

# Dipole fluid as a basic model for the equation of state of ionic liquids in the vicinity of their critical point

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A model of dipole fluid for ionic liquids similar to molten NaCl is proposed. The estimates for the critical parameters are obtained with the help of the van der Waals equation of state. The influence of the rotation on the characteristics of a dipole pair and the location of the critical point is discussed. The dissociation of such a fluid near the critical point is considered.

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## INTRODUCTION

The critical behavior of systems with direct Coulombic interaction attracts much attention because of its significance both for theoretical understanding and for possible applications. One obvious example of such systems is liquid metals. Here the electronic subsystem effectively screens out interionic Coulombic interaction, giving rise to a short-ranged pseudopotential. It is well known that the liquid-vapor critical point for such systems is of the Ising universality class. Moreover, a simple van der Waals (vdW) theory for such systems is as good a mean field approximation as for molecular liquids [1,2]. On the other hand, pure molecular liquids such as H<sub>2</sub>O and HgCl<sub>2</sub> become ionized in the higher-density region above the critical point [3,4], therefore the internal degrees of freedom of the molecules should be taken into consideration. In Ref. [5] it was proposed that satisfactory predictions of the vdW model for liquid metals and the similarity of the compressibility factor critical value  $Z_c = P_c/\rho_c T_c$  for liquid metals and alkali-metal halides allow us to apply the vdW model for the description of the critical behavior of ionic liquids. Additionally, in Ref. [5] it was noted that the assumption about complete association below the critical point for alkali-metal halides (NaCl, KCl) gives a more adequate description of the experimental data on binodal obtained in Ref. [6].

There is the strong indication for the existence of the liquid-gas critical point in ionic liquids such as molten NaCl. The main model for such systems is called the primitive model or its restricted version (RPM), where the characteristics (mass, diameter, etc.) of the opposite charges are the same. Because of the formation of associated ionic pairs, the derivation of the mean field equation of state in the rigorous thermodynamic approach is yet unsolved. The existence of additional constraints, the so-called sum rules [7], makes the problem of finding thermodynamically consistent mean field theory difficult compared to the molecular liquid case. Various approaches have been proposed recently for the derivation of equation of state (EOS) for the RPM. Mostly they are based either on the improvements of the classical Debye-

Hückel (DH) [8] and Bjerrum [9] theory of association or mean spherical approximation (MSA) [10], taking into account the association and various effective interactions. For the reviews of the results see Refs. [3,11–14].

The location of the critical point for the RPM varies depending on the interactions included in the free energy. It is accepted that the following dimensionless parameters for the temperature  $T$ , particle number density  $n$ , and pressure  $P$  are used:

$$T^* = \frac{k_B T}{q^2/a}, \quad \rho^* = n a^3, \quad P^* = \frac{P}{q^2/a^4}, \quad (1)$$

where  $a$  is the diameter of an ion and  $q$  is the absolute value of the charge. The characteristic value for  $T_c^*$  takes the values in the interval  $0.05 \leq T_c^* \leq 0.08$ . The situation with the critical density  $\rho_c$  is less definite. Its value varies from  $\rho_c = 0.02$  to  $\rho_c = 0.08$ . It should be noted that most of the analytical results predict a low-density ( $\rho_c = 0.026$ ) and “high-temperature” ( $T_c^* = 0.06$ – $0.08$ ) critical point. It cannot be excluded that such a low value for  $\rho_c^*$  is connected with the small association taken into account with the help of the thermodynamic perturbation theory. However the reliability of such estimates is not quite clear. The Monte Carlo (MC) simulation studies [15–17] performed in recent years give a high-density ( $\rho_c = 0.07$ – $0.08$ ) and low-temperature ( $T_c^* = 0.04$ – $0.05$ ) critical point. Despite the 100% uncertainty in the value of the critical density for the RPM, the compressibility factor takes the value between 0.2 and 0.3, which is quite reasonable in view of the vdW value  $Z_c = 0.375$  of this parameter. Therefore, the development of the alternative approach based on the dipole fluid model seems to be expedient.

In the present paper we estimate the coordinates of the critical point. We will also show that the change of molecular parameters due to rotations influences essentially the location of the critical point of the ionic molten salt in the framework of the dipole fluid approach.

## I. QUALITATIVE ANALYSIS OF THE CRITICAL BEHAVIOR OF THE DIPOLE LIQUID

NaCl is the simplest example of an ionic liquid. In solid state it is an ionic crystal. Above the melting point the posi-

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tions of ions become unfixed, but this liquid remains strongly dissociated. Due to thermal expansion at increasing temperature, the dissociation degree diminishes and the molten salt becomes a dipole liquid. At further increasing temperature and decreasing density of the molten salt the dissociation degree grows again and the molten salt becomes a completely ionized system. Thus, at some temperature ( $T_1, T_2$ ) and density ( $n_1, n_2$ ) intervals, molten NaCl can be considered as a dipole liquid. Also, additional arguments for this assumption will be given.

