Influence of charge fluctuations on the critical behavior of electrolyte solutions

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The effective Hamiltonian of electrolyte solution near its critical point is constructed. The vapor-liquid critical point is investigated in detail. The strong dependence of the Landau-Ginsburg number on the concentration of electrolyte is demonstrated. It is shown that the charge fluctuations in electrolytes essentially suppress the fluctuation of the order parameter and broaden the region of classical behavior.
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I. INTRODUCTION

In recent years critical phenomena in systems with Coulombic interaction between particles have been the object of great interest of many experimental [1–6] and theoretical [7–9] works. In [7] it was noted that the infinite range of Coulombic interaction may lead either to mean-field behavior with classical exponents or to Ising-like behavior. Another type of critical behavior seems to be unrealistic both from theoretical grounds and experimental evidence [7]. At first, the conclusion that the Coulombic interaction suppresses the fluctuations of an order parameter in solutions of the electrolytes is confirmed by the experimental data of Refs. [1,10]. At the same time some electrolyte solutions [6] show crossover from mean field to Ising behavior.

It is difficult to solve the problem of the type of critical behavior of a system in experiments. The main question here is the estimation of the Ginsburg number Gi, which controls the width of the asymptotic region $t_\times$. Its magnitude depends on the microscopic parameters of a system and as follows from experiments it varies in a wide range. In [2] the crossover from classical to Ising-like behavior was clearly observed at $t_\times \approx 10^{-2}$. In [1,3,4] the data were fitted by classical asymptotics up to $t_\times \approx 10^{-4}$ near the critical point. The molecular-dynamics simulations of molten salt [5] also show classical behavior of an order parameter for $\tau \approx 10^{-2}, \tau = (T - T_c)/T_c$, although the influence of finite-size effects does not allow us to say exactly whether the crossover does take place or not. In all cases, the width of the fluctuation region is smaller than the one for molecular liquids. In [6], the dependence of the width of the crossover region on the dielectric permittivity ϵ of a solvent was investigated. It was observed that the crossover region becomes smaller as ϵ is decreased. There are no physical reasons for the existence of such ϵ^* that $\mathrm{Gi}(\epsilon) \to 0$ as $\epsilon \to \epsilon^* > 1$. In case of $\epsilon^* = 1$, we deal with the plasma phase transitions [11]. Here we should note that liquid metals show Ising-class critical behavior [12], although they are the systems with pure Coulombic interaction. It is possible that this interaction is a precondition for the strong asymmetry of a binodal both for electrolytes and liquid metals. The shape of a binodal in the considered system is much more asymmetric than in the case of molecular liquids. This circumstance is connected with the choice of an appropriate order parameter, which restores the symmetrical shape of a binodal. Otherwise, the $\sim \tau^{2\beta}$ term, which is absent in standard variants of the asymptotic equation of state [13], should be introduced to fit the experimental data in laboratory variables [14].

In such a situation it is necessary to construct the effective Landau-Ginsburg Hamiltonian (LGH) of electrolyte solution in such a way that it takes into account (a) the long-range Coulombic interaction and (b) the short-range character of the charge-charge correlation functions. The first attempt in this direction was undertaken in [15]. In that work the initial Hamiltonian had the form

$$H[\eta(\vec{r}),q(\vec{r})] = H_s[\eta(\vec{r})] + H_{\text{ch}}[q(\vec{r})] + H_{\text{int}}[\eta(\vec{r}),q(\vec{r})], \tag{1}$$

where the first two terms describe the Landau-Ginsburg Hamiltonian for a solvent and the Hamiltonian for the Coulombic subsystem, respectively. The third term describes the interaction between the order parameter $\eta(\vec{r})$ and fluctuations of charge density $q(\vec{r})$. Near the vapor-liquid critical point $\eta(\vec{r}) = n(\vec{r}) - n_c$, where n is the density of a solvent, n_c is its critical value, and

$$H_s[\eta(\vec{r})] = \int dV \left[\frac{1}{2} c_0 [\vec{\nabla}\eta(\vec{r})]^2 + \frac{1}{2} a_2^{(0)} \eta(\vec{r})^2 + \frac{1}{4} a_4^{(0)} \eta(\vec{r})^4 \right], \tag{2}$$

where $a_2^{(0)} = \alpha_0 (T - T_c)/T_c \equiv \alpha_0 \tau$. The second term H_{ch} was modeled by the expression

$$H_{\text{ch}}[\eta(\vec{r})] = \int \frac{q(\vec{r}_1) q(\vec{r}_2)}{\epsilon_0 |\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2, \tag{3}$$

where ϵ_0 is the dielectric permittivity of a solvent. The contact form for H_{int},

$$H_{\text{int}} = -g \int d\vec{r}\, \eta(\vec{r}) q(\vec{r}), \tag{4}$$

is least evident. As a result, the predictions made in [15] have not been confirmed experimentally [7].

A new attempt to construct the LGH and to calculate the Ginsburg number for a system with Coulombic interaction was undertaken quite recently in [16,17]. However, the fluctuations of dielectric permittivity which is directly connected with density fluctuations were ignored. As we will see further, the account of this coupling leads to essential renormalization of the coefficients in the effective LGH and should be taken into account.

In the present work we construct the effective LGH for electrolyte solution near its vapor-liquid critical point starting from a modernized form of the initial Hamiltonian (1)–(4). First of all, we ignore $H_{\rm int}$ in the form (4) and take into account the spatial inhomogeneity of dielectric permittivity near the critical point, which is caused by its dependence on an order parameter:

$$\epsilon \to \epsilon(\vec{r}) = \epsilon + \frac{\partial \epsilon}{\partial \eta}\eta(\vec{r}) + \cdots, \tag{5}$$

where ϵ is the equilibrium value for the dielectric permittivity of a solvent. Due to Eq. (5), the expression (3) for $H_{\rm ch}$ is only the first term in a series on $\epsilon'(\vec{r}) = \epsilon(\vec{r}) - \epsilon$. The terms of higher orders describing the most essential polarization effects have the form

$$H_{\rm ch}[q(\vec{r}),\epsilon'(\vec{r})] = \int U(\vec{r}_1,\vec{r}_2|\epsilon(\vec{r}))q(\vec{r}_1)q(\vec{r}_2)d\vec{r}_1 d\vec{r}_2, \tag{6}$$

where

$$\begin{aligned} U(\vec{r}_1,\vec{r}_2|\epsilon(\vec{r})) &= \sum_{p\geqslant 0}\int d\vec{x}_1\cdots d\vec{x}_p K_p(\vec{r}_1,\vec{r}_2|\vec{x}_1,\ldots,\vec{x}_p) \\ &\quad \times \epsilon'(\vec{x}_1)\cdots\epsilon'(\vec{x}_p) \end{aligned} \tag{7}$$

and

$$K_0(\vec{r}_1,\vec{r}_2) = \frac{1}{\epsilon_0|\vec{r}_1 - \vec{r}_2|}.$$

In Sec. II we determine the explicit form of kernels $K_p, p > 1$ and the corresponding coefficients of the LGH. In Sec. III we analyze the dependence of the Ginsburg number and critical exponents on electrolyte concentration. A comparison with experiments is also given. In Secs. IV and V we propose theoretical explanations for the concentration dependence of the shift of the critical point and the degree of asymmetry of the equation of state. Some new problems are outlined in the Conclusion.

