SCALING TRANSFORMATION HYPOTHESIS FOR SPATIALLY BOUNDED TWO-COMPONENT LIQUID MIXTURES

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The hypothesis of scaling transformation for spatially bounded two-component liquid mixtures in the critical domains of vapor formation (vapor — liquid) and stratification (liquid — liquid) is proposed. The concept of spatial boundedness of systems in the critical domain is introduced, and the hypothesis of scaling transformation for spatially unbounded two-component liquid mixtures with the usage of different independent variables is discussed. Some consequences of the scaling hypothesis that is formulated in the paper (in particular, the limiting transition to a spatially bounded system and the critical behavior of the order parameter in a system with bounded geometry) are considered.

Introduction

Last time, the influence of spatial boundedness on the course of phase transitions and critical phenomena has aroused a considerable interest of both theorists and experimentalists (see, for example, [1—3]).

Achievements of the modern physics of phase transitions and critical phenomena were associated, first of all, with the formulation of the scaling hypothesis. Its main idea is reduced to establishing the transformation laws of physical quantities that are characterized by anomalous fluctuations of the order parameter of a system in the critical domain and, when passing to a new scale, to the determination of the correlation radius of these fluctuations ξ. At first, the scaling hypothesis was formulated for spatially unbounded one-component liquids and magnetic materials [4]. Later on, it was extended on the spatially unbounded two-component systems with the usage of the isomorphism hypothesis [5, 6].

In this paper, we consider spatially bounded systems. The scaling hypothesis for one-component liquids and magnetic materials with bounded geometry was proposed, for the first time, in [1] (see also [3]). In accordance with this hypothesis, the fluctuation part of thermodynamic potential turns out to be dependent not only on the reduced temperature τ, the external field h, and the conjugated order parameter φ as it occurs in spatially unbounded systems (really, it happens in systems whose linear sizes are much more than the correlation radius), but on the typical size L of a system in the direction of its spatial boundedness. Specific features of the critical behavior of equilibrium and nonequilibrium physical properties of spatially bounded liquids have been studied in many papers [1—3, 7—12]. The aim of this work is to formulate the scaling hypothesis for spatially bounded two-component liquid mixtures in the critical domains of vapor formation (vapor — liquid) and stratification (liquid — liquid). At first, we introduce the notion of spatial boundedness of a system in the critical domain. Further, we discuss the scaling hypothesis in different independent variables for the spatially unbounded two-component liquid mixtures. In conclusion, we formulate the scaling hypothesis for binary mixtures of classical liquids with spatially bounded geometry and discuss some consequences of this hypothesis (in particular, the limiting transition to a spatially bounded system and the critical behavior of the order parameter in such a system).

1. The Concept of a System Spatially Bounded in the Critical Domain

Although the concept of spatial boundedness of a system is clear on the intuitive level, it requires, to our mind, a more precise definition. We call the system to be spatially bounded near the critical point or in the vicinity of the critical point (line) of a second-order phase transition if its typical linear dimensions in the direction of spatial boundedness do not exceed the maximum value of the correlation radius of fluctuations of the order parameter that could be reached in the given experiment. We note that the role of the order parameter is played by fluctuations of the density of one-component liquids in the critical domain, fluctuations of the concentration of a liquid mixture near the critical state of the liquid — liquid system, etc.

At first, we consider *classical* one-component liquids in the critical domain. In this case, the correlation radius of density fluctuations ξ in the zero external field or in the near vicinity of the critical isochore is defined by the following temperature dependence: $\xi = \xi_0 \tau^{-v}$, where $\tau = (T - T_c)/T_c$ is the deviation of temperature T from its critical value T_c, $v = 0.63$ is the critical index, and ξ_0 is the correlation radius amplitude that is of the order of 1-10 nm for classical liquids. In modern experiments with the classical liquids, approaching to the critical point as close as $T - T_c \approx 10^{-2} - 10^{-3}$ is rather real [6, 7]. Then, for the liquids with critical temperature $T_c \approx 10^3$ K, we obtain that the enlarging factor of the correlation radius $\xi/\xi_0 = \tau^{-v}$ is 10^3. Therefore, the liquid systems such as thin films, cylindrical pores, spherical specimens, etc. can be considered as spatially bounded in the critical domain if their linear sizes in the direction of spatial boundedness are about 1-10 μm.

