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Thermodynamics and phase transitions of electrolytes on lattices with different discretization parameters

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Lattice models are crucial for studying thermodynamic properties in many physical, biological and chemical systems. We investigate the lattice restricted primitive model (LRPM) of electrolytes with different discretization parameters in order to understand thermodynamics and the nature of phase transitions in systems with charged particles. A discretization parameter is defined as a number of lattice sites that can be occupied by each particle, and it allows one to study the transition from the discrete picture to the continuum-space description. Explicit analytic and numerical calculations are performed using the lattice Debye–Hückel approach, which takes into account the formation of dipoles, the dipole–ion interactions and correct lattice Coulomb potentials. The gas–liquid phase separation is found at low densities of charged particles for different types of lattices. The increase in the discretization parameter lowers the critical temperature and the critical density, in agreement with Monte Carlo computer simulation results. In the limit of infinitely large discretization our results approach the predictions from the continuum model of electrolytes. However, for the very fine discretization, where each particle can only occupy one lattice site, the gas–liquid phase transitions are suppressed by order–disorder phase transformations.

1. Introduction

Electrostatic interactions are important in various physical, chemical and biological processes [1]. However, a full thermodynamic description of systems with charged particles is still far from complete. In the last decade, this subject has attracted a lot of attention due to controversial theoretical and experimental issues on the nature of phase transitions in ionic fluids [2–4].

Lattice models have been used extensively for investigations of different phenomena in chemistry, physics and biology. For example, the Ising model, which is a lattice gas model, is fundamental for understanding critical phenomena in non-charged systems. This observation has strongly stimulated many studies of ionic fluids utilizing the discretized lattice models [5–18]. There are several advantages in using the lattice approach for systems with the particles interacting via long-ranged Coulomb potentials. The production of ion pairs and dipole–ion interactions can be described better than in continuum-space models

[10, 13]. Lattice models are also computationally much more efficient with respect to the time and length scales [6, 7, 14, 15]. Monte Carlo computer simulations of charged systems on discretized lattices are faster by a factor of 5–100 than the corresponding continuum models [6, 7, 15].

If we define a diameter of a charged particle as σ and the lattice cell size as a, then a discretization parameter $\zeta = \sigma/a$ specifies how close the lattice system approaches the continuum behaviour. The case of $\zeta = 1$ corresponds to the standard lattice model of electrolytes where each particle occupies no more than one lattice site. When the discretization parameter becomes very large the system of charged particles does not feel the underlying lattice anymore and its thermodynamic properties become indistinguishable from the properties of continuum electrolytes.

Theoretical investigations of thermodynamics and phase behaviour of lattice models of electrolytes have followed several different approaches [8–13, 16, 17]. The hierarchical reference theory [9] utilized the renormalization group methods to calculate thermodynamic properties of ionic fluids on lattices. Ciach and co-worker [12, 16, 17] used the field-theoretical methods to analyse different properties of

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lattice electrolytes. Other field-theory approaches for lattice and off-lattice electrolytes use the Hubbard–Stratonovich transformation [19] or method of collective variables [20, 21]. However these methods are mathematically very complicated and the predictions for lattice systems, as compared with Monte Carlo simulations [6, 22], are mostly of qualitative nature. A different theoretical method [10, 11, 13, 22] is based on the physically more transparent Debye–Hückel (DH) approach. In this method the free energies of lattice electrolytes are obtained by solving the lattice versions of the usual Debye–Hückel equations for general dimensions. This method can provide a reasonable thermodynamic description of different lattice models of charged particles, such as charge-asymmetric [13] and anisotropic lattices [11, 22], as compared with computer simulations and other theoretical approaches [16, 17].