Let us consider the general properties of this liquid and, in particular, its main critical parameters: the critical temperature and density. The interparticle interaction in the dipole system takes the form

$$U(1,2) = U_w(1,2) + U_{dd}(1,2), \quad (2)$$

where the first term describes the van der Waals interaction between molecules and

$$U_{dd} = \frac{1}{\epsilon r_{12}^3} \left( \mathbf{d}_1 \cdot \mathbf{d}_2 - 3 \frac{(\mathbf{d}_1 \cdot \mathbf{r}_{12})(\mathbf{d}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right) \quad (3)$$

the proper dipole-dipole interaction,  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  is the interparticle spacing. Note that the dipole moment of a pair is some function of the equilibrium distance between ions in a pair:

$$\mathbf{d}_i = d(r_{12}) \mathbf{n}_i, \quad \mathbf{n}_+ = \frac{\mathbf{r}_+^{(i)} - \mathbf{r}_-^{(i)}}{|\mathbf{r}_+^{(i)} - \mathbf{r}_-^{(i)}|},$$

$i = 1, 2$ ,  $\epsilon$  is the dielectric permittivity.

It is easy to check that the inequality  $|U_w(r_{12})| \ll U_d(\sigma/r_{12})^6$  takes place at all  $r_{12}$ . Therefore in the following, the contribution  $|U_w|$  will be ignored.

Because the dipole-dipole interactions are relatively weak, the angular distribution of dipole moments  $\mathbf{d}_i$  is close to the isotropic one. More exactly, we assume that the two-particle distribution function  $g(\mathbf{d}_1, \mathbf{d}_2)$  can be approximated by the first two terms in the expansion:

$$g(\mathbf{d}_1, \mathbf{d}_2) = 1 - \beta U_{dd}(1,2) + \dots, \quad \beta = \frac{1}{k_B T}. \quad (4)$$

The approximation of such a kind allows us to exclude the orientational degrees of freedom in the configurational integral with the help of the perturbation theory. Another way is to use the analog of the standard quantum mechanical derivation of van der Waals potential for the case of two molecules. Here the averaging over rotational degrees of freedom for both molecules leads to the vanishing of the interaction in the first order of perturbation theory. Then the

second order leads to the attractive  $1/r^6$  potential. In fact both procedures are equivalent to the usage of the isotropic potential

$$U(r_{12}) = \langle U(1,2) \rangle = U_w(r_{12}) - U_d \left( \frac{\sigma}{r_{12}} \right)^6, \quad (5)$$

$$U_d = \frac{2}{3} \beta \frac{\langle \langle d^2 \rangle \rangle^2}{\epsilon^2 \sigma^6}.$$

Here  $\sigma \approx a_+ + a_- \approx 2a$ ,  $a_+$  and  $a_-$  are the diameters of ions Na and Cl correspondingly and for simplicity we put  $a_+ = a_-$ ,  $\langle \langle \dots \rangle \rangle$  denotes the average with the quasiclassical internal partition function of a pair [18],

$$\langle \langle d^2 \rangle \rangle = \frac{4\pi \int_0^R d^2(r) \exp[-\beta U_{eff}(r)] r^2 dr}{\Xi(T^*, R)},$$

where  $\Xi(T^*, R)$  is the internal partition function of a pair, which is chosen to be proportional to the partition function of the isolated pair. Due to the mass action law, it determines the association constant  $K(T)$  which governs the ionization equilibrium. The electronic degrees of freedom of the ions do not contribute to thermodynamics because the characteristic energies are out of the thermodynamic domain of interest. Thus the partition function in the quasiclassical approximation reads as

$$\Xi(T^*, R) = 4\pi \int_0^R \exp[-\beta U_{eff}(r)] r^2 dr, \quad (6)$$

where  $U_{eff}$  is the effective internal energy of a pair. Its explicit form will be discussed below.

The integrand in Eq. (6) tends to infinity at  $r \rightarrow \infty$ , because  $U_{eff} \rightarrow 0$ . Therefore, the integration region should be bounded from above by some value  $R$ . The approximation (6) is adequate until  $R$  remains less than the average intermolecular distance. The appearance of such a cutoff in Eq. (6) is inevitable for any realistic interionic potential and shows the only shortcoming of the model of the chemical equilibrium used to calculate the degree of ionization in a system.

Note that in the two-dimensional (2D) case the situation is opposite: (1) the logarithmic growth of the electrostatic potential allows us to put  $R = \infty$ ; and (2) to prevent the annihilation of a pair in Ref. [19] the big positive value of the chemical potential was included in  $U_{eff}$ .

