

Lattice models of ionic systems with charge asymmetry

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The thermodynamics of a charge-asymmetric lattice gas of positive ions carrying charge q and negative ions with charge $-zq$ is investigated using Debye–Hückel theory. Explicit analytic and numerical calculations, which take into account the formation of neutral and charged clusters and cluster solvation by the residual ions, are performed for $z=2, 3$, and 4 . As charge asymmetry increases, the predicted critical point shifts to lower temperatures and higher densities. This trend agrees well with the results from recent Monte Carlo simulations for continuum charge-asymmetric hard-sphere ionic fluids and with the corresponding predictions from continuum Debye–Hückel theory. © 2003 American Institute of Physics. [DOI: 10.1063/1.1558311]

I. INTRODUCTION

The nature of critical phenomena in ionic systems has been a subject of numerous theoretical studies in recent years.^{1–4} Due to the long-range nature of Coulombic interactions, construction of a full renormalization group treatment, which was so successful in describing the critical behavior of nonionic fluids, meets both conceptual and technical difficulties.¹ However, in recent years some progress has been achieved in obtaining physically reasonable, well-based mean-field theories for ionic systems.^{1–5} These theoretical studies have been supported and, sometimes in substantial part, initiated by intensive Monte Carlo simulations^{6–11} of charged systems.

To investigate the thermodynamics of ionic fluids, two main mean-field approaches have been developed. The first one^{1,3} extends the pioneering work of Debye and Hückel¹² (DH) on dilute solutions of strong electrolytes, while the second approach² relies on integral equations for correlation functions. Analysis of thermodynamic energy bounds and comparison with the best Monte Carlo estimates for the critical parameters suggests that the DH-based theory gives a better description of the thermodynamics of electrolytes, at least in the critical region.^{3,13}

The simplest model of ionic fluids, the so-called restrictive primitive model (RPM), considers a system of spherical equisized charged particles, half of them carrying a charge q and the other half with charge $-q$. The charge symmetry of this model plays a crucial role in the determination of its universality class and in the ability to obtain analytic solutions. This raises the question of how the breaking of the symmetry will affect the thermodynamics and critical properties of electrolyte systems. An important extension of the RPM is the charge-asymmetric primitive model, where the sizes of negative and positive particles are the same while absolute values of charges for positive and negative ions are different. Recent Monte Carlo simulations^{8,10} have revealed that, as charge asymmetry increases, the critical temperature T_c of the gas–liquid transition decreases, while the critical

density ρ_c grows. However, most of the current theories give different predictions. Simple DH theory and the mean-spherical approximation (MSA) both predict no dependence on the asymmetry parameter z .^{3,14} In symmetric Poisson–Boltzmann and modified Poisson–Boltzmann integral equation methods¹⁵ the charge asymmetry hardly changes T_c , while ρ_c increases. However, the absolute values of the critical parameters are very different from Monte Carlo estimates. A field theoretical approach by Netz and Orland¹⁶ predicts large increases in critical temperatures and, similarly, a large decrease in critical densities, in sharp contrast with computer simulations trends. The only theory that produces reasonable results for the effect of charge asymmetry on thermodynamics and criticality of ionic systems, as judged by comparison with Monte Carlo computer simulations, is the DH approach augmented by Bjerrum cluster formation and cluster–ion interactions (DHBjCI).¹⁷

Lattice models, such as the Ising model, have played an important role in understanding criticality in nonionic systems. In recent years, lattice models have also attracted the attention of researchers as a tool for investigating thermodynamics and criticality in Coulomb systems.^{1,18–22} A systematic study of electrolytes on lattices, which utilizes the Debye–Hückel approach, has been presented recently.²⁰ In this work the thermodynamics of a d -dimensional system of equal numbers of positive and negative ions, i.e., a charge-symmetric lattice RPM, has been investigated. Specific calculations for Coulomb systems on three-dimensional lattices, which included ion pairing and ion–dipole interactions, predicted a gas–liquid phase separation at low densities. However, taking into account the lattice symmetry yielded a different scenario—the phase diagrams of electrolytes on simple cubic and body-centered-cubic lattices show order-disorder phase transitions with a tricritical point, while gas–liquid phase separation is suppressed. The introduction of charge asymmetry in lattice models of ionic fluids tends to suppress the possibility of order–disorder phase transitions,

and gas–liquid phase coexistence reappears, although the position of critical point may change.

In this paper, we present a thermodynamic investigation of charge-asymmetric lattice models of electrolytes. By explicitly including the clustering of oppositely charged particles and ion–cluster interactions, we obtain phase diagrams for 2:1 and 3:1 lattice electrolytes, and we locate the critical point for the 4:1 ionic system. Our results accord well with the trend obtained in recent Monte Carlo simulations and the continuum DHBjCI theory.¹⁷ The paper is organized as follows: In Sec. II we present an overview of our thermodynamic approach to multicomponent charged species mixtures and we outline the pure Debye–Hückel theory. The full theory, which accounts for charged and neutral cluster formation and their interactions with the residual ions, for a 2:1 system is presented in detail in Sec. III. Section IV describes the general scheme of thermodynamic calculations for 3:1 and 4:1 lattice electrolytes. Finally, the results are discussed in Sec. V and our conclusions are given in Sec. VI.

II. LATTICE DEBYE–HÜCKEL THEORY OF CHARGE-ASYMMETRIC ELECTROLYTES

A. Thermodynamic overview

Consider a system of charged particles on a three-dimensional simple cubic lattice with a unit cell length a , which initially has N_0 ions carrying a charge $-zq$ and zN_0 ions with a charge q : i.e., the total number of ions is $N=(z+1)N_0$. Because of the electrostatic interactions, ions with opposite charges tend to form clusters. As a result, there will be many species present in the system: dimers, trimers, etc., with respective charges $(-z+1)q, (-z+2)q, \dots, 0$. If the number of particles of type i is given by N_i , then we define $\rho_i=N_i/V$ and $\rho_i^*=\rho_i v_0$ to be the number density and the reduced density of the i th species, with $v_0=a^3$ being the unit lattice cell volume.