A full thermodynamic investigation of the continuum ($\zeta = \infty$) restricted primitive model (RPM), which is a system of equal-size hard-sphere ions carrying positive and negative charges, using the Debye–Hückel approach has shown that in the system there are gas–liquid phase transitions driven by electrostatic interactions [23]. However, a systematic study of the lattice version of the RPM [10] (with $\zeta = 1$) indicates that these phase transitions are suppressed on simple-cubic (sc) and body-centred cubic (bcc) lattices because of thermodynamically more favourable charge-ordering phase transformations. These theoretical observations are in agreement with the predictions from Monte Carlo computer simulations [6, 22]. The different thermodynamic properties of lattice and continuum models of electrolytes raised the question of crossover phase behaviour of ionic systems with intermediate lattice discretization. Ciach and co-worker [12, 16, 17], using mean-field arguments and renormalization group methods, discussed some features of phase transitions for these lattice models. However, full thermodynamic and phase properties of these systems are not investigated yet. The goal of this article is to fill this gap.

In this paper we study the lattice models of charged particles with different discretization parameters by applying the Debye–Hückel approach. In addition, we modify the original lattice model of electrolytes [10] ($\zeta = 1$) that utilized a mean-field assumption about electrostatic potentials and led to several unphysical features at high densities of ions. The paper is organized in the following way. In section 2 we provide a general description of lattice models of electrolytes using the Debye–Hückel method. Specific calculations and discussions of thermodynamic properties of charged systems for lattices with different discretization

parameters are given in section 3. Our results and conclusions are summarized in section 4.

2. General lattice DH theory

Consider the lattice restricted primitive model (LRPM) of electrolytes in three dimensions. Note that our method can be easily generalized in d dimensions [10], however, for clarity we prefer to explain the details using three-dimensional lattices. The model consists of an equal number of oppositely charged particles, with charges q_0 or $-q_0$, correspondingly. Due to the overall neutrality, the densities of positive and negative ions are equal to each other, $\rho_+ = \rho_- = (1/2)\rho_1$. The particles have a spherical shape with the charge located in the centre of the sphere. The diameter of the particle is given by $a\zeta$, where a is a nearest neighbour lattice distance and ζ is the discretization parameter: see figure 1. Thus, in the special case $\zeta = 1$ each ion occupies a single site, while $\zeta = \infty$ corresponds to a continuum model. All particles interact only through Coulombic potential and hard-core exclusion. Then the free energy of the system can be written as a sum of two terms, $F = F^{\text{id}} + F^{\text{el}}$. It allows one to calculate the
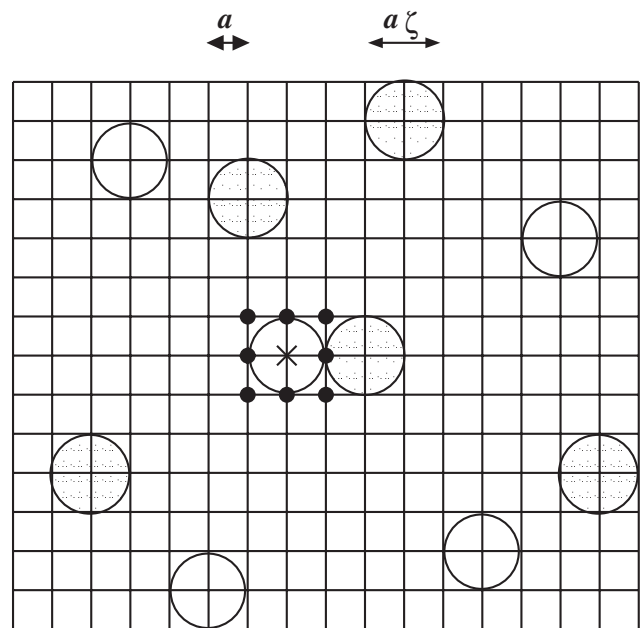

Figure 1. A schematic picture of the lattice model of electrolytes with different discretizations. Large empty circles denote the positive particles, while large grey circles correspond to the negative ions. The ions are spheres with the diameter $a\zeta$, where a is the distance between the nearest lattice sites. The position of the origin is marked by a cross. Small filled circles indicate the position of lattice sites in the exclusion zone of the central positive ion.

thermodynamic properties of the system, such as chemical potentials and the pressure, as given by [10, 23]

$$\bar{f} \equiv -\frac{F}{k_B T V},$$

$$\bar{\mu}_i \equiv \frac{\mu}{k_B T} = -\frac{\partial \bar{f}}{\partial \rho_i},$$

$$\overline{P} \equiv \frac{P}{k_B T} = \bar{f} + \sum_i \rho_i \bar{\mu}_i. \tag{1}$$

