

Critical behavior of ionic liquids

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The renormalization of the Landau-Ginzburg Hamiltonian for a system with Coulombic interactions caused by spatially inhomogeneous polarizational effects is discussed. It is shown that for ionic liquids with a strong dependence of the degree of dissociation on density, the nonclassical fluctuation region is significantly narrowed. The essential role of the association of ions is noted.

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INTRODUCTION

Critical phenomena in fluids with nondispersive Coulombic interactions have attracted much attention in the last decade owing to a diversity of experimental results (see [1–3]). The variety of systems studied experimentally can be divided into two groups.

Pure ionic fluids such as molten salts NaCl, KCl, etc. form the first group. The liquid-vapor critical point of these systems is located at very high temperatures ($T_c \approx 10^3$ K). This makes the experiments very difficult. From this point of view the ionic (quasi) binary mixtures with low critical temperatures ($T_c \approx 300$ K) of decomposition used in the experiments by Pitzer and co-workers are more suitable [1,2,4,5]. The basic model for these systems is the restricted primitive model (RPM). The latter is the system of equal number of positive and negative charges, immersed in a structureless solvent of dielectric permittivity ϵ . Various theoretical approximations and numerical simulations predict the liquid-vapor critical point at very low dimensionless temperatures and densities [6–8]. The nature of critical fluctuations in this model has not been studied much. The main difficulty here is the interaction between number density and charge fluctuations.

The renormalization-group analysis of this problem based on the theoretical field analog of the RPM taking into account hard-core repulsion was done in [9]. It was shown that the investigated model may exhibit either a first-order transition or Ising-like critical behavior depending on the starting values of the coefficients of the Landau-Ginzburg Hamiltonian (LGH). According to the study of Ref. [9] these two types are formed due to the existence of a tricritical surface in the space of the coefficients of the Hamiltonian. But the estimate for the width of the fluctuational region was not given. In addition, the value of the coefficient in the ϕ^6 term is chosen without any physical grounds, although as was noted all the coefficients at $\phi^n, n < 22$ in the LGH obtained are negative.

The possibility of the tricritical nature of observed peculiarities was also discussed in [6,10]. For such a conjecture to be valid the additional scale competitive with the correlation length of an order parameter must exist [6]. For example, in polymer blends the apparent second scale is the size of a molecule [11], which may lead to the crossover. The physical meaning of its analog, if there exists one, for an electrolyte solution is not clear [12].

Analogous problems arise for the second group which in-

cludes dilute solutions of electrolytes, such as aqueous electrolytes ($\text{H}_2\text{O} + \text{NaCl}$ etc.) [13,14], and quasibinary solutions [12]. Here the admixture of ions changes the parameters of the critical point of a pure solvent. Thus the critical behavior of a pure solvent is perturbed by the Coulombic subsystem of ions. The critical behavior of these systems may exhibit a crossover from mean-field to Ising-like asymptotics within the temperature interval of an experiment. In particular, experimental data for some solutions were fitted with a mean-field exponential law up to $\tau \approx 10^{-4}$ [3], i.e., the fluctuation region is much less in comparison with that for simple liquids ($Gi \approx 0.1 - 1$).

To process such data, the different assumptions in [15,16] and [17] were considered. These affected the conclusions about the existence of the crossover in such systems. The results of [17] show the nonclassical behavior through the temperature interval without any crossover. In [15,16] the experimental data were fitted by a classical equation of state (EOS).

In [18] it was shown that accounting for the fluctuations of dielectric permittivity of a solvent is very important for constructing the proper LGH and Ginzburg criteria for the analysis of the influence of the Coulombic subsystem on critical behavior of a solvent. In particular, the “square root” concentration dependence for the shift of the critical point locus for small concentrations observed in [14] was explained.

In this work we investigate the influence of inhomogeneous polarizational effects on the criticality of ionic liquids. The charge-density coupling in these systems arises owing to the fluctuations of dielectric permittivity caused by the fluctuations of density. The part of the dielectric permittivity of ionic fluid which depends on density is formed mainly by the polarizability of ionic cores and neutral ionic pairs. Taking account of the local dependence of this part of dielectric permittivity leads to fluctuations of local electrostatic energy in the regions with characteristic size of the density-density correlation length. These charge fluctuations effectively renormalize the coefficients of the LGH of a system. In principle, the rigorous solution of the RPM should include these effects. However in the absence of the exact solution, the polarization effects can be taken into account with the help of the effective LGH.

I. CHARGE FLUCTUATIONS IN A SYSTEM

We consider a system of charged particles with charges Z_+, Z_- , masses m_+, m_- , and diameters $a_+ \approx a_- = a$. The

global electroneutrality condition

$$Z_+ N_+ - Z_- N_- = 0 \quad (1)$$

is assumed, where N_i are the numbers of corresponding ions. Since Coulombic forces do not allow a critical point of decomposition into charged phases in our conceptual system we will discuss only the liquid-vapor critical point.

At the beginning we analyze some general properties of charge fluctuations in a molten salt and their change at approaching the liquid-vapor critical point.