The Helmholtz free energy is central for the determination of the thermodynamic behavior of charge-asymmetric lattice electrolytes. It can be approximated by summing consecutively the free energies describing the interactions between different species,

$$F = F^{\text{Id}} + \sum_i F_i, \tag{1}$$

where F^{Id} is the ideal lattice gas (entropic) term and F_i is the electrostatic energy of the i th species. Once the reduced free energy density $\bar{f} \equiv -F/k_B T V$ is known, the reduced chemical potentials for every component $\bar{\mu}_i \equiv \mu/k_B T$ can be computed via

$$\bar{\mu}_i = -\partial \bar{f} / \partial \rho_i. \tag{2}$$

Finally, the reduced pressure is given by

$$\bar{p} \equiv p/k_B T = \bar{f} + \sum_i \rho_i \bar{\mu}_i. \tag{3}$$

Then the possible phase equilibria are defined by matching pressures and chemical potentials for each component in different phases.

In multicomponent systems with charged particles it is the electrochemical potential that must be equal in coexisting vapor (v) and liquid (l) phases,¹⁷ namely,

$$\mu_{i,v} + q_i \phi_v = \mu_{i,l} + q_i \phi_l, \tag{4}$$

where $\phi_{v(l)}$ is the electrostatic potential in the corresponding phase, where, in general, there is a nonzero Galvani potential difference $\Delta \phi = \phi_v - \phi_l$ between the phases.²⁴ However, for calculating phase equilibria in multicomponent systems of charged particles, it is more convenient to use the single-component thermodynamic picture.¹⁷ Since every thermodynamic phase is electroneutral, the multicomponent system with $N=(z+1)N_0$ ions can be viewed as a single-component system of N_0 molecules, each of them consisting of one negative ion and z positive ions. Then phase equilibrium between the liquid and vapor at temperature T is ensured by

$$P(T, \rho_v) = P(T, \rho_l), \quad \mu(T, \rho_v) = \mu(T, \rho_l), \tag{5}$$

where ρ_v and ρ_l are the overall particle densities in gas and liquid phases, respectively, while $\mu = \mu_- + z\mu_+$. The pressure in each phase can still be calculated using Eq. (3). This approach accounts for the electroneutrality of each phase and utilizes only one chemical potential, which significantly simplifies calculations of phase diagrams.

B. Pure DH theory of charge-asymmetric lattice electrolytes

As a first approximation, assume that there is no clustering between oppositely charged particles and that only free ions are present in the system. The free energy density can be written as $\bar{f} = \bar{f}^{\text{Id}} + \bar{f}^{\text{DH}}$, where the first term is the entropic ideal gas contribution, which is given by

$$\bar{f}^{\text{Id}} = -\frac{\rho_+^*}{v_0} \ln \rho_+^* - \frac{\rho_-^*}{v_0} \ln \rho_-^* - \frac{1-\rho^*}{v_0} \ln(1-\rho^*). \tag{6}$$

The subscripts “+” and “-” denote positive and negative ions, respectively. Owing to overall electroneutrality in the system, the densities of free ions are related to each other by

$$\rho_+^* = z\rho_-^*/(1+z), \quad \rho_-^* = \rho^*/(1+z). \tag{7}$$

The second term in the free energy density is the electrostatic contribution $\bar{f}^{\text{DH}} = \bar{f}_+(\rho_+) + \bar{f}_-(\rho_-)$, which is the result of ion–ion Coulombic interactions. By solving the lattice version of the linearized Poisson–Boltzmann equation for the electrostatic potential and subsequently applying the Debye charging procedure, as was done for the charge-symmetric lattice model of electrolytes,²⁰ it can be easily shown that

$$\bar{f}^{\text{DH}} = \frac{1}{12v_0} \int_0^{x^2} \left[P(1) - P\left(\frac{6}{x^2+6}\right) \right] d(x^2), \tag{8}$$

where

$$P(\zeta) = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \frac{d\mathbf{k}}{1 - \frac{\zeta}{3}(\cos k_1 + \cos k_2 + \cos k_3)} \tag{9}$$

'is the integrated lattice Green's function for the simple cubic lattice^{25,26} and $x^2 = \kappa^2 a^2$ with the reciprocal squared Debye screening length given by

$$\kappa^2 = \frac{4\pi}{Dk_B T} (\rho_+ q_+ + \rho_- q_-^2) = \frac{4\pi z q^2 \rho}{Dk_B T}. \quad (10)$$

Now the chemical potential for each type of ion can be easily calculated through Eq. (2), which yields

$$\bar{\mu}_i = \ln\left(\frac{\rho_i^*}{1 - \rho^*}\right) + \frac{\pi}{3T^*} \left[P\left(\frac{6}{x^2 + 6}\right) - P(1) \right], \quad (11)$$

where we have defined the reduced temperature by

$$T^* = \frac{Dk_B T a}{z q^2}, \quad (12)$$

which is related to the reduced density as $\rho^* = x^2 T^* / 4\pi$. Then for the chemical potential of the neutral "molecule," consisting of one negative and z positive ions, we obtain

$$\begin{aligned} \bar{\mu} = & (1+z) \ln\left(\frac{\rho^*}{1 - \rho^*}\right) + (1+z) \frac{\pi}{3T^*} \\ & \times \left[P\left(\frac{6}{x^2 + 6}\right) - P(1) \right] + C(z), \end{aligned} \quad (13)$$

where the density-independent constant is $C(z) = [z \ln z - (1+z) \ln(1+z)]$. Having the chemical potentials and free energy, we can calculate the pressure using Eq. (3) to obtain

$$\begin{aligned} \bar{p} v_0 = & -\ln(1 - \rho^*) + \frac{1}{12} \left[x^2 P\left(\frac{6}{x^2 + 6}\right) \right. \\ & \left. - \int_0^{x^2} P\left(\frac{6}{x^2 + 6}\right) d(x^2) \right]. \end{aligned} \quad (14)$$

