Anisotropic Lattice Models of Electrolytes

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Systems of charged particles on anisotropic three-dimensional lattices are investigated theoretically using Debye-Hückel theory. It is found that the thermodynamics of these systems strongly depends on the degree of anisotropy. For weakly anisotropic simple cubic lattices, the results indicate the existence of order-disorder phase transitions and a tricritical point, while the possibility of low-density gas-liquid coexistence is suppressed. For strongly anisotropic lattices this picture changes dramatically: the low-density gas-liquid phase separation reappears and the phase diagram exhibits critical, tricritical and triple points. For body-centered lattices, the low-density gas-liquid phase coexistence is suppressed for all degrees of anisotropy. These results show that the effect of anisotropy in lattice models of electrolytes amounts to reduction of spatial dimensionality.
I. INTRODUCTION

Understanding thermodynamic properties of electrolyte systems is a long-standing problem which, in recent years, has attracted increased attention due to controversial results on the nature of criticality in Coulomb systems. Experiments suggest that the critical region of solutions of some organic salts can be well described by classical behavior, while for other electrolyte systems the Ising-like description with non-classical behavior is more appropriate. This dichotomy has greatly stimulated theoretical attempts to understand the thermodynamics of ionic systems.

Criticality in simple nonionic fluids can be successfully described and analyzed by the renormalization group (RG) method, and it is reasonable to suggest that this method could also be used to investigate also Coulomb systems. However, in order to proceed with RG calculations, a physically meaningful and well based mean-field theory should be developed. Most theoretical studies of ionic systems concentrate on the simplest model of electrolytes, the so called restricted primitive model (RPM), in which ions are viewed as equal size particles of positive and negative charges of equal magnitude. Currently, there are two theoretical directions in the development of the mean-field description of ionic fluids. The first approach is based on integral equations for correlation functions, while the second approach extends the original Debye-Hückel (DH) theory. Comprehensive theoretical analysis which utilizes for example thermodynamic energy bounds, and comparison with current Monte Carlo simulations indicate that theories based on DH theory may provide a better description of the thermodynamics of electrolytes in critical regions.

So far most of the theoretical efforts in the investigation of charged systems have been devoted to continuum models. However, lattice models are also important for understanding the criticality in Coulomb systems, since the Ising model, which is a lattice gas model, has been crucial for the description of critical phenomena in nonionic systems. There are few numerical and analytical results for lattice ionic systems which show that the phase diagram differs significantly from continuum models. The structures of simple cubic (sc) and body-centered cubic (bcc) lattices allow for charge distribution with the appearance of a long-range order phase at low temperatures similar to that of an ionic crystal. However, this ordering decreases entropy and for high temperatures the disordered phase is thermodynamically more stable. As a result, there is an order-disorder phase
transition line which ends up at the tricritical point\cite{11,14,17,18} while for continuum RPM systems only a gas-liquid coexistence can be found.

Recently, a systematic investigation of lattice models of electrolytes has been presented\cite{14}. In this investigation the lattice restricted primitive model (LRPM), with charged particles occupying sites on a general $d$-dimensional lattice, has been considered using Debye-Hückel theory. By solving exactly the lattice version of the Debye-Hückel equation, closed expressions for thermodynamic properties of general $d$-dimensional ionic systems have been obtained. For three-dimensional lattice Coulombic systems specific calculations, which included pairing and dipole-ion solvation, yielded a gas-liquid phase separation at low densities. However, by taking into account the lattice symmetry, it has been shown that for sc and bcc lattices this gas-liquid phase separation is thermodynamically unfavorable, and the order-disorder phase transitions with the tricritical point will dominate, in agreement with Monte Carlo simulation results\cite{17,18}.

The thermodynamics of lattice anisotropic ionic systems have not been studied yet, although they may provide important information on thermodynamics of real electrolytes. In addition, the lattice stretching, which leads to anisotropy, can be viewed as analogous of lowering the spatial dimensionality of the system. However, DH-based calculations for the continuum\cite{11} and lattice\cite{14} models of electrolytes predict an increase of gas-liquid critical temperatures for lower dimensions. Thus, for lattice anisotropic models, gas-liquid phase separation may reappear along with distinct order-disorder phase transitions. This possibility raises the question of the precise determination of phase diagrams for ionic systems on anisotropic lattices.