For *quantum* liquids (for example, liquid He^4 in the vicinity of the λ-point), this evaluation of spatial boundedness is considerably underestimated. In fact, for liquid He^4 in the vicinity of the λ-point, the following experimental values are known [13,14]: the correlation radius amplitude $\xi_0 = 0.36$ nm below the temperature of the second-order phase transition at $T_\lambda = 2.17$ K and $\xi_0 = 0.14$ nm above it, respectively. At the same time, the critical index of the temperature dependence of the correlation radius is $v = 0.671$. The minimal temperature approach to the second-order phase transition of liquid He^4 in the λ-point, which was obtained in the experiment in [15], is the record in smallness and equals $\Delta T = T - T_\lambda = 2$ nK. For the dimensionless temperature deviation, this gives $\tau = (T - T_\lambda)/T_\lambda \approx 10^{-9}$. Correspondingly, the enlarging temperature factor of the correlation radius $\xi/\xi_0 = \tau^{-v}$ is 10^6 with regard for the experimental values of τ and v or by three orders larger than that for classical liquids. As a result, the correlation radius of fluctuations of the order parameter in liquid He^4 reaches macroscopic values: $\xi = 0.36$ mm and $\xi = 0.14$ mm while approaching the λ-point from the lower and higher temperatures, respectively. Therefore, in the specific experiment [15], the film of liquid helium $L \approx 0.1 - 0.3$ mm in thickness has to be considered as a spatially bounded system in the vicinity of the λ-point.

2. Scaling Hypothesis for Spatially Unbounded Two-component Liquid Mixtures

Let a two-component liquid mixture be spatially unbounded. This means that the typical sizes of its volume (in all directions) are much larger than the maximum (under the given thermodynamic conditions) value of the correlation radius $\xi_max >> L$. While formulating the scaling hypothesis (as well as the isomorphism hypothesis) [5, 6], which establishes a definite correspondence between the critical behavior of two- or multicomponent liquid solutions and the idealized models such as the Ising model, model of lattice gas, model of incompressible binary alloy, etc., it is necessary to distinguish what kind of variables (field ones or density variables) are chosen as complementary with respect to the variables of the above-specified idealized systems. We recall that the *field variables* are those that take the same values in the coexisting phases (temperature, pressure, chemical potential, or the chemical potentials of binary mixture components, and so on). The *density variables* are those that change their values by step when passing through the interface (entropy, volume, concentration, or densities of binary mixture components, etc.) [5—7].

The critical state of a liquid-liquid system. In the vicinity of this critical state, a binary liquid mixture is isomorphic to the idealized model of incompressible binary alloy, which is described by the independent variables “temperature T — concentration x” and becomes ordered below the order-disorder phase transition. In this case, the pressure P becomes a complementary natural variable for a two-component liquid mixture. But the system under consideration has compressibility that tends theoretically to infinity while approaching the critical state unlike the indicated idealized model.

To formulate the scaling hypothesis, it is convenient to use the thermodynamic potential that, in this case, is the Gibbs free energy $G(T,P,x)$ calculated per one mole [i.e., the chemical potential $\mu = G/N$, where N is the number of moles (in our case, $N = 1$)]:

$$G(T,P,x) = \mu(T,P,x) = \mu_1(1-x) + \mu_2 x = \mu_1 + \mu^* x. \tag{1}$$

Here, μ_1 and μ_2 are the chemical potentials of one mole of a pure solvent and a dissolved substance; $\mu^* = \mu_2 - \mu_1 = (\partial G/\partial x)_{T,P}$ is the difference of chemical potentials that is the field variable of the double solution as well as the pressure P; $x = (\partial G/\partial \mu^*)_{T,P}$ is the concentration of the dissolved substance.