Near the liquid-vapor critical point due to strong density fluctuations the system becomes spatially inhomogeneous. The charge contributions to the free energy are generalized (see details in [18]):

$$\begin{aligned} \delta f_{ch} = & \int d\vec{r}' \int d\vec{r}'' \int d\vec{r}_1 \cdots \int d\vec{r}_p K_p(\vec{r}', \vec{r}'' | \vec{r}_1, \dots, \vec{r}_p) \\ & \times \delta\epsilon(\vec{r}_1) \cdots \delta\epsilon(\vec{r}_p), \end{aligned} \quad (2)$$

where $\delta\epsilon(\vec{r})$ is a deviation of dielectric permittivity from its equilibrium value, K_p is the kernel function, determined from the Poisson equation. In the so-called local approximation, when the contributions generated by the nonlinear term $(\vec{\nabla} \delta\epsilon)(\vec{\nabla} \delta\phi)$ of the Poisson equation for the potential increment $\delta\phi$ are ignored, δf_{ch} is equal to

$$\delta f_{ch} \approx \int d\vec{r} \int d\vec{r}' \frac{\langle \delta\rho(\vec{r}) \delta\rho(\vec{r}') \rangle}{\epsilon |\vec{r} - \vec{r}'|} \frac{1}{1 + \delta\tilde{\epsilon}(\vec{r})}, \quad (3)$$

where $\delta\tilde{\epsilon}(\vec{r}) = \delta\epsilon/\epsilon$. As a result, δf_{ch} is approximated by the expression

$$\delta f_{ch} = \delta f_{ch}^{(eq)} + \frac{\delta f_{ch}^{(eq)}}{V} \int d\vec{r} \left(\frac{1}{1 + \delta\tilde{\epsilon}(\vec{r})} - 1 \right), \quad (4)$$

where $\delta f_{ch}^{(eq)}$ is the charge contribution to the free energy far away from the critical point. In the simplest case $f_{ch}^{(eq)}$ can be approximated by the Debye-Huckel (DH) law

$$\beta \delta f_{ch}^{(eq)} = - \frac{1}{12\pi} \Gamma_c^3, \quad (5)$$

in which

$$\Gamma = \frac{a}{r_s} < 1$$

is the inverse screening length amplitude.

Further, it is very essential that the fluctuations of dielectric permittivity are mainly caused by the density fluctuations, which are connected with the order parameter $\eta(\vec{r})$ according to $\eta(\vec{r}) = [n(\vec{r}) - n_c]/n_c$, where n_c is the critical value of density. Thus, the following relation between fluctuations of density and dielectric permittivity exists:

$$\epsilon \rightarrow \epsilon(\vec{r}) = \epsilon(1 + \lambda_1 \eta(\vec{r}) + \lambda_2 \eta^2(\vec{r}) + \dots), \quad (6)$$

where

$$\lambda_k = \left. \frac{n_c^k \partial^k \epsilon}{\epsilon_c \partial n^k} \right|_{n=n_c}, \quad (7)$$

$\epsilon = \epsilon(n)$ is the equilibrium value for dielectric permittivity.

Thus the difference $H_{ch} = \delta f_{ch} - \delta f_{ch}^{(eq)}$ can be represented in the form

$$H_{ch} \approx \int d\vec{r} \sum_{n=1}^{\infty} \frac{1}{n} a_n^{(pol)} \eta^n(\vec{r}), \quad (8)$$

where

$$\begin{aligned} a_1^{(pol)} &= -\lambda_1, & a_2^{(pol)} &= -\lambda_2 + \lambda_1^2, \\ a_3^{(pol)} &= -\lambda_3 + 2\lambda_1\lambda_2 - \lambda_1^3, \end{aligned} \quad (9)$$

$$a_4^{(pol)} = -\lambda_4 + 2\lambda_3\lambda_1 + \lambda_2^2 - 3\lambda_2\lambda_1^2 + \lambda_1^4, \dots \quad (10)$$

In fact after neglecting the terms of order $n > 4$, this gives an addition to the primary LGH of the system:

$$\begin{aligned} H^{(0)}[\eta] = & \int d\vec{r} \left[\frac{1}{2} a_2^{(0)} \eta(\vec{r})^2 + \frac{1}{2} b_2^{(0)} [\vec{\nabla} \eta(\vec{r})]^2 \right. \\ & \left. + \frac{1}{4} a_4^{(0)} \eta(\vec{r})^4 \right]. \end{aligned} \quad (11)$$

Note that as long as expression (4), which accounts for polarizational effects, is used the polarizational contribution to a_4 is negative. It follows that (a) the dielectrical permittivity is a monotonic function of the density, (b) the Coulombic potential is a convex function of the dielectric permittivity, and (c) the excess free energy for ionic systems is negative. This becomes quite clear if we choose $\eta = (\epsilon - \epsilon_c)/\epsilon_c$ as the order parameter. The inclusion of Eq. (4) to the effective LGH leads to the diminishing of the value of a_4 , thus reducing the Ginzburg number.

The results obtained above serve as the background for the analysis of the Ginzburg number in molten salt.