In this article, we present a theoretical investigation of anisotropic lattice models of electrolytes using the Debye-Hückel method\cite{14} which has the advantage that it accounts for both electrostatic screening and sublattice ordering in a unified framework. We investigate the ionic systems on three-dimensional lattices obtained by anisotropic stretching of simple cubic and body-centered cubic lattices. The paper is organized as follows. In Sec. II we provide a combined DH and mean-field ordering description of ions on simple tetragonal lattices. The similar analysis for stretched body-centered lattices is given in Sec. III. A discussion and conclusions are presented in Secs. IV and V.
II. DEBYE-HÜCKEL THEORY FOR SIMPLE TETRAGONAL LATTICES

A. Pure DH theory

Our derivation for anisotropic lattice electrolytes follows closely the Debye-Hückel approach for isotropic lattice ionic systems. We consider a system of equal numbers of positive and negative ions with the total density $\rho = \rho_- + \rho_+$ on a tetragonal lattice, which is obtained by stretching the simple cubic lattice, with unit cell dimensions $a \times a \times b$ with an anisotropy factor defined as the ratio of lattice parameters, $\alpha = a/b$. The case $\alpha = 1$ corresponds to the isotropic simple cubic lattice electrolytes which have been studied in detail earlier. The Debye-Hückel approach implies that we can construct the total free energy of the system by summing consecutively the terms which describe interactions between different species. Charged particles interact through the lattice Coulomb potential, otherwise they behave as ideal particles with additional hard-core on-site exclusions. Thus the total free energy density is given by $f = f^{Id} + f^{DH}$. The ideal lattice gas contribution can be written as

$$\bar{f}^{Id} = -\frac{F}{k_BTV} = -\frac{\rho^*}{v_0} \ln \rho^* - \frac{(1 - \rho^*)}{v_0} \ln(1 - \rho^*),$$

where $\rho^* = \rho v_0$ is the reduced dimensionless density and $v_0 = a^2b$ is the unit lattice cell volume.

The other term in $f$ comes from the Coulombic interactions of the free ions and includes the effect of screening. In order to find an expression for the Debye-Hückel contribution to the free energy density, we need the electric potential felt by an ion due to all other ions. This potential can be found by fixing an arbitrary ion at the origin and solving the linearized Poisson-Boltzmann equation

$$\Delta \varphi(r) = \kappa^2 \varphi(r) - (C_d q / D v_0) \delta(r),$$

where $\kappa^2 = C_d \beta q^2 / D$ is the inverse squared Debye screening length, with $\beta = 1/k_B T$ and $C_d = 4\pi$ for three-dimensional lattices. The lattice Laplacian used in Eq. (2) can be presented in the form which incorporates the geometry of the lattice,

$$\Delta \varphi = \Delta_x \varphi + \Delta_y \varphi + \Delta_z \varphi,$$
with
\[ \Delta_i \varphi(r) = \frac{1}{a_i^2} [\varphi(r - a_i e_i) - 2\varphi(r) + \varphi(r + a_i e_i)], \]
(4)
where \( i = x, y, z; a_x = a_y = a, a_z = b \) and \( e_i \) are the unit vectors along the corresponding lattice directions. Then Eq. (2) can be easily solved by Fourier transformation to yield for \( r > 0 \)
\[ \varphi(r) = \frac{2\pi qa^2}{3Dv_0} \int_k \frac{e^{ikr}}{(x^2 + 4 + 2\alpha^2)/6 - J(k, \alpha^2)}, \]
(5)
where we introduced the anisotropic lattice function
\[ J(k, \gamma) = \frac{1}{c_0} \sum_{mn} e^{ik a} = \frac{1}{3} (\cos k_1 + \cos k_2 + \gamma \cos k_3), \]
(6)
\( c_0 = 6 \) is the number of nearest neighbors, and \( \int_k \equiv (2\pi)^{-d} \int_{-\pi}^{\pi} d^d k \) and \( x = \kappa a \). Note that the vectors \( k = (k_1/a, k_2/a, k_3/b) \) describe the reciprocal lattice.