II. EFFECTIVE LANDAU-GINSBURG HAMILTONIAN

The electrolyte solution near its vapor-liquid critical point is characterized by two independent scales: (a) the screening length $r_{\rm scr}$, which in the Debye approximation is

$$r_{\rm scr} \approx r_D = \sqrt{\frac{\epsilon k_B T}{\sum 4\pi e_a^2 z_a n_a}}, \tag{8}$$

where e is the electronic charge, z_a and n_a are the valence and the number density for the ions of type ''a,'' T is the temperature, and k_B is the Boltzmann constant; (b) the correlation length r_c for density fluctuations in a solvent,

$$r_c = r_0\tau^{-\nu}, \quad \nu = \begin{cases} 0.5 & \text{classical region,} \\ 0.63 & \text{fluctuation region.} \end{cases} \tag{9}$$

The critical behavior of a solution depends on the interplay of these scales. For experiments where

$$r_{\rm scr} \gg r_c,$$

the interionic electric field acts as the additional pressure which changes the position of the critical point. The character of the fluctuations of an order parameter for a system does not change and the range for the crossover of critical exponents is determined by the Ginsburg number for a solvent. In the more important second case when

$$r_{\rm scr} < (\ll) r_c, \tag{10}$$

the electric field of charge fluctuations polarizes a solvent and as a result leads to a variation of interaction constants in the LGH and also to the appearance of additional terms in it.

This consideration is based on the important fact that the screening length remains finite while approaching the liquid-gas critical point. Such a conclusion is a direct consequence of the isomorphism principle for the critical phenomena in multicomponent mixtures and simple liquids. In accordance with it, the only extensive variable of state is strongly fluctuating in the vicinity of the critical point (see Appendix A). The level of fluctuations for others, which are orthogonal to it, is bounded. ''Switching on'' the Coulombic interaction for the electroneutral system additionally suppresses the long-range fluctuations of the variable connected with the charge fluctuations.

The lower bound for the concentration range where Debye screening is not destroyed by the thermal fluctuations is

$$x_{\rm min} = v\,\epsilon\left(\frac{k_B T}{e^2}\right)^3 \approx 10^{-6}, \tag{11}$$

where v is the volume per molecule of a solvent.

The electric field of charge fluctuations polarizes the solvent. Because of this, the local electrostatic energy is fluctuating on the scales of density-density correlation length. The account of this contribution renormalizes the interaction constants in the LGH. To construct the corresponding LGH, we will use the interrelation (5) between fluctuations of density and dielectric permittivity,

$$\epsilon \to \epsilon(\vec{r}) = \epsilon[1 + \lambda_1\eta(\vec{r}) + \lambda_2\eta^2(\vec{r}) + \cdots], \tag{12}$$

$$\lambda_k = \frac{\rho_c^k}{\epsilon(\rho_c)}\left.\frac{\partial^k \epsilon}{\partial \rho^k}\right|_{\rho=\rho_c}, \quad \eta = \rho/\rho_c - 1. \tag{13}$$

Here, ϵ is the equilibrium value for the dielectric permittivity. We can obtain the effective LGH as follows. For a homogeneous system, the density of energy is a sum of the non-Coulombic contribution $h_{\rm nC}$ and that for the Coulombic subsystem h_C. Far away from the critical point, the latter has the structure

$$h_C = -\frac{1}{8\pi}\Gamma_c^3 \frac{1}{(\epsilon/\epsilon_c)^{3/2}}, \tag{14}$$

where n is the particle density, Γ is the inverse screening length, and the index ''c'' indicates that the values are taken in the critical point. To take into account the large-scale inhomogeneity of a system, we assume that the condition

$$r_c > r_{\mathrm{scr}}$$

is fulfilled, where r_c is the correlation length for the fluctuations of an order parameter. We can use the analogous expressions for h_{nC} and h_C in which local values of ϵ and n,

$$\begin{aligned} n &\to n[1+\tilde{\eta}(\mathbf{r})], \\ \epsilon &\to \epsilon[1+\tilde{\epsilon}(\mathbf{r})], \end{aligned} \tag{15}$$

should be substituted. As a result the fluctuational contribution of the Coulombic subsystem into the energy of a system is equal to

$$\beta h_C(\mathbf{x}) = -\frac{\Gamma_c^3}{8\pi}\left[\frac{1}{[1+\tilde{\epsilon}(\vec{x})]^{3/2}} - 1\right]. \tag{16}$$

The formal derivation of the quasilocal approximation (16) from the microscopic point of view is given in Appendix A. Adding the quasilocal term

$$\beta h^{(ql)} = \frac{b^2}{2}[\nabla\eta(\mathbf{r})]^2, \tag{17}$$

we assume that the value of b can be evaluated with the help of results [16,18].

Using the dimensionless form of the coefficients of the LGH, the formulas (15) and (16) yield the following:

$$\beta H_{\mathrm{eff}}[\eta(\vec{x})] = \int d\vec{x}\left(\frac{b}{2}[\vec{\nabla}\eta(\vec{x})]^2 + \sum_{m=1}^{\infty}\frac{a_m}{m}\eta^m(\vec{x})\right), \tag{18}$$

where

$$a_m = a_m^{(0)} + a_m^{(el)}x^{3/2}, \quad m \geqslant 1, \quad a_m^{(0)} = 0, m \geqslant 5, \tag{19}$$

$$b = (c_0 + c)\sigma, \tag{20}$$

and according to Eq. (2),

$$a_1^{(0)} = a_3^{(0)} = 0.$$

Here σ is the diameter of a molecule in a solvent. The values of $a_m^{(el)}$ are determined from Eq. (16) and are equal to

$$a_m^{(el)} = \frac{(-1)^{m+1}}{16\pi}\frac{(2m+1)!!}{(2m-2)!!}(\Gamma_*\sigma)^3, \quad \Gamma_* = \frac{\Gamma}{\sqrt{x}}. \tag{21}$$

The calculation of the LGH without taking into account polarization effects was done in [16,17] based on different models. The obtained Ginsburg criterion did not show the existence of crossover (Gi$\simeq$10).