II. EFFECTIVE LANDAU-GINZBURG HAMILTONIAN OF A SYSTEM

According to Eqs. (8)–(11) the effective LGH of molten salt NaCl takes the structure

$$\beta H_{eff}[\eta(\vec{r})] = \int d\vec{r} \left(\frac{b_2}{2} (\vec{\nabla}[\eta(\vec{r})])^2 + \sum_{m=1}^4 \frac{a_m}{m} \eta^m(\vec{r}) \right), \quad (12)$$

where

$$a_m = a_m^{(0)} + a_m^{(pol)} \quad (13)$$

and

$$b_2 = b_2^{(0)}. \quad (14)$$

The coefficients $a_2^{(0)}$ and $a_4^{(0)}$ are connected with the derivatives of pressure with respect to density by the relations

$$a_2^{(0)} = \left. \frac{\partial P}{\partial n} \right|_T, \quad a_4^{(0)} = \left. \frac{\partial^3 P}{\partial n^3} \right|_T, \quad (15)$$

in which P includes the contributions of both short-range repulsive and Coulombic interactions. Almost all equations of state for the RPM lead to very small values of the coefficients $a_i^{(0)}$ compared with those for molecular fluids at least by an order of magnitude [19,20],

$$\frac{a_2^{(RPM)}}{a_2^{(LJ)}} = 0.01 - 0.1, \quad \frac{a_4^{(RPM)}}{a_4^{(LJ)}} = 0.001 - 0.01. \quad (16)$$

The only exception is the Debye-Huckel-Bjerrum model, where the values of these coefficients are of the same order as for molecular fluid. To calculate $a_m^{(pol)}$ we use the formulas (9) and (10) with coefficients λ_k , determined with the help of the canonical form for dielectric permittivity,

$$\frac{\epsilon - 1}{\epsilon + 2} = \lambda(1 + \eta), \quad (17)$$

where

$$\lambda = \frac{4\pi}{3} \alpha_{eff} \rho_c^* \quad (18)$$

and $\rho^* = na^3$. Here n is the overall number density. In accordance with Eq. (17) the parameter λ satisfies the inequality $\lambda < 1$. The value of ϵ does not exceed 1.2 (in vapor phase) [8,21].

The effective polarizability α_{eff} is mainly formed by the associated ionic pairs,

$$\alpha_{eff} = \frac{1 - \Delta}{6} \delta^2 \frac{1}{T^*}, \quad (19)$$

where

$$\Delta = \frac{n_+}{n_0} = 1 - \frac{n_{dim}}{n_0} \quad (20)$$

is the degree of dissociation of the system, n_0 is the number density of the ions of a particular type, i.e., $n = 2n_0$, T^* is the dimensionless temperature $T^* = k_B T / (e^2/a)$ and $\delta = l/a$ is the dimensionless size of an ionic pair ($d_0 = el$ being its dipole moment) and we put $Z_+ = Z_- = 1$ for simplicity. The condition $\lambda < 1$ holds for all cases since ρ_c^*/T_c^* is sufficiently small. In addition, if $9T_c^*/2\pi\delta^2\rho_c^* < 1$, we can get the low estimate for Δ at the critical point:

$$1 - \frac{9T_c^*}{2\pi\delta^2\rho_c^*} < \Delta_c. \quad (21)$$

This estimate is natural for three-dimensional Coulombic systems, which apparently cannot undergo Kosterlitz-

Thouless transition [22], where $\Delta = 0$ with r_s divergence. Thus the model (17) is acceptable from this point of view even for the critical point located at high density ($\rho_c^*/T_c^* > 1$). Note that as δ grows, the degree of dissociation Δ_c at the critical point becomes closer to 1, which is pretty natural from the physical point of view.

Further analysis of the polarizational induced terms into LGH coefficients is sensible with respect to the coordinates (ρ_c^*, T_c^*) of the critical point. To estimate ρ_c^* and T_c^* , different models for the EOS: DH, MSA, DH taking into dimerization (Bjerrum approach), hard-core interactions, etc. were used (see [6,19,20]). There are also the computer simulations of the phase diagram [22,23]. The values of parameter ρ_c^*/T_c^* obtained with the help of analytical methods are small, $0.5 < \rho_c^*/T_c^* < 1$ (low critical density case). Unlike these analytical estimates recent computer calculations give the values $1 < \rho_c^*/T_c^* < 2$ [23]. Basing on the estimate (21) one can see that both these cases are consistent ($\lambda < 1$) with the model. Note that model EOS such as MSA with different corrections [8] and numerical Monte Carlo calculations [23,22] also show high degree of dissociation near critical point. The expressions for $a_2^{(pol)}$ and $a_4^{(pol)}$, which follow from Eqs. (9) and (17), read as

$$a_2^{(pol)} = 9 \frac{\lambda^2}{(1+2\lambda)^2(1-\lambda)^2} \beta_c f_{ch}^{(eq)},$$

$$a_4^{(pol)} = \frac{27}{2} \frac{\lambda^4}{(1+2\lambda)^4(1-\lambda)^4} \beta_c f_{ch}^{(eq)}. \quad (22)$$

It follows from Eq. (3) that polarizational contribution to a_4 is negative, therefore the Ginzburg number decreases after taking account of polarization effects. Here the approximation $\Delta \approx \Delta_c$ was used. Using the dimensionless form of coefficients of the LGH obtained in works [19,20] we calculate the Ginzburg temperature for ionic fluid,

$$Gi = \frac{9a_4^2}{8\pi^2 \tilde{a}_2} \left(\frac{a}{b} \right)^6, \quad (23)$$

where

$$\tilde{a}_2 = \lim_{\tau \rightarrow 0} \frac{a_2}{\tau}, \quad \tau = \frac{T - T_c}{T_c}. \quad (24)$$

It is useful to rewrite Eq. (23) in the following form:

$$Gi = Gi_0 \left(1 + \frac{a_4^{(pol)}}{a_4^{(0)}} \right)^2, \quad (25)$$

where Gi_0 is the Ginzburg temperature without accounting for the inhomogeneous polarization. Here we neglect the renormalization of the coefficients \tilde{a}_2 and b of the LGH. It appears that in this approximation Gi slightly decreases in comparison with the initial value because the value of λ is actually small (< 0.1), since ϵ is close to 1.