To compute the electric potential at the origin due to the surrounding ions, it is recalled that no other ion can be placed at that site, and hence the appropriate equation is the Laplace’s equation,
\[ \Delta \varphi(r = 0) = 0. \]
(7)
This enables us to write
\[ \Delta_x \varphi(r = 0) = \Delta_y \varphi(r = 0) = \Delta_z \varphi(r = 0) = 0, \]
(8)
which yields
\[ \varphi(0) = (\varphi(r - ae_x) + \varphi(r + ae_x))/2 \]
\[ = (\varphi(r - ae_y) + \varphi(r + ae_y))/2 \]
\[ = (\varphi(r - ae_z) + \varphi(r + ae_z))/2 \]
(9)
Then from Eqs. (5) and (9) it follows that
\[ \varphi(0) = \frac{2\pi qa^2}{Dv_0(2 + \alpha^2)} \int_k \frac{J(k, \alpha^2)}{(x^2 + 4 + 2\alpha^2)/6 - J(k, \alpha^2)}. \]
(10)
Following the DH approach for isotropic lattices, we introduce the integrated anisotropic lattice Green’s function

$$P(z, \alpha) = \int \frac{1}{1 - zJ(k, \alpha^2)},$$

which has been evaluated exactly in terms of a product of two complete elliptic integrals of the first kind by Joyce. Then the total potential at the origin due to the surrounding ions, $$\psi(0) = \varphi(0) - \varphi(0)|_{x=0}$$, takes the form

$$\psi = \frac{2\pi q}{Db(2 + \alpha^2)} \left[ x^2 P \left( \frac{6}{x^2 + 4 + 2\alpha^2}, \alpha \right) - P \left( \frac{6}{4 + 2\alpha^2}, \alpha \right) \right].$$

By using the Debye charging procedure, the reduced electrostatic free energy density can be calculated explicitly, yielding

$$\bar{f}^{DH} = \frac{1}{4(2 + \alpha^2)v_0} \left[ x^2 P \left( \frac{6}{4 + \alpha^2}, \alpha \right) - x^2 \int_0 P \left( \frac{6}{x^2 + 4 + \alpha^2}, \alpha \right) d(x^2) \right].$$

The chemical potential, $$\bar{\mu} = \mu/k_B T = -\partial \bar{f}/\partial \rho$$, is then given by

$$\bar{\mu} = \ln \rho^* - \ln(1 - \rho^*) - \frac{\pi}{(2 + \alpha^2)T^*} \left[ P \left( \frac{6}{4 + \alpha^2}, \alpha \right) - P \left( \frac{6}{x^2 + 4 + \alpha^2}, \alpha \right) \right],$$

where, following the continuum DH theory and the DH theory for isotropic cubic lattices, the reduced temperature is defined as

$$T^* = \frac{Dbk_BT v_0}{q^2 a^2} = \frac{Db}{q^2 \beta} = \frac{Da}{q^2 \beta \alpha},$$

and for the reduced density we obtain

$$\rho^* = \frac{x^2 T^*}{4\pi}.$$  

Knowing the free energy density and the chemical potential allows us to calculate the pressure, $$\bar{p} = p/k_B T = \max_{\rho} [\bar{f} + \bar{\mu} \rho]$$, yielding

$$\bar{p}v_0 = -\ln(1 - \rho^*) + \frac{1}{4(2 + \alpha^2)} \left[ x^2 P \left( \frac{6}{x^2 + 4 + 2\alpha^2}, \alpha \right) - x^2 \int_0 P \left( \frac{6}{x^2 + 4 + 2\alpha^2}, \alpha \right) d(x^2) \right].$$

Eqs. (1), (13), (14) and (17) provide a full thermodynamic description of the simple tetragonal lattice model of electrolytes. The thermodynamics at the critical region can be
investigated by analyzing the spinodal, which is determined by the condition $\rho \partial_{\rho} \mu = 0$. Using Eq. (14) we obtain

$$T^*_s = \frac{2\pi}{(2 + \alpha^2)} \frac{\zeta(1 - \zeta)\partial P(\zeta)/\partial \zeta}{2 + (1 - \zeta)^2 \partial P(\zeta)/\partial \zeta},$$

with $\zeta = 6/(x^2 + 4 + 2\alpha^2)$.