It is essential that the averaging procedure restricts the applicability region of the potential (5) by interparticle spacings  $\sigma \leq r_{12}$ , which gives the size of the ‘‘averaged’’ dipole of order  $2a$ . The value of  $\sigma$  may be slightly less than  $2a$  since rotating dipoles are not the same as hard spheres of diameter  $2a$ . It is quite clear in view of the scattering cross section for the hard rotating dumbbells. At this level  $\sigma$  should be considered as the parameter (in general, temperature dependent) of the dipole-dipole potential. The procedure of its fixing in the critical point will be discussed later.

To describe the properties of molten NaCl within the interval, where it can be considered as a dipole liquid, we can use the hard wall potential:

$$U(r_{12}) = \begin{cases} \infty, & r_{12} < \sigma \\ -U_d \left( \frac{\sigma}{r_{12}} \right)^6, & \sigma \leq r_{12}. \end{cases} \quad (7)$$

Such a potential leads to the van der Waals equation of state

$$P = \frac{n_d k_B T}{1 - n_d b} - A(T) n_d^2, \quad (8)$$

where

$$A(T) = -\pi \int_{\sigma}^{\infty} U(r) r^2 dr = \frac{\pi \sigma^3}{3} U_d, \quad b = \frac{2\pi}{3} \sigma^3, \quad (9)$$

and  $n_d$  is the pair number density. Therefore the overall density is  $n = 2n_d$ . In dimensionless form, Eqs. (8) and (9), read as

$$P^* = \frac{\rho^* T^*}{2 - b \rho^*} - \frac{\tilde{A}(T^*)}{4} \rho^{*2} \quad (10)$$

and

$$\tilde{A}(T^*) = \frac{2\pi}{9 T^{*3} \sigma^3} r_d^4. \quad (11)$$

Here all spatial parameters are given in units of a hard-core diameter  $a$ . The parameter  $r_d$  determines the square of spacing between the effective charges in the dipole pair:

$$r_d^2 = \frac{\langle\langle d^2(r) \rangle\rangle}{q^2}.$$

The value of parameter  $r_d$  depends on the internal structure of the pair, which is determined by the standard quantum mechanical methods (see, e.g., Ref. [20]).

Though by the order of magnitude  $r_d \approx 1$ , from Ref. [21] it follows that the characteristic values of dipole moments correspond to  $r_d < 1$ . In fact this is because the effective charge of the ion in a pair is less than the charge of a free ion.

Since  $\sigma$  is connected with the size of the pair, we model its temperature dependence via the relation

$$\sigma = r_d \delta, \quad (12)$$

where  $\delta$  is the fitting parameter.

Note that  $\sigma$  is temperature dependent, which we assume the same as that for  $r_d$ . Note that the vapor phase in contact with the liquid one is the gas of dipole molecules. The van der Waals EOS is an appropriate approximation for the EOS for such vapor phase. Thus we can get the critical parameters of this system using the van der Waals theory of the critical point.

Equation (8) leads to the following equations for the critical temperature and density (note that  $n_d = n/2$ , where  $n$  is the total number density):

$$T_c^* = \frac{2\sqrt{2}}{9\sigma^3} r_d^2, \quad \rho_c^* = \frac{1}{\pi\sigma^3}. \quad (13)$$

The estimates for these parameters are straightforward if we put  $\sigma = 2$  and take into account that due to the small dipole moment of NaCl,  $r_d = 1$  (in units of  $a$ ):

$$T_c^* = \frac{\sqrt{2}}{36} \approx 0.04, \quad \rho_c^* = \frac{1}{8\pi} \approx 0.04, \quad P_c^* = \frac{\sqrt{2}}{1536\pi} \approx 3 \times 10^{-4}, \quad (14)$$

$$Z_c = \frac{P_c^*}{\rho_c^* T_c^*} = \frac{3}{16} \approx 0.19,$$

which are in satisfactory agreement with the values

$$T_c^* = 0.055, \quad \rho_c^* = 0.026, \quad P_c^* = 3.6 \times 10^{-4}, \quad (15)$$

$$Z_c = 0.25$$

obtained within the extended Debye-Hückel-Bjerrum theory [12] augmented with the ion-dipole interaction. Our value of the critical density is greater due to neglecting the dissociation of the dipole pairs.

Now we need to consider the dipole pair by itself, since the parameters of the potential (16) actually are the averages over the internal partition function of a pair and, therefore, are temperature-dependent functions.