Note that the expression for the pressure is independent of the charge asymmetry and the chemical potential of the "molecule" is $(1+z)/2$ times the value for the 1:1 electrolytes [if we neglect the constant $C(z)$, which does not affect the thermodynamics of the system]. Then the predicted phase separation and critical point

$$T_c^* = 0.1018, \quad \rho_c^* = 0.0996 \quad (15)$$

are the same as for the charge-symmetric lattice electrolytes. This result fully agrees with the pure DH theory in continuum space,¹⁷ which also predicts no change in the critical parameters for charge-asymmetric electrolytes.

III. LATTICE DEBYE-HÜCKEL THEORY WITH CLUSTERING AND CLUSTER-IONS INTERACTIONS FOR 2:1 ELECTROLYTES

A. Bjerrum clustering

One of the main deficiencies of the pure DH theory, which describes the system of free positive and negative ions, is the total neglect of the ion clustering. Oppositely charged particles attract each other and form clusters in order to reduce the free energy. This process significantly decreases the number of free ions. In charge-symmetric lattice electrolytes in the critical region the number of neutral ion pairs is 2–3 times larger than the number of free ions,²⁰ and

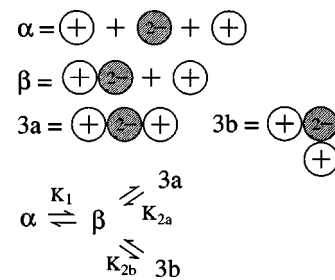


FIG. 1. Different charged and neutral particles and chemical reactions in 2:1 lattice electrolyte systems.

one can expect that for charge-asymmetric ionic systems this ratio should be even larger because of the larger free energy gain for clusters with the increase of the parameter z .

The importance of ion pairing in charged particles systems was first recognized by Bjerrum.^{23,27} In his original approach a cutoff distance between two oppositely charged ions was introduced to define a bound pair. Later, the definition of a pair became a subject of many discussions.^{1,3} However, as was shown in a careful analysis by Levin and Fisher,³ the precise value of this cutoff distance has little influence on the critical parameters and coexistence curves (less than 0.5%). Meanwhile, the further problem of calculation of the electrostatic energy of the dipole particle poses another, new technical difficulty, since the ion pair does not possess spherical symmetry and the problem cannot be solved exactly analytically or numerically. By approximating the ideal bispherical exclusion zone by a symmetrically centered sphere, Levin and Fisher³ succeeded in obtaining a precise, numerically tractable solution. For three- or four-particle clusters in charge-asymmetric continuum ionic fluids, the same strategy also yields reasonable results,¹⁷ although the technical complexity of computations increases significantly.

In lattice systems the situation is intrinsically simpler because of the discrete rather than continuous symmetry. In 1:1 electrolytes it allows one to define clearly an ion pair as two oppositely charged particles sitting on neighboring lattice sites.²⁰ Similarly, for charge-asymmetric lattice electrolytes we can easily define different cluster configurations. These particles may be viewed as independent chemical species, and the processes of clustering can be considered as a set of chemical reactions between them.

To illustrate our approach, consider a 2:1 lattice ionic fluid in which clusters are allowed to form. Then, following Ref. 17, in addition to the free positive particles with charge $+q$ and free negative ions with charge $-2q$, we suppose it suffices to consider three basic types of clusters: specifically we include dimers carrying a charge $-q$ (with the number density ρ_2^*) and two possible configurations of neutral trimers, linear and angular, with number densities ρ_{3a}^* and ρ_{3b}^* , respectively (see Fig. 1).

In the spirit of Bjerrum's approach, we assume first that neutral clusters do not interact with charged particles. Then these neutral particles contribute only to the ideal free energy, and the total free energy density is given by

$$\bar{f} = \bar{f}^{\text{Id}}(\rho_+, \rho_-, \rho_2, \rho_{3a}, \rho_{3b}) + \bar{f}_+^{\text{El}} + \bar{f}_-^{\text{El}} + \bar{f}_2^{\text{El}}. \quad (16)$$

To calculate the free energy of the charged dimers f_2^{El} , we adopt a view of them as a combination of neutral symmetric (+, -) dipoles, which occupy two neighboring sites, and single-site particles (with the charge $-q$) which sit on the top of negative part of the dipoles, i.e., (+, 2-) = (+, -) + (-). Then the electrostatic free energy densities for the free ions and charged dimers are given by the corresponding expressions from the pure DH theory, although with a different inverse squared Debye screening length, namely,

$$\kappa^2 = \frac{4\pi}{Dk_B T} (\rho_+ q^2 + 4\rho_- q^2 + \rho_2 q^2). \quad (17)$$