Below critical point, the system separates into liquid and gaseous phases with different densities because of strong density fluctuations. These phases have different degrees of dissociation Δ_{liq} and Δ_{gas} , since thermodynamically the degree of dissociation Δ is a function of T^* and ρ^* . At the very critical point $\Delta^{(liq)} = \Delta^{(gas)}$ but below $\Delta_{liq} \neq \Delta_{gas}$ because of $\rho_{liq}^* \neq \rho_g^*$. From the physical point of view one can expect the non-Ising-like asymptotics for the critical behavior only if density fluctuations strongly interact with the ones for charge. This interaction occurs only if the dipoles exist, since their number fluctuations are directly connected with fluctuations of density. Thus the very fact that below critical point $\Delta^{(liq)} \neq \Delta^{(gas)}$ means that the number fluctuations of neutral pairs are strong and therefore the polarizational effects should be taken into account. Since the density fluctuations are strong the fluctuations of dipole number are strong too. That means that the fluctuations of charge numbers are also strong though mutually correlated due to the neutrality condition ($\delta n_+ = -\delta n_-$). Indeed one could expect the peculiarities for the critical behavior in ionic liquids if the degree of dissociation strongly depends on the density near the critical point. From the standard thermodynamical equilibrium consideration one can get [8]

$$2 \frac{1-\Delta}{\Delta^2} = (1+\eta)K(T^*)\exp[\beta(\mu_+^{(ex)} + \mu_-^{(ex)} - \mu_{dip}^{(ex)})],$$

$$\eta = \frac{\rho^* - \rho_c^*}{\rho_c^*}, \quad (26)$$

where $\mu_k^{(ex)}$, $k = +, -, dip$, are the excess chemical potentials for the corresponding type of particles, $K(T)$ is the parameter of association-dissociation equilibrium. Therefore, to consider the case of strong interaction between charge and density fluctuations, we should not neglect density dependence of Δ near the critical point. It is clear that this dependence is very essential for the dielectric permittivity as has been noted above. Here we use the linear approximation for such dependence:

$$\Delta(\rho, \tau) = \Delta_c + \Delta_1 \eta + o(\eta). \quad (27)$$

The estimate for Δ_1 can be obtained from [8], where we can find that for different EOS $0 < \Delta_1 < 10$. The coefficients $a_2^{(pol)}$ and $a_4^{(pol)}$ take the values

$$a_2^{(pol)} = 9 \frac{(\lambda - \Delta_1)^2}{(1 + 2\lambda)^2 (1 - \lambda)^2} \beta_c f_{ch}^{(eq)},$$

$$a_4^{(pol)} = \frac{27}{2} \frac{(\lambda - \Delta_1)^4}{(1 + 2\lambda)^4 (1 - \lambda)^4} \beta_c f_{ch}^{(eq)}. \quad (28)$$

Note that Eq. (28) corresponds to the linear approximation for the $\epsilon(\eta)$ dependence. The main result, the diminishing of the Ginzburg temperature, appears in this approximation. Actually to construct $a_4^{(pol)}$ the terms up to fourth order in the η expansion for $\epsilon(\eta)$ should be included. Sure the explicit expressions for $a_2^{(pol)}$ and $a_4^{(pol)}$ become very com-

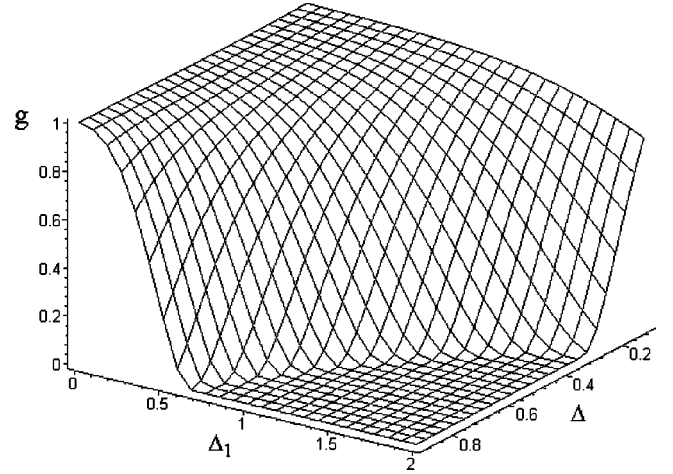


FIG. 1. The dependence of the Ginzburg temperature $g = Gi/Gi_0$ obtained with Eq. (17) on the degree of ionization Δ and Δ_1 at $a_4^{(0)} = 0.01$, $\delta = 1$, $\rho_c^*/T_c^* = 0.5$.