## II. THE ROTATION OF DIPOLES

In the preceding section the model of an undissociated ionic liquid consisting of rotating dipoles has been introduced. Here we investigate the internal structure of the bound pair of ions. We take into account the fact that the energy of interaction of a pair should include centrifugal energy together with the Coulombic potential, as in the standard problem of two bodies interacting via a central field. First we consider the structure of the dipole within the RPM model, i.e., the ions are modeled by the hard charged spheres. In other words the effective potential energy of interaction between the nuclei is

$$U_{eff}(r) = \begin{cases} \infty, & r < 1 \\ -\frac{q^2}{r} + \frac{L^2}{2\mu r^2}, & 1 \leq r. \end{cases} \quad (16)$$

It includes the Coulombic interaction and centrifugal energy,  $\mu = (m_+ m_-)/(m_+ + m_-)$  is the reduced mass. The hard-core diameter is taken as unity and describes the impenetrability of inner electronic shells.

Let us consider the question of the size of a pair within the picture formulated above. We note that for the specific systems of interest,  $T/(\hbar^2/2\mu r^2) \approx 10^4$  (for NaCl the rota-

tional quantum  $\hbar^2/2\mu r^2$  corresponds to temperature  $T_{rot} = 0.31$  K), and therefore the rotational degrees of freedom can be treated classically:

$$E_{rot} = \langle \langle L^2/(2\mu r^2) \rangle \rangle = kT. \quad (17)$$

The equilibrium distance between ions in a pair caused only by the Coulombic and centrifugal forces is determined by the equation

$$U'_{eff}(r) = \frac{q^2}{r_{eq}^2} - \frac{L^2}{\mu r_{eq}^3} = 0.$$

From here it follows that

$$r_{eq} = \frac{L^2}{\mu q^2}$$

and at the condition (17), we obtain

$$\langle \langle 1/r_{eq} \rangle \rangle = \frac{2}{q^2} \langle \langle L^2/(2\mu r^2) \rangle \rangle = \frac{2kT}{q^2} \geq \frac{1}{\langle \langle r_{eq} \rangle \rangle}.$$

If the oscillations of nuclei within a pair are ignored, then finally we get

$$\langle \langle r_{eq} \rangle \rangle = \frac{1}{2T^*}.$$

The obtained result is valid ( $r_{eq} > 1$ ) only if  $T^* < 1/2$ . This result exactly coincides with the Bjerrum size of a pair [9] (see also Ref. [12]),

$$R^{Bj} = \begin{cases} \frac{1}{2T^*}, & T^* \leq 1/2 \\ 1, & T^* > 1/2. \end{cases} \quad (18)$$

The choice of Eq. (18) as the size of the ionic pair is inappropriate from the physical point of view at low temperatures  $T^* \ll 1$  [12]. It is natural that with lowering  $T$  the size of a pair should become smaller tending to the close contact value  $a$  at  $T \rightarrow 0$ . That is why Eq. (18) is used as the size of a pair for  $1/T^* \geq 2$  only. Within the picture of rotating dipoles such a behavior is quite clear.

The question about the size of an ionic pair is very important because it is determinative for the consideration of ionization equilibrium. For the Coulomb potential there is no explicit border between the bound states and those of scattering. Note that the problem of the rigorous physical criterion of a pair arises even in the quantum mechanical approach, which takes into account the internal degrees of a bound state of two ions. Here the division of the discrete spectrum of the two-particle Hamiltonian into strongly and weakly bounded states is used [22]. This is analogous to the introduction of an upper cutoff in the classical partition function of a molecule, Eq. (6). Therefore within the proposed model, we will include the rotational energy in the association constant.

To define the size of a pair following Bjerrum, we investigate the extreme points of the integrand in Eq. (6). They are

$$R_-(T^*) = \frac{1 - \sqrt{1 - 16T^*\lambda}}{4T^*}, \quad R_+(T^*) = \frac{1 + \sqrt{1 - 16T^*\lambda}}{4T^*}, \quad (19)$$

where the coefficient  $\lambda$  is

$$\lambda = \frac{L^2/(2\mu a^2)}{q^2/a}$$

and will be chosen below.

Here  $R_+$  is the solution of the Bjerrum type [minimum of the integrand in Eq. (6)]:

$$R_+(T^*) = \frac{1}{2T^*} [1 - 4\lambda T^* + o(T^*)], \quad (20)$$

which, as has been said above, is inappropriate. Since a pair is a bound state, the centrifugal energy is less than the potential one, therefore  $\lambda < 1$ .

Another solution,

$$R_-(T^*) = 2\lambda [1 + 4\lambda T^* + o(T^*)], \quad (21)$$

corresponds to the maximum of the integrand and is caused by the appearance of the minimum for the effective potential. This means that  $R_-$  determines the most probable value of the internuclear distance in a pair. It is easy to check that asymptotically, for low values of the temperature  $T^*$ , the value of  $K(T^*)$  is formed mainly by the very maximum of the integrand. From the physical point of view it is natural that in the limit  $T^* \rightarrow 0$  a pair is in hard-core contact configuration and has the size 1 (in dimensionless units). Since  $R_-$  has quite reasonable values and correct behavior at low  $T^*$ , we should put  $\lambda = 1/2$ . This value of  $\lambda$  is also in full accordance with the virial theorem, according to which for the Coulomb interaction the average value of the kinetic energy equals the opposite one-half of the average potential energy [18].