The phase transitions and the gas-liquid coexistence can be studied by analyzing the pressure and the chemical potential in different phases. The predicted gas-liquid coexistence curves for simple tetragonal lattices are shown in Fig.1. The critical temperature increases monotonically as the anisotropy parameter decreases and reaches the value of $T_c^* = 1/2$ at $\alpha = 0$: see Fig.2a. At the same time, the critical density shows a non-monotonic behavior with two maxima and a minimum, and finally approaches the value $\rho_c^* = 0$ at $\alpha = 0$, as shown in Fig.2b. Lowering the anisotropy parameter can be visualized as the stretching the lattice along one direction, and the limit of $\alpha \to 0$ corresponds to an infinite distance between the layers. Thus the anisotropic lattice model at $\alpha = 0$ is equivalent to the 2D Coulomb system on square lattice, for which the pure DH theory\cite{14} predicts the critical parameters to be $T_c^* = 1/4$ and $\rho_c^* = 0$. The apparent discrepancy between our results for the critical temperature and the results for two-dimensional lattice electrolytes\cite{14} can be easily explained by analyzing the linearized Poisson-Boltzmann Eq.(2). In our calculations we used the three-dimensional coefficient $C_d = 4\pi$, while in two dimensions this coefficient is equal to $2\pi$, which explains the factor 2 in the difference in the corresponding values of the critical temperatures.

At the limit of large $\alpha$ the lattice is stretched along 2 directions, and thus the anisotropic lattice with $\alpha = \infty$ corresponds to the 1D lattice Coulomb system. Our predictions for critical parameters in this case are $T_c^* = 0$ and $\rho_c^* = 0$, while for one-dimensional lattice electrolytes the DH-based calculations give $T_c^* = \infty$ and $\rho_c^* = 0$. In this case, the difference in critical temperatures can be attributed to our definition of the reduced temperature in Eq.(15). Note, however, that the DH method is incorrect in describing one-dimensional ionic systems\cite{14}. The overall agreement between our estimates of critical parameters of strongly anisotropic lattice models of electrolytes and the results for 1D and 2D ionic lattice systems supports our arguments that anisotropic stretching is analogous to lowering of spatial dimensionality for simple cubic lattices.

A surprising feature of the predicted coexistence curves is the critical density dependence...
on the lattice anisotropy as exhibited in Fig.2b. It shows two maxima (at $\alpha = 0.4$ and $\alpha = 4.175$) and one minimum (at $\alpha = 1$); this picture is probably the result of geometric and packing effects.

**B. Sublattice Ordering**

The Debye-Hückel approach presented above describes only the low-density behavior of the system. To obtain the full thermodynamic description of simple tetragonal lattices we have to take into account the lattice symmetry. A simple tetragonal lattice, similarly to a simple cubic lattice, can be viewed as consisting of two intercalated sublattices. Ions of opposite signs can be distributed unequally between these sublattices, thus reducing the electrostatic contribution to the free energy. At the same time, unequal distribution of charged particles lowers the entropy which leads to an increase in the total free energy. The competition between these factors determine the thermodynamics and phase behavior of the system.

We consider again a simple tetragonal cubic lattice with $N$ charged particles. The overall system is neutral, and there are $N_A^+ (N_A^-)$ positive (negative) particles in sublattice $A$, and $N_B^+ (N_B^-)$ positive (negative) particles in sublattice $B$. Assuming that sublattice $A$ has an excess of positive ions, the corresponding order parameter can be defined as

$$y = \frac{N_A^+ - N_A^-}{N_A^+ + N_A^-} = -\frac{N_B^+ - N_B^-}{N_B^+ + N_B^-}. \quad (19)$$

This order parameter has a positive value in the ordered phase, while it equals to zero in the disordered phase.