Now it is desirable to reduce the initial Hamiltonian of an electrolyte (18) in the vicinity of the critical point ($r_D \ll r_c$) to the Landau-Ginsburg form. Usually such a reduction is performed by omitting all local terms $\sim\eta^n, n \geqslant 5$. However, this step is connected with the loss of important information about corrections to the leading asymptotic terms [19]. A more suitable way is connected with the attraction of catastrophe theory [20], which states that the nonlinear transformation of the order parameter

$$\eta \to \tilde{\phi} = \eta + \gamma_2\eta^2 + \gamma_3\eta^3 + \cdots \equiv \hat{P}_t\eta \tag{22}$$

and the shift transformation

$$\tilde{\phi} \to \phi = \tilde{\phi} - \phi_0 \equiv \hat{P}_s\tilde{\phi} \tag{23}$$

reduce the infinite series

$$h = \sum_{n=1}\frac{1}{n}A_n\eta^n \tag{24}$$

to the canonical form

$$h(\eta(\phi)) = A_1^{(c)}\phi + \frac{1}{2}A_2^{(c)}\phi^2 + \frac{1}{4}A_4^{(c)}\phi^4 \equiv h^{(c)}(\phi). \tag{25}$$

The coefficients $A_k^{(c)}$ are the definite nonlinear functions of the initial ones (see [19,21]):

$$A^{(c)} = \hat{P}_c A, \quad \hat{P}_c = \hat{P}_s\hat{P}_t. \tag{26}$$

In the fluctuation region the situation is more complex since the behavior of a system is described by a configuration integral:

$$Q = \int \exp\{-\beta H_{\mathrm{eff}}[\eta(\vec{x})]\}D\eta(\vec{x}). \tag{27}$$

In this case the transformation (22) has a local character and is accompanied by Jacobian terms. The Landau-Ginsburg Hamiltonian of a system is a result of the iterative procedure generated by the elementary transformations (22):

$$\beta H_{\mathrm{can}}[\psi(\vec{x})] = \frac{b}{2}\int(\vec{\nabla}\psi(\vec{x}))^2 d\vec{x} + \int d\vec{x}\left(-a_1^{(c)}\psi(\vec{x}) + \frac{1}{2}a_2^{(c)}\psi^2 + \frac{1}{4}a_4^{(c)}\psi^4\right). \tag{28}$$

Here

$$\psi = T_c\eta = \gamma_0 + \eta + \frac{1}{2}\gamma_2\eta^2 + \cdots, \quad a^{(c)} = \hat{T}_c A. \tag{29}$$

The details of these transformations can be found in [19,21].

III. GINSBURG CRITERION FOR ELECTROLYTE SOLUTIONS

It is well known [13] that the crossover from classical to Ising-like critical behavior of a system occurs at the temperature

$$\tau \approx \text{Gi}, \tag{30}$$

where

$$\text{Gi} = \frac{a_4^{(c)^2} T_c^2}{\alpha b^3}, \quad \alpha = \left. \frac{d a_2^{(c)}}{d\tau} \right|_{T=T_c}. \tag{31}$$

Values α_0 ($a_2^{(0)} = \alpha_0 \tau$) and $a_4^{(0)}$ for the initial Hamiltonian can be extracted from the van der Waals equation (see [19]):

$$\alpha_0 \simeq \beta_c \Phi \delta^2, \quad a_4^{(0)} \simeq \delta^4, \tag{32}$$

where $\delta = n_c \sigma^3$ is the dimensionless density and $-\Phi$ is the minimum value of the interparticle potential for a solvent. Using Eqs. (21) yields

$$\frac{a_4^{(c)}}{a_4^{(0)}} = 1 - \tilde{a}_4 x^{3/2} + o(x^{3/2}),$$

$$\frac{\alpha}{\alpha_0} = 1 + \tilde{\alpha} x^{3/2} + o(x^{3/2}), \tag{33}$$

$$\frac{b}{c_0} = 1 + \lambda_1 x^{1/2} + o(x^{1/2}),$$

where

$$\tilde{a}_4 \simeq \frac{1}{a_4^{(0)}} (\Gamma_* \sigma)^3 \delta^4 \left(\frac{\partial \ln \epsilon}{\partial \ln \rho} \right)^4 \simeq 0.1\text{–}1,$$

$$\tilde{T} = \frac{T_c - T_c^{(0)}}{T_c^{(0)}} \simeq 0.01,$$

$$\tilde{\alpha} \simeq \frac{1}{\alpha_0} (\Gamma_* \sigma)^3 \delta^2 \left(\frac{\partial \ln \epsilon}{\partial \ln \rho} \right)^2 \simeq 1, \tag{34}$$

$$\lambda_1 \simeq \frac{1}{c_0} (\sigma \Gamma_*) \simeq 0.1.$$

The numerical estimations for $\tilde{a}_4$, $\tilde{T}$, $\tilde{\alpha}$, and λ_1 are obtained for the following values of the parameters:

$$\delta \simeq 0.33, \quad \beta_c \Phi \simeq 1.$$

We assume that $\partial \ln \epsilon / \partial \ln \rho$ can be approximated by the formula

$$\frac{\partial \ln \epsilon}{\partial \ln \rho} = \frac{A \rho}{\epsilon} \tag{35}$$

and the coefficient A is equal to 280 cm^3/g for water in accordance with [22], at least by the order of magnitude $\Gamma_* \sigma < 1$. Using Eqs. (31) and (33), we obtain the following renormalized value of the Ginsburg number:

$$\text{Gi}(x) \approx \text{Gi}^{(0)} \frac{(1 - \tilde{a}_4 x^{3/2})^2}{(1 + \tilde{\alpha} x^{3/2})(1 + \lambda_1 x^{1/2})^3}, \tag{36}$$

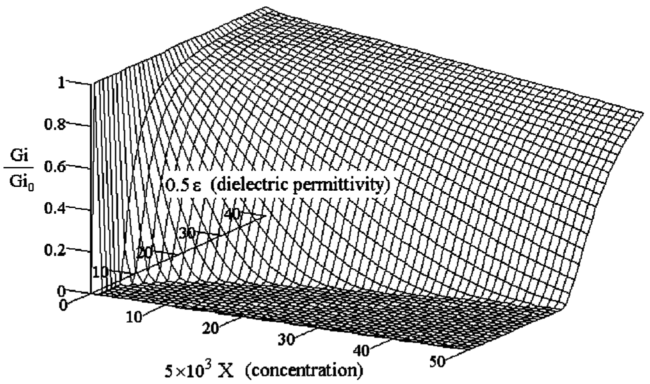

FIG. 1. The relative value Gi/Gi_0 of the Ginsburg number as a function of concentration (x axis) and dielectric permittivity (y axis) calculated by formula (36). The scales on the x and y axes equal to 1:0.0002 and 1:2, respectively.