All these facts confirm that we can treat the quantity  $R_-$  as the size of the pair up to the temperatures  $T^* \leq 0.1$ . In addition,  $R_-$  never exceeds 2 (see Fig. 1), i.e., the interparticle distance when the influence of other pairs and charges on the effective potential can be treated as the external field. So we put  $R_-$  as the physical cutoff for Eq. (6):

$$R = R_-(T^*).$$

The existence of a length scale that is much shorter than the Bjerrum length was noted in Ref. [12] based on the numerical analysis of the function  $K(T^*, R)/K(T^*, R^{Bj})$ , though only the Coulomb potential was included in the Boltzmann factor. This heuristic scale gives the point near which  $K(T^*, R)$  grows very rapidly approaching its plateau value [12]. In our case we find the same behavior of  $K(T^*, R)$  at small temperatures,  $T^* < 0.04$  (see Fig. 2). The function

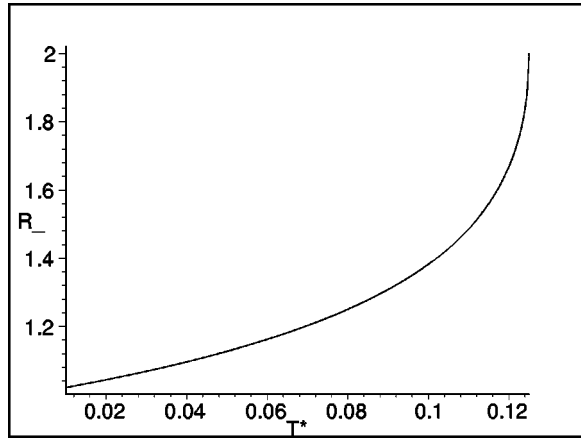


FIG. 1. The temperature dependence of  $R_-$ .

$$\tilde{K}(R, T^*) = K(T^*, R_+) / K(T^*, R), \quad R = R_-(T^*) \delta$$

is close to 1 at  $T^* < 0.04$  and  $\delta > 1.2$ .

The formulas (19) are applicable if

$$T^* \leq \frac{1}{8}. \tag{22}$$

We can consider this temperature interval as the one where the dipole fluid exists as the stable phase.

It is surprising that the simple model of dipole fluid considered above leads to the sharp phase transition at  $T^* = 1/8$  between conducting and insulating phases. From this point of view there is some similarity with the transition in the 2D Kosterlitz-Thouless (KT) model. This analogy is not occasional since within the KT model the chemical potential prevents the annihilation of opposite charges and can be interchanged with the centrifugal energy for the rotating pair. In this case as it can be shown by arguments similar to those of Ref. [19], that the value of the temperature for the KT transition remains invariable.

Note that the temperature  $T_{diss}^* = 1/8$  reminds us that for Kosterlitz-Thouless transition in 2D case and corresponds to dissociation-association transition in low-density approximation. However, in contrast to 2D case in 3D case there is no divergence in the size of the pair and therefore in its polarizability. The derivative of the latter on the temperature has

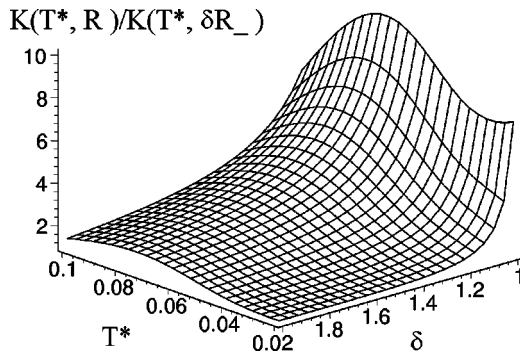


FIG. 2. The ratio  $\tilde{K} = K(T^*, R_+) / K(T^*, \delta R_-)$  as a function of  $\delta$  and  $T^*$ .

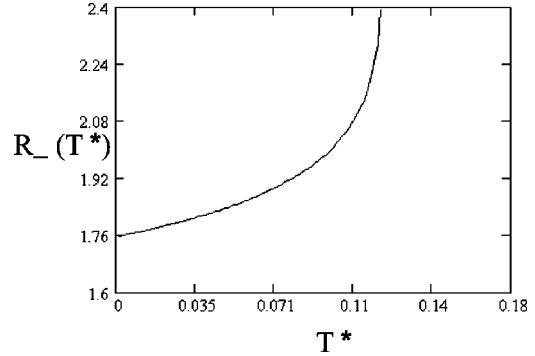


FIG. 3. The temperature dependence of  $R_-$  for  $U_{rep}$  of the type given by Eq. (23);  $U_0 = 10$ ,  $n = 12$ .

singular behavior. This fact directly follows from the dimensionality reasons. Indeed, the polarizability  $\alpha$  in our picture is proportional to  $R_-(T^*)^3$ . Therefore

$$\frac{d\alpha(T^*)}{dT^*} \propto \frac{1}{\sqrt{T_{diss}^* - T^*}}.$$

In other words the temperature derivative of the dielectric permittivity  $\epsilon$  is singular but not the dielectric permittivity itself in such a picture where the dissociation-association transition is sharp because of neglecting the influence of other pairs and charges.

