SUSCEPTIBILITY OF FINITE-SIZE BINARY LIQUID MIXTURES IN THE CRITICAL REGION

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The scaling hypothesis for finite-size binary liquid mixtures is used to study the susceptibility in the liquid-liquid and liquid-vapor critical regions. The dependence of the susceptibility on temperature and field variables as well as on the scaling densities φ_1, φ_2 and the linear size of a system is found to determine the consequences which can be verified experimentally. A change of the critical behavior of susceptibilities determined by the correlators $\langle\varphi_1\varphi_1\rangle$, $\langle\varphi_2\varphi_2\rangle$, and $\langle\varphi_1\varphi_2\rangle$ has to exist for the liquid-vapor critical state in a finite-size binary liquid mixture. The limiting transition from the susceptibility of a finite-size binary liquid mixture to that of a system where all its linear sizes become infinite is examined.

Introduction

Resent achievements of the physics of phase transitions and critical phenomena are resulted, first of all, from the fundamental ideas which use scaling transformations and a renormalization group approach, as well as from the results of precise experiments [1—5]. All this enables one to formulate the fundamental laws of transformations of physical quantities, which are determined by the strong interaction between the order parameters of an investigated system at large spatio-temporal distances. These laws had been based upon the scale invariance hypothesis which has been defined, for the first time, for infinite-size individual substances [1, 6], and then it was extended to finite-size binary mixtures [3] because of the isomorphism hypothesis. The physical meaning of the scale invariance hypothesis consists in the realization of a consequent scale transition from interatomic lengths to the correlation length of fluctuations of the system order parameter, a new parameter in the critical region that has the dimension of length.

The nature of phase transitions and critical phenomena in various systems, particularly in individual liquids and binary or multicomponent liquid mixtures, essentially changes in the cases where the investigated systems become finite-size. Such systems, the investigation of which is of not only a theoretical, but great practical interest, include various surfaces, transient layers (interfaces), pores, as well as vitally important biological objects — biomembranes, synaptic junctions, etc.

The scaling hypothesis for finite-size individual systems (one-component liquids and magnetics) was established in [7] (see also [8]). In [9], the scaling hypothesis was extended to the case of finite-size binary liquid mixtures in the critical region.

In the present work, the scaling hypothesis which was established in [9] will be used for the investigation of the susceptibility of finite-size binary liquid mixtures in the critical regions of mixing–stratification (liquid-liquid) and vaporization (liquid-vapor) with the purpose to get those consequences that can be verified experimentally.

Liquid-Liquid Critical State

For the critical state of binary liquid mixtures with a finite-size configuration, it is necessary to consider two different cases depending on which additional variable — a field one or the density— is fixed under experimental conditions. According to [10], the field variables mean such physical quantities which take on equal values in coexistent phases (the pressure, temperature, chemical potential of mixture components, etc.). Unlike the field variables, there are the density-related ones which reveal a discontinuity when passing through an interface (the densities of components, mixture concentrations, specific entropy, etc.). The fixation of an additional field variable in a binary liquid mixture makes this system isomorphic (similar) to a one-component liquid. In the opposite case where a density variable is fixed, the critical indices of a binary mixture can be renormalized under certain conditions in comparison with the critical indices of one-component liquids [3, 7].

Let us examine binary liquid mixtures with a finite-size configuration near the liquid–liquid (mixing–stratification) critical state. For this case, we pick out a field variable — the chemical potential $\mu^* = \mu_2 - \mu_1$, where μ_1 and μ_2 are, respectively, the potentials of a pure solvent and a solute per mole — as a variable additional to the independent ones, the temperature T and the pressure P which describe the thermodynamics of a one-component system. As mentioned above, the isomorphism of the critical behavior of a binary liquid mixture and an individual liquid has to take a place for the independent variables T, P, and μ^*.

Using the rules of selection of isomorphic thermodynamic quantities (for more details, see [3]), we have

a) The thermodynamic potential which depends on this additional field variable μ^* is the chemical potential $\mu_1(T,P,\mu^*) = \Phi - \mu^* x$, and its total differential is $d\mu_1^* = -SdT - VdP - xd\mu^*$, where Φ is the Gibbs free energy, S is the entropy, and V is the volume;

b) The order parameter φ is a deviation of the concentration from the critical value, i.e. $\varphi = x - x_c(P)$;

c) The external ordering field h which is conjugated to the order parameter φ in the thermodynamic sense is determined by the difference μ of the chemical potentials of a mixture as follows: $h = [\mu^* - \mu^*(x_c, T)]/RT_c$.