To determine the ideal gas (entropic) contribution to the free energy one needs to know the corresponding densities and chemical potentials. As shown in Fig. 1, we identify five different species in the 2:1 lattice Coulombic system. Let us define α as a set of free positive and negative ions, β as a set of negatively charged dimers and free positive ions, $3a$ as the linear neutral trimers, and $3b$ as the neutral angular trimers. Then the clustering in these system can be described by three chemical reactions



with the corresponding equilibrium constants K_1 , K_{2a} , and K_{2b} . The chemical equilibrium in the system is described by the following relations between chemical potentials

$$2\mu_+ + \mu_- = \mu_\alpha + \mu_2 = \mu_{3a} = \mu_{3b}. \quad (21)$$

The chemical potential for each particle can be computed by first separating the entropic and electrostatic parts, i.e., $\bar{\mu}_i = \bar{\mu}_i^{\text{Id}} + \bar{\mu}_i^{\text{El}}$, where the latter is determined simply by $\bar{\mu}_i^{\text{El}} = -\partial \bar{f}^{\text{El}} / \partial \rho_i$. For the ideal-gas parts of the chemical potentials the situation is more complex. For free single-site ions the chemical potentials can be easily found applying the potential distribution theorem²⁸ or, from simple entropic considerations,

$$\bar{\mu}_+^{\text{Id}} = \ln \rho_+^* - \ln(1 - \rho_+^* - \rho_-^* - 2\rho_2^* - 3\rho_{3a}^* - 3\rho_{3b}^*), \quad (22)$$

$$\bar{\mu}_-^{\text{Id}} = \ln \rho_-^* - \ln(1 - \rho_+^* - \rho_-^* - 2\rho_2^* - 3\rho_{3a}^* - 3\rho_{3b}^*). \quad (23)$$

However, for dimers and trimers there are no similar exact expressions. Nevertheless, these entropic contributions to the chemical potentials can be estimated by applying the Bethe approximation,²⁹ which has been successful in the DH theory of 1:1 lattice electrolytes.²⁰ Note that in lattice electrolyte systems phase transitions predominantly take place in the low-density regimes, and thus the error in using the Bethe approximation is expected to be small.

Defining the activities of the particles via z_i , for every species we have

$$z_i = \zeta_i / \Lambda_i^{3n} e^{\mu_i}, \quad (24)$$

where n is the number of sites occupied by the particle, ζ_i is the corresponding internal partition function, and Λ_i is the de Broglie wavelength (see Ref. 3). For the latter the equality $\Lambda_+ = \Lambda_- = \Lambda_2 = \Lambda_{3a} = \Lambda_{3b}$ holds. We refer to the Appendix for a detailed calculation of the dimer and trimer activity using the Bethe approximation method, and we give here only the final expressions for activities:

$$z_2 = \frac{\rho_2^* (1 - \frac{1}{3}\rho_2^*)}{(1 - \rho_+^* - \rho_-^* - 2\rho_2^* - 3\rho_{3a}^* - 3\rho_{3b}^*)^2} e^{\bar{\mu}_2^{\text{El}}}, \quad (25)$$

$$z_{3a} = \frac{\rho_{3a}^* (1 - \frac{1}{2}\rho_2^*)^2}{(1 - \rho_+^* - \rho_-^* - 2\rho_2^* - 3\rho_{3a}^* - 3\rho_{3b}^*)^3} e^{-1/(2-\rho_{3a})} e^{\bar{\mu}_{3a}^{\text{El}}}, \quad (26)$$

$$z_{3b} = \frac{\rho_{3b}^* (1 - \frac{1}{2}\rho_2^*)^2}{64(1 - \rho_+^* - \rho_-^* - 2\rho_2^* - 3\rho_{3a}^* - 3\rho_{3b}^*)^3} e^{-1/(2-\rho_{3b})} e^{\bar{\mu}_{3b}^{\text{El}}}. \quad (27)$$

Once the activities are known, the chemical potentials are derived by utilizing Eq. (24) for each species, and the free energy is obtained by integrating the chemical potentials. Finally, we arrive at the chemical potential of an α ‘‘molecule’’ (which consists of two positive and one negative ions) in the form

$$\bar{\mu}_\alpha^{\text{DHBj}} = 2\ln \rho_+^* + \ln \rho_-^* - 3 \ln(1 - \rho_+^* - \rho_-^* - 2\rho_2^* - 3\rho_{3a}^* - 3\rho_{3b}^*) + \bar{\mu}^{\text{El}} \quad (28)$$

and the reduced pressure

$$\begin{aligned} \bar{p}^{\text{DHBj}}_{V_0} = & -\ln(1 - \rho_+^* - \rho_-^* - 2\rho_2^* - 3\rho_{3a}^* - 3\rho_{3b}^*) \\ & + 3 \ln(1 - \rho_2^*/3) + 3 \ln(1 - \rho_{3a}^*/2) \\ & + 3 \ln(1 - \rho_{3b}^*/2) - \frac{\rho_{3a}^*}{2 - \rho_{3a}^*} - \frac{\rho_{3b}^*}{2 - \rho_{3b}^*} + \bar{p}^{\text{El}}_{V_0}. \end{aligned} \quad (29)$$

The electrostatic part of the chemical potential and the pressure have the same form as in the pure DH theory (14), namely,

$$\bar{\mu}^{\text{El}} = \frac{\pi}{3T^*} \left[P\left(\frac{6}{x^2+6}\right) - P(1) \right], \quad (30)$$

$$\bar{p}^{\text{El}} = \frac{1}{12} \left[x^2 P\left(\frac{6}{x^2+6}\right) - \int_0^{x^2} P\left(\frac{6}{x^2+6}\right) d(x^2) \right], \quad (31)$$

where $x^2 = \kappa^2 a^2$ with κ^2 given by Eq. (17).