Relation (1) may be considered as the Legendre transformation from the Gibbs free energy G(T,P,x) to the chemical potential of a pure solvent $\mu_1(T,\mu_*)$ since

$$dG(T,P,x) = -SdT + VdP + \mu^* dx,$$
$$d\mu_1(T,P,\mu^*) = -SdT + VdP - x d\mu^*. \tag{2}$$

The Gibbs free energy consists of two terms: $G = G_0 + G_{\text{sing}}$. The first term ($G_0$) is the regular part of the thermodynamic potential that has no singularities in the critical state. The second term (G_{sing}) is the fluctuation (singular) part that is determined by the interaction of strongly developed fluctuations of the order parameter. In the vicinity of the liquid-liquid critical state, the order parameter is $\varphi(P) = x - X_c(P)$, i.e., the deviation of the concentration x from the critical value $x_c(P)$. The above-presented results concerning the Gibbs energy are completely related to the chemical potential of a pure solvent $\mu_1(T,P,\mu^*)$, i.e., $\mu_1 = \mu_{\text{reg}} + \mu_{\text{sing}}$.

The generalization of the scaling hypothesis formulated for a one-component liquid to the case of a two-component liquid mixture being in the vicinity of the critical liquid-liquid state (stratification) in the spatially unbounded system can be written as [6]

$$G_{\text{sing}}(T,P,x) = [\tau(P)]^{2-\alpha}\psi_1[\varphi(P)/\tau^{\beta}(P)], \tag{3a}$$

where $\tau(P) = [T - T_c(P)]/T^c(P)$ is the reduced temperature or dimensionless temperature “distance” to the critical point (line) $T^c(P), \alpha \approx 0.1$ and $\beta \approx 1/3$ are critical indices.

The scaling hypothesis can be reformulated with the help of the following formulas that are completely equivalent to expression (3a)

$$G_{\text{sing}}(T,P,x) = [\varphi(P)]^{\delta+1}\psi_2[\tau(P)/\varphi^{1/\beta}(P)], \tag{3b}$$

$$G_{\text{sing}}(T,P,x) = [\tau(P)]^{2-\alpha}\psi_3[h/\tau^{\beta\delta}(P)], \tag{3c}$$

where $h = [\mu^* - \mu^*(x_c(P),T)]/\mu^*(x_c(P),T)$ is the field that orders the system and is conjugated to the order parameter $\varphi(P) = x - x_c(P)$; and the critical index $\delta \approx 4.7 \div 5.0$.

The scaling functions $\psi_1(y)$, $\psi_2(z)$, and $\psi_3(v)$ that enter formulas (3) satisfy the following asymptotics:

$$\psi_1(y \to 0) = \text{const}, \quad \psi_1(y \to \infty) \sim y^{\delta+1}; \tag{4a}$$

$$z_2(z \to 0) = \text{const}, \quad \psi_2(z \to \infty) \sim z^{2-\alpha}; \tag{4b}$$

$$\psi_3(v \to 0) = \text{const}, \quad \psi_3(v \to \infty) \sim v^{1+1/\delta}. \tag{4c}$$

The substitution of the asymptotic expressions (4) in formulas (3) of the scaling hypothesis allows one to obtain the known scaling-based results for the fluctuation part of the thermodynamic potential (Gibbs free energy):

$$G_{\text{sing}} \sim \tau^{2-\alpha} \quad \text{for} \quad P = P_c, \quad x = x_c;$$
$$G_{\text{sing}} \sim (x - x_c)^{\delta+\alpha} \quad \text{for} \quad T = T_c, \quad P = P_c;$$
$$G_{\text{sing}} \sim (\mu^* - \mu^*_c)^{1+1/\alpha} \quad \text{for} \quad T = T_c, \quad x = x_c. \tag{5}$$

We underline that the Gibbs free energy $G(T,P,x)$ and the chemical potential of a pure solvent $\mu_1(T,P,\mu^*)$ are expressed through the so-called isomorphic variables, because the complementary variable, pressure P, that is used with respect to the variables of the idealized model of incompressible binary alloy, is the field variable. It is precisely the case, in accord with the isomorphism hypothesis [5, 6], where there is no renormalization of the critical indices of a two-component liquid mixture near the critical liquid-liquid state as compared with the known critical indices of the chosen idealized model. In particular, this is confirmed by formulas (5).

