{(b)}(x)}{f_1^{(a)}(x)} + \left( \frac{\partial\mu}{\partial p} \right)_\rho^0 \right] / \left( \frac{\partial\mu}{\partial\rho} \right)_p^0, \\ \varphi_2(y) &= p_c \left[ \frac{f_2^{(b)}(y)}{f_2^{(a)}(y)} + \left( \frac{\partial\mu}{\partial p} \right)_\rho^0 \right] / \left( \frac{\partial\mu}{\partial\rho} \right)_p^0. \end{aligned} \quad (17)$$

Note that, in order to obtain formula (16), we used the relations  $a_s = a_s^0 \Delta\rho^{-\nu/\beta} = a_s^0 \Delta p^{-\nu/\beta\delta}$  and  $b_s = b_s^0 \Delta\rho^{-\nu/\beta} = b_s^0 \Delta p^{-\nu/\beta\delta}$ , where  $a_s^0$  and  $b_s^0$  are the amplitudes of singular parts of kinetic coefficients. Whence,

assuming that, in vicinities of the critical isobar ( $x \rightarrow 0$ ) and the isochore ( $y \rightarrow 0$ ), the ratios between the scale functions in relations (16) are equal to the ratio between the amplitudes of singular parts of Onsager kinetic coefficients  $a_s$  and  $b_s$ , i.e.,

$$\frac{f_1^{(b)}(x)}{f_1^{(a)}(x)} \approx \frac{f_2^{(b)}(y)}{f_2^{(a)}(y)} \approx \frac{b_s^0}{a_s^0},$$

we obtain the following formula for the amplitude of barodiffusion ratio:

$$k_p^0 = p_c [b_s^0/a_s^0 + (\partial\mu/\partial p)_\rho^0]/(\partial\mu/\partial\rho)_p^0 = const. \quad (18)$$

Therefore, according to expressions (16)–(18), the barodiffusion ratio  $k_p$  has a “strong” divergence in the fluctuation region, similar to that for the isothermal or isobaric compressibility of a one-component liquid, if the effects of spatial dispersion are not taken into account. For the specific numerical values of critical indices, we obtain the following formulas for  $k_p$ :

(i) in a vicinity of the critical isobar,

$$k_p \approx k_p^0 \Delta\rho^{-1.85} (1 + C_1 \Delta p/\Delta\rho^5), \quad (19)$$

(ii) in a vicinity of the critical isochore,

$$k_p \approx k_p^0 \Delta p^{-0.37} (1 + D_1 \Delta\rho/\Delta p^{0.2}). \quad (20)$$

#### 4.2. Crossover region

In this region, where  $a_s \approx a_r$  and  $b_s \approx b_r$ , the ratio between Onsager kinetic coefficients remains the same as it was in the fluctuation region, since  $b/a = (b_s + b_r)/(a_s + a_r) \approx 2b_s/2a_s \approx 2b_r/2a_r = b_s^0/a_s^0$ . Hence, formulas (19) and (20) remain invariable, whereas the barodiffusion ratio  $k_p$ , according to them, decreases, as the distance from the critical point increases, which is accompanied by the growth of deviations of the density,  $\Delta\rho$ , and the pressure,  $\Delta p$ .

**Table 2**

$\Delta p$	$D$	$\Delta\rho$	$D$
$10^{-12}$	$8.35 \times 10^{-14}$	$10^{-7}$	$2.58 \times 10^{-22}$
$10^{-10}$	$4.58 \times 10^{-13}$	$10^{-5}$	$1.21 \times 10^{-18}$
$10^{-8}$	$2.30 \times 10^{-12}$	$10^{-3}$	$6.49 \times 10^{-15}$
$10^{-6}$	$2.55 \times 10^{-12}$	0.1	$3.24 \times 10^{-11}$
$10^{-4}$	$1.39 \times 10^{-11}$	0.5	$1.70 \times 10^{-10}$
$10^{-2}$	$4.14 \times 10^{-10}$	0.75	$7.82 \times 10^{-10}$
1	$2.30 \times 10^{-9}$	1	$2.30 \times 10^{-9}$

