

Chapter 2

Dimensional Crossover in Liquids in Reduced Geometry

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Abstract Problem of finding the pair correlation function G_2 and correlation length ξ of order parameter fluctuations in liquids in restricted geometry is discussed. Two types of dimensional crossover (DC) are studied. The 1st type (DC-1) corresponds to transition from 3D bulk to 3D bounded liquids. In this case the dependence of physical properties on thermodynamic variables (temperature, density, pressure, etc.) in bulk liquids with linear sizes $L \gg \xi$ may convert into dependence of these properties on linear sizes in bounded liquids with $L < \xi$. The 2nd type (DC-2) corresponds to the case when a further decreasing of linear sizes in confined liquids may be treated under certain conditions as the change of spatial dimensionality D (for example, $3D \Leftrightarrow 2D$ crossover in slit-like pores or $3D \Leftrightarrow 1D$ crossover in cylindrical pores). Smooth transition of effective critical exponents (say, from $\nu = 0.625$ for $D = 3$ to $\nu = 1$ for $D = 2$) as well as theoretical results versus experimental data are examined for liquids in reduced geometry.

2.1 Introduction

Phase transitions and critical phenomena in reduced geometry have been actively investigated in recent years. Many systems of experimental and theoretical interest are spatially bounded and have different forms of reduced geometry, such as thin surface layers, interfaces, porous media, biological membranes, vesicles, synaptic clefts, etc. This review paper is aimed at studying peculiarities of dimensional crossover in liquid systems in reduced geometry.

The problem going to be mainly discussed: how results of 3D systems transfer to results of 2D systems and vice versa. Obviously, such a $3D \Leftrightarrow 2D$ transition which may be called “dimensional crossover” or “dimensionality crossover” should be

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smooth and without discontinuities. While describing such a dimensional crossover (DC), one has to take into account the main theoretical ideas of bulk scaling and finite-size scaling (FSS) as well as experimental results (see e.g. [1–15]).

The topics under consideration are as follows: (a) pair correlation function and correlation length of order parameter fluctuations in liquids in reduced geometry; (b) effects of spatial limitation and two types of dimensional crossover; (c) comparison of theoretical results and experimental data in liquids in reduced geometry.

2.2 Pair Correlation Function and Correlation Length of Order Parameter Fluctuations

The major problem of the statistical physics approach is to find the pair correlation function G_2 and correlation length ξ of order parameter fluctuations in bounded systems undergoing phase transitions and critical phenomena. This problem is studied in liquid volumes in reduced geometry in the form of plane-parallel layers and cylindrical samples [4, 16].

To receive *the pair correlation function* of scalar order parameter fluctuations, namely density fluctuations for a single-component liquid near the critical point, one can use the well-known method of the statistical physics based on the Ornstein-Zernike (OZ) equation

$$G_2(r) = C(r) + \langle \rho \rangle \int G_2(r - r') C(r') dr'. \quad (2.1)$$

Here $C(r)$ is the direct correlation function and $\langle \rho \rangle$ is the average density. The direct correlation function $C(r)$ is usually short-range for real intermolecular potentials. It allows using the following differential equation instead of the integral (2.1):

$$(\Delta - \kappa^2)G_2(r) = -C(r)/C_2, \quad (2.2)$$

where $\kappa^2 = (1 - C_0)/C_2$ is the quantity related to the inverse isothermal compressibility, while $C_0 = \langle \rho \rangle \int C(r) dr$, $C_2 = \frac{1}{6} \langle \rho \rangle \int C(r) r^2 dr$ are the zero and the second spatial moments of the direct correlation function.

In order to obtain the pair correlation function $G_2(r)$ one usually substitutes the short-range direct correlation function $C(r)$ in (2.2) with the delta function $\delta(r)$. Then $G_2(r)$ can be found as the Green function for the Helmholtz operator $\hat{L} = \Delta - \kappa^2$, where Δ is the Laplacian.

Using this method, it is easy to obtain the OZ correlation function

$$G_2(r) = A \exp(-r/\xi)/r \quad (2.3)$$

for the 3-dimensional infinite system with zero boundary conditions. One has indeed for the pair correlation function $G_2(r) \rightarrow 0$ if $r = |r_1 - r_2| \rightarrow \infty$. Here in (2.3) A is the constant coefficient, $\xi = \kappa^{-1}$ is the correlation length of order parameter fluctuations. It is important to mention that the anomalous growth of the correlation length ξ and the long-range behavior of the pair correlation function $G_2(r) \sim r^{-1}$ take place at the phase transition or critical points only for spatially infinite systems.

Let us consider the geometry of our problem in the form of a **plane-parallel layer**: $-\infty < x, y < \infty$, $-L_0 < z < L_0$. It is possible to find the Green's function of the Helmholtz operator for such a layer with zero boundary conditions at the surfaces $z = \pm L_0$ in the following form [4]:

$$G_2(\rho, z) = \frac{1}{4\pi L_0} \sum_{n \geq 0} [1 - (-1)^n] * \quad (2.4)$$

$$K_0 \left[\rho (\kappa^2 + n^2 \pi^2 / 4L_0^2)^{3/2} \right] \cos(n\pi z / 2L_0),$$

where $\rho = (x^2 + y^2)^{1/2}$ and $K_0(u)$ is the cylindrical Macdonald function.

The pair correlation function $G_2(r)$ may be obtained also by another method based on the result of acting the inverse Helmholtz operator \hat{L}^{-1} on the delta function $\delta(r)$. It first requires the expression for the delta function constructed of orthonormal eigenfunctions of the operator \hat{L} with zero boundary conditions and with eigenvalues λ_n satisfying the relation $\lambda_n = k_x^2 + k_y^2 + k_z^2 + \kappa^2$. Components of wave vector k_x, k_y change continuously ($-\infty < k_x, k_y < \infty$), while k_z is discrete ($k_z = n^2 \pi^2 / 4L_0^2$, $n = 0, 1, 2, \dots$). The following formula for $\delta(r)$ satisfies all these conditions:

$$\delta(r) = \frac{1}{8\pi L_0} \sum_{n \geq 0} \iint [1 - (-1)^n] \cos(n\pi z / 2L_0) \exp[i(k_x x + k_y y)] dk_x dk_y. \quad (2.5)$$

With taking (5) into account, an expression for $G_2(r)$ can be obtained in the form

$$G_2(r) = \hat{L}^{-1} \delta(r)$$

$$= \frac{1}{8\pi^2 L_0^2} \sum_{n \geq 0} \iint \frac{\cos(n\pi z / 2L_0) e^{i(k_x x + k_y y)}}{k_x^2 + k_y^2 + (n\pi / 2L_0)^2 + \kappa^2} dk_x dk_y. \quad (2.6)$$

Using polar coordinates $k_x = k_{xy} \cos \varphi$, $k_y = k_{xy} \sin \varphi$ and integrating (6) with such formulae for cylindrical functions

$$\exp(ik\rho \cos \varphi) = J_0(k\rho) + 2i \cos \varphi J_1(k\rho) + 2i^2 \cos 2\varphi J_2(k\rho) + \dots,$$

$$\int_0^\infty \frac{k J_0(k\rho) dk}{k^2 + a^2} = K_0(\rho a).$$

one can obtain the result given by formula (2.4) for the pair correlation function of a plane-parallel layer.