plex and we will not give them here. These results are represented in Fig. 1. The key feature is the vanishing of the Ginzburg number at low dielectric permittivity values and small screening length, while the value of Δ_1 is high enough and Δ is close to 1. This region of parameters naturally corresponds to the state of the ionic liquid with a high degree of dissociation at the critical point. Thus the account of polarizational effects caused by the density fluctuations is very essential for the analysis of asymptotical behavior of ionic fluids, which was pointed in [24]. Using other model equations of state such as the nonlimiting DH (NDH) approximation

$$F - F_{id} = -\frac{1}{4\pi} [\ln(1 + \Gamma) - \Gamma + \Gamma^2/2] \quad (29)$$

and MSA equation

$$F - F_{id} = -\frac{1}{12\pi} [2 + 6\Gamma + 3\Gamma^2 - 2(1 + 2\Gamma)^{3/2}] \quad (30)$$

for constructing the LGH does not change the results significantly. Namely, the difference between the results obtained with the help of Eqs. (29) and (30) does not exceeds 5%. The DH approximation gives qualitatively the same results with the difference in comparison with MSA and NDH EOS up to 20% for $\Gamma_c < 0.3$. It directly follows from Eq. (4), which shows that all polarizational corrections to the LGH are proportional to $\beta \delta f_{ch}^{(eq)}$. Since the DH EOS is valid only for low density systems the usage of this EOS should be treated as mere illustrative.

For comparison we also give the results (see Fig. 2) for the Ginzburg temperature calculated based on the Onsager formula for dielectric permittivity [35]:

$$\epsilon = \frac{1}{4} \left(1 + 3x + 3 \sqrt{1 + \frac{2x}{3} + x^2} \right), \quad (31)$$

where

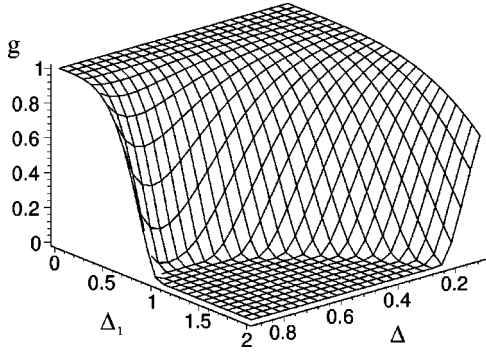


FIG. 2. The dependence of the Ginzburg temperature $g = Gi/Gi_0$ obtained with Eq. (31) on the degree of ionization Δ and Δ_1 at $a_4^{(0)} = 0.01$, $\delta = 1$, $\rho_c^*/T_c^* = 0.5$.

$$x = \frac{2\pi d^2(1 - \Delta - \Delta_1 \eta)}{3T^*}.$$

As it follows from the obtained results for Gi , the steep increase of the degree of ionization with density may result in significant lowering of Gi . For sufficiently great values of $\Delta_1 = \partial\Delta/\partial\eta$ the Ginzburg temperature may vanish. The value of Δ_1 at which $Gi=0$ increases if the locus parameter ρ_c^*/T_c^* decreases. This is quite natural, since for the Coulombic criticality to occur at low density a stronger density dependence for the degree of dissociation is needed.

In other words the Coulombic driven criticality is characterized by a small value of Gi caused by strong density dependence of the degree of dissociation at the critical region. The following scenarios are possible.

(1) Δ is continuous at the critical point but $\partial\Delta/\partial\rho|_{\rho^*=\rho_c^*, T=T_c^*}$ is very large. Note that due to very low estimates for ρ_c^* in different mean-field approximations, even if $\Delta_1 \approx 1$ the value of $\partial\Delta/\partial\rho|_{\rho^*=\rho_c^*} \approx 10^2$. Here an anomalously small value of Gi is observed but the critical behavior is Ising-like. The polarizability of a system also renormalizes the coefficient b . As has been noted above, the Coulombic interactions prevent the spatial separation of opposite charges in a system. Therefore in quasilocal approximation the energy of a system with inhomogeneous dielectric permittivity should be higher than that for a homogeneous one. In other words the polarization contribution increases the value of b . Thus we obtain the upper estimate for Gi .

(2) Δ is continuous at the critical point but its fluctuations are essential $\sqrt{\langle(\delta\Delta)^2\rangle} \approx \langle\Delta\rangle$. In general, Δ is the sum of the thermodynamical equilibrium part $\Delta^{(eq)}(\rho^*, T^*)$ and the fluctuation one $\Delta^{(fl)}$: $\Delta = \Delta^{(eq)}(\rho^*, T^*) + \Delta^{(fl)}$. Therefore the quantity $\Delta_{liq} - \Delta_g$ includes the part orthogonal to the density fluctuations and can be considered as a concurrent order parameter, and a type of critical behavior distinct from Ising-like behavior can be expected. In particular, if the coefficient of the gradient term $c(\partial\Delta)^2$ tends to zero the spatial inhomogeneous phase with respect to Δ and possibly the density is expected. The analog of such a phase in condensed matter is the excitonic drops [25]. In such a case the initial liquid-vapor critical point can transform to a peculiar point

similar to Lifshitz one [26]. Note that spatial inhomogeneity of Δ in no way means the spatial separation of charges, i.e., the charge-density wave phase. In addition, this scenario is closely connected with the metal-insulator transition [22].

(3) The discontinuity of the density dependence of Δ at the mean-field critical point. According to the definition at the point of the second order phase transition the difference between phases disappears. If there is a discontinuity in Δ at the critical point, then it is not a second order phase transition. This case needs detailed investigation.