The nonzero charge density on each sublattice produces an additional “background” potential $\Phi(r)$ which, however, does not change the correlation functions. This potential can be found using the linearized Poisson-Boltzmann equation

$$\Delta \Phi(r_A) = -\frac{4\pi}{D}\rho y q. \quad (20)$$

Because of the symmetry between sublattices, we have $\Phi(r_A) = -\Phi(r_B)$. By using the definition of the lattice Laplacian (3)-(4), and following the approach outlined for isotropic lattice electrolytes, we obtain for the potential $\psi$ due to all ions except the one fixed at
the origin the following expression

$$\psi(r_A) = -\frac{\pi}{2 + \alpha^2} \frac{\rho^s y q}{Db} + \psi^{DH},$$

(21)

where $\psi^{DH}$ is given in Eq.(12). The electrostatic part of the total free energy then follows again from the Debye charging process, while the entropic contribution can be calculated as for isotropic lattices \[3,4\] yielding

$$\bar{f} = \bar{f}^{Id} + \bar{f}^{DH} + \bar{f}^{Ord} \text{ with}$$

$$\bar{f}^{Ord} = \frac{\pi}{2(2 + \alpha^2) v_0 T^*} \rho^s y^2 - \frac{\rho^s}{2v_0} \left[ (1 + y) \ln(1 + y) + (1 - y) \ln(1 - y) - 2 \ln 2 \right],$$

(22)

where $\bar{f}^{Id}$ and $\bar{f}^{DH}$ are given by Eqs.(1) and (13).

The knowledge of the total free energy allows us to investigate the possibility of sublattice ordering. It can be done by looking for minima of $\bar{f}^{Ord}$ for nonzero values of the order parameter $y$. This procedure leads us to the equation describing the $\lambda$-line, along which second-order phase transitions occur,

$$\rho^*_\lambda = \frac{2 + \alpha^2}{\pi} T^*.$$

(23)

The anticipated tricritical point can be found by calculating the intersection of the $\lambda$-line with the spinodal $\partial \bar{p} / \partial \rho^* = 0$, and this analysis yields the equation for the tricritical point \[3,4\]

$$\frac{4(2 + \alpha^2)}{\rho^*_{tri}} \left[ \frac{\partial P_s}{\partial (x^2)} \right]_{x^2=4(2+\alpha^2)} + \frac{1}{1 - \rho^*_{tri}} - \frac{3}{2} = 0.$$

(24)

The resulting tricritical densities and temperatures for different values of the anisotropic parameter $\alpha$ are presented in Figs.2a and 2c. The tricritical temperature is a decreasing function of the anisotropy parameter, and it reaches its maximal value of $T_{tri} = 0.5960$ at $\alpha = 0$, which is exactly twice the value of the tricritical temperature for the ionic system on the two-dimensional square lattice (see Eq.(70) of Ref.\[14\]). This deviation is again the result of using different dimension-dependent coefficients $C_d$, as was argued above. Both critical and tricritical temperatures vanish at large anisotropies, however, $T_{tri}$ becomes smaller than $T_c$ for $\alpha > 4.25$. The behavior of the tricritical density is different. It has a minimal value for the isotropic lattice ($\alpha = 1$), and it reaches the maximal values of $\rho_c = 0.3794$ and $\rho_c = 0.416$ for $\alpha = 0$ and $\alpha = \infty$ respectively.

The phase diagrams for simple tetragonal lattices are presented in Fig.3. For weakly anisotropic lattices there are only order-disorder phase transitions, while for strongly anisotropic lattices the gas-liquid phase separation reappears at low densities.
III. THEORY FOR BODY-CENTERED TETRAGONAL LATTICE

Consider a system of equal numbers of positive and negative ions on the body-centered tetragonal lattice with \( 2a \times 2a \times 2b \) unit lattice cell. Using the symmetry of the lattice and applying Eqs. (3) and (4) the lattice Laplacian for tetragonal body-centered lattice is given by

\[
\Delta \varphi(r) = \frac{2(2 + \alpha^2)}{3c_0a^2} \sum_{a_{nn}} [\varphi(r + a_{nn}) - \varphi(r)],
\]

(25)

where \( \alpha = a/b \) and the summation runs over all \( c_0 = 8 \) neighbors in a cell. When \( a = b \) this reduces to the well known lattice Laplacian for the body centered cubic lattice. Because of the special symmetry of body-centered lattice, the lattice function

\[
J_b(k) = \frac{1}{c_0} \sum_{a_{nn}} e^{i \mathbf{k} \cdot a_{nn}} = \cos k_1 \cos k_2 \cos k_3,
\]