Then, taking into account the results obtained in [7—9] and using the isomorphic variables T, P, and μ^*, the scaling hypothesis for a finite-size binary mixture near the liquid-liquid critical state looks like

$$\mu_1(T,P,\mu^*)_{\text{singul}} = L^{-d} f_\mu(a\varphi^{1/\beta}L^{1/\nu}, bhL^{\beta\delta/\nu}), \qquad (1)$$

$$\xi = L f_\xi(a\varphi^{1/\beta}L^{1/\nu}, bhL^{\beta\delta/\nu}). \qquad (2)$$

In Eqs. (1)—(2), the following notations are introduced: $\mu_1(T,P,\mu^*)_{\text{singul}}$ is the singular part of the thermodynamic potential per mole, which is the chemical potential of a solvent in this case; ξ is the correlation length of fluctuations of the order parameter (the concentration) of a binary liquid mixture; h is the external field which is conjugated to the order parameter; L is the typical linear size of a dish with the investigated mixture; d is the spatial dimension of a system (since we investigate the three-dimensional liquid mixtures limited in one, two, or three directions in the present work, $d = 3$); $f_\mu(y,z)$ and $f_\xi(y,z)$ are the corresponding scaling functions; β, δ, and ν are the critical indices; a and b are the non-universal (different for different mixtures) constants.

The scaling functions $f_\mu(y,z)$and $f_\xi(y,z)$ which appear in Eqs. (1), (2) for the scaling hypothesis for finite-size binary liquid mixtures are characterized by the following asymptotic formulae as $L \to \infty$:

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

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

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

$$f_\mu(z \to \infty) \sim z^{-\nu/\beta\delta} \sim h^{-\nu/\beta\delta}, \qquad (3)$$

where $\tau = [T - T_c(P)]/T_c(P)$ is the divergence of the temperature of a mixture T from the critical value $T_c(P)$.

Thus, under the transition to an unbounded system where the specific linear size L becomes infinite, the dependence on L disappears in the scaling hypothesis (1), (2) for finite-size systems, just as expected. Actually, the using of asymptotics (3) in Eqs. (1), (2) results in the following estimates for the fluctuation part of the thermodynamic potential of a solvent and for the correlation length of fluctuations of the concentration of a solute in a binary liquid mixture:

$$\mu_{1\text{singul}} \sim \varphi^{\delta+1} \sim \tau^{2-\alpha} \sim h^{\delta+1/\delta},$$

$$\xi \sim \tau^{-\nu} \sim h^{-\nu/\beta}. \qquad (4)$$

Here, the following relations for critical indices are used: $-d + (2\beta + \gamma)/\nu = 0$, $d\nu = 2 - \alpha$, $\alpha + 2\beta + \gamma = 2$, $\beta(\delta - 1) = \gamma$. Estimates (4) demonstrate the realization of a limiting transition from the scaling hypothesis (1)—(2) for the systems with a finite-size configuration to one for the unbounded systems [1—5].

To obtain the susceptibility χ of a finite-size binary liquid mixture in the critical region, it is necessary to calculate the second partial derivative of the singular part of the thermodynamic potential (1) with respect to the chemical potential μ^*, i.e.

$$\chi_{P,T} = -RT_c(\partial^2 \mu_{1\text{singul}}/\partial \mu^{*2})_{P,T}, \qquad (5)$$

since, in the investigated case, the susceptibility is $\chi_{P,T} = -RT_c(\partial x/\partial \mu^*)_{P,T}$ and the concentration is $x = -(\partial \mu_1/\partial \mu^*)_{P,T}$. Taking into account that the chemical potential μ^* is determined by the external field