Note that spatially modulated charge density and order parameter waves was predicted in [27]. There quite a different system was considered, namely, an electrolyte solution of small concentration, with strong contact interaction between neutral density fluctuations and the charged subsystem. However a similar character of the intermode interaction cannot be justified. Unlike this, the possibility of the appearance of the microhomogeneous state in molten salt NaCl is connected with realistic polarizational effects and independent (uncorrelated) fluctuations of the degree of dissociation, not leading to spatial separation of charges. The case of the repulsive hard-core driven criticality [6,28] is characterized by an insignificant change in Gi and a weak density dependence of the degree of dissociation.

III. CONDUCTIVITY OF THE ELECTROLYTES

Above it was shown that the peculiarities of the critical behavior of ionic liquids are determined by the density dependence $\Delta(\rho^*)$ of the degree of dissociation near the critical point. The criticality of the conductivity σ for highly concentrated ionic mixtures and other electrolytes has been studied much less compared with their equilibrium thermodynamical properties [29,30]. The measurements of the conductivity for highly concentrated nonaqueous electrolytes was presented in [30].

It is well known (see [31]) that for magnetic systems with Ising symmetry for an order parameter and conjugated field, the critical fluctuations lead to a singularity for the conductivity σ similar to that of entropy on the critical isochor [31]:

$$\sigma = \sigma_c + A_r \tau + A_s \tau^{1-\alpha} + \dots \quad (32)$$

Formally the appearance of the singular term is easily explained with the help of a thermodynamic relation between the variations of the conductivity, $\delta\sigma$, and the entropy, δs ,

$$\delta\sigma \propto -\omega_{rel}(\mathbf{k}=0) \frac{T}{\langle j^2 \rangle} \sigma^2 \delta s, \quad (33)$$

where ω_{rel} is the characteristic relaxation rate for the conductivity, provided that it is nonzero at the critical point, i.e., no critical slowing down for the conductivity occurs. This is certainly true for scenario (1) above. Let us consider this case in more detail focusing on the connection of the singular term for the conductivity with the behavior of the key parameter Δ . As is known, the conductivity of a system is determined by

$$\sigma = \frac{\beta}{3} \int_0^\infty \int_V \langle \mathbf{j}(\mathbf{r}, t) \cdot \mathbf{j}(0, 0) \rangle d\mathbf{r} dt, \quad (34)$$

where $\mathbf{j}(\mathbf{r}, t)$ is the electrical current density,

$$\mathbf{j}(\mathbf{r}, t) = e \rho_{ch}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t), \quad (35)$$

and $\rho_{ch}(\mathbf{r}, t)$ is the density fluctuation of the charged component. The overall density n is a sum of the density of the charged component (free carriers) and the double density of dipole pairs. The density fluctuation is the sum of the fluctuations of these terms. To calculate Eq. (34) we can use the arguments of [32]. Due to screening effect, the correlation of charge fluctuations separated by distance $r > r_s$ is negligible. Due to this, in DH approximation we get

$$\langle \rho_{ch}(\mathbf{r}, t) \rho_{ch}(0, 0) \rangle \approx \frac{1}{4\pi\beta r_s^2} \left(\frac{\partial \rho_{ch}}{\partial \mu} \right)_T \frac{e^{-r/r_s}}{r} f(\omega_{osc}), \quad (36)$$

where

$$\frac{\partial \rho_{ch}}{\partial \mu} = n_c \frac{\partial \Delta}{\partial \mu} + \Delta_c \frac{\partial n}{\partial \mu}. \quad (37)$$

n is the overall density and f is a function without singularities. We will not be interested in the time relaxation of charge fluctuations here. The peculiarities of the critical behavior of the conductivity are mainly determined by the derivative $\partial \rho_{ch} / \partial \mu$. Since the number of charges is $N = N_0 \Delta(\rho, T)$ the singularity of $\partial \Delta / \partial \mu|_{T=T_c}$ can be obtained from the analysis of $\partial N / \partial \mu|_{T_c}$. The last is given by the thermodynamic identity (see, e.g., [26])

$$\left(\frac{\partial N}{\partial \mu} \right)_T = \frac{\left(\frac{\partial N}{\partial T} \right)_\mu}{\left(\frac{\partial S}{\partial T} \right)_\mu - \frac{C_V}{T}}, \quad C_V = T \left(\frac{\partial S}{\partial T} \right)_{V, N}, \quad T = T_c(1 + \tau), \quad (38)$$

where in the vicinity of the critical point $C_V = C_V^{(reg)} + C_V^{(sing)}$, where on the critical isochor $C_V^{(sing)} \propto \tau^{-\alpha}$. The value $\partial N / \partial \mu|_{T_c}$ is nonzero because of the condition of ionization equilibrium. Therefore the leading divergent terms in the denominator cancel out, but other less singular terms such as $\tau^{1-\alpha}$ do not. The later terms are responsible for the singular terms in the conductivity.

DISCUSSION

In the present work the important role of polarizational effects in the critical behavior of ionic melts is demonstrated. It is established that if the key parameters of a system take the values $r_s = 1 - 5, \Delta_1 > 0.5$, the coefficient a_4 of the effective LGH reduces considerably or vanishes.