As in the previous case of a plane-parallel layer, let us find a solution of the differential OZ equation for a spatially restricted system in the form of a **cylindrical sample** ($0 \leq x, y \leq a, -Z_0 < z < Z_0, Z_0 \gg a$). The cylinder radius a is supposed to be much smaller than distance Z_0 along the cylinder axis. While solving the OZ equation in cylindrical coordinates

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial G_2}{\partial r} + \frac{\partial G_2}{\partial z^2} - \kappa^2 G_2 = 0, \quad (2.7)$$

the nonsingular solution can be found as follows [16]:

$$G_2(r, z) = \sum_{n \geq 1} D_n J_0(\mu_n \frac{r}{a}) \exp \left[-(\kappa^2 + \mu_n^2/a^2)^{1/2} |z| \right]. \quad (2.8)$$

Here $J_0(u)$ is the Biessel function, μ_n are its nodes, i.e. the solutions of the equation $J_0(\mu_n) = 0$, and D_n are coefficients. The solution (2.8) is valid for all r except the nearest vicinity of the point $r = 0$.

The iterative procedure was proposed to find a non-singular solution of the OZ equation in [17]. The first iterations for the pair and direct correlation functions of scalar order parameter fluctuations near the critical point were found for bounded systems with geometry of a cylinder. These results, being valid even at $r = 0$, were used to study the shifts of the critical parameters.

The main contributions in both expressions (2.6) and (2.8) for the pair correlation function are given by the first terms with small n . Therefore, one has in the case of a plane-parallel layer

$$G_2(\rho, z) = \frac{1}{2\pi L_0} K_0 \left[\rho(\kappa^2 + n^2\pi^2/4L_0^2)^{1/2} \right] \cos(\pi z/2L_0), \quad (2.9)$$

and in the case of a cylindrical sample

$$G_2(r, z) = D_1 J_0(\mu_1 r/a) \exp \left[-(\kappa^2 + \mu_1^2/a^2)^{1/2} |z| \right]. \quad (2.10)$$

Correlation functions (2.4) and (2.8) demonstrate an oscillatory behavior in the z direction for plane-parallel layers and in the r direction for cylindrical samples confirming the theoretical results and computer-simulation studies (see e.g. [18, 19]) for the radial distribution function $g(r)$ in liquids in restricted geometry).

The limiting case of the Ornstein-Zernike approximation (2.3) for an infinite system can be obtained from formulae (2.4) and (2.8) for G_2 with zero boundary conditions

$$\begin{aligned}
G_2(\rho, z) &= \frac{1}{4\pi L_0} \left(\frac{2L_0}{\pi} \right)^2 \int_0^\infty K_0 \left[\rho(\kappa^2 + n^2 \pi^2 / 4L_0^2)^{1/2} \right] \cos(k_z z) dk_z \\
&= \frac{1}{4\pi} \exp \left[-\kappa(\rho^2 + z^2)^{1/2} \right] / (\rho^2 + z^2)^{1/2}, \\
G_2(r, z) &= \int_1^\infty e^{-x|z|} J_0(r\sqrt{x^2 - \kappa^2}) dx = \frac{\exp(-\kappa\sqrt{r^2 + z^2})}{\sqrt{r^2 + z^2}},
\end{aligned}$$

in geometries of plane-parallel layers and cylindrical samples, correspondingly.

As is seen from (2.4), (2.8–2.10), the pair correlation functions of liquids in reduced geometry have a non-exponential shape. Therefore, it is natural to determine **the correlation length** ζ of order parameter fluctuations in such bounded liquids according to the following relation:

$$\zeta = \sqrt{M_2}, M_2 = \frac{\int G_2(r) r^2 dr}{\int G_2(r) dr}, \quad (2.11)$$

where M_2 is the second normalized spatial moment of the pair correlation function.

In the case of **a plane-parallel layer**, taking into account the formula (2.9) for the pair correlation function $G_2(r)$ and expression for the cylindrical Macdonald function $K_\nu(u)$ and gamma-function $\Gamma(u)$ [20]

$$\int_0^\infty x^\mu K_\nu(ax) dx = 2^{\mu-1} a^{-\mu-1} \Gamma\left(\frac{1+\mu+\nu}{2}\right) \Gamma\left(\frac{1+\mu-\nu}{2}\right),$$

one can derive the following formula for the correlation length ζ of order parameter fluctuations:

$$\zeta = \zeta_0 \left[\frac{4}{\kappa^2 + \pi^2 / 4L_0^2} + \frac{1}{4} (1 - 8/\pi^2) S^2 \right]^{1/2}. \quad (2.12)$$

In the case of **a cylindrical geometry** in accordance with the main contribution for pair correlation function (2.10) and values of integrals [20]

$$\begin{aligned}
\int_0^a J_0(a/\alpha) r dr &= (a/\alpha) J_1(\alpha a), \\
\int_0^a J_0(\alpha r) r^3 dr &= \frac{a}{\alpha} \left(\alpha^2 - \frac{1}{\alpha^2} \right) J_1(\alpha a) + 2\alpha^2 a^2 J_0(\alpha a),
\end{aligned}$$

the correlation length ξ can be written as

$$\xi = \xi_0 \left[\frac{2}{(\xi_0^{-1}\kappa)^2 + \mu_1^2/S^2} + \left(1 - \frac{4}{\mu_1^2}\right)S^2 \right]^{1/2}. \quad (2.13)$$

The correlation length ξ in (2.12) and (2.13) depends not only upon thermodynamic variables (because of relationships between κ and temperature, density, etc.) but also on the thickness $d = 2L_0$ or the radius a , i.e. on the geometric factors $S = d/\xi_0$ or $S = a/\xi_0$ related to the number of molecular monolayers along the direction of spatial limitation.