where $\text{Gi}^{(0)}$ is the Ginsburg number for a solvent. In fact, the Ginsburg number essentially depends on the ratio of the amplitude of correlation length r_0 and the Debye screening length. In accordance with what was said above, the Ginsburg number is a monotone decreasing function of concentration. Besides this, it also depends on the temperature as a parameter. Summarizing our arguments for the regions $r_D < (>) r_c$, we can write

$$\text{Gi}(x|\tau) = \begin{cases} \text{Gi}^{(0)}, & x \ll x_D(\tau), \\ \text{Gi}(x), & x_D(\tau) \ll (<) x, \end{cases} \tag{37}$$

where

$$x_D(\tau) = \left(\frac{1}{\Gamma_* r_0} \right)^2 \tau^{2\nu} \tag{38}$$

is the limit concentration of an electrolyte, which determines the applicability region of our polarization model. The concentration dependences of Gi at some fixed τ and different values of the dielectric permittivity are presented in Fig. 1. Note that the greater the value of the dielectric permittivity is, the greater is Gi. This fact was noted experimentally in [6]. Figure 2 shows the concentration dependence of Gi for

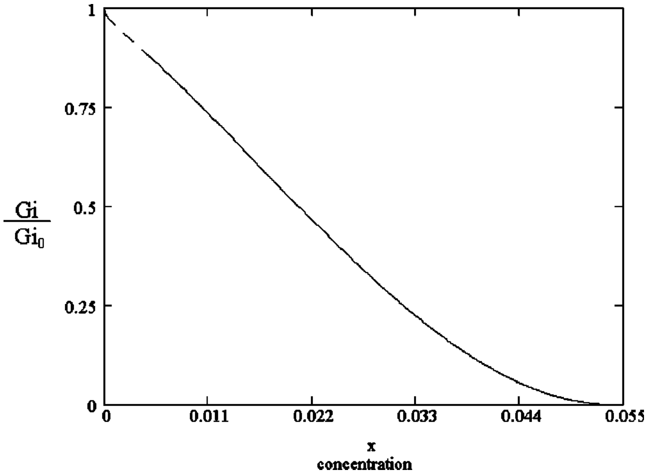

FIG. 2. Concentration dependence of the Ginsburg number for parameters given in the text.

electrolyte solution with $\epsilon = 80$ and $\Gamma_* \sigma = 0.5$. The qualitative behavior of $\mathrm{Gi}(x)$ near x_D is shown by a dashed line. Essentially, the value of a_4 vanishes and the system loses its stability at the concentration of an electrolyte:

$$x_* = \tilde{a}_4^{-2/3}. \tag{39}$$

Obviously this possibility is realized only if $\tilde{a}_4 > 1$ [see Eq. (33)]. In this case one can expect the multicritical behavior of a system [7].

Using the formula (37) is not convenient since usually experiments are carried out at fixed concentration. Let us illustrate this situation considering the values of the critical exponent. According to Eq. (37) we have

$$\nu = \begin{cases} 0.5 \quad \text{for} \quad \begin{array}{llllll} \mathrm{Gi}^{(0)} & < & \tau_D(x) & < & \tau & \text{(a)} \\ \mathrm{Gi} & < & \tau & < & \tau_D(x) & \text{(b)}, \end{array} \\ \\ 0.625 \quad \text{for} \quad \begin{array}{llllll} \tau & \ll & \mathrm{Gi}^{(0)} & < & \tau_D(x) & \text{(c)} \\ \tau & \ll & \mathrm{Gi} & < & \tau_D(x) & \text{(d)}, \end{array} \end{cases} \tag{40}$$

where

$$\tau_D = (r_0 \Gamma_* \sqrt{x})^{1/\nu} \sim x. \tag{41}$$

At the end of this section, let us complete the obtained results with qualitative arguments. By order of magnitude [13]

$$\mathrm{Gi} = \left(\frac{r_s}{r_0} \right)^6, \tag{42}$$

where r_s is the interparticle spacing. The addition of an electrolyte leads to the augmentation of the correlation length amplitude because of its renormalization by charge-charge fluctuations. It is clear that the behavior of strongly concentrated electrolytes is expected to be similar to that of simple liquids or liquid metals.

IV. FLUCTUATION-INDUCED SHIFT OF THE CRITICAL POINT IN A SOLUTION OF ELECTROLYTES

An anomalous curvature of the T-x and P-x projections of the critical line of electrolyte solution at very small mole fractions of an electrolyte $\mathrm{NaCl} + \mathrm{H_2O}$ was observed in many experimental works [23–25]. But the nature of very big values of $dT_c(x)/dx$ was not clarified.

We will show that the shift of the critical point of a high diluted solution from the locus of a pure solvent is governed predominantly by the charge-charge fluctuations. The ‘‘square root’’ concentration law for such a shift is a direct consequence of the polarizational charge-density coupling theory proposed in previous sections. The dependence of the coefficients of the effective LGH at low concentrations is given by Eq. (33). In the mean-field approximation, the shift of the critical temperature as it follows from Eq. (33) is

$$\Delta^{(\mathrm{mean})} T_c \simeq x^{3/2}. \tag{43}$$

But the fluctuations change slightly the value of the critical temperature. This fluctuation-induced shift of the critical temperature (the locus of the critical point in general) is proportional to

$$\Delta^{(\mathrm{fl})} T_c \simeq \sqrt{x}. \tag{44}$$

Indeed, let us define the renormalized order parameter so that the coefficient at the gradient term is equal to unity:

$$\phi(\mathbf{r}) = \sqrt{c(x)}\, \eta(\mathbf{r}). \tag{45}$$

The LGH for the new order parameter reads as follows:

$$\beta H_{\mathrm{eff}}[\phi] = \int dV \left(\frac{1}{2} [\nabla \phi(\mathbf{r})]^2 + \tilde{a}_1(T,x) \phi(\mathbf{r}) + \frac{1}{2} \tilde{a}_2(T,x) \phi^2(\mathbf{r}) + \frac{1}{4} \tilde{a}_4(T,x) \phi^4(\mathbf{r}) \right), \tag{46}$$

where

$$\tilde{a}_k(T,x) = [c(x)]^{-k/2} a_k(T,x). \tag{47}$$

In the first order of perturbation theory on fluctuation coupling constant $\tilde{a}_4$ [27], we have

$$\tilde{a}_2^R(T,x) = \tilde{a}_2(T,x) + 3 \tilde{a}_4(T,x) \frac{d}{d\Lambda} \int_0^\Lambda G_0(\mathbf{q}) d\mathbf{q} \bigg|_{\Lambda = 1},$$

$$G_0(\mathbf{q}) = \frac{1}{\tilde{a}_2(T,x) + \mathbf{q}^2}. \tag{48}$$

From Eq. (44) it follows that

$$\frac{dT_c(x)}{dx} \simeq \frac{1}{\sqrt{x}}, \tag{49}$$

which explains the anomalously big values of $dT_c(x)/dx$ observed in [23–25]. Note that such a term was used purely empirically in [26] to process the experimental data. The same conclusion on the existence of $\sqrt{x}$ terms is valid for other coordinates of the critical point, such as pressure and density.