$h = [\mu^* - \mu^*(x_c, T)]/RT_c$ which appears in the second scale argument $z = bhL^{\beta\delta/\nu}$ of the function $f_\mu(y,z)$ of the singular part of the thermodynamic potential in Eq. (1), we get

$$\chi = -RT_c(\partial^2\mu_{1\text{singul}}/\partial^2 z)_{P,T}(\partial z/\partial h)^2(\partial h/\partial\mu^*)^2_T =$$

$$= (-RT_c)^{-1}L^{-d}(\partial^2 f_\mu(y,z)/\partial^2 z)_y b^2 L^{2\beta\delta/\nu} =$$

$$= L^{\gamma/\nu} f_\chi(y,z), \tag{6}$$

where the susceptibility scaling function is $f_\chi(y,z) = -b^2(RT_c)^{-1}(\partial^2 f_\mu(y,z)/\partial z^2)_y$ and the well-known relation between critical indices $-d + 2\beta\delta/\nu = \gamma/\nu$ is also used.

Let us use the asymptotic formulae for the scaling function $f_\chi(y,z)$ as $L \to \infty$ which appears in Eq. (6) to determine the limiting transition from the susceptibility χ of a finite-size medium to the susceptibility of an infinite-size medium:

$$f_\chi(y \to \infty) \sim y^{-\gamma},$$

$$f_\chi(z \to \infty) \sim z^{-\gamma/\beta\delta}. \tag{7}$$

As a result of the using of such asymptotes, we get the power dependences of a susceptibility $\chi(L \to \infty) \sim \tau^{-\gamma} \sim h^{-\gamma/\beta\delta}$ on the temperature τ and the field variable h for a finite-size medium which are known from [1—5].

Liquid-Vapor Critical State

Consider the vaporization (liquid-vapor) critical state, whose thermodynamics is described by such a set of independent variables: T (the temperature), μ_1 (the chemical potential of a solvent) and μ^* (the difference between the chemical potentials of a solvent and a solute). The order parameter is a divergence of the total molar density ρ of a mixture from the critical value ρ_c, i.e. $\varphi\Delta\rho = [\rho - \rho_c(\mu^*)]/\rho_c(\mu^*)$, and the external field conjugated to the order parameter is the quantity $h = [\mu_1 - \mu_1(\rho_c, T)]/RT_c$ [3,11]. For the indicated independent variables, the thermodynamic potential Ω per unit volume, i.e. the pressure $P = -\Omega/V$, satisfies the relation

$$dP = \rho S dT + \rho d\mu_1 + \rho x d\mu^*, \tag{8}$$

where ρS is the entropy density, S is the molar entropy, and x is the molar concentration of a solute.

The singular part of a pressure $P_{\text{singul}} = P - P_{\text{reg}}$ (P is the total pressure, and P_{reg} is the regular part of a pressure which has no singularities and is an analytical function of the variables T, μ_1, and μ^*) is determined by anomalous fluctuations of a density and satisfies the following scaling hypothesis for a finite-size binary liquid mixture near the liquid—vapour critical state:

$$P_{\text{singul}} = \tau^{2-\alpha} f_p^{(1)}(a\tau L^{1/\nu}, bhL^{\beta\delta/\nu}), \tag{9}$$

$$\xi = L f_\xi^{(1)}(a\tau L^{1/\nu}, bhL^{\beta\delta/\nu}). \tag{10}$$

Hence, the isomorphic susceptibility of such a system is described as follows:

$$\chi_{T,\mu*} = \frac{RT_c}{\rho_c}\left(\frac{\partial^2 p}{\partial\mu_1^2}\right)_{T,\mu^*} = \frac{RT_c}{\rho_c}\left(\frac{\partial^2\rho}{\partial\mu_1}\right)_{T,\mu^*} =$$

$$= L^{-d}\left(\frac{\partial^2 f_p^{(1)}}{\partial z^2}\right)_y \left(\frac{\partial z}{\partial h}\right)^2 \left(\frac{\partial h}{\partial\mu_1}\right)^2 =$$

$$= L^{-d} b^2 L^{2\beta\delta/\nu}(RT_c)^{-2}\left(\frac{\partial^2 f_p^{(1)}}{\partial z^2}\right)_y = L^{\gamma/\nu} f_\chi(y,z), \tag{11}$$

where the scaling function is $f_\chi = b^2(RT_c)^{-2}\times$ $\times(\partial^2 f_p^{(1)}/\partial z^2)_y$, $y = a\tau L^{1/\nu}$, $z = bhL^{\beta\delta/\nu}$. It is easy to see that, according to the isomorphism hypothesis, susceptibility (11) has a critical behaviour $\chi_{T,\mu*}(L \to \infty) \sim \tau^{-\gamma}$ when proceeding to an infinite system and is equal to the isothermal susceptibility of a one-component liquid in the critical region.