The analysis of reliability of this inference needs further consideration. Additional support for the conjecture of intensive breaking of dipole pairs at the critical point is provided by the results of numerical experiments [15].

The physical status of the size  $R_-(T^*)$  becomes more clear if we interchange the hard core by some regular repulsive potential function, e.g.,

$$U_{rep}(r) = \frac{U_0}{r^n}, \tag{23}$$

where the potential is dimensionless and given in units of  $q^2/a$ . In this case a deep minimum of the effective energy appears and the oscillatory degrees of freedom should be taken into consideration. Therefore in this case  $\lambda < 1/2$ .

The extrema of the integrand in Eq. (6) are given by the equation

$$2T^* - rU'_{eff}(r) = 0,$$

so that at  $T^* = 0$  the only root is the minimum of the effective energy caused by the repulsive and the Coulombic potentials. At  $T^* \neq 0$  exactly,  $R_-(T^*)$  corresponds to this minimum, while the Bjerrum length has quite another meaning. It is clear that the softening of a hard core shifts the distance of maximal probability  $R_-(T^*)$  to higher values (see Fig. 3).

Let us consider the role of oscillations within the adiabatic approximation (see, e.g., Ref. [20]). For the oscillation energy, the following estimate takes place ( $\hbar = 1$ ,  $k_B = 1$ ):

$$\omega_0 = \sqrt{\frac{E''(R)}{\mu}} \approx \frac{1}{r_0} \sqrt{\frac{E}{\mu}}.$$

Since the energy of the electronic term  $E$  is proportional to  $m_e$  and internuclear spacing  $r_0 \sim 1/m_e$  we obtain

$$\frac{\omega_0}{T_{diss}} \sim \sqrt{\frac{m_e}{\mu}} \approx \frac{1}{30}. \quad (24)$$

The depth of the minimum determines the dissociation temperature of a molecule itself, which is rather high (for NaCl  $T_{diss} \approx 46000$  K). This is typical for molecules with ionic bonding [2]. Taking into account Eq. (24), in dimensional units the formula (22) can be represented as the following:

$$T_{diss} \leq \frac{q^2}{8a} \approx (3-4)\omega_0.$$

Therefore the domain of existence of the dipole fluid covers the region where the dissociation due to the excitation of vibrational modes occurs.

It should be noted also that the effective charge of ions in a bound state is less than their charge  $q$  in a free state due to the distribution of charge determined by the wave function of the external electron. That is why the effective charge of an ion in a pair  $q_*$  is not equal to the charge of a free ion  $q$ . It is also confirmed by the experimental data on the dipole moment of NaCl [21]:

$$d = q_* r_0 \approx (5-10) \times 10^{-18} \text{ esu cm},$$

where  $r_0$  is the equilibrium distance between nuclei for a given electronic term. Actually  $q_*$  also depends on  $r_0$  since the electronic term is determined by the internuclear distance. For example, for NaCl in the dissociated state it is clear that  $q_* = 1$ . Using the data (see, e.g., Ref. [21]), we obtain

$$q_*/e \approx 0.4-0.9.$$

From here it follows that  $T_{diss}$  reduces to value  $T_{diss} \leq (1-2)\omega_0$ .

### III. DISINTEGRATION OF AN IONIC PAIR AND DIELECTRIC PROPERTIES

The behavior of a bounded pair in the condensed state is determined by its surrounding. It changes the spectrum of energy of a pair acting as an external field. The spectrum of states is determined by the two-particle Hamiltonian

$$\hat{H}(\mathbf{r}) = \hat{H}^{(0)}(\mathbf{r}) + \hat{H}_{int}(\mathbf{r}),$$

where  $\hat{H}^{(0)}$  is the Hamiltonian of an isolated pair and  $\hat{H}_{int}$  is the part due to the action of the surrounding. Thus for two-particle energy we have

$$\mathcal{E} = \langle \hat{H}(\mathbf{r}) \rangle = \mathcal{E}^{(0)} + \mathcal{E}_{int}.$$