Critical liquid-vapor state. In the vicinity of the critical state of vapor formation (liquid-vapor), a two-component liquid mixture is isomorphic to the idealized model of lattice gas. This model is usually described by the independent variables “temperature T — density ρ or volume V” and the relevant thermodynamic potential is Helmholtz's free energy. Based upon the lattice gas model, we have to choose the concentration x (as the natural density variable of the binary solution) or the difference of the chemical potentials of the solute and solvent $\mu^* = \mu_2 - \mu_1$ (the field variable conjugated to the concentration) as the complement variable for the binary liquid mixture (with respect to variables T, ρ or T, V). We emphasize that Helmholtz's free energies for two collections of variables T, ρ, x and T, ρ, μ^* are equivalent since they are connected by the Legendre transformation: $F(T, \rho, x) = F(T, \rho, \mu^*) + \mu^* x$. At the same time, in accord with the isomorphism hypothesis, the independent variables T, ρ, μ^* have considerable advantage. In this case, under fixation of the complementary field variable $\mu^* = \text{const}$, the critical behavior of a two-component liquid mixture near the critical state of vapor formation and that of the lattice gas model are identical. Moreover, it is important that the same is true for the critical behavior of the one-component liquid near the isolated critical point, the system being isomorphic to the lattice gas model.

The order parameter of a two-component mixture near the critical liquid-vapor state is a deviation of the mixture density from its critical value, $\varphi(\mu^*) = [\rho - \rho_c(\mu^*)]/\rho_c(\mu^*)]$. The field conjugated to this parameter is a dimensionless deviation of the chemical potential of the solvent from its value on the critical isochore, $h = [\mu_1 - \mu_1(\rho_c(\mu^*), T)]/\mu_1(\rho_c(\mu^*), T)$.

Keeping this in mind, we can write down the scaling hypothesis for a two-component liquid mixture in the vicinity of the critical liquid-vapor state (vapor formation) in the spatially unbounded system analogously to formulas (3):

$$F_{\text{sing}}(T, \rho, \mu^*) = [\tau(\mu^*)]^{2-\alpha} \psi_1^*[\varphi(\mu^*)/\tau^{\beta}(\mu^*)], \tag{6a}$$

$$F_{\text{sing}}(T, \rho, \mu^*) = [\varphi(\mu^*)]^{\delta+1} \psi_2^*[\tau(\mu^*)/\varphi^{1/\beta}(\mu^*)], \tag{6b}$$

$$F_{\text{sing}}(T, \rho, \mu^*) = [(\tau\mu^*)]^{2-\alpha} \psi_3^*[h(\mu^*)/\tau^{\beta\delta}(\mu^*)]. \tag{6c}$$

Here, $(\mu^*) = [T - T_c(\mu^*)]/T_c(\mu^*)$ is the relative temperature deviation. The scaling functions $\psi_1^*(y), \psi_2^*(z)$, and $\psi_3^*(v)$ have the same asymptotics that are valid for the scaling functions $\psi_1(y), \psi_2(z)$, and $\psi_3(v)$ [see formulas (4)].

Application of these asymptotic expressions to formulas (6) of the scaling hypothesis to a two-component mixture near the critical state of vapor formation allows us to obtain the following scaling results for the fluctuation part of Helmholtz's free energy:

$$F_{\text{sing}} \sim [T - T_c(\mu^*)]2 - \alpha$$

at

$$\mu_1 = \mu_1[\rho_c(\mu^*), T], \rho = \rho_c(\mu^*);$$

$$F_{\text{sing}} \sim [\rho - \rho_c(\mu^*)]^{\delta+1}$$

at

$$T = T_c(\mu^*), \mu_1 = \mu_1[\rho_c(\mu^*), T];$$

$$F_{\text{sing}} \sim [\mu_1 - \mu_1(\rho_c(\mu^*), T]^{1+1/\delta}$$

at

$$T = T_c(\mu^*), \quad \rho = \rho_c(\mu^*). \tag{7}$$

For both the critical states of mixing-stratification (liquid-vapor) and vapor formation (liquid-vapor), the choice of independent variables has to take in to take into account the specific conditions of the experiment. For example, in studying the critical state of vapor formation for a spatially unbounded two-component mixture in the gravitation field, the isomorphic variables "temperature T — density ρ — chemical potential μ^*" are the simultaneously independent experimental variables (see, for example, [7, 16—18]). For a similar "gravitation experiment", the condition for the fixation of a complementary field variable ($\mu^* = \text{const}$) is valid under natural conditions. That is, the isomorphism conditions for a binary liquid mixture and a one-component liquid near the critical state of vapor formation (liquid-vapor) are realized experimentally without additional restrictions. These are precisely the factors which determine the advantages of studying the critical phenomena in liquid mixtures in the Earth's gravitation field without the effects of mixing of liquids that are frequently used by experimentalists.

3. Scaling Hypothesis for Two-component Liquid Mixtures with Spatially Bounded Geometry

Now we consider a two-component mixture near the liquid-liquid or liquid-vapor critical state in the volume that is spatially bounded in a number of directions: (i) one (a plane-parallel layer), (ii) two (a cylindrical specimen), (iii) three (a specimen of the spherical or cubic geometry or a parallelepiped). Let typical linear sizes of the system L in all directions of spatial boundedness be at most the correlation radius of fluctuations of the order parameter $\xi (L \leq \xi)$.

The critical liquid-liquid state. In this case, the expansion of the scaling hypothesis to one-component systems with spatially bounded geometry formulated in [1—3] is given by the following results for the singular part of the thermodynamic potential

G_{sing} (Gibbs free energy) per one mole or the chemical potential of a pure solvent $\mu_{1\mathrm{sing}}(T,P,x)$) and for the correlation radius of concentration fluctuations ξ:

$$\mu_{1\mathrm{sing}}(T,P,x)=L^{-d}f_{\mu}[a\varphi^{1/\beta}(P)L_{1/v},bhL^{\beta\delta/v}], \tag{8}$$

$$\xi(T,P,x)=L^{-d}f_{\xi}[a\varphi^{1/\beta}(P)L_{1/v},bhL^{\beta\delta/v}]. \tag{9}$$

Here d is the spatial dimension of the system, $f_{\mu}(y,z)$ and $f_{\xi}(y,z)$ are the corresponding scaling functions. As was noted in the previous section, the order parameter of the system under consideration is the deviation of the concentration from its critical value $\varphi(P)=x-x_c(P)$ that enters into (8), (9). The field conjugated to $\varphi(P)$ is $h=[\mu^*-\mu^*(x_c(P),T)]/\mu^*(x_c(P),T)$.

The first scaling argument $y=a\varphi L^{1/v}$ of the scaling functions f_{μ} and f_{ξ} in (8), (9) can be obtained from the following relations:

$$\xi\sim\tau^{-v},\quad \tau\sim\xi^{1/v},\quad \varphi\sim\tau^{-\beta},\quad \tau\sim\varphi^{1/\beta},$$

$$y\sim\xi\sim\frac{\varphi^{1/\beta}}{\xi^{-1/v}}\sim\varphi^{1/\beta}L^{1/v},\quad L=\xi. \tag{10}$$

Analogously, we can obtain an expression for the second scaling argument $z=bhL^{\beta\delta/v}$ keeping in mind the relations:

$$\xi\sim\tau^{-v}\sim\varphi_{-v\beta}\sim h^{-v\beta\delta},\quad \varphi\sim\tau^{\beta},\quad \varphi\sim h^{1},$$

$$\tau\sim\varphi^{1/\beta},\quad h\sim\xi^{-\beta\delta/v},\quad z\sim\frac{h}{\xi^{-\beta\delta/v}}\sim hL^{\beta\delta/v}\quad L\approx\xi. \tag{11}$$