In terms of activities, the chemical equilibrium conditions (21) can be presented in the form of laws of mass action

$$z_+^2 z_- K_1 = z_2 z_+, \quad (32)$$

$$z_2 z_+ K_{2a} = z_{3a}, \quad (33)$$

$$z_2 z_+ K_{2b} = z_{3b}. \quad (34)$$

As can be seen from the chemical equilibrium conditions (21) and the definition of activities (24), the association constants in Eqs. (32)–(34) are relaxed to the internal partition functions of dimers and trimers:

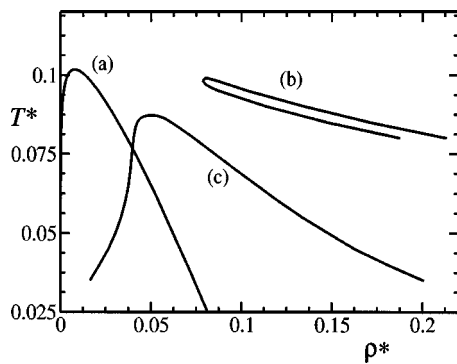


FIG. 2. Phase diagrams for 2:1 lattice electrolyte: (a) pure DH theory, (b) DHBj approximation, and (c) DHBjCI theory.

$$K_1 = \zeta_1(T), \quad K_1 K_{2a} = \zeta_{3a}(T), \quad K_1 K_{2b} = \zeta_{3b}(T). \quad (35)$$

The above definitions of the association constants lead to the expressions

$$\zeta_i = v_0 c_i \sum_{j=1}^n e^{-u_{ji}/k_B T}, \quad (36)$$

where $u_{ji} = q_j \varphi_j$ is the electrostatic energy of the j th ion of a cluster particle i in the potential φ_j , which is due to the other ions entering the multimer cluster. The coefficient c_i in Eq. (36) is an entropic factor which takes into account all allowable configurations of the cluster. The electrostatic potentials φ_j can be determined by solving the lattice version of the linearized Poisson–Boltzmann equation

$$\Delta \varphi_j = - \frac{4\pi}{Dv_0} \sum_{k \neq j} q_k \delta(\mathbf{r}_k), \quad (37)$$

in which q_k and \mathbf{r}_k are the charge and the position of the k th ion entering the multimer cluster. Since lattice Coulomb potentials can be calculated exactly in numerical terms,²⁰ we obtain the following expressions for association constants:

$$K_1 = 6v_0 \exp\left[\frac{1.08152}{T^*}\right], \quad (38)$$

$$K_{2a} = v_0 \exp\left[\frac{0.812033}{T^*}\right], \quad (39)$$

$$K_{2b} = 4v_0 \exp\left[\frac{0.734737}{T^*}\right]. \quad (40)$$

Substituting Eqs. (38)–(40) and the expressions for activities (25)–(27) into the expressions for chemical equilibrium (32)–(34) yields a set of equations, which define implicitly the dimer and trimer densities ρ_2^* , ρ_{3a}^* , and ρ_{3b}^* in terms of the monomer densities ρ_+^* and ρ_-^* . The electroneutrality of the system requires that $\rho_+^* = 2\rho_-^* + \rho_2^*$. Then the chemical potential and the pressure can be expressed in terms of only one variable, the total reduced density $\rho^* = \rho_+^* + \rho_-^* + 2\rho_2^* + 3\rho_{3a}^* + 3\rho_{3b}^*$, which allows for the construction of the coexistence curve (see Fig. 2).

As in the case of charge-symmetric continuum³ and lattice²⁰ electrolytes, the coexistence curve in the DHBj approximation has an unphysical bananalike shape. This is related to the fact that, as the temperature is lowered, the num-

ber of neutral clusters quickly grows, and this depletes the number of free charges present in the system. Since it is the density of free charges that plays the role of the order parameter and governs the gas–liquid transition, the phase separation takes place at higher overall densities. At this level of approximation, neutral clusters are electrically inactive and, hence, contribute only to the hard-core part of the free energy, which is the same for both phases. Thus DHBj theory simply superimposes the pressure of ideal gas of clusters on the pure DH pressure, and both sides of the coexistence curve shift to higher densities by equal amounts. The critical density is now substantially higher, $\rho_c^* \approx 0.0807$, while the critical temperature slightly decreases, $T_c^* \approx 0.099$.

B. Cluster-ion interactions

The predictions of DHBj theory for lattice ionic systems are thermodynamically unreasonable and should be corrected by taking into account the effects of interactions between multimers in clusters and free ions.^{3,20} As shown earlier for continuum and lattice electrolytes,^{3,20} these solvation effects eliminate the unphysical banana-shape phase coexistence curves. It is reasonable to expect that these cluster–ion interactions are even more important in charge-asymmetric ionic systems due to a larger fraction of neutral clusters in equilibrium with free ions.

The exact calculations of interactions between the multimers and free ions are very complicated. Instead, we use a reasonable assumption to obtain closed analytic expressions. We approximate the neutral clusters as a set of overlapping noninteracting symmetric dipoles. For example, the neutral trimers can be viewed as a combination of two dipoles, i.e., $(+, 2-, +) = (+, -) + (-, +)$. The charged clusters, as we discussed above, are approximated as symmetric dipoles overlapping with free ions, i.e., $(+, 2-) = (+, -) + (-)$. We expect that differences between our approximation and the exact cluster–ion interaction contribution to the free energy to be small since the corrections correspond to higher-order dipole–dipole interactions and thus can be neglected.