Let us summarize the approximations used to derive expressions for the pair correlation function G_2 and correlation length ξ :

- (a) Here two methods have been used: (1) method of the OZ integral (2.1) which was transformed into the differential (2.2) with two spatial moments of the short-range direct correlation function. This method is quite equivalent to the well-known OZ approximation in the fluctuation theory of critical phenomena giving the critical exponent $\eta = 0$ in an scaling formula for the pair correlation function $G_2(r) = A \exp(-r/\xi)/r^{1+\eta}$ [21]; (2) method of the inverse Helmholtz operator $\hat{L} = \Delta - \kappa^2$ acting on the delta function and giving G_2 as the Green function for this operator.
- (b) We used here only the main contributions to correlation function G_2 given by the first terms in (2.4) and (2.8). It was shown [22, 23] that next contributions, say, for a cylindrical sample are decreasing with the growth of number n of the Biessel function nodes μ_n ($\mu_1 = 2.4048$, $\mu_2 = 5.5201$, $\mu_3 = 8.8537$, $\mu_4 = 11.7915$, etc.) and due to reduction of cylindrical and exponential functions in (2.8) and (2.10) with increasing of their arguments. So, at $|z|/\kappa a \approx 1$ ratios of successive terms in (2.8) have such orders of magnitudes: $a_2/a_1 \approx 10^{-1} \sim 10^{-2}$, $a_3/a_1 \approx 10^{-3}$, $a_4/a_1 \approx 10^{-4}$.
- (c) The pair correlation functions (2.4), (2.8–2.10) in liquids in reduced geometry are obtained for zero boundary conditions. The case of the arbitrary boundary conditions for the pair correlation function $G_2(r=a, z) = F(z)$ was studied for a cylindrical geometry in [22, 23]. Numerical values of the arbitrary function $F(z)$ depend on the concrete problems and change within the interval $0 \leq F \leq 1$. The case $F = 0$ corresponds to “hydrophobic” surfaces, the case $F = 1$ – to “hydrophilic” surfaces. The intermediate case $0 < F < 1$ describes obviously the situation of the so-called “incomplete wetting”. Omitting immaterial details, one can receive finally the solution of the OZ differential (2.2) in the form (2.8) with the only important difference: values μ_n , being the nodes of the Biessel function and satisfying the equation $J_0(\mu_n) = 0$, have to be substituted in the formula (2.8) for the arbitrary boundary conditions by values ξ_n which are the nodes of the transcendental equation $J_0(\xi_n) = F(z) \exp[-(\kappa^2 + \xi_n^2/a^2)^{1/2}|z|]$.

2.3 Comparison with the Fisher Scaling Hypothesis, Anisotropic Effects in Finite-Size Scaling

Fisher [2] and other authors (see e.g. [8–10, 12, 13]) have proposed the *FSS hypothesis for systems in reduced geometry*. According to this hypothesis (here we shall formulate it for classical liquids), the fluctuation part of the thermodynamic potential $\Delta\Phi_s$ and the correlation length ξ depend not only on the thermodynamic variables (the reduced temperature τ , etc.) and external fields h but on the linear size L of a system:

$$\Delta\Phi_s = L^{-d} f_\Phi(a\tau L^{1/v}, bhL^{\beta\delta/v}), \quad \xi = L f_\xi(a\tau L^{1/v}, bhL^{\beta\delta/v}), \quad (2.14)$$

where a and b are nonuniversal constants (amplitudes).

The first scaling argument in (2.14) $x = a\tau L^{1/v}$ in both scaling functions f_Φ and f_R can be obtained from the following formulae:

$$\xi \sim \tau^{-n}, \tau \sim \xi^{-1/v}, x \sim \frac{\tau}{\xi^{-1/v}} \sim \tau L^{1/v} \quad (\xi \rightarrow L). \quad (2.15)$$

In analogous way one can easily obtain the expression for the second scaling argument $y = bhL^{\beta\delta/v}$ with taking such formulae into account

$$\begin{aligned} \xi \sim \tau^{-v} \sim \varphi^{-v/\beta} \sim h^{-v/\beta\delta}, \quad \varphi \sim \tau^\beta, \quad \varphi \sim h^{1/\delta}, \quad \tau \sim \varphi^{1/\beta}, \\ h \sim \xi^{-\beta\delta/v}, \quad y \sim \frac{h}{\xi^{-\beta\delta/v}} \sim hL^{\beta\delta/v} \quad (\xi \rightarrow L). \end{aligned} \quad (2.16)$$

Here $\varphi = (\rho - \rho_c)/\rho_c$ is the order parameter for classical liquids, i.e. the reduced density.

The isothermal compressibility of liquids in reduced geometry in nonzero external fields may be written as

$$\begin{aligned} \beta_T = (\partial^2 \Delta\Phi_s / \partial h^2)_\tau = L^{-d+2\beta\delta/v} f_\beta(x, y), \quad f_\beta = b(f_\Phi)''_h, \\ -d + 2\beta\delta/v = \gamma/v. \end{aligned} \quad (2.17)$$

The Fisher FSS hypothesis formulated for the susceptibility χ in [2]

$$\chi = S^\omega F(S_\tau^\theta). \quad (2.18)$$

Equation (2.18) was stated for systems in reduced geometry in a zero external field. Here $S = L/a_0$ is the geometric factor and $F(x)$ is the scaling function of the susceptibility (the isothermal compressibility in liquids).

The most important consequences of (2.18) are as follows:

- the critical exponent $\omega = 2 - \eta$;
- the critical exponent $\theta = 1/\nu$;
- the scaling function $F(x)$ has such an asymptotic formula for large arguments $x = S^\theta \tau \gg 1$: $F(x) \sim x^{-\gamma}$, where $\gamma = (2 - \eta)\nu$ is the critical exponent of the susceptibility for bulk systems.

Let us compare the Fisher FSS hypothesis for the susceptibility with results obtained above for liquids in reduced geometry of a plane-parallel layer. In accordance with the formula (2.12), one has such an expression for the susceptibility for a plane-parallel layer

$$\chi = \chi_0 S^2 \left\{ 4[S^2 \tau^{2\nu} f_1(x) + \pi^2]^{-1} + (1 - 8/\pi^2)/4 \right\}, \quad (2.19)$$

where χ_0 is the amplitude of the susceptibility.

Equation (2.19) has the form analogous to the FSS hypothesis (2.18). Comparison between these formulae gives the following results:

- According to (2.18) and (2.19) the critical exponent $\omega = 2$. Taking into account $\omega = \gamma/\nu = 2 - \eta$ and the fact that the Helmholtz differential operator $\hat{L} = \Delta - \kappa^2$ corresponds to the OZ approximation with zero value of the critical exponent η , this result confirms the first consequence of the Fisher FSS hypothesis (2.18).
- Scaling function $F(x)$ in (2.19) depends on the argument $x = S^{2/\nu} \tau$ for a zero external field, i.e. in the vicinity of the critical isochore. Therefore, for $\eta = 0$ one has $2/\nu = 1/\nu = \theta$ in accordance with the second consequence of the scaling hypothesis (2.18).
- With increasing the thickness of a plane-parallel layer one has the following result for the scaling function $F(x)$ from (2.19) for large arguments $x = S^{2/\nu} \tau \gg 1$: $F(x) \sim x^{-1} \sim x^{-\gamma}$ in accordance with the third consequence of the FSS hypothesis (2.18).