(26)

in contrast to the simple tetragonal lattice, is independent of the anisotropy parameter \( \alpha \). Thus the isotropic bcc lattice Green’s function \( P_b(z) = \int_{\mathbf{k}} \frac{1}{1 - z J_b(k)} \) can be used for calculation of the thermodynamic properties. Then the potential at the origin due to the surrounding ions takes the form

\[
\psi = \frac{2\pi q}{Dv_0} \frac{3a^2}{(2 + \alpha^2)} \left[ P_b \left( \frac{4 + 2\alpha^2}{x^2 + 4 + 2\alpha^2} \right) - P_b(1) \right],
\]

(27)

and the electrostatic free energy is given by

\[
\bar{f}^{DH} = \frac{1}{4(2 + \alpha^2)v_0} \left[ x^2 P_b(1) - \int_0^{x^2} P_b \left( \frac{4 + 2\alpha^2}{x^2 + 4 + 2\alpha^2} \right) d(x^2) \right].
\]

(28)

Furthermore, the ordering free energy does not depend on the type of lattice and is the same both for the simple and body centered lattices. Therefore we can use the corresponding expression from (22) and estimate the tricritical point from Eq.(24) by using \( P_b \left( \frac{4 + 2\alpha^2}{x^2 + 4 + 2\alpha^2} \right) \) instead of the simple tetragonal Green’s function \( P \left[ \frac{6}{x^2 + 4 + 2\alpha^2}, \alpha \right] \). Phase diagrams for electrolytes on the tetragonal body-centered lattices are shown in Fig.4.

Analysis of phase diagrams for the body-centered lattice models of ionic systems indicate that both critical and tricritical densities are independent of the degree of lattice stretching, while \( T^*_c \) and \( T^*_tri \) are decreasing functions of \( \alpha \). These relations can be understood by analyzing the corresponding equation for the spinodal,

\[
T^*_s = \frac{2\pi}{(2 + \alpha^2)} \frac{\zeta (1 - \zeta) \partial P_b(\zeta)/\partial \zeta}{2 + (1 - \zeta)^2 \partial P_b(\zeta)/\partial \zeta},
\]

(29)
where $\zeta = (4 + 2\alpha^2)/(x^2 + 4 + 2\alpha^2)$. Since the lattice Green’s function $P_b(\zeta)$ is independent of the anisotropy parameter $\alpha$, the critical point can be described by the parameter $x_c^2 = 2(2 + \alpha^2)(1 - \zeta_c)/\zeta_c$ with $\zeta_c$ being independent of $\alpha$, while $T_c^* \propto 1/(2 + \alpha^2)$. Then, utilizing Eq.(16) the critical density $\rho_c = x_c^2 T_c^*/4\pi$ is also independent of $\alpha$. Similar arguments can now be applied for the analysis of the tricritical point. The thermodynamic behavior of the tetragonal body-centered lattice electrolytes is then different from that of the simple tetragonal lattice ionic systems. Since critical and tricritical temperature decay at the same rate as functions of the anisotropy parameter $\alpha$, while $\rho_c^*$ and $\rho_{tri}^*$ are constant, the possible low-density gas-liquid coexistence is suppressed by order-disorder phase transitions with a tricritical point at any degree of anisotropy, as shown in Fig.4.

IV. DISCUSSION.

Our analysis of simple tetragonal lattice models of electrolytes based on the DH approach indicates that, similarly to isotropic sc ionic lattice systems, at weak anisotropies ($0.385 < \alpha < 2.113$) the possible low-density gas-liquid phase separation is metastable, and the sublattice ordering is always thermodynamically more favorable. However, for strongly anisotropic simple lattices ($\alpha < 0.385$ or $\alpha > 2.113$) the gas-liquid coexistence reappears and the phase diagram becomes more complex, with critical, tricritical and triple points, as shown in Fig.3. The explanation of this phenomenon is the following. For weakly anisotropic lattices the ordering of ions of opposite signs on different sublattices decreases significantly the total free energy, and order-disorder phase transitions with a tricritical point determines the phase diagram of the system. For strongly anisotropic lattices this ordering is less significant at low densities and the gas-liquid phase separation is restored. Another way of looking at this phenomenon, as was discussed above, is the analogy between lattice stretching and lowering of the space dimensionality. As was shown before, at low dimensions the critical temperature is increasing and thus gas-liquid coexistence occurs again at low densities.