According to our approximation the reduced density of dipoles from all cluster particles in the system is equal $\rho_2^* + 2\rho_{3a}^* + 2\rho_{3b}^*$. Since the energy of solvation of a single free dipole in the lattice electrolyte system is known exactly,²⁰ the cluster–ion interactions contribute to the free energy density as

$$\begin{aligned} \bar{f}^{\text{CI}} = & (\rho_2^* + 2\rho_{3a}^* + 2\rho_{3b}^*) \frac{\pi q^2 a^2}{21Dk_B T v_0^2} \\ & \times \left[-\frac{x^2}{2} + \frac{1}{x^2} \int_0^x G(x^2) d(x^2) \right], \end{aligned} \quad (41)$$

where

$$G(x^2) = \frac{x^2(x^2 + 7)}{x^2 + 6} P\left(\frac{6}{x^2 + 6}\right). \quad (42)$$

Then the corresponding contributions to the chemical potentials and pressure are given by

$$\bar{\mu}_\alpha^{\text{CI}} = \frac{2\pi^2(\rho_2^* + 2\rho_{3a}^* + 2\rho_{3b}^*)}{21(T^*)^2} \left[\frac{1}{2} - \frac{1}{x^2} G(x^2) + \frac{1}{x^4} \int_0^{x^2} G(x^2) d(x^2) \right] \quad (43)$$

and

$$\bar{p}^{\text{CI}} v_0 = \bar{\mu}_\alpha^{\text{CI}} x^2 T^* / 4\pi, \quad (44)$$

which must be added to the values provided by Eqs. (28) and (29) in order to obtain the complete expressions for the chemical potential and pressure.

The full DHBjCI theory predicts a phase separation as exhibited in Fig. 2. As in the charge-symmetric lattice and continuum electrolytes,^{3,20} taking into account the solvation of clusters by the residual free ions eliminates the unphysical bananalike shape of the coexistence curve. The critical parameters are now given by

$$T_c^* = 0.08735, \quad \rho_c^* = 0.05001, \quad (45)$$

$$Z_c \equiv p_c / \rho_c k_B T = 0.2431.$$

Comparison with the critical parameters of 1:1 lattice ionic system indicates that the critical temperature is about 11% lower, while the critical density is 1.67 times higher. These trends—the decrease in the critical temperature and increase in the critical density—are in agreement with the results of continuum calculations for charge-asymmetric electrolytes.¹⁷

It is interesting to estimate the relative amounts of different species in the critical region. In terms of molar fractions $y_i = n_i \rho_i^* / \rho^*$ (n_i is the size of the particle), our theoretical approach predicts

$$y_+ = 0.1002, \quad y_- = 0.0388, \quad y_2 = 0.0452, \quad (46)$$

$$y_{3a} = 0.0075, \quad y_{3b} = 0.8083.$$

As expected, the fraction of neutral trimers significantly exceeds the fraction of free charges. Also, the number of charged dimers is very low, which can be attributed to their propensity to combine with free ions to form energetically more favorable neutral trimers. What is surprising, at first glance, is that the ratio of linear trimers to angular trimers is much less than unity. Indeed, because electrostatic interactions favor a linear arrangement of the ions in a trimer cluster, these clusters are more energetically stable and should prevail over angular trimers. However, these naive arguments do not take into account the entropic considerations. First of all, the angular trimers have more different possible configurations than the linear trimers. In addition, they are more compact and can be packed more densely. As a consequence, there are more ways to arrange angular trimers on the lattice and they dominate trimer clusters.

IV. LATTICE DHB/CI THEORY FOR 3:1 AND 4:1 ELECTROLYTES

The thermodynamic calculations for $z=3$ asymmetric lattice electrolytes can be performed following the method presented in full detail in Sec. III. As shown in Fig. 3, there are seven basic clusters to be considered in this system—namely, single-site positive and negative ions, dimers with

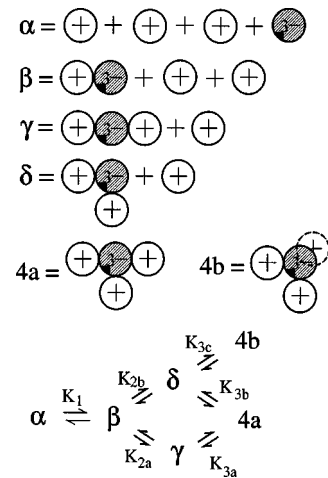


FIG. 3. Different charged and neutral particles and chemical reactions in 3:1 lattice electrolyte.

the charge $-2q$, linear and angular trimers (with the charge $-q$), and two types of neutral tetramers, which are connected by the network of six chemical reactions. Note that we do not consider clusters with bonds between the same charges. For example, we assume that charged trimers have the configurations $(+, 3-, +)$, but not $(+, +, 3-)$. Indeed, these particles are less stable and their contributions to free energies can be neglected.

In addition, as in the case of 2:1 lattice Coulombic systems, we view the clusters as combinations of noninteracting $(+, -)$ symmetric dipoles and single-site charges. The activities of multimers are calculated by applying the Bethe approximation method outlined in the Appendix. These approximations allow us to calculate the free energy of the system as a sum of the corresponding entropic, electrostatic, and cluster solvation terms for each particle. The resulting phase coexistence curve is given in Fig. 4. The critical parameters are

$$T_c^* = 0.0688, \quad \rho_c^* = 0.0847. \quad (47)$$

The molar fractions of different clusters in the critical region are

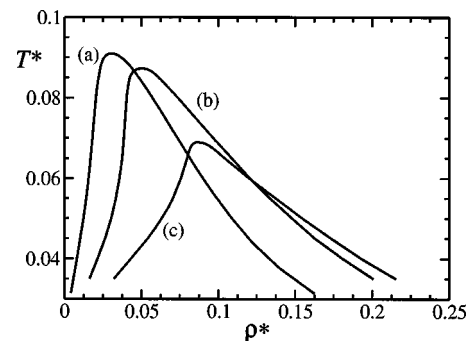


FIG. 4. Phase diagrams of (a) 1:1, (b) 2:1, and (c) 3:1 lattice electrolytes in DHBjCI theory.