Idea of **universality** and **isomorphism** seems to be one of the most important features in the physics of critical phenomena and phase transitions. [5, 9–11, 24]. Within a certain universality class, critical behaviour of physical properties in bulk and confined systems is similar and allows generalizing on systems not only physical but also other nature.

There is another problem that is actively discussed in physics of the critical phenomena for bulk and confined systems [25–29]. Namely, **influence of anisotropy** on such quantities as ratios of amplitudes and scaling functions. Influence of anisotropy and universality on FSS was investigated in [25] on the basis of analysis of the critical Binder cumulant of a 2D Ising model. The Binder cumulant [26] characterizes the distribution of order parameter fluctuations and is defined by such a relation $U = 1 - \langle M^4 \rangle / (3 \langle M^2 \rangle^2)$, where M is the magnetization per spin, $\langle M^2 \rangle$ and $\langle M^4 \rangle$ are its second and fourth spatial moments. Results obtained

in [25] support the validity of universal FSS for critical behavior of physical properties in the presence of a weak anisotropy. It is worthy to mention, that in our present approach using integral equations for the pair correlation function with the short-ranged direct correlation, the critical Binder cumulant $U = 1$ because of the OZ approximation in which $\langle M^4 \rangle = 0$. Correlative behavior of anisotropic binary liquid system were studied by the methods of integral equations in the three-moment approximation in [27] with taking into account the 3rd spatial moment of the direct correlation function.

Important results related to the problem of universality and effects of anisotropy were obtained in supercooled water [28] and in ionic fluids [29]. The authors [28] analyzed the critical behavior of supercooled water on the basis of two models: (1) the lattice-gas model used to describe the physical properties of liquid-vapor transitions, and (2) the lattice-liquid model, associated with an entropy-driven separation. The critical behavior of supercooled water appeared to be closer to the lattice-liquid model behavior, while the critical behavior of the lattice-gas model being equivalent to the critical behavior of Ising model for incompressible anisotropic ferromagnets.

The correlation length ξ in (2.12), (2.13) demonstrates an anisotropic behavior. Consider for definition the case of a plane-parallel layer, then correlation length ellipse related to (2.12) is determined by two contributions $\xi = (\xi_{xy}^2 + \xi_z^2)^{1/2}$ where $\xi_{xy} = 2/(\kappa^2 + \pi^2/4S_0^2)^{1/2}$ is the correlation length in the xy plane, and $\xi_z = (S_0/2)(1 - 8/\pi^2)^{1/2}$ is the correlation length in the z direction. In certain sense this result reminds the correlation length ellipse for a 2D Ising model with weak anisotropy caused by different amplitudes $\xi_{0,>}$ and $\xi_{0,<}$ above and below the critical point [25].

2.4 Effects of Spatial Limitation, Two Types of Dimensional Crossover

Spatial limitation of systems undergoing critical phenomena and 2nd order phase transitions causes the change of critical parameters and critical exponents. The most important feature of critical phenomena in bulk systems is the divergence of the bulk correlation length ξ in the critical point according to the formula

$$\xi = \xi_0 |\tau|^{-\nu}, \quad (2.20)$$

where ξ_0 is the amplitude of correlation length which has the same order of magnitude as a_0 , $\tau = (T - T_c(\infty))/T_c(\infty)$ is the temperature variable for a bulk liquid with the critical temperature $T_c(\infty)$.

However, the natural desire of investigators to study critical phenomena in systems in reduced geometry and perfect experimental technique allow one to realize a situation in which the correlation length becomes the same order of magnitude as the characteristic linear size of the sample. Thereby, theoretical and

experimental results in such bounded systems yield not bulk critical parameters and bulk theoretical critical exponents but its effective values depending on linear sizes.

Here the problem of critical behavior of systems in reduced geometry is discussed for single-component liquids with scalar order parameters. Special attention is given to the dimensional crossover (DC) effects of two types as follows [30]:

1. **The first type of dimensional crossover (DC-1)** corresponds to transition from 3D bulk to 3D liquids in reduced geometry. In this case one has a situation in which dependence of physical properties on thermodynamic variables (temperature, density, pressure, etc.) in bulk liquids with linear sizes $L \gg \xi$ may convert into dependence of these properties on linear sizes in confined liquids with $L < \xi$.
2. **The second type of dimensional crossover (DC-2)** corresponds to the case when a further decreasing of linear sizes in confined liquids may be treated under certain conditions as the change of spatial dimensionality D (for example, $3D \Leftrightarrow 2D$ crossover in slitlike pores or $3D \Leftrightarrow 1D$ crossover in cylindrical pores).

2.4.1 Dimensional Crossover DC-1

Let us first consider the *shifts of the critical parameters in liquids in reduced geometry*. Table 2.1 contains formulae for the temperature $T_c(S)$, density $\rho_c(S)$ and pressure $P_c(S)$ in bounded single-component liquids (3rd column) which are analogous to the critical temperature $T_c(\infty)$, critical density $\rho_c(\infty)$ and critical pressure $P_c(\infty)$ in bulk liquids (2nd column). An important difference between these parameters of bulk and confined liquids consist in as follows: while the critical parameters $T_c(\infty)$, $\rho_c(\infty)$, $P_c(\infty)$ of bulk liquids characterize coordinates of singularities for physical properties on the thermodynamic space, the analogous parameters $T_c(S)$, $\rho_c(S)$, $P_c(S)$ give coordinates of points in which these physical properties have only its rounding maxima or minima.

As an example, the shift of the critical temperature can be calculated for a slitlike pore with the geometric factor $S = 10$ and the pore's thickness $H \approx 3$ nm filled by water with the bulk critical temperature $T_c(\infty) \approx 647$ K. The result of calculation of $T_c(S)$ according to (21) for the critical exponent $\nu = 0.628$ gives $T_c(S) \approx 587$ K. In this case the shift of the critical temperature is negative and rather large: $\Delta T_c = T_c(S) - T_c(\infty) \approx -60K$. Analogues of other critical parameters—the critical

Table 2.1 Critical parameters for bulk and confined systems

Critical parameters	Bulk systems	Confined systems	
Critical temperature	$T_c = T_c(\infty)$	$T_c(S) = T_c(\infty)[1 + (G/S)^{1/\nu}]^{-1}$	(2.21)
Critical density	$\rho_c = \rho_c(\infty)$	$\rho_c(S) = \rho_c(\infty)[1 + (G/S)^{\beta/\nu}]^{-1}$	(2.22)
Critical density	$P_c = P_c(\infty)$	$P_c(S) = P_c(\infty)[1 + (G/S)^{\beta\delta/\nu}]^{-1}$	(2.23)

density and pressure—may be calculated for any liquid in reduced geometry with help of formulae (2.22) and (2.23).