We put

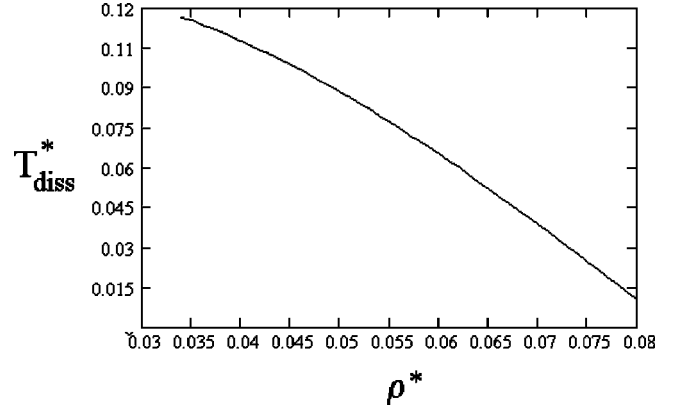


FIG. 4. The density dependence of  $T_{diss}^*$ .

$$\mathcal{E}^{(0)} = U_{eff}(r)$$

and treat  $\mathcal{E}_{int}$  as the fluctuational part of the energy due to the surroundings. Within the thermodynamic approach it determines the accuracy of determination of the energy level of a pair interacting with the surrounding as a thermostat.

To estimate the influence of the surroundings on the disintegration of a dipole pair one can use the following reasons. Due to dipole-dipole interaction, the internal energetic levels of a molecule broaden. The width of this broadening is as follows:

$$|\Delta E| = z \sqrt{\langle U_{dd}^2 \rangle}, \quad (25)$$

where  $U_{dd}$  is the energy of dipole-dipole interaction (3),  $z$  is the number of nearest neighbors. For the estimation we take that  $\langle 1/R_{12}^3 \rangle \sim \rho^*$ . Then Eq. (25) reads

$$|\Delta E| \approx z \rho^* \langle \langle r^2 \rangle \rangle, \quad (26)$$

where for the 3D system we put  $z = 6$ .

Taking into account that the thermal and dipole-dipole channels of broadening the levels act together, we can write the equation for the density dependence of the temperature of dissociation:

$$|\Delta E| + T^* = -\langle \langle U_{eff} \rangle \rangle. \quad (27)$$

This dependence is shown in Fig. 4. From the results obtained above we can conclude that the dipole fluid of rotating dipoles exists at low densities ( $\rho < 0.085$ ) and temperatures ( $T < 0.1$ ). These results depend on  $z$ , i.e., the structure factor of the phase. Note that qualitatively the results obtained above within the model of the dipole fluid are in good agreement with the results of the MC simulation of the RPM [15]. The manifestation of the dipole-dipole mechanism in the broadening of spectral lines in nuclear magnetic resonance is discussed in Ref. [23].

Let us consider the behavior of the dielectric permittivity near the critical point. To describe the dielectric permittivity, we use its canonical form (see details in Ref. [24]):

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\pi}{6} \rho^* \left( \alpha_{el}^* + \frac{r_d^2}{3T^*} \right). \quad (28)$$

With good accuracy  $\alpha_{el}$  can be evaluated as the sum of electronic polarizabilities for Ar and Ne (see, e.g., Ref. [25]), which have similar inner electronic shell structures. The estimates show that this contribution is negligibly small in comparison with the second one.

As was noted above, the value of  $r_d$  is less than the geometric distance between ions. In accordance with Ref. [21]  $r_d$  takes values 0.5–1. For dipole fluids such as KCl and NaCl near their critical points, this leads to the values of dielectric permittivity  $\epsilon \approx 1.2$ –1.3. The electronic terms of a molecule are functions of the temperature due to the interionic spacing  $R(T^*)$ . Therefore the peculiarities of the temperature dependence of the dielectric permittivity are expected on the line  $T_{diss}^*(\rho^*)$ , where intensive breaking of the dipoles occurs. If this line is assumed to intersect with the binodal then the corresponding behavior of  $\epsilon$  should be observed near the critical point, since the derivative  $\partial\epsilon/\partial T$  has a maximum along  $T_{diss}^*(\rho^*)$  and diverges at the critical point. We believe that this behavior was observed in numerical simulations [15,16].

To give the additional arguments in favor of the dipole fluid model, let us study the minimum of the free energy  $f(T^*, \rho^*, r)$  per pair as a function of the spacing between the ions in a pair. The free energy has the structure

$$f(T^*, \rho^*, r) = U(T^*, \rho^*, r) - T^*S, \quad (29)$$

where

$$U(T^*, \rho^*, r) = U_0(T^*, \rho^*) + U_{rep}(r) - \frac{1}{\epsilon r} \quad (30)$$

is the internal energy of a pair ( $U_0$  is the contribution independent of the distance between the ions) and

$$S = \ln(r^3/\sigma^3) \quad (31)$$

is the simplest approximation for its entropy. Within the proposed dipole model, the repulsive part  $U_{rep}$  can be modeled as the centrifugal energy. The dielectric permittivity  $\epsilon$  is given by Eq. (28).