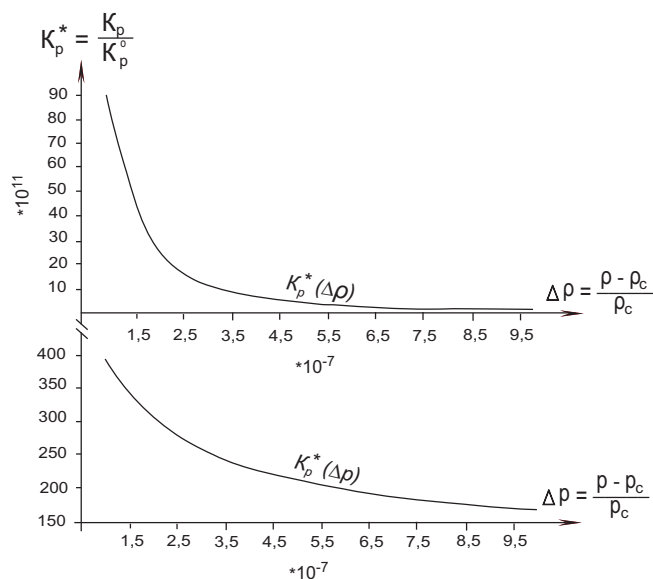


Fig. 3. Dependences of the barodiffusion ratio on the order parameter  $\Delta\rho$  in a vicinity of the critical isobar and the order parameter  $\Delta p$  in a vicinity of the critical isochore

#### 4.3. Regular region

All that was written above about the crossover region is equally applicable to the regular one, where  $b/a = b_r/a_r = b_s^0/a_s^0$ . A unique quantity that remains dependent on  $\Delta\rho$  and  $\Delta p$  is the derivative  $(\partial\mu/\partial\rho)_p$  in the denominator of formula (15), which ensures that formulas (19) and (20) hold true. Figure 3 illustrates the dependence of the barodiffusion ratio on the density and the pressure presented by Eqs. (19) and (20), respectively, in wide intervals of their variation.

At the same time, since the regular region is contiguous with the region, where deviations of the thermodynamic parameters from their critical values are large ( $\tau \geq 1$ ,  $\Delta\rho \geq 1$ , and  $\Delta p \geq 1$ ), this circumstance requires that the additional regular contributions providing the “matching” between the expressions for the barodiffusion ratio  $k_p$  in the regions ( $\tau \leq 1$ ,  $\Delta\rho \leq 1$ ,  $\Delta p \leq 1$ ) and ( $\tau \geq 1$ ,  $\Delta\rho \geq 1$ ,  $\Delta p \geq 1$ ) should be taken into account. In other words, it is necessary to provide a transition (crossover) from formulas (19) and (20), in which the power-law relations  $(\partial\mu/\partial\rho)_p \sim \tau^\gamma \sim \Delta\rho^{\gamma/\beta} \sim \Delta p^{\gamma/\beta\delta}$  were used, to corresponding formulas, in which the inverse isobaric compressibility (the isobaric modulus) is given, for example, by the Tait or another regular (non-scaling) state equation. By the way, the same also concerns the self-diffusion coefficient in the regular region.

## 5. Conclusion

To summarize, we would like to note that the results of this research provide a basis for the further study of features of the pressure gradient influence on diffusion processes, which is of not only theoretical, but also practical interest. In particular, barodiffusion processes must play an important role in the precision medical techniques of ultrasonic diagnostics and therapy [19].

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## БАРОДИФУЗІЙНІ ЯВИЩА В РІДИННИХ СИСТЕМАХ ПОВЛИЗУ КРИТИЧНОЇ ТОЧКИ

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Р е з ю м е

Представлено результати теоретичних досліджень бародифузійних явищ в однокомпонентних рідинах для різних областей наближення до критичної точки, а саме: 1) для динамічної флуктуаційної області, де сингулярні внески в кінетичні коефіцієнти Онзагера переважають їх регулярні внески ( $a_s \gg a_r$  і  $b_s \gg b_r$ ); 2) для динамічної кросоверної (перехідної) області, де  $a_s \approx a_r$  і  $b_s \approx b_r$ ; 3) для динамічної регулярної області, де  $a_s \ll a_r$  і  $b_s \ll b_r$ . Додатково до температури динамічного кросовера  $\tau_D$  введено тиск  $\Delta p_D$  і густину  $\Delta \rho_D$  динамічного кросовера, для яких наведено чисельні оцінки. Досліджено особливості критичної поведінки коефіцієнта самодифузії  $D$  та бародифузійного відношення  $k_p$ .