It is necessary to note that the scaling arguments $y=a\varphi L^{1/n}$ and $z=bhL^{\beta\delta/v}$ contain two nonuniversal constants a and b. They are different for different substances and may be connected with the nonuniversal amplitude of the correlation radius 0 in the relation $\xi=\xi_{0\tau-V}$ and with one more nonuniversal constant B_0 in the formula for the phase coexistence curve $\varphi=B_{0\tau\beta}$. The scaling functions $f_{\phi}(y,z)$ and $f_{\xi}(y,z)$ in (8), (9) satisfy the asymptotic expressions at $L\to\infty$:

$$f_{\mu}(y\to\infty)\sim y^{\beta(\delta+1)}\sim\varphi^{\delta+1}\sim\tau 2-a,$$

$$f_{\mu}(z\to\infty)\sim z^{1+1/\delta}\sim h^{1+1/\delta},$$

$$f_{\xi}(y\to\infty)\sim y^{-v}\sim\varphi^{-v/\beta}\sim\tau{-}v,$$

$$f_{\xi}(z\to\infty)\sim z^{-v/\beta\delta}\sim h^{-v/\beta\delta}. \tag{12}$$

From these relations, we see that, when passing to an unbounded system, $L\to\infty$, the dependence of the scaling hypothesis (8), (9) on a linear size L disappears for spatially bounded systems. In fact, the substitution of asymptote (12) into (8), (9) gives

$$G_{\mathrm{sing}}\sim\mu_{1\mathrm{sing}}\sim L^{-d}y^{\beta(\delta+1)}\sim L^{-d}\varphi^{\delta+1}L^{\beta(\delta+1)/v}\sim$$

$$\sim\varphi^{\delta+1}L^{-d+(2\beta+y)/v}\varphi^{\delta+1}L_0\sim\varphi^{\delta+1}\sim\tau^{\beta(\delta+1)}\sim\tau^{2-a},$$

$$G_{\mathrm{sing}}\sim\mu_{1\mathrm{sing}}\sim L^{-d}z^{(\delta+1)\delta}\sim L^{-d}h^{(\delta+1)\delta}L^{\beta(\delta+1)/v}\sim$$

$$\sim h^{(\delta+1)\delta}L^{0}h^{(\delta+1)\delta},$$

$$\xi\sim Ly^{-v}\sim L\varphi^{-v/\beta}L^{-1}\sim\varphi^{-v\beta}L^{0}\sim\varphi^{-v/\beta}\ \sim\tau^{-v},$$

$$\xi\sim Lz^{-v/\beta\delta}\sim Lh^{-v/\beta\delta}L^{-1}\sim h^{-v\beta\delta}L^{0}\sim h^{-v/\beta\delta}. \tag{13}$$

Therefore, we have obtained a limiting transition from the scaling hypothesis for a spatially bounded two-component liquid mixture to the scaling hypothesis for a similar system with spatially unbounded geometry.

The critical liquid-vapor state. Analogously to the previous case where a spatially bounded two-component system was in the vicinity of the critical liquid-liquid state, we can write down the scaling hypothesis for this system in the vicinity of the critical liquid-vapor state for the singular part of the thermodynamic potential, Helmholtz's free energy per one mole $F_{\mathrm{sing}}(T,\rho,\mu^*)$, and for the correlation radius of fluctuations of the order parameter $\xi(T,\rho,\mu^*)$:

$$F_{\mathrm{sing}}(T,\rho,\mu^*)=L^{-d}f_{F}[a\varphi^{1/\beta}(\mu^*)L^{1/v},bh(\mu^*)L^{\beta\delta/v}], \tag{14}$$

$$\xi(T,\rho,\mu^*)=Lf_{\xi}[a\varphi^{1/\beta}(\mu^*)L^{1/v},bh(\mu^*)L^{\beta\delta/v}]. \tag{15}$$

In this case, the order parameter and the field conjugated to it are the deviations of the mixture density $(\mu^*)=[\rho-\rho_c(\mu^*)]/\rho_c(\mu^*)$ and the chemical potential of a solvent $h=[\mu_1-\mu_1(\rho_c(\mu^*),T)]/\mu_1(\rho_c(\mu^*),T)$ from their values on the critical isochore. The scaling functions of Helmholz's free energy $f_F(y,z)$ and the correlation radius $f_{\xi}(y,z)$ have the asymptotes that are given by formulas (12).