V. ASYMMETRY OF A BINODAL FOR ELECTROLYTE SOLUTIONS

In this section we will show that the addition of electrolyte leads to essential additional asymmetry of the vapor-liquid coexistence curve. We establish this fact in an evident form within the framework of the canonical formalism [19,21], which gives a clear motivation for all standard asymptotic terms of the equation of state as well as for those of form $\tau^{n\beta}$ introduced in [14].

As follows from the scale-invariant theory of critical phenomena, the singular part of the equation of state is given by the expression

$$\langle P\rangle = |h_2|^{\beta} g_s\left(\frac{h_1}{|h_2|^{\beta+\gamma}}\right). \tag{50}$$

The order parameter P and conjugated fields h_1, h_2 within the canonical formalism should be identified with ψ and the coefficients $a_1^{(c)}, a_2^{(c)}$ of the Hamiltonian (28). As a result, Eq. (50) takes the form

$$\langle \psi\rangle = |a_2^{(c)}|^{\beta} g_s\left(\frac{a_1^{(c)}}{|a_2^{(c)}|^{\beta+\gamma}}\right). \tag{51}$$

Here the brackets $\langle\ \rangle$ designate the averaging on the volume of the correlation sphere ($\propto r_c^3$). In particular, the equation of a binodal including the additional Wegner's term [28] is as follows:

$$\langle \psi\rangle_{\text{bin}} = \pm |a_2^*|^{\beta} g_s(0)(1 + b_2|a_2^*|^{\Delta} + \cdots), \tag{52}$$

where $a_2^* = a_2^{(c)}|_{a_1^{(c)}=0}$. Its ''liquid'' and ''gas'' branches in variables (ψ, a_2^*), as is clear from Eq. (51), are absolutely symmetric. But this symmetry disappears if we return to the initial (''laboratory'') variables (η, τ) [19,21]. Indeed, using Eqs. (22) and (23) one can get

$$\langle \eta\rangle = C + \langle\psi\rangle + \frac{1}{2}\Gamma_2\langle\psi^2\rangle + \cdots. \tag{53}$$

Since (see [13])

$$\langle \psi^2\rangle = \langle\psi\rangle^2 + |h_2|^{1-\alpha} l_s\left(\frac{h_1}{|h_2|^{\beta+\gamma}}\right),$$

where the function $l_s(x)$ is inverse to $g_s(x)$, Eq. (53) in the asymptotic region transforms to

$$\tfrac{1}{2}(\langle\eta\rangle_{\text{bin}}^{+} - \langle\eta\rangle_{\text{bin}}^{-}) = g_s(0)|a_2^*|^{\beta}(1 + b_2|a_2^*|^{\Delta} + \cdots) + \cdots, \tag{54}$$

$$\tfrac{1}{2}(\langle\eta\rangle_{\text{bin}}^{+} + \langle\eta\rangle_{\text{bin}}^{-}) = C + \tfrac{1}{2}\Gamma_2[g_s^2(0)|a_2^*|^{2\beta} + l_s(0)|a_2^*|^{1-\alpha}] + \cdots.$$

Note that Eq. (54) besides standard terms [13] includes an additional contribution $\propto|\tau|^{2\beta}$ (as well as other terms $\propto|\tau|^{n\beta}, n>2$). The latter was introduced in works [14] due to empirical reasons. This new term with $\beta=0.5$ appears in the mean-field approximation [29] as well. Essentially, the asymmetry of the coexistence curve is determined by a product of universal multipliers $g_s(0)$ and $l_s(0)$ and the coefficient Γ_2 describing the individual properties of liquids and solutions. The temperature and concentration dependences of coefficients C, Γ_2, a_2^* are determined by the expressions (21) and

$$\begin{aligned} C &\simeq C_0 + C_1\tau + \cdots,\\ C_i &\simeq C_i^{(0)} + C_i^{(el)}, \quad i=0,1,\\ \Gamma_2 &\simeq \Gamma_2^{(0)} + \Gamma_2^{(el)},\\ a_2^* &\simeq a_2^{(0)} + a_2^{(el)}, \end{aligned} \tag{55}$$

where $C_i^{(0)}, \Gamma_2^{(0)}, a_2^{(0)}$ are the values of the respective coefficients in the absence of electrolyte. The values of the terms induced by electrolyte impurity in Eqs. (55) are of $\propto x^{3/2}$ order and strongly depend on the parameter $\Gamma_*\sigma$. If $\Gamma_*\sigma < (\ll) 0.1$, they can be omitted. In the opposite cases, an account of additional terms is rather essential. It occurs due to the decrease of the value of a_4 (see the formulas below). The coefficient C_1 is equal to the tangent of the slope angle of the rectilinear diameter with respect to the temperature axis in the mean-field approximation. Approximate values for C_0 and C_1 as well as for Γ_2^0 and $\Gamma_2^{(el)}$ can be calculated with the help of formulas

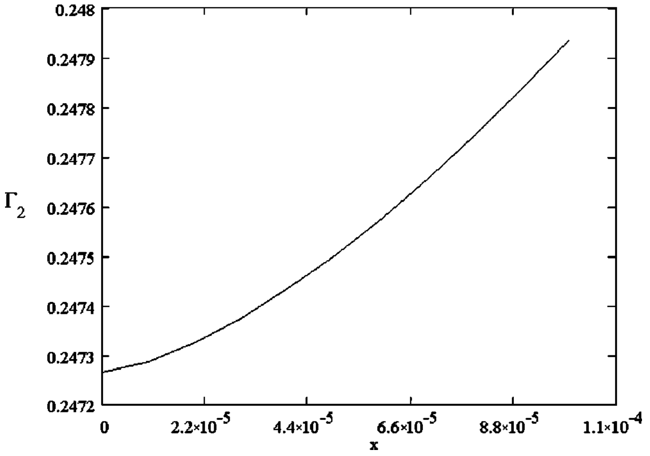

FIG. 3. The concentration dependence of coefficient Γ_2 (53) determining the nonuniversal contribution to the amplitude of rectilinear diameter singularity.