A similar situation is also characteristic for the critical behavior of electrolyte solutions. There the charge fluctuations of admixed ions can essentially renormalize the co-

efficient $a_4^{(0)}$ of the initial LGH for a solvent. At definite concentration x_* of the electrolyte, $a_4(x_*) = 0$. For higher concentrations the standard scenario of the critical behavior becomes inapplicable and additional investigations are necessary. In connection with this we note the result obtained experimentally in [33] for a ternary aqueous solution of sodium bromide. A fluctuation region was observed at salt concentration 0.17 (mass fraction), less than 10^{-5} . To interpret this as the well as specific dip on the line of the lower critical points, the conjecture about the existence of competing microheterogeneous phases was put forward. In principle, it is possible that at some concentration the line of the lower critical points may touch the virtual phase spinodal, whose branches are directed to lower temperatures. Then between the branches of the spinodal the state of the electrolyte solution should be heterogeneous according to the thermodynamic demands.

The main peculiarities of the critical behavior of molten NaCl salt are determined by the density dependence of the degree of dissociation Δ and its fluctuations. When the fluctuations of Δ are relatively small, the critical behavior of the ionic liquid should be Ising-like. From the thermodynamic point of view it is supported by the fact that the system is characterized by two thermodynamic degrees of freedom [34]. The specificity of the system is displayed only in the numerical value of the Ginzburg number: it is the lesser, the more the derivative $\partial \Delta / \partial \rho|_T$ is.

If the fluctuations of Δ become strong, $\sqrt{\langle (\delta \Delta)^2 \rangle} \approx \langle \Delta \rangle$, the deviations from the Ising-like behavior can be considerable. First of all, the system can demix on the parameter Δ . In other words, the formation of drops with different values of Δ is possible. Since Δ is a crucial parameter, the change of the type of the critical behavior seems to be probable.

It is not excluded that the phase diagram of molten salt NaCl near its liquid-vapor critical point will be more complex in comparison with that for a one-component liquid with simple intermolecular interaction. In particular, the derivative $\partial^3 P / \partial n^3|_{T=T_c}$ can be close to zero, which can lead to a change of the type of the critical point, e.g., tricritical behavior. However the vanishing of a_6 is impossible. The behavior of conductivity can serve as an additional test of the type of the critical behavior. So the sharp change of the conductivity could testify the point of phase transition different from the second order.

Most crucial for the critical behavior is the dependence of a_4 on the degree of dimerization Δ of the system, which directly influences the polarizability. The density of the ionic liquid is formed by the density of free charges and bounded states. The density of the nondissociated molecules (dipoles) is determined by the thermodynamical parameters of the state of the system (e.g., temperature and specific volume). In particular, the results of Monte Carlo simulations indicate that the proximity of these two transitions could explain the crossover phenomena in ionic fluids [22]. Note that our consideration is based on mean-field treatment. Therefore a thorough analysis of fluctuation effects is needed to determine the type of critical behavior if $a_4 = 0$.

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APPENDIX: CANONICAL FORM OF THE DIELECTRIC PERMITTIVITY

There exist many approaches to the problem of dielectric permittivity. Based on different assumptions they allow to describe with the most completeness only one or several characteristic contributions. Unfortunately applying to model representations too early lead to hard to control errors. In particular, it can change the character of inequalities and essentially influence the values of the density derivatives of dielectric permittivity. Therefore the discussion of the general structure of dielectric permittivity as well as the nature of main contributions to it seems to be appropriate. By definition, dielectric permittivity for an isotropic medium [35] is equal to

$$\epsilon - 1 = 4\pi \frac{P}{E}, \quad (\text{A1})$$

where $P = |\mathbf{P}|$, \mathbf{P} is the polarizability vector, and E is the strength of the Maxwell electric field ($\mathbf{P} \parallel \mathbf{E}$). In general, we should calculate \mathbf{P} and E as functions of the external field strength E_0 . However for a specimen of spherical shape the connection between E and E_0 is especially simple:

$$\mathbf{E} = \frac{3}{\epsilon + 2} \mathbf{E}_0. \quad (\text{A2})$$

Therefore we can write

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{P(E_0)}{E_0} \equiv \frac{4\pi}{3} n \alpha_{eff}. \quad (\text{A3})$$

Since the effective polarizability α_{eff} is a characteristic of a medium, but not of the shape of the specimen, Eq. (A3), connecting ϵ and α_{eff} , is of general character. The left side of Eq. (A3) is always less than unity, so the inequality

$$\frac{4\pi}{3} n \alpha_{eff} < 1$$

should hold well.

To make a further conclusion about α_{eff} and ϵ , we rewrite the formula (A3) in the form

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{\langle \mathbf{D} \rangle_0 + \frac{1}{3} \langle \mathbf{D}^2 \rangle_0 E_0}{VE_0}, \quad (\text{A4})$$

where \mathbf{D} is the dipole moment of a system, V is its volume, and the angular brackets designate the average over the equilibrium Gibbs distribution. Note that the matter within the spherical example is homogeneously polarized. In general, the dipole moment has the structure

$$\mathbf{D} = \mathbf{D}_0 + \hat{\alpha} \mathbf{E}_0, \quad (\text{A5})$$

where \mathbf{D}_0 is the dipole moment of the isolated system and $\hat{\alpha}$ is its polarizability. Following Fisher [36] $\hat{\alpha}$ can be represented in a form