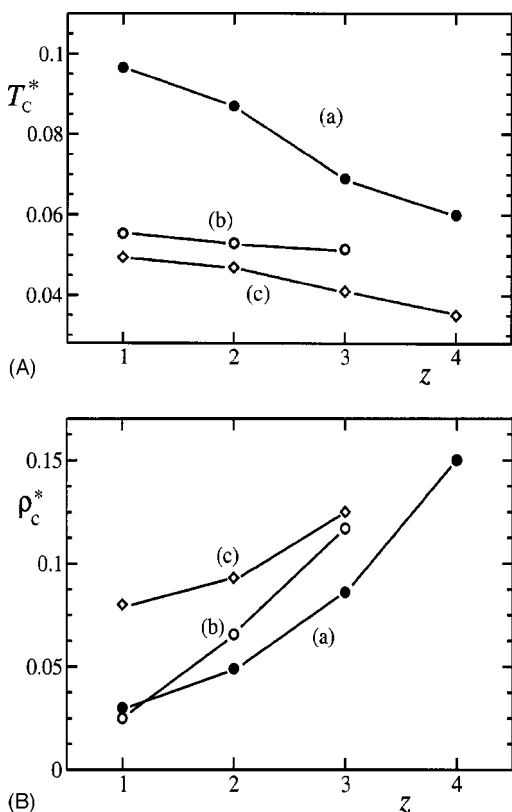


FIG. 5. (A) Critical temperatures T_c^* and (B) critical densities ρ_c^* as functions of charge asymmetry: (a) our lattice DHBjCI predictions, (b) continuum DHBjCI predictions (Ref. 17), and (c) Monte Carlo simulations (Refs. 8, 10, and 11).

$$\begin{aligned}
 y_+ &= 0.08872, & y_- &= 0.00347, & y_2 &= 0.0088, \\
 y_{3a} &= 0.0033, & y_{3b} &= 0.2049, & y_{4a} &= 0.3043, \\
 y_{4b} &= 0.3864.
 \end{aligned}
 \quad (48)$$

As expected, neutral clusters again dominate.

Analogous thermodynamic calculations can be done for 4:1 lattice electrolytes. However, the number of different types of clusters and the number of chemical reactions between them become fairly large, and the full thermodynamic analysis is difficult to complete. Instead, we focus on the critical region of the system where calculations can be completed. The resulting critical parameters are

$$T_c^* = 0.060, \quad \rho_c^* = 0.148. \quad (49)$$

The relative density of all neutral clusters here is about 87%.

Full phase diagrams for $z:1$ lattice ionic systems ($z = 1, 2, \text{ or } 3$) calculated using DHBjCI approach are exhibited in Fig. 4.

V. DISCUSSION

Our analysis of charge-asymmetric lattice electrolytes using Debye–Hückel theory with Bjerrum clustering and cluster–ion interactions indicates that charge asymmetry strongly influences the thermodynamics, especially in the critical region. It is found that critical temperatures decrease while critical densities increase with charge asymmetry. Our theoretical predictions for critical parameters are compared

in Fig. 5 with the results of continuum Monte Carlo simulations^{8,10,11} and with the predictions of the continuum DHBjCI theory.¹⁷

Clearly, the overall consistency between the lattice and continuum DHBjCI approaches and computer simulations results indicates that the Debye–Hückel method correctly captures the physics of phase transitions in these ionic systems. In Coulomb systems with charge asymmetry the formation of clusters is strongly favored. Clusters contribute to electrostatic interactions much less than free ions, and the effective electrostatic energy per particle decreases. However, the phase separation is driven by charged particles, and the temperature is normalized by the strongest electrostatic interaction between the positive and negative ions [see Eq. (12)]. Therefore, the reduced critical temperature falls.

Cluster formation also significantly depletes the number of free ions. At the critical point, the molar fractions of free single-site positive and negative ions are 21.0%, 13.8%, 9.2%, and 4.2% for 1:1, 2:1, 3:1, and 4:1 lattice electrolyte systems, respectively. As a consequence, larger overall densities are required to achieve the phase separation, and the reduced critical density increases.

At the same time, the relative numbers of neutral particles as a function of charge asymmetry shows a nonmonotonic behavior. The molar fractions of neutral clusters are equal to 79% in 1:1 ionic system, 81% in 2:1 electrolytes, 69.1% in 3:1 ionic system, and about 88% in 4:1 electrolytes. The decrease of the molar fraction of neutral clusters in the critical region in the 3:1 system as compared to 2:1 electrolytes has also been found in continuum calculations.¹⁷ The actual number of neutral clusters depends on two factors: the free energy gain of cluster formation and the temperature (through the equilibrium constant). It is possible that in 3:1 electrolytes the lowering of the critical temperature is not enough to overcome the repulsion between the positive ions in neutral tetramers, while in 4:1 ionic systems the decrease in critical temperature is enough to favor more strongly the formation of neutral clusters.

The absolute values of the critical temperature in our charge-asymmetric lattice models is larger than the Monte Carlo simulation data^{8,10} by a factor of 1.68–1.94, with lesser factors corresponding to higher z . This agrees with the general feature of lattice models to overestimate the values of critical temperatures in comparison with continuum models. Note, however, that the simulations are performed with the continuum potential, while our theory employs the lattice Coulombic potentials. In addition, the reduced temperature (12) is normalized by the energy of two ions interaction via *continuum* or $1/r$ Coulombic potential. However, the lattice potential differs from $1/r$ at short distances,²⁰ and normalizing the temperature by the energy of lattice Coulombic interactions of nearest neighbors would lower the temperatures by an additional 8%.

The absolute values of the critical densities in our theoretical approach are only 38%–69% of the current Monte Carlo estimates.^{8,10} This fact reflects the discrete nature of the lattices and that not all possible clusters have been taken into account.