Let us now derive relationships between thermodynamic variables in bulk and confined liquids. Namely, between the dimensionless deviation of temperature from its critical value $\tau = [T - T_c(\infty)]/T_c(\infty)$ in a bulk liquid system and the temperature variable $\tau(S) = [T - T_c(S)]/T_c(S)$ in a confined liquid system. For this purpose one has to substitute the formula (2.21) for the analogue of critical temperature $T_c(S)$ into $\tau(S)$ and obtains the following expression as a result of obvious algebraic transformations:

$$\tau(S, \xi) = (G/S)^{1/\nu} + [1 + (G/S)^{1/\nu}]|\tau| \text{sign} \tau. \quad (2.24)$$

Taking (2.20) into account, the formula (2.24) for the temperature variable in a confined system can be rewritten in a quite equivalent form

$$\tau(S, \xi) = (G/S)^{1/\nu} + [1 + (G/S)^{1/\nu}](\xi_0/\xi)^{1/\nu} \text{sign} \tau. \quad (2.25)$$

Here in (2.24) and (2.25) G is the geometrical factor depending on the low crossover dimensionality (geometrical form) of a liquid volume (thus, for plane-parallel layers or slit-like pores $G = \pi$, while for cylindrical samples $G = \mu_1 = 2.4048$ being the first zero of the Bessel function $J_0(z)$); $S = L/a_0$ is the number of molecular layers, where L is a linear size such as a layer's thickness or cylinder's radius in direction of system's spatial limitation, a_0 is an average diameter of molecule.

Quantity $\tau(S, \xi)$ in (2.24) and (2.25) can be considered as the **temperature variable for confined systems**. For relatively large sizes $L \gg \xi$ it is easy to find from (2.25) that due to factor $S = L/a_0 \gg 1$ the correlation length ξ is approaching its bulk value $\xi = \xi_0 \tau^{-\nu}$. In reduced geometry if an opposite inequality $L \ll \xi$ is valid, the first term in (2.25) becomes more important than the second one. It means that the correlation length ξ does not depend on thermodynamic variables and equals a system's linear size.

Similar to the temperature variable $\tau(S, \xi)$ in liquids in reduced geometry given by (2.25), the **density** $\Delta\rho(S, \xi)$ and **pressure** $\Delta p(S, \xi)$ **variables** may be introduced according to the following formulae:

$$\Delta\rho(S, \xi) = \left(\frac{G}{S}\right)^{\frac{\beta}{\nu}} + \left(1 + \left(\frac{G}{S}\right)^{\frac{\beta}{\nu}}\right) \left(\frac{\xi_0}{\xi}\right)^{\frac{\beta}{\nu}} \text{sign} \Delta\rho, \quad (2.26)$$

$$\Delta p(S, \xi) = \left(\frac{G}{S}\right)^{\frac{\beta\delta}{\nu}} + \left(1 + \left(\frac{G}{S}\right)^{\frac{\beta\delta}{\nu}}\right) \left(\frac{\xi_0}{\xi}\right)^{\frac{\beta\delta}{\nu}} \text{sign} \Delta p. \quad (2.27)$$

Equations (2.26) and (2.27) give correct asymptotical expressions for the correlation length in bulk liquids with $L \gg \xi$, namely $\xi = \xi'_0 \Delta\rho^{-\nu/\beta}$, $\xi = \xi''_0 \Delta p^{-\nu/\beta\delta}$.

Here the amplitudes ξ'_0, ξ''_0 of the correlation length have such relationships with the amplitude ξ_0 : $\xi'_0 = \xi_0 B_0^{v/\beta}$, $\xi''_0 = \xi_0 (B_0/D_0)^{v/\beta\delta}$. The coefficients B_0 and D_0 characterize the shapes of the coexistence curve $\Delta\rho = B_0|\tau|^\beta$ and the critical isotherm $\Delta\rho = D_0\Delta\rho^{1/\delta}$ in the close vicinity of the bulk critical point.

Let us illustrate effects of spatial limitation and dimensional crossover of the 1st type (DC-1) on the temperature dependence of **diffusion coefficient** described by the following formula in confined liquids:

$$D = \{a_R + a_s^0[\tau(S, \xi)]^{-v}\}(\partial\mu/\partial\rho)_T^0[\tau(S, \xi)]^\gamma. \quad (2.28)$$

Here a_R is the regular part and a_s^0 is the amplitude of the singular part of the Onsager coefficient, $(\partial\mu/\partial\rho)_T^0$ is the amplitude of the inverse isothermal susceptibility. For small volumes ($\xi \gg L$) the term $(G/S)^{1/\nu}$ for $\tau(S, \xi)$ in (2.25) will prevail. This is a reason why the diffusion coefficient D in formula (2.28) is decreasing at the fixed temperature with increasing linear sizes S of liquid volumes. For large volumes ($L \gg \xi$) the term $(1/\xi)^{1/\nu}$ for $\tau(S, \xi)$ in (2.25) has a greater role with increasing linear sizes $S = L/a_0$. That is why the diffusion coefficient D in (2.28) will increase and asymptotically approach its value D_0 for spatially infinite liquid volumes.

Another important consequences of finite-size effects on the critical behavior of the diffusion coefficient are as follows: the temperature variable $\tau_M(S) = [T_M - T_c(\infty)]/T_c(\infty)$ corresponding to the minimum value of the diffusion coefficient, i.e. the shift of the critical temperature in liquids in restricted geometry, (i) has a negative value in agreement with the FSS theories [2, 8–10, 12, 13]; (ii) goes to zero with increasing the geometric factor S (linear size L) of a system; (iii) increases with transition from plane-parallel to cylindrical geometry, in other words, while the lower crossover dimensionality d_{LCD} decreases.

Table 2.2 explains the notion of the **lower crossover dimensionality** which has to be introduced to characterize the type of restricted geometry [30, 31]. For real confined 3D systems (1st column) the lower crossover dimensionality d_{LCD} (2nd column) determines the spatial dimensionality of limiting geometrical objects (3rd column) for cases when system's linear sizes in directions of spatial limitation are approaching its minimum possible value.

The **effects of spatial dispersion** (nonlocality) being neglected gives unreal consequences for physical properties with approaching the critical and 2nd order phase transitions points in bulk systems as well as its analogous points in confined systems.