$$\hat{\alpha} = \sum_{i=1}^N \sum_{k=1,2} \hat{\alpha}_1^{(k)}(\mathbf{r}_i) + \sum_{1 \leq i, j \leq N} \sum_{k_1, k_2=1,2} \hat{\alpha}_2^{(k_1, k_2)}(\mathbf{r}_i, \mathbf{r}_j) + \dots, \quad (\text{A6})$$

where $\hat{\alpha}_1^{(k)}(\mathbf{r}_i)$ is the tensor of one-particle polarizability for the i th ion of type k , $\hat{\alpha}_2^{(k_1, k_2)}(\mathbf{r}_i, \mathbf{r}_j)$ is the tensor of irreducible two-particle polarizability for i th and j th ions of types k_1 and k_2 , correspondingly, and so on. A similar expansion is characteristic for the dipole moment:

$$\mathbf{D}_0 = \sum_{1 \leq i, j \leq N} \sum_{k_1, k_2=1,2} \mathbf{d}_2^{(k_1, k_2)}(\mathbf{r}_i, \mathbf{r}_j) + \dots. \quad (\text{A7})$$

Note that within such an approach the central problem is the calculation of irreducible contributions of different orders to $\hat{\alpha}$ and \mathbf{D} but not the problem of the acting field [35]. From symmetry reasons it follows that

$$\langle \hat{\alpha}_1^{(k)}(\mathbf{r}_i) \rangle_0 = \alpha_1^{(k)} \hat{I}, \quad (\text{A8})$$

$$\langle \hat{\alpha}_2^{(k_1, k_2)}(\mathbf{r}_i, \mathbf{r}_j) \rangle_0 = \frac{1}{3} \langle \text{Sp} \hat{\alpha}_2^{(k_1, k_2)}(\mathbf{r}_i, \mathbf{r}_j) \rangle_0 \hat{I}, \quad k=1,2, \quad (\text{A9})$$

where the angular brackets $\langle \dots \rangle_0$ designate the averaging over the equilibrium distribution function and we suppose that one-ion polarizability is a scalar. The contributions of higher order polarizabilities are relatively small and will be ignored further. Since $\langle \mathbf{D}_0 \rangle_0 = \mathbf{0}$ the average $\langle \mathbf{D} \rangle_0 = \mathbf{0}$ can be approximated by the expression

$$\langle \mathbf{D} \rangle_0 = n \left[\alpha_+ + \alpha_- + \frac{z}{12} (\alpha_{++} + \alpha_{--} + 2\alpha_{+-}) \right], \quad (\text{A10})$$

where z is the coordination number and, for example, $\alpha_{++} = \text{Sp} \hat{\alpha}_2^{(+, +)}$ is the binary polarizability of two positive ions, which are nearest neighbors ($r_{12} \approx a$). Taking into account that the main contribution to $\hat{\alpha}_2^{(+, +)}$ is caused by the dipole interactions, we can get the characteristic inequality

$$\alpha_{++} \leq \frac{\alpha_+^2}{a^3} \leq \frac{1}{8} \alpha_+, \quad (\text{A11})$$

since $\alpha_+ \sim (a/2)^3$. Therefore we conclude that the contribution of the binary polarizability in Eq. (A10) cannot exceed $\frac{1}{3}$ of that from the contribution of one-particle ones.

To calculate $\langle \mathbf{D}^2 \rangle$ at small E_0 we use the following assumptions: (1) $\langle \mathbf{D}^2 \rangle_0 \approx \langle \mathbf{D}_0^2 \rangle_0$; (2) the dipole moments of ions

are strongly correlated only within the region whose size on the average is equal to r_s ; (3) the characteristic dipole moment for this region has order of the dipole moment \mathbf{d}_0 for isolated molecule NaCl. As a result we can write

$$\langle \mathbf{D}^2 \rangle_0 \approx V \frac{d_0^2}{r_s^3}. \quad (\text{A12})$$

All these estimates allow us to conclude that

$$\alpha_{eff} \approx \alpha_+ + \alpha_- + \frac{1}{3} \frac{d_0^2}{k_B T} \left(\frac{a}{r_s} \right)^3. \quad (\text{A13})$$

The values α_+ and α_- can be approximated by the polarizabilities of Ne and Ar. Using for r_s the estimate obtained above in such a way, we get

$$\alpha_- + \alpha_+ \ll \frac{d_0^2}{k_B T} \left(\frac{a}{r_s} \right)^3. \quad (\text{A14})$$

Hence the estimate of the dielectric permittivity and its derivatives with respect to density can be obtained with the help of formulas of Lorentz-Lorenz type:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n \frac{d_0^2}{k_B T} \left(\frac{a}{r_s} \right)^3. \quad (\text{A15})$$

The specific form of the relation between dielectric permittivity and the effective polarizability is especially important for the calculation of the derivatives $\partial^k \epsilon / \partial n^k$. From this point of view the formula of Lorentz-Lorenz type is obtained from first principles and should be considered as a physically grounded result. If the dissociation is not complete the formula (AA15) takes the form

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n \frac{d_0^2}{k_B T} \left[\frac{1 - \Delta}{2} + \Delta \left(\frac{a}{r_s} \right)^3 \right]. \quad (\text{A16})$$

The last term in Eq. (AA16) is essential only in the close vicinity of the critical point. In other situations its influence is negligible. Then

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{2\pi}{3} n \frac{d_0^2}{k_B T} (1 - \Delta). \quad (\text{A17})$$

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