The equilibrium size of a pair is the solution of the equation

$$\left. \frac{\partial f}{\partial r} \right|_{T^*, \rho^*} = 0, \quad (32)$$

and is given by

$$r_-^{(eq)} = \frac{1}{6\epsilon T^*} (1 - \sqrt{1 - 12T^* \epsilon^2}). \quad (33)$$

Thus the equilibrium size of a pair does not exceed  $2\epsilon$  (in dimensionless units). The second root

$$r_+ = \frac{1}{6\epsilon T^*} (1 + \sqrt{1 - 12T^* \epsilon^2}) \quad (34)$$

of Eq. (32) corresponds to the maximum of the free energy and is similar to the Bjerrum length. Using Eqs. (33) and (28) the self-consistent equation for the dielectric permittivity can be obtained. This question will be considered elsewhere.

In the 2D case of point charges of low density, Eq. (32) gives the following. If the short range repulsive potential  $U_{rep}$  is less singular than  $\ln R$  at  $R \rightarrow 0$ , then for  $T^* > 1/2$  the dipole pair is unstable (free charges dominate), since the free energy (29) has no minimum. For  $T^* < 1/2$  the dipoles are stable. In the low-density limit it clearly corresponds to the equation of state of the 2D Coulombic gas obtained in Ref. [26] (see also Ref. [27]).

Finally we estimate the Ginzburg number by the formula used for the molecular liquids [18]:

$$Gi = \left( \frac{r_0}{\xi_0} \right)^6, \quad (35)$$

where  $r_0 = \langle\langle r \rangle\rangle \approx a$  is the interparticle spacing within the ionic pair and  $\xi_0$  is the amplitude of the correlation length for density fluctuations. Since the density fluctuations are connected with those for dipole pairs we set it to  $\xi \geq \sigma$ . Using the parameters of the dipole fluid model, from Eq. (35) we get the estimate:

$$Gi \leq 0.04. \quad (36)$$

## DISCUSSION

The ionic and dipole liquids form two natural approximations to describe the critical properties of the systems similar to molten NaCl. In our paper we have estimated the main critical parameters for the liquid with a hard dipole as well as considered the influence of the effects arising due to the softness of a dipole molecule. In particular, the latter is very important for describing the dielectric properties of a system near the critical point.

Here we should emphasize that the rotation of molecules plays the key role in the behavior of molten NaCl in the critical region. The rotational motion at some temperature  $T_{diss}$  leads to the disintegration of molecules in the low-density vapor phase. Due to dipole-dipole interactions between molecules, the value of  $T_{diss}$  decreases with the density. In this way, the region of stability of such a dipole phase of molten salts such as NaCl can be established. At the same time dipole-dipole interactions form the deep minimum for the effective intermolecular potential, determining the equation of state of NaCl vapor. The position of the critical point obtained from this equation of state falls into the region of stability of the dipole phase. Since the effective size  $\sigma$  of the molecules and the depth of the potential well depends on the temperature, the position of the critical point and the characteristics of the rotational motion should be studied in the self-consistent way. It was shown that the coordinates of the critical point for a fluid of rotating dipoles are of the same magnitudes as those obtained for the models of the RPM type. Also it was noticed that the critical temperature for the dipole fluid is of the same order as the  $T_{diss}$  for molecular

alkali-metal halides. Such a proximity explains the abrupt change in the degree of dissociation observed in numerical experiments.

It is not excluded that the quantum corrections to internal states of the dipole pairs will also slightly change the estimates. In particular, the temperature dependence of the vibrational contributions to the heat capacity can also be studied. The following step is to construct the equation of state for small “soft” dipole molecules and to take into account the dissociation process with the help of perturbation theory. The combination of such an approach with that developed in Ref. [28] on the basis of the ionic liquid allows us to narrow the region of the most probable values for the critical parameters.

Our estimate for the critical temperature correlates with the known analytical results. Note that most of the analytical approaches are based on the EOS for low-density Coulombic systems (DH, MSA, etc.), where the dissociation is taken into account perturbatively.

Within the dipole liquid approach we have obtained the

estimate for the Ginzburg temperature and have shown that it is less than 1 for the simple liquid by a factor of  $10^{-2}$ – $10^{-1}$ . The approximation of the dipole liquid allows us to analyze in an evident form the contribution of the polarizational effects [28]. One can show that these effects lead to the further considerable decrease of the Ginzburg temperature.

Note also the possibility for the appearance of an inhomogeneous phase near the critical point of ionic liquids. Since the dissociation temperature  $T_d$  is near  $T_c$ , the system can disintegrate in the regions with essentially different values of the ionization degree  $\Delta$ : the drops of ionic and dipole liquids. As a consequence, the region with the Ising-like behavior cannot be reached. Thorough investigation of this scenario is needed. These and other questions will be the subject of further work.

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