Table 2.2 Lower crossover dimensionality

Real confined 3D systems	Lower crossover dimensionality	Limiting geometric objects
Plane-parallel layer, slit-like pore, membrane, synaptic cleft	2	Molecular plane
Cylindrical pore, bar, ionic channel	1	Molecular line
Sphere, cube, vesicle	0	Point (one molecule)

Namely, in bulk systems the isothermal compressibility, magnetic susceptibility, isobaric and isochoric heat capacities have infinite values, while the diffusion coefficient, thermal conductivity, and sound velocity approach zero values. To take effects of spatial dispersion into account, such an idea has to be used [32]: spatial dispersion contributions must be added to the quantities which become zero in the bulk critical point (e.g. added to the diffusion coefficient or to the reverse isothermal compressibility, etc.). Thus, the self-diffusion coefficient has a minimum nonzero value at the bulk critical temperature in accordance with the following formula [30]:

$$D_{\min}(L_{\max}) = D_0 \frac{(G/S_{\max})^{\gamma/\nu} + 4\pi B/L_{\max}^2}{(G/S_{\max})^{\gamma/\nu} + 4\pi b/L_{\max}^2}. \quad (2.29)$$

Here $S_{\max} = L_{\max}/a_0$ is the number of molecular layers in the direction of a maximum system's linear size L_{\max} , B and b are the coefficients describing the effects of spatial dispersion in the Ornstein-Zernike approximation.

Figure 2.1 illustrates this result. Here, the solid curve corresponds to bulk liquids. The data are also presented for a plane-parallel (dotted curve) and cylindrical (curve with points) reduced geometry.

As is seen from Fig. 2.1, the self-diffusion coefficient $D(\tau, S, k)$ demonstrates an asymmetrical behavior with change of sign of the temperature variable $\tau = [T - T_c(\infty)]/T_c(\infty)$ in accordance with the inequalities $D(\tau, S, k) > D(-|\tau|, S, k)$, $D_{0, \tau > 0} > D_{0, \tau < 0}$. Such an asymmetry of the self-diffusion coefficient is confirmed by theoretical studies in [33].

2.4.2 Dimensional Crossover DC-2

While describing the dimensional crossover DC-2, the fact of different numerical values of the critical exponents in 3D and 2D liquids [11] (see Table 2.3) and the results of computer experiment [15] are taken into account.

For definition let us consider confined liquids in slitlike pores. While reducing linear sizes L (for plane-parallel geometry—the thickness H of pores or number of its molecular layers $S = H/a_0$, a liquid system will transfer from 3D to 2D geometry. This transition should be resulting in change of the critical exponents of classical liquids belonging to the Ising-model universality class. For example, the critical index ν describing the temperature dependence of the correlation length ξ has to shift its value from 0.638 to 1.0 (see Table 2.3).

The following expression for any effective critical exponents n_{eff} is proposed to study a smooth transition between its 3D value n_3 and 2D value n_2 [30]:

$$n_{eff} = n_3 + \left[\frac{2}{\pi} \arctan(ax - b) - 1 \right] \frac{n_3 - n_2}{2}. \quad (2.30)$$

Fig. 2.1 Relative self-diffusion coefficient in bulk D/D_0 versus the temperature variable $\tau = (T - T_c(\infty))/T_c(\infty)$ in bulk and confined liquids

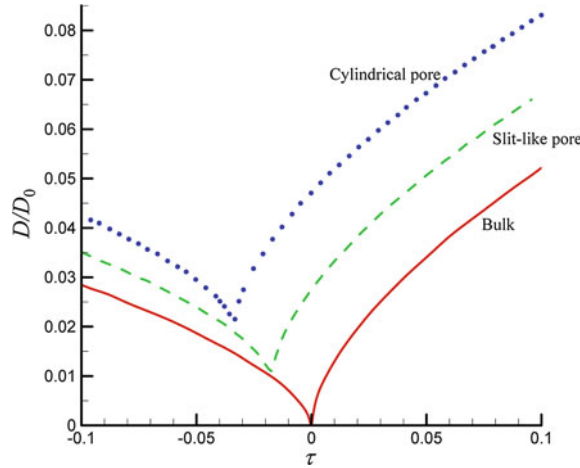


Table 2.3 Numerical values of critical exponents in 3D and 2D Ising models [11]

Physical property	Critical exponents	3D Ising model	2D Ising model
Heat capacity	α	0.125 ^a	$0(C_v \sim \ln \tau)$
		0.110 ^b	
Coexistence curve	β	0.3125 ^a	1/8
		0.325 ^b	
Isothermal compressibility	γ	1.250 ^a	7/4
		1.241 ^b	
Critical isotherm	δ	5.0 ^a	15
		4.8 ^b	
Correlation length	ν	0.638 ^a	1
		0.630 ^b	
Correlation function	η	0.041 ^a	1/4
		0.031 ^b	

^a sum of series; ^b RG-approach

Here in (2.30) $x = H/H_{cr}$ is the dimensionless size (in fact—thickness H) of a plane-parallel layer; H_{cr} is the layer’s thickness at which the $3D \Leftrightarrow 2D$ crossover occurs (authors [15] consider $H_{cr} \approx 2, 4$ nm for a slitlike pore filled by water molecules).

As an example, formula (2.30) illustrates the $3D \Leftrightarrow 2D$ crossover for the critical exponent ν of the correlation length ξ in a slitlike pore. Figure 2.2 shows the theoretical dependence $\nu(S)$ on number of monolayers S in accordance with (2.30).

As is mentioned before, there are always factors which distort the idealized bulk critical behavior and give the effective values of critical parameters and exponents. Among these factors: effects of spatial limitation, crossover effects, external fields, temperature gradients, impurities, multiple-scattering effects, etc. [34–39].

Fig. 2.2 Dimensional $3D \Leftrightarrow 2D$ crossover in the critical exponent ν versus number of molecular layers S

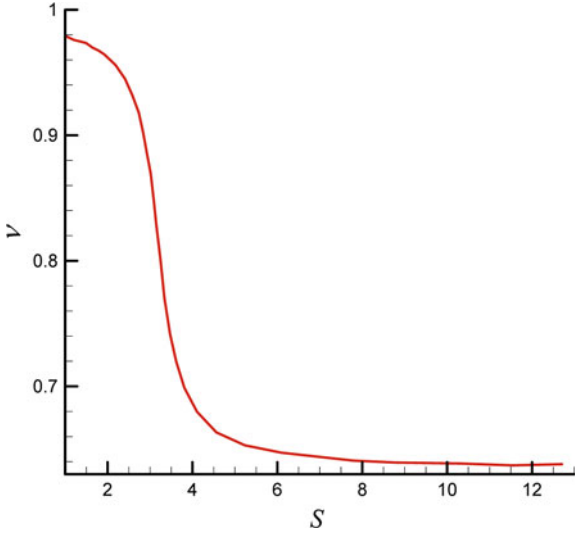


Table 2.4 Dependence of the effective critical exponent ν_{eff} on S

S	1.0	2.4	3.1	3.5	5.6	8.0
H , (nm)	0.3	0.7	0.9	1.1	1.7	2.4
ν_{eff}	1.0	0.95	0.85	0.75	0.65	0.64

The problem of the effective critical parameters and critical exponents is examined in detail in a number of papers (see e.g. references in [14]).