$$\begin{gathered} C \approx -\frac{\tilde{A}_3}{4\tilde{A}_4},\\ \Gamma_2^{(0)} \approx -\frac{2a_5^{(0)}}{5a_4^{(0)}}, \quad \Gamma_2^{(el)} \approx 0.4\frac{a_5^{(el)}a_4^{(0)} - a_4^{el}a_5^{(0)}}{a_4^{(0)}(a_4^{(0)} + a_4^{(el)})}. \end{gathered} \tag{56}$$

Here $\tilde{A}_n$ are the coefficients of the Hamiltonian

$$\mathbf{h}_4(\tilde{\phi}) = P_t[h(\eta(\tilde{\phi}))] = \tilde{A}_1\tilde{\phi} + \frac{1}{2}\tilde{A}_1\tilde{\phi}^2 + \frac{1}{3}\tilde{A}_1\tilde{\phi}^3 + \frac{1}{4}\tilde{A}_4\tilde{\phi}^4$$

obtained from Eq. (24) with the help of transformation (22).

The results of numerical calculations of the concentration dependences for the coefficients Γ_2 and C_1 are shown in Figs. 3 and 4, respectively. Figure 4 indicates that the addition of electrolyte leads to the increase of asymmetry of the coexistence curve, which is in qualitative agreement with experiments [5,10,30].

VI. DISCUSSION

The main attention in this paper is focused on the detailed account of polarization effects in electrolyte solutions near their vapor-liquid critical points. It is shown that the essential renormalization of coefficients of the Landau-Ginsburg Hamiltonian takes place. The renormalization of coupling constant $a_4^{(c)}$ is especially significant. For some solvents at definite concentration of an electrolyte, the coefficient $a_4^{(c)}$

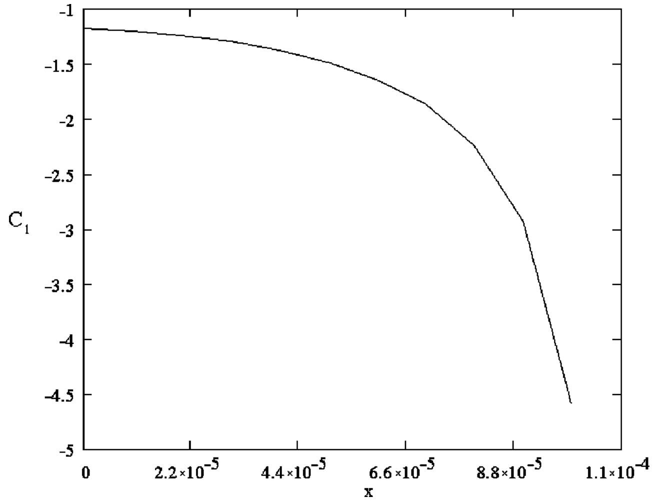

FIG. 4. Tangent of the slope of rectilinear diameter with respect to temperature axis vs electrolyte concentration according to Eq. (56) at $\epsilon=80$ and $\Gamma\sigma=0.5$.

can reach zero and further become negative. This means that respective systems can lose their stability. The decrease of $a_4^{(c)}$ at the addition of electrolyte also leads to the considerable diminishing of the Ginsburg number. As a result, the applicability region of mean-field theory of fluctuations expands. Besides, it is shown that the addition of electrolytes augments the asymmetry degree of the equation of state. Unfortunately, the verification of these predictions is now impossible since the needed experimental data are absent in the literature.

The approach developed in this paper can be applied to solutions of electrolytes or dipole impurities in binary mixtures near their consolute points. In fact, the respective change of formalism is inessential. But reliable information about the coefficients of the initial Landau-Ginsburg Hamiltonian is also absent. However, one qualitative fact discovered in [31] attracts our attention. It was shown, in particular, that the critical exponent ν of the correlation length near the double critical point (DCP) takes the following value:

$$\nu=2\nu_0, \qquad \nu_0=0.5,$$

where ν_0 is the respective exponent far away from the DCP. The classical value of ν_0 can be easily explained in our approach. The systems investigated in [31,32] went beyond the vicinity of the DCP under the influence of a small quantity of electrolyte or dipole impurity. Their addition leads to the narrowing of the region where the fluctuations have scale-invariant character. Besides, these impurities lead to additional asymmetry of the equation of state. This is in qualitative agreement with the results of [1].

The essential focus from our point of view has detailed an account of polarizational effects within the restricted primitive model [7]. Besides, the use of collective variables [18] allows us to analyze main screen effects in a more direct way. The results of our consideration of this question will be presented separately.

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APPENDIX A

It is known [33] that the fluctuation part δF of the free energy for a binary mixture in the quadratic approximation has the structure

$$\delta f=\frac{1}{2}\left(-\frac{1}{\beta_T}\xi_0^2+\frac{\partial\mu_2}{\partial c}\xi_1^2\right)+\cdots, \tag{A1}$$

where

$$\xi_0=\frac{\delta n_1}{n_1^{(0)}}+\frac{\delta n_2}{n_2^{(0)}}, \qquad \xi_1=\frac{\delta n_1}{n_1^{(0)}}-\frac{\delta n_2}{n_2^{(0)}} \tag{A2}$$

describe the fluctuations of the density and the composition in the system, and $n_1^{(0)}$ and $n_2^{(0)}$ are the equilibrium densities of the components.

In a general case, according to Eq. (A1), critical phenomena in binary mixture can be of two types: (a) liquid-vapor and (b) ''decomposition.'' The critical points of the first type are located on the surface determined by the equation

$$\beta_T^{-1}=0, \tag{A3}$$

and the second is located on the surface,

$$\frac{\partial\mu_2}{\partial c}=0. \tag{A4}$$

Near the vapor-liquid critical point, the variable ξ_0 is strongly fluctuating while the fluctuations of ξ_1 are bounded. We call such a variable weakly fluctuating. The case of multicomponent mixtures differs only in the number of weakly fluctuating variables. The boundness of fluctuations for ξ_1 means that fluctuations of $n_1^{(0)}$ and $n_2^{(0)}$ leading to strong fluctuations of ξ_0 obey the condition

$$\frac{\delta n_1}{n_1^{(0)}}-\frac{\delta n_2}{n_2^{(0)}}\ll\min\left(\frac{\delta n_1}{n_1^{(0)}},\frac{\delta n_2}{n_2^{(0)}}\right). \tag{A5}$$

Near the consolution point, the situation is inverse.