This ensures the limiting transition to a spatially unbounded liquid mixture near the critical state of vapor formation according to formulas completely analogous to (13).

The order parameter of a binary liquid mixture. In conclusion, we obtain one of the consequences that follows from the scaling hypothesis (2), (3) for liquid mixtures in media with bounded geometry and can be verified experimentally. Let us consider the equilibrium value of the order parameter $\varphi_0 = x_0 - x_c(P), [\rho_0 - \rho_c(\mu^*)]/\rho_c(\mu^*)$ that can be obtained by differentiating the singular part of the thermodynamic potential per one mole (Gibbs free energy $G_{\text{sing}} = \mu_{1\text{sing}}(T, P, x)$ for the liquid-liquid critical state or Helmholtz's free energy $F_{\text{sing}}(T, \rho, \mu^*)$ for the critical liquid-vapor state) with respect to the external field h conjugated to the order parameter. As a result, we get

$$\varphi_0 = (\partial G_{\text{sing}}/\partial h)_\tau = (\partial F_{\text{sing}}/\partial h)_\tau =$$

$$= L^{-d+\beta\delta/v} f_\varphi(y, z) = L^{-\beta/v} f_\varphi(y, z), \qquad (16)$$

where the scaling function $f_\varphi(y, z)$ is determined in terms of the derivatives of the scaling function f_μ in formula (8) or the scaling function f_F in formula (14) with respect to another argument z as follows: $f_\varphi = b\partial f\mu/\partial z = b\partial f_F/\partial z$. The combination of critical indices in exponent (16) equals $-d + \beta\delta/v = -\beta/v$, because there are the following relations between critical indices: $3v = 2 - d, a + 2\beta + \gamma = 2, \quad \beta\delta = \beta + \gamma$. Formula (16) allows us to propose the following method for obtaining the dependence of any physical quantity (let it be N) on the typical size L of a spatially bounded system [19]:

$$N \sim \tau^{-n} \sim \xi^{-n/v} \sim L^{-n/v}. \qquad (17)$$

The relation (17) leads to the following conclusion: if an arbitrary physical quantity (equilibrium or nonequilibrium one) in a spatially unbounded system has the temperature singularity $N(\tau) \sim \tau^{-n}$, then, in view of the relations $\xi \sim \tau^{-v}$, $\tau \sim \xi^{-1/v}$, and $\xi \approx L$, the dependence of this quantity on the linear size L in spatially bounded systems near the critical points and the points of phase transitions has the form $N(L) \sim L^{-n/v}$. For example, the equilibrium value of the order parameter in a spatially unbounded system is $\varphi_0(\tau) \sim \tau^\beta$. Then, in the spatially bounded system with linear size L (for example, a cube with side L), the order parameter depends on L as $\varphi_0(L) \sim L^{-\beta/v}$. This is confirmed by formula (17) as well. With the help of result (17) for the equilibrium value of the order parameter, we can easily obtain the limiting transition to a spatially unbounded system. In fact, the linear size L in the latter system is infinite, and the correlation radius can unlimitedly grow at $\tau \to 0$ or at the phase transition point. It follows from (17) that a value of the equilibrium order parameter $\varphi_0 \to 0$ at $\tau \to 0$, $L \to \infty$ in agreement with the physical argumentation.

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ГІПОТЕЗА МАСШТАБНОГО ПЕРЕТВОРЕННЯ ДЛЯ ПРОСТОРОВО ОБМЕЖЕНИХ ДВОКОМПОНЕНТНИХ РІДКИХ СУМІШЕЙ

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Резюме

Запропоновано гіпотезу масштабного перетворення для просторово обмежених двокомпонентних рідких сумішей в критичних областях пароутворення (рідина—пара) та розшарування (рідина—рідина). Введено поняття просторової обмеженості системи в критичній області та обговорено гіпотезу масштабного перетворення для просторово необмежених двокомпонентних рідких сумішей з використанням різних незалежних змінних. Розглянуто деякі наслідки сформульованої в роботі гіпотези (зокрема, граничний перехід до просторово необмеженої системи, а також критичну поведінку параметра порядку в системі обмеженої геометрії).