Table 2.4 demonstrates the dependence of the effective critical exponent ν_{eff} on number of molecular layers S (dimensionless thickness H of a slitlike pore) calculated in accordance with (2.30) for water molecules.

Parameters a and b characterizing slope and position of the $3D \Leftrightarrow 2D$ crossover were chosen to fit the following condition: 2D value of the critical exponent $\nu = 1$ corresponds to a system's thickness consisting of almost one molecular layer.

Such an interpolation (2.30) looks similar in a certain sense to approach used in [40] to receive the crossover between hydrodynamic and fluctuation regions for the central Rayleigh component of the light-scattering spectrum in mode-mode coupling version of the dynamical theory of critical phenomena.

2.5 Theoretical Results Versus Experimental Data in Confined Liquids

In this section the relationship between theoretical and experimental data will be analyzed with taking into account effects of spatial limitation and dimensional crossover in liquids in reduced geometry.

Table 2.5 Diffusion coefficient of water molecules in cylindrical pores [41, 42]

R (nm)	62.5	88.0	117.0	130.0	150.0
$D_{\text{exp}} \cdot 10^{-9} \text{ (m}^2/\text{s)}$	1.59	1.95	2.13	2.19	2.30
$D_{\text{theor}} \cdot 10^{-9} \text{ (m}^2/\text{s)}$	1.79	2.00	2.11	2.14	2.17

Experimental studies (see e.g. references in [41]) of *the size dependence of the diffusion coefficient D* of water molecules in a porous glass allow considering the dimensional crossover of the 1st type (DC-1) in cylindrical pores. These results give also an opportunity to investigate the asymptotical transition of the diffusion coefficient D from its values in liquid in restricted geometry to the bulk value $D_0 = 2.3 \cdot 10^{-9} \text{ m}^2/\text{s}$ for water molecules. Table 2.5 demonstrates the size experimental dependence of $D_{\text{exp}}(R)$ on the pore's radius R together with results of the theoretical calculation $D_{\text{theor}}(R)$ for $G = 2.4048$ and $S = R/\xi_0$ in the case of a large pore's radius ($R \gg \xi$) [42].

Thus, asymptotical transition of the diffusion coefficient D of water molecules to its bulk value takes place in cylindrical pores if a pore's radius $R \geq 150 \text{ nm}$. It is possible to conclude that experimental and theoretical results of study the dependence of water diffusion coefficient on size of cylindrical pores demonstrate not only qualitative, but also quantitative agreement with average deviation about 4,8 %.

The computer experiment [15] allows verifying the interpolation formula (2.30) with taking into account *the size dependence of the critical temperature of a fluid in a pore*. Figure 2.3 (see black circles) demonstrates computer experiment results for dependence of the critical temperature $T_c(H)/T_c(\infty)$ on the pore's size, i.e. on the thickness H of a slitlike pore filled by water.

To compare the interpolation formula (2.30) with results of computer experiment [15], we substitute the size dependence of the critical exponent $\nu(H)$ into formula (2.21) for the critical temperature $T_c(H)$ of a fluid in a pore. The agreement between computer experiment data and theoretical calculations seems to be quite good. The lowest experimental point corresponds to the critical temperature of almost 2D water in slitlike pore with its thickness $H = 0.5 \text{ nm}$. This value of thickness H refers to almost one monolayer plane with taking into account that the diameter of water molecule equals $d \approx 0.3 \text{ nm}$. It is interesting to stress that the beginning of the dimensional crossover DC-2 from 3D to 2D critical behavior takes place at the slitlike pore's thickness $H_{cr} \approx 2.4 \text{ nm}$. This value of H_{cr} was mentioned in [15] and corresponds to approximately 8 molecular layers of water molecules in slitlike pores.

Finally we would like to compare theoretical and experimental *shifts of the critical temperature in confined liquids*. Table 2.6 (2nd line) contains experimental results for shifts of the water critical temperature $\Delta T_c = T_c(\infty) - T_c(R)$ in cylindrical pores of different radius R obtained by different experimental methods (see references in review [15]). Results of theoretical calculation $\Delta T_c = T_c(\infty) - T_c(R) \sim (\mu_1 \xi_0 / R)^{1/\nu}$ in accordance with the formula (2.21) are presented in the 3rd line of Table 2.6 [23, 43].

Fig. 2.3 Related critical temperature of a fluid in a pore $T_c(H)/T_c(\infty)$ versus the thickness H of a slitlike pore (black circles correspond to the data computer experiment [15]; solid curve was obtained using the formulae (2.21) for $T_c(H)$ and (2.30) for ν [30])

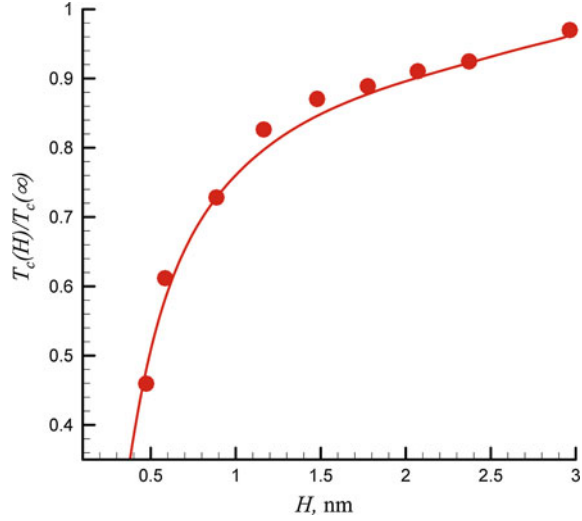


Table 2.6 Experimental and theoretical shifts of the critical temperature

Pore radius R (nm)	3.9	5.0	11.0	12.1	15.7
$(\Delta T_c/T_c)_{\text{exp}}$	0.047	0.044	0.033	0.029	0.0015
$(\Delta T_c/T_c)_{\text{theor}}$	0.065	0.044	0.013	0.011	0.0071

In spite of that is qualitative agreement between experimental and theoretical data, these and other results demonstrate a considerable enough distinction of the data received by different methods for the same liquid in pores with approximately equal radius.

2.6 Conclusion

In this paper we studied critical phenomena in liquid in restricted geometry. Thermodynamic, kinetic and correlation properties of confined liquids are essentially different from those properties of bulk systems. The influence of spatial limitation effects (among them—effects of dimensional crossover) is more pronounced in cases when linear sizes L of systems are less or the same order of magnitude as the correlation length ζ of order parameter fluctuations.