However, the thermodynamic behavior of Coulomb systems on body-centered tetragonal lattices is very different. At all degrees of anisotropy, the sublattice ordering is thermodynamically more stable, and gas-liquid phase separation is always suppressed. This is the result of the special symmetry of body-centered lattices.

Our pure Debye-Hückel treatment of anisotropic lattice electrolytes assumed that there
are only free ions and empty sites in the system. However, at low temperatures the formation of strongly bound neutral dimers, or Bjerrum pairs, is a highly favorable process. Such pairing can be viewed as a reversible chemical reaction and this process can be treated in a systematic way. Another important contribution to the free energy of electrolytes is the ion-dipole solvation energy. The formation of ion pairs and their interactions with single ions have a strong effect on the thermodynamic properties and phase diagrams of electrolytes. Our theoretical method can be extended to include these effects, although, due to anisotropy of the lattice system, there will be more than one type of bound neutral dimers. Based on the comparison with the continuum and isotropic lattice electrolytes, we predict that, if we take these effects into account, both critical and tricritical temperatures will decrease, while critical and tricritical densities will increase. However, this means that our qualitative conclusions on thermodynamics and phase diagrams of anisotropic cubic lattices will not change.

It is interesting to note that similar phase diagrams of lattice electrolytes have been obtained by Ciach and Stell. They considered a mean-field theory of electrolytes with single-ion lattice potential on the isotropic sc lattice and additional short-range interactions. Note that this treatment neglects the cooperative screening, which is thermodynamically important and which is included in our DH-based theory. However, the origins of similar complex phase diagrams in both models are different. In the model of Ciach and Stell the gas-liquid phase coexistence is driven by short-range interactions, while in our model the lattice stretching makes the sublattice ordering less thermodynamically favorable at low densities and, as a result, gas-liquid phase separation is restored.

V. CONCLUSIONS

We have extended the Debye-Hückel method to treat three-dimensional anisotropic lattice models of electrolytes. Phase diagrams for different degrees of anisotropy have been obtained. For weakly anisotropic simple tetragonal lattices, the order-disorder phase transitions with a tricritical point suppress the possibility of low-density gas-liquid phase transitions. However, for strongly anisotropic lattices gas-liquid phase coexistence is restored. Thus the lattice anisotropy for simple tetragonal lattices mimics the lowering of the spatial dimensionality. However, the thermodynamics of the body-centered tetragonal lattice ionic
systems is very different. There is no gas-liquid separation and the phase diagram has only order-disorder phase transitions for all degrees of anisotropy. This is the consequence of the special symmetry of body-centered lattices.

The relevance of our results for understanding the thermodynamics of real ionic fluids remains unclear. However, our method may be more useful for description of the thermodynamics of real ionic crystals with defects. Furthermore, numerical simulations of the anisotropic lattice ionic models with lattice Coulombic potentials are clearly needed in order to check the validity of our theoretical predictions.

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Figure Captions

Fig.1. Gas-liquid coexistence curves for simple tetragonal cubic lattices predicted by pure DH theory for different values of the lattice anisotropy parameter $\alpha$.

Fig.2. Critical parameters as a function of degree of anisotropy: (a) critical and tricritical temperatures; (b) critical density; (c) tricritical density.

Fig.3. Phase diagrams of electrolytes on simple tetragonal lattices with sublattice ordering for different degrees of anisotropy: (a) for $\alpha = 1$ and $\alpha = 0.1$; (b) for $\alpha = 15$. Dashed lines show the metastable gas-liquid coexistence curves predicted by pure DH theory.

Fig.4. Phase diagrams for ionic systems on body-centered tetragonal lattices with sublattice ordering. The gas-liquid coexistence curves predicted by pure DH theory are shown by dashed lines.
Fig. 1
Fig. 2a
Fig. 2b
Fig. 2c
Fig. 3a
Fig. 3b
Fig. 4