An interesting example of a binary mixture is salt molten, in which neutral salt molecules are fully dissociated into ions of only two types. In this case, $n_1^{(0)}$ and $n_2^{(0)}$ satisfy the electroneutrality condition

$$z_1 n_1^{(0)}=z_2 n_2^{(0)}, \tag{A6}$$

where z_i, $i=1,2$, is the valency of an ion. Strictly speaking, the latter are also connected with first variable.

Due to strong Coulombic interactions, only the vapor-liquid critical point is possible in such salt molten. For the same reason, the inequality for fluctuations ξ_1 becomes stronger. Therefore, it is expedient to move on to new variables

$$\delta\rho = z_1 n^{(0)} \xi_1, \tag{A7}$$

$$\delta\phi = \frac{n^{(0)}}{\xi_0 - \xi_1} \simeq \frac{n_1^{(0)}}{2}\xi_0, \tag{A8}$$

which describe the fluctuations of charge and electroneutral density, respectively.

APPENDIX B

It is essential that due to Eq. (10) the corresponding polarizational contributions to the LGH can be obtained by the averaging of Eq. (6) over the charge fluctuations. Collecting in Eq. (6) the contributions of different types of ions, we get

$$\begin{aligned}\langle \beta H_{\mathrm{ch}}[q(\vec{r}),\tilde{\epsilon}(\vec{r})]\rangle &= \frac{e^2 n_0^2}{2k_B T \epsilon^2}\sum_{a,b} x_a x_b \\ &\times \int dV_1 dV_2 f_{a,b}(\vec{r}_a,\vec{r}_b|\tilde{\epsilon}(\vec{r}))u_{a,b}(\vec{r}_1,\vec{r}_2|\epsilon(\vec{r})).\end{aligned} \tag{B1}$$

Here

$$f_{a,b}(\vec{r}_a,\vec{r}_b) = \langle q_a(\vec{r}_1)q_b(\vec{r}_2)\rangle = z_a z_b e^2 D(\vec{r}_1,\vec{r}_2|\tilde{\epsilon}) \tag{B2}$$

is the pair correlation function of ions of types "a,b," n_0 is the particle density, and

$$\tilde{\epsilon}(x) = \frac{\epsilon'(x)}{\epsilon}. \tag{B3}$$

The interionic potential $u_{a,b}$ can be extracted from the Poisson equation

$$\hat{K}_x G(\vec{x},\vec{y}) = -4\pi\delta(\vec{x}-\vec{y}), \quad u_{a,b}(\vec{r}_a,\vec{r}_b) = z_a z_b G(\vec{r}_a,\vec{r}_b), \tag{B4}$$

where

$$\hat{K}_x = [\vec{\nabla}\cdot\epsilon(\vec{x})]\vec{\nabla}. \tag{B5}$$

In accordance with [29], the function $f_{a,b}(\vec{r}_a,\vec{r}_b)$ can be found from the equation

$$\frac{\partial f_{a,b}}{\partial \vec{r}_b} = -\frac{1}{k_B T}\frac{\partial u_{a,b}}{\partial \vec{r}_b} - \frac{1}{k_B T}\sum_d x_d \int \frac{\partial u_{b,d}}{\partial \vec{r}_b} f_{a,b,d} dV_d. \tag{B6}$$

Here $f_{a,b,d}$ is the triple correlation function. Now different closures may be used. For small concentrations, $x > x_{\min}$, of electrolyte, Kirkwood's superposition approximation [29] for $f_{a,b,d}$ can be used. But this step needs a certain amount of caution in the case of low concentrations for highly asymmetric electrolytes, for which $d_+/d_- \ll (\gg) 1$, where d_i is the diameter of the ith ion as follows from the results of [34].

Multiplying Eq. (B6) on $[1+\tilde{\epsilon}(\vec{x})]$ and applying the operator $\vec{\nabla}$ with the help of Eq. (B4), we get

$$K_x D(\vec{x},\vec{y}|\tilde{\epsilon}) - \Gamma_{\mathrm{loc}}^2 D(\vec{x},\vec{y}|\tilde{\epsilon}) = 4\pi\delta(\vec{x}-\vec{y}), \tag{B7}$$

where

$$\Gamma_{\mathrm{loc}} = \frac{\Gamma}{\sqrt{1+\tilde{\epsilon}(\vec{x})}}$$

is the local value of inverse screening length and Γ is its value in homogeneous media. In the Debye approximation, Γ is

$$\Gamma = \frac{1}{r_D}.$$

Obviously both $f_{a,b}$ and $u_{a,b}$ are functionals of the dielectric permittivity. So we can write Eq. (B1) as

$$\langle \beta H_{\mathrm{int}}\rangle = \frac{\Gamma^4}{32\pi^2}\int d\vec{x}\, d\vec{y}\, G(\vec{x},\vec{y}|\tilde{\epsilon})D(\vec{x},\vec{y}|\tilde{\epsilon}). \tag{B8}$$

In a local approximation for Eq. (B8) we get

$$\langle \beta H_{\mathrm{int}}^{(l)}\rangle = -\frac{\Gamma^3}{8\pi}\int d\vec{x}\frac{1}{[1+\tilde{\epsilon}(\vec{x})]^{3/2}}. \tag{B9}$$

This result could be written down immediately since the integrand is the local energy in the Debye approximation. In the case of small gradients of the dielectric permittivity, the quasilocal contribution to the energy of a system can be written as

$$\langle \beta H_{\mathrm{int}}^{(ql)}\rangle = \frac{c}{2}\int (\vec{\nabla}\eta(\vec{x}))^2 dV. \tag{B10}$$

In this section we set $\eta(\vec{x}) \equiv \tilde{\epsilon}(\vec{x})$. To obtain the value of c, we represent $G(\vec{x},\vec{y})$ and $D(\vec{x},\vec{y})$ as the expansions on $(\vec{\nabla}\tilde{\epsilon})^2$:

$$\begin{aligned}G(\vec{x},\vec{y}) &= G_0(\vec{x},\vec{y}) + \frac{[\vec{\nabla}\tilde{\epsilon}(\vec{x})]^2}{2}G_2(\vec{x},\vec{y}) + \cdots, \\ D(\vec{x},\vec{y}) &= D_0(\vec{x},\vec{y}) + \frac{[\vec{\nabla}\tilde{\epsilon}(\vec{x})]^2}{2}D_2(\vec{x},\vec{y}) + \cdots.\end{aligned} \tag{B11}$$