The study of critical phenomena and 2nd order (continuous) phase transitions in systems in reduced geometry allows one to formulate important conditions of universality classes for confined soft matter. Namely, to the following well-known basic conditions of universality classes in bulk systems with $L \gg \zeta$:

- (a) the same space dimensionality;
- (b) the same dimensionality of order parameter;

- (c) the same type of intermolecular interaction (short- or long-range);
- (d) the same symmetry of Hamiltonian (fluctuation part of thermodynamic potential), it is necessary to add the following conditions of universality classes in confined systems with $L \leq \xi$;
- (e) the same type of system's geometry (lower crossover dimensionality);
- (f) the same type of boundary conditions;
- (g) the same type of physical properties under consideration.

The last factor appears to be important because coordinates of maxima or minima in systems in restricted geometry, being analogues of bulk critical parameters, are different (nonuniversal) for various physical properties.

The verification of theoretical results for critical phenomena in confined systems needs experimental studies which are much more complicated than those experimental studies in bulk systems. Nevertheless, we hope that the attractive FSS hypothesis of finite-size scaling for the diverse critical phenomena and phase transitions in the nano- and mesoscale world around and inside us will prove experimentally to be correct.

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References

1. L.P. Kadanoff, Phys. **2**, 263 (1966)
2. M.E. Fisher, ed. by M.S. Green (Academic Press, New York, 1971)
3. H.E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Glarendon Press, Oxford, 1971)
4. E.L. Lakoza, V.M. Sysoev, A.V. Chalyi, JETP **65**, 605 (1973) Sov.Phys.-JETP, **38**, 298 (1974)
5. M.E. Fisher, Rev. Mod. Phys. **46**, 597 (1974)
6. K.G. Wilson, J. Kogut, Phys. Rep. **12**, 75 (1974)
7. A.Z. Patashinskii, V.L. Pokrovskii, *The Fluctuation Theory of Phase Transitions* (Pergamon Press, Oxford, 1979)
8. M.N. Barber, ed. by C.Domb and J.L. Lebowitz (Academic Press, 1983), p.145
9. V. Privman, M.E. Fisher, Phys. Rev. B **30**, 322 (1984)
10. V. Privman, ed. by V. Privman (World Scientific, Singapore, 1990), p.1
11. M.A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Gordon & Breach, Philadelphia, 1991)
12. V. Privman, P.C. Hohenberg, A. Aharony, ed. by C. Domb and J.L. Lebowitz (Academic, New York, 1991)
13. K. Binder, Annu. Rev. Phys. Chem. **43**, 33 (1992)
14. A.V. Chalyi, A.V. Lebed, *Non-Homogeneous Liquids Near the Critical Point and the Boundary of Stability and Theory of Percolation in Ceramics* (Harwood Academic Publishers, London, 1993)
15. I. Brovchenko, A. Oleinikova, Handb. Theor. Comput. Nanotechnol. **62**, 1 (2005)
16. A.V. Chalyi, J. Mol. Liquids **58**, 179 (1993)
17. A.V. Chalyi, A.N. Vasilev, J. Mol. Liquids **84**, 203 (2000)

18. I.Z. Fisher, *Statistical Theory of Liquids* (Fizmatgiz, Moscow, 1961)
19. V.Y. Antonchenko, A.S. Davydov, V.V. Ilyin, *Basic Principles of Physics of Water* (Naukova Dumka, Kiev, 1991)
20. I.S. Gradshtein, I.M. Ryzhik, *Tables of Integrals, Sums, Series and Products* (Nauka, Moscow, 1971)
21. M.E. Fisher, J. Math. Phys. **5**, 944 (1964)
22. L.A. Bulavin, A.V. Chalyi, K.A. Chalyy, L.M. Chernenko, L.G. Grechko. Preprint of the Bogolyubov Institute for Theoretical Physics, ITP-93-15E, Kiev (1993)
23. A.V. Chalyi, Y.V. Tsekhmister, K.A. Chalyy, *Processes of Ordering and Self-organization in Fluctuation Models of Open Systems* (Vipol, Kiev, 2001)
24. M.A. Anisimov, A.V. Voronel, and E.E. Gorodetskii, Sov.Phys.-JETP, **33**, 605 (1971)
25. B. Kastening, Phys. Rev. E **86**, 041105 (2012); arXiv: 1209.0105v2 [cond-mat.stat-mech] (2013)
26. K. Binder, Phys. Rev. Lett. **47**, 693 (1981)
27. A.V. Chalyi, A.N. Vasilev, Ukr. Phys. J. **45**, 118 (2000)
28. C.E. Bertrand, M.A. Anisimov, J. Phys. Chem. B **115**(48), 14099 (2011)
29. H. Weingartner, W.Schroer, ed. by I.Prigogine, S.A.Rice (Interscience Publications, Wiley, 2001)
30. A.V. Chalyi, L.A. Bulavin, V.F. Chekhun et al., Condens. Matter Phys. **16**, 23008 (2013)
31. M.O. Kimball, K.P. Mooney, F.M. Gasparini, Phys. Rev. Lett. **92**, 15301 (2004)
32. V.M. Sysoev, A.V. Chalyi, Theor. Math. Phys. **26**, 126 (1976)
33. W. Koch, V. Dohm, Phys. Rev. E **58**, R1179 (1998)
34. A.V. Chalyi, L.M. Chernenko, JETP **87**, 187 (1984)
35. E.K. Riedel, F.J. Wegner, Phys. Rev. Lett. **29**, 349 (1972)
36. S.D. Landau, V.G. Mukhailovsky, A.V. Chalyi, Ukr. Phys. J. **15**, 423 (1971)
37. M.A. Anisimov and J.V. Sengers, ed. by E.Kivan, P.G. Debenedetti, C.J. Peters (Kluwer, Dordrecht, 2000), 89121
38. Y.C. Kim, M.A. Anisimov, J.V. Sengers, E. Luijten, J. Stat. Phys. **110**, 591 (2003)
39. M.A. Anisimov, Condens. Matter Phys. **16**, 1 (2013)
40. K. Kawasaki, ed. by C. Domb, M.S. Green (Academic Press, New York, 1976)
41. L.A. Bulavin, T.V. Karmazina, V.V. Klepko, V.I. Slisenko, *Neutron Spectroscopy of Condensed Systems* (Academperiodyka, Kiev, 2005)
42. L.A. Bulavin and K.A. Chalyy, Bulletin of the Kiev University (Phys.&Math.), №1, 328 (2006)
43. L.A. Bulavin, K.A. Chalyy, *Neutron Optics of Mesoscale Liquids* (Naukova Dymka, Kiev, 2006)

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