VI. CONCLUSIONS

We have investigated the effects of charge asymmetry on thermodynamics and critical properties of the lattice ionic systems using Debye–Hückel theory with Bjerrum clustering and cluster–ion interactions. Phase diagrams for $z:1$ lattice electrolytes have been obtained for $z=2$ and 3, while for $z=4$ the location of the critical point was determined. Our results agree well with the Monte Carlo simulations and with the continuum Debye–Hückel theory,¹⁷ predicting that the increase in the charge asymmetry lowers the critical temperature and increases the critical density.

Our theoretical approach may be extended in several directions. In this paper we investigated charge asymmetric electrolyte systems on the simple cubic lattices. It is interesting to consider the lattices with different symmetry such as body-centered-cubic and face-centered-cubic lattices, for which thermodynamic calculations for charge symmetric systems are already performed.²⁰ Another interesting question is how the charge asymmetry will affect the ionic systems in two dimensions, where interesting phase transitions may appear.

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APPENDIX: THE BETHE APPROXIMATION FOR MULTIMERS

Consider a system of N_m multimers (each particle occupies m lattice sites), which interact with each other only via on-site exclusion, on a simple cubic lattice with the total number of sites, N . We can calculate the entropy of the multimer distribution following a direct method of counting probabilities in the Bethe approximation employed by Nagle.²⁹ (For other methods of calculating the partition function for lattice systems see Refs. 30 and 31.) The Bethe approximation does not take into account any correlations around cycles, and thus it is exact for lattices with only tree-like paths (Bethe lattices). However, for three-dimensional cubic lattices this approximation gives fairly good results.

Consider, first, a system consisting only of dimers. Then the number of ways to arrange $N_2=N\rho_2^*$ dimers on the simple cubic lattice can be approximated by²⁹

$$W_2(\rho_2^*) = \left[\binom{N}{2N\rho_2^*} 6^{2N\rho_2^*} \right] \left[\left(\frac{2\rho_2^*}{6} \right)^{1/2} \left(1 - \frac{2\rho_2^*}{6} \right)^{5/2} \right]^{2N\rho_2^*} \times \left[\left(1 - \frac{2\rho_2^*}{6} \right)^{6/2} \right]^{N(1-2\rho_2^*)}. \quad (\text{A1})$$

Here the first set of square brackets represents the total number of ways to arrange $N\rho_2^*$ dimer vertices on the lattice,

taking into account six possible orientations for each dimer, provided one its vertex is fixed. The second set of brackets gives the probability that a dimer vertex configuration is compatible with all its nearest-neighbor vertex configurations. Here $2\rho_2^*/6$ is the probability of finding dimer’s edge along certain lattice direction starting from a given point, and $(1-2\rho_2^*/6)^5$ ensures there is only one dimer at this point. The third set of square brackets is the probability that no dimers occupy $N(1-2\rho_2^*)$ empty lattice sites. The square roots are taken in order not to compute the probabilities twice. The Bethe approximation for dimer’s activity on the simple cubic lattice then yields

$$z = \exp \left(- \frac{1}{N} \frac{d}{d\rho_2^*} \ln W_2(\rho_2^*) \right) = \frac{\rho_2^*/3(1-\rho_2^*/3)}{(1-2\rho_2^*)^2}. \quad (\text{A2})$$

Similar calculations can be performed for the systems containing trimers, tetramers, or higher-order multimers. However, since now not all multimer vertices are equivalent, we have to account for each type of vertex separately.

In particular, consider the system with $N_3=N\rho_3^*$ trimers. Then there are $3N\rho_3^*$ trimer vertices, with $N\rho_3^*$ “center” and $2N\rho_3^*$ “end” vertices. For linear trimers the number of possible orientations is 3 if we fix a “center” vertex and 6 if we fix an “end” vertex. Then the number of ways to arrange linear trimers on the lattice is given by

$$W_3(\rho_3^*) = \left[\binom{N}{3N\rho_3^*} 6^{2N\rho_3^*} 3^{N\rho_3^*} \right] \left[\left(\frac{3\rho_3^*}{6} \right)^{1/2} \times \left(1 - \frac{3\rho_3^*}{6} \right)^{5/2} \right]^{2N\rho_3^*} \left[\left(\frac{3\rho_3^*}{6} \right)^{2/2} \left(1 - \frac{3\rho_3^*}{6} \right)^{4/2} \right]^{N\rho_3^*} \times \left[\left(1 - \frac{3\rho_3^*}{6} \right)^{6/2} \right]^{N(1-3\rho_3^*)}. \quad (\text{A3})$$

Again the first set of square brackets gives the maximum possible number of distinct trimer vertices configurations, the second set of square brackets accounts for the probability that all “end” vertex configurations are compatible with their nearest-neighbor configurations, the third set of brackets corresponds to the “center” vertices’ compatibility, and the last factor ensures that there are $N(1-3\rho_3^*)$ lattice sites free of trimers. Then the activity of linear trimers is given by

$$z_{3a} = \frac{\rho_{3a}^*(1-3\rho_{3a}^*/6)^2}{(1-3\rho_{3a}^*)^3} e^{-1/(2-\rho_{3a}^*)}. \quad (\text{A4})$$

For angular trimers, the only difference is that now there are 24 distinct trimer orientations if we start from the “end” vertices and 12 orientations if we start from the “center” vertex. This yields

$$z_{3b} = \frac{1}{64} \frac{\rho_{3b}^*(1-3\rho_{3b}^*/6)^2}{(1-3\rho_{3b}^*)^3} e^{-1/(2-\rho_{3b}^*)}. \quad (\text{A5})$$

Similarly, the activity of tetramers is given by

$$z_4 = C \frac{\rho_4^*(1-2\rho_4^*/3)^3}{(1-4\rho_4^*)^4} e^{-1/(1-2\rho_4^*/3)}, \quad (\text{A6})$$

where the coefficient C equals $1/96$ for planar tetramers and $C = 1/128$ for nonplanar tetramers.

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