The functions $G_0(\vec{x},\vec{y})$ and $D_0(\vec{x},\vec{y})$ are determined by the local terms of the Poisson equation and can be represented in the form

$$G_0(\vec{x},\vec{y}) = \begin{cases} \dfrac{1}{1+\tilde{\epsilon}(\vec{x})}\dfrac{1}{|\vec{x}-\vec{y}|}, & |\vec{x}-\vec{y}| \leq r_c, \\ \dfrac{1}{|\vec{x}-\vec{y}|}, & |\vec{x}-\vec{y}| \geq r_c, \end{cases} \tag{B12}$$

$$D_0(\vec{x},\vec{y})$$

$$=\begin{cases}\dfrac{1}{|\vec{x}-\vec{y}|}\exp(-\Gamma_{\mathrm{loc}}|\vec{x}-\vec{y}|)\,\dfrac{1}{1+\tilde{\epsilon}(\vec{x})}, & |\vec{x}-\vec{y}|\leqslant r_c\,,\\ \dfrac{1}{|\vec{x}-\vec{y}|}\exp(-\Gamma|\vec{x}-\vec{y}|), & |\vec{x}-\vec{y}|\geqslant r_c\,.\end{cases}$$

Functions $G_2(\vec{x},\vec{y})$ and $D_2(\vec{x},\vec{y})$ are not equal to zero when $|\vec{x}-\vec{y}|\leqslant r_c$. So we have

$$G_2(\vec{x},\vec{y})=\begin{cases}-\dfrac{|\vec{x}-\vec{y}|}{2}, & |\vec{x}-\vec{y}|\leqslant r_c\,,\\ 0, & |\vec{x}-\vec{y}|\geqslant r_c\,,\end{cases}\tag{B13}$$

$$D_2(\vec{x},\vec{y})=\begin{cases}\dfrac{1}{2|\vec{x}-\vec{y}|}\exp(-\Gamma|\vec{x}-\vec{y}|), & |\vec{x}-\vec{y}|\leqslant r_c\,,\\ 0, & |\vec{x}-\vec{y}|\geqslant r_c\,.\end{cases}$$

In Eqs. (B12) and (B13) it is taken into account that on scales $|\vec{x}-\vec{y}|\geqslant r_c$, the media are spatially homogeneous. Substituting Eqs. (B11), (B12), and (B13) in Eq. (B8), we get

$$c=\frac{3}{16\pi}\Gamma.\tag{B14}$$

[1] K.S. Pitzer, Acc. Chem. Res. **23**, 333 (1990).

[2] T. Narayanan and K.S. Pitzer, Phys. Rev. Lett. **73**, 3002 (1994).

[3] R.R. Singh and K.S. Pitzer, J. Chem. Phys. **92**, 6775 (1990).

[4] K.C. Zhang, M.E. Briggs, R.W. Gammon, and J.M.H. Levelt, J. Chem. Phys. **97**, 8692 (1992).

[5] Y. Guissani and B. Guillot, J. Chem. Phys. **101**, 490 (1994).

[6] T. Narayanan and K.S. Pitzer, J. Chem. Phys. **102**, 8118 (1995).

[7] M.E. Fisher, J. Stat. Phys. **75**, 1 (1994).

[8] G. Stell, J. Stat. Phys. **78**, 197 (1995).

[9] J.S. Høye and G. Stell, J. Phys. Chem. **94**, 7899 (1990).

[10] L.A. Bulavin, A.V. Oleynikova, and A.V. Petrovitskij, Int. J. Thermophys. **17**, 138 (1996).

[11] W.-D. Kraeft, D. Kremp, W. Ebeling, and G. Röpke, *Quantum Statistics of Charged Particle System* (Akademie-Verlag, Berlin, 1986).

[12] F. Hensel, J. Phys.: Condens. Matter Suppl. A **2**, 33 (1990).

[13] A.Z. Patashinskii and V.L. Pokrovsky, *Fluctuation Theory of Critical Phenomena* (Pergamon, Oxford, 1979).

[14] A. Martin, I. Lopez, F. Monroy, A.G. Casielles, F. Ortega, and R. Rubio, J. Chem. Phys. **101**, 6874 (1994).

[15] V.M. Nabutovskii, N.A. Nemov, and Yu.G. Peisakovich, Zh. Éksp. Teor. Fiz. **79**, 2196 (1980) [Sov. Phys. JETP **52**, 111 (1980)].

[16] M.E. Fisher and B.P. Lee, Phys. Rev. Lett. **77**, 3561 (1996).

[17] W. Schroer and V.C. Weiss, J. Chem. Phys. **109**, 8504 (1998).

[18] I.R. Yukhnovsky and M.F. Golovko, *The Statistical Theory of Classical Equilibrium Systems* (Naukova, Dumka, 1980).

[19] V.L. Koulinskii and N.P. Malomuzh, J. Phys.: Condens. Matter **9**, 29 (1996).

[20] T. Poston and I.N. Stewart, *Catastrophe Theory and Its Applications* (Pitman, London, 1978), Surveys and Reference Works in Math. 2.

[21] V.L. Koulinskii and N.P. Malomuzh, J. Mol. Struct. **38**, 199 (1996).

[22] M. Neumann, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972).

[23] K.S. Pitzer, J.L. Bischoff, and R.J. Rosenbauer, Chem. Phys. Lett. **134**, 60 (1987).

[24] K.S. Pitzer and J.C. Tanger, Int. J. Thermophys. **9**, 635 (1988).

[25] W. Marshall, J. Chem. Soc., Faraday Trans. **86**, 1807 (1990).

[26] A.A. Povodyrev, M.A. Anisimov, J.V. Sengers, and J.M.H. Levelt Sengers, Physica A **244**, 298 (1997).

[27] S.K. Ma, *Modern Theory of Critical Phenomena* (W.A. Benlamin, Inc., London, 1976).

[28] F.J. Wegner, Phys. Rev. B **5**, 4529 (1982).

[29] L.D. Landau and E.M. Lifshitz, *Statistical Physics* (Nauka, Moscow, 1976), Vol. 5, Pt. 1.

[30] K.S. Pitzer, J. Phys. Chem. **99**, 13 070 (1995).

[31] I.L. Fabelinsky, S.V. Krivokhizha, and L.L. Chaikov, Usp. Fiz. Nauk **149**, 328 (1986) [Sov. Phys. Usp. **29**, 572 (1986)].

[32] S.V. Krivokhizha, I.L. Fabelinsky, and L.L. Chaikov, Izv. Vuzov. Radiofiz. **30**, 308 (1987).

[33] T. Hill, *Statistical Mechanics. Principals and Selected Applications* (McGraw Hill Book Company, Inc., New York, 1956).

[34] M. Lozada-Cassou and E. Diaz-Herrera, J. Chem. Phys. **93**, 1386 (1990).