The scaling hypothesis (9), (10) for a finite-size binary mixture near the vaporization critical state can be restated in another way

$$\Delta P_{\text{singul}} = L^{-d} f_p^{(2)}(z_1, z_2),$$

$$\xi = L f_\xi^{(2)}(z_1, z_2), \tag{12}$$

where the corresponding scaling function $f_p^{(2)}$ depends on the arguments $z_1 = h_1 L^{\beta\delta/\nu}$ and $z_2 = h_2 L^{1/\nu}$. In Eq. (12), we used two scaling fields h_1 and h_2 [11,12],

$$h_1 = a_1\Delta\mu_1 + a_2\tau + a_3\Delta\mu^*,$$

$$h_2 = b_1\tau + b_2\Delta\mu_1 + b_3\Delta\mu^*, \tag{13}$$

and also the dimensionless quantities for the singular part of a pressure $\Delta P_{\text{singul}} = P_{\text{singul}}/\rho_c RT_c$, the chemical potential of a solvent $\Delta\mu_1 = (\mu_1 - \mu_{1c})/\mu_{1c}$, and the difference between the chemical potentials of a solvent and a solute $\Delta\mu^* = (\mu^* - \mu^*_c)/\mu^*_c$.

The density-related scaling quantities φ_1 and φ_2 which are conjugated to the fields h_1 and h_2 are determined by the equations

$$\varphi_1 = \left(\frac{\partial \Delta P_{\mathrm{singul}}}{\partial h_1}\right)_{h_2} = L^{-d+\beta\delta/\nu}\left(\frac{\partial f_p^{(2)}}{\partial z_1}\right)_{z_2} =$$

$$= L^{-\beta/\nu}\left(\frac{\partial f_p^{(2)}}{\partial z_1}\right)_{z_2}, \tag{14}$$

$$\varphi_2 = \left(\frac{\partial \Delta P_{\mathrm{singul}}}{\partial h_2}\right)_{h_1} = L^{-d+1/\nu}\left(\frac{\partial f_p^{(2)}}{\partial z_2}\right)_{z_1} =$$

$$= L^{(\alpha-1)/\nu}\left(\frac{\partial f_p^{(2)}}{\partial z_2}\right)_{z_1}, \tag{15}$$

which were derived with regard for the relations $d\nu = 2-\alpha$, $\beta(\delta-1)=\gamma$, $-2+\alpha+\beta+\gamma=-\beta$, $1-d\nu=\alpha-1$. It follows from Eq. (14) that the density-related scaling quantity plays the role of the order parameter, since $\varphi_1 \sim L^{-\beta/\nu} \sim \tau^{\beta}$ according to the results of work [9] on the relation between the spatial dependence of some physical quantity in a finite-size system and the temperature dependence of this quantity in an infinite-size system in the critical region.

Now we can obtain the required relations for the susceptibilities of a finite-size binary mixture as follows.

1. For the susceptibility χ_1 which determines the critical behavior of the order parameter correlator $\langle\varphi_1^2\rangle$, we have

$$\chi_1 = \left(\frac{\partial^2 \Delta P_{\mathrm{singul}}}{\partial h_1^2}\right)_{h_2} = \left(\frac{\partial \varphi_1}{\partial h_1}\right)_{h_2} = \left(\frac{\partial \varphi_1}{\partial z_1}\right)_{z_2}\frac{\partial z_1}{\partial h_1} =$$

$$= L^{-(\beta-\delta)/\nu}\left(\frac{\partial^2 f_p^{(2)}}{\partial z_1^2}\right)_{z_2} = L^{\gamma/\nu} f_\chi^{(1)}(z_1,z_2), \tag{16}$$

where the scaling functions of a susceptibility and a pressure are related by the relation $f_\chi^{(1)}(z_1,z_2) = \left(\frac{\partial^2 f_p^{(2)}}{\partial z_1^2}\right)_{z_2}$. One can see that, under the transition to an infinite-size system, the susceptibility χ_1 which is similar to the isomorphic susceptibility $\chi_{T,\mu*}$ [see Eq. (11)] is characterized by the strong divergence $\chi_1(L\to\infty)\sim\tau^{-\gamma}$, where $\gamma\approx 5/4$.

2. For the susceptibility χ_2 which determines the critical behavior of the correlator of the second density-related scaling quantity $\langle\varphi_2^2\rangle$, we get

$$\chi_2 = \left(\frac{\partial^2 \Delta P_{\mathrm{singul}}}{\partial h_2^2}\right)_{h_1} = \left(\frac{\partial \varphi_2}{\partial h_2}\right)_{h_1} = \left(\frac{\partial \varphi_2}{\partial z_2}\right)_{z_1}\frac{\partial z_2}{\partial h_2} =$$

$$= L^{(\alpha-1)/\nu}\left(\frac{\partial^2 f_p^{(2)}}{\partial z_2^2}\right)_{z_1} L^{1/\nu} = L^{\alpha/\nu} f_\chi^{(2)}(z_1,z_2), \tag{17}$$

where the scaling function $f_\chi^{(2)}(z_1,z_2) = \left(\frac{\partial^2 f_p^{(2)}}{\partial z_2^2}\right)_{z_1}$. It is evident that, under the transition to an infinite-size system, the susceptibility χ_2 shows a weak divergence, namely $\chi_2(L\to\infty)\sim\tau^{-\alpha}$, where $\alpha\approx 0.1$ According to the results of the fluctuation theory of phase transitions [1], this means that the correlator $\langle\varphi_2^2\rangle$ defines thermal fluctuations or fluctuations of the system energy.

3. Along with the susceptibilities χ_1 and χ_2, we can also introduce the so-called cross susceptibility

$$\chi_3 = \frac{\partial^2 \Delta P_{\mathrm{singul}}}{\partial h_1 \partial h_2} = \left(\frac{\partial \varphi_1}{\partial h_2}\right)_{h_1} = \left(\frac{\partial \varphi_2}{\partial h_1}\right)_{h_2} =$$

$$= L^{(1-\beta)/\nu} f_\chi^{(3)}(z_1,z_2), \tag{18}$$

where the scaling function $f_\chi^{(3)}(z_1,z_2) = \frac{\partial^2 f_p^{(2)}}{\partial z_1 \partial z_2}$. It is clear that the susceptibility χ_3 defines a behavior of the correlator $\langle\varphi_1\varphi_2\rangle$ which is nonzero for liquid systems (unlike magnetics) [1]. According to Eq. (18), the temperature dependence of the correlator $\langle\varphi_1\varphi_2\rangle$ for an infinite-size system is $\langle\varphi_1\varphi_2\rangle \sim \tau^{\beta-1}$, where the exponent is $\beta - 1 \approx -2/3$. So, the susceptibility χ_3 should show a critical behavior which is intermediate between those of susceptibilities χ_1 and χ_2.

The experimental confirmation of the existence of various critical behaviors of the susceptibility of a finite-size binary mixture should be expected when investigating the optical spectra of critical opalescence, i.e. a dynamical dispersion of light near the liquid—vapor critical state.

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СПРИЙНЯТЛИВІСТЬ ПРОСТОРОВО ОБМЕЖЕНИХ БІНАРНИХ РІДКИХ РОЗЧИНІВ У КРИТИЧНІЙ ОБЛАСТІ

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Резюме

Гіпотезу масштабної інваріантності для просторово обмежених бінарних рідких розчинів застосовано для визначення сприйнятливості в критичних областях рідина-рідина та рідина-пара. З метою отримання тих наслідків, котрі можуть бути перевірені експериментально, знайдено залежності сприйнятливості від температурної та польової змінних, а також від густинних скейлінгових величин φ_1, φ_2 та лінійного розміру досліджуваної системи. Для критичного стану пароутворення просторово обмеженого бінарного розчину повинна існувати зміна критичної поведінки сприйнятливостей, які визначаються кореляторами $\langle\varphi_1\varphi_1\rangle$, $\langle\varphi_2\varphi_2\rangle$ і $\langle\varphi_1\varphi_2\rangle$. Отримано граничний перехід від сприйнятливості просторово обмеженого бінарного рідкого розчину до сприйнятливості цієї системи, коли всі її лінійні розміри прямують до нескінченності.