Since every positively charged particle has a corresponding negatively charged ion, we can introduce new hypothetical particles with chemical potential $\overline{\mu}_1 = \overline{\mu}_- + \overline{\mu}_+$. Then the two-component system is easily mapped into the one-component system with an overall density of hypothetical particles given by ρ_1. The conditions for phase transitions are specified by

$$\overline{\mu}_1(T, \rho_{\text{liq}}) = \overline{\mu}_1(T, \rho_{\text{vap}}), \quad \overline{P}(T, \rho_{\text{liq}}) = \overline{P}(T, \rho_{\text{vap}}). \tag{2}$$

Let us take an arbitrary particle and assume that its charge q_i is in the centre of the coordinates. Then all lattice sites in the system can be divided into three groups with respect to the position of this fixed particle as shown in figure 1. The first one consists of just one lattice site, $\mathbf{r} = (0, 0, 0)$, where the charge of the particle is located. The second group is made of other lattice sites in the exclusion zone where no centres of other particles can be found. All lattice sites outside the exclusion zone are in the third group. To determine the average electrostatic potential at each lattice site we can derive the linearized lattice Poisson–Boltzmann equations following the standard Debye–Hückel procedures [10, 24]. For the central lattice site we obtain

$$\Delta\varphi(\mathbf{r} = (0, 0, 0)) = -\frac{4\pi}{D v_0} q_i, \tag{3}$$

with v_0 being a unit cell volume. In this equation $\Delta\varphi$ is the lattice Laplacian which is defined as follows [10],

$$\Delta\varphi(\mathbf{r}) = -\frac{6}{c_0 a^2} \sum_{nn} [\varphi(\mathbf{r} + \mathbf{a}) - \varphi(\mathbf{r})], \tag{4}$$

where $\mathbf{a}$ is a nearest-neighbour vector and the summation runs over all c_0 nearest neighbours.

The number of the lattice sites in the exclusion zone (the second group) is determined by the discretization parameter ζ and the type of lattice. For example, for sc lattices with $\zeta = 1, 2, 3, 4$ or 5 these numbers are 0, 26, 92, 250 and 484, correspondingly [6]. Since there are no charges in the exclusion zone outside of the central

lattice site, the linearized lattice Poisson–Boltzmann equations have a simple form [10, 24],

$$\Delta\varphi(\mathbf{r}_{\text{ex}}) = 0, \tag{5}$$

where $\mathbf{r}_{\text{ex}}$ specifies the lattice sites in the exclusion zone but not the central point.

Similarly, for the lattice sites in the third group, i.e. outside of the exclusion zone, the linearized lattice Poisson–Boltzmann equations are given by [10, 24]

$$\Delta\varphi(\mathbf{r}_{\text{out}}) = \kappa^2 \varphi(\mathbf{r}), \tag{6}$$

where $\mathbf{r}_{\text{out}}$ describes the lattice points outside the exclusion zone and $\kappa^2 = 4\pi\beta\rho_1 q_0^2/D$ is the inverse squared Debye screening length with $\beta = 1/k_B T$.

Linearized lattice Poisson–Boltzmann equations (3), (5) and (6) can be written in a unified way as

$$\Delta\varphi(\mathbf{r}) = \kappa^2 \varphi(\mathbf{r}) - A_0 \delta(\mathbf{r}) - \sum_{\mathbf{r}_{i,\text{ex}}} A_i \delta(\mathbf{r} - \mathbf{r}_{i,\text{ex}}), \tag{7}$$

where the coefficients A_0 and A_i are determined explicitly from equations (3), (5) and (6), and the summation is over all lattice sites from the second group. Note that $\delta(\mathbf{r})$ is a lattice delta-function defined as

$$\delta(\mathbf{r} - \mathbf{r}_0) = \begin{cases} 1, & \mathbf{r} = \mathbf{r}_0; \\ 0, & \mathbf{r} \neq \mathbf{r}_0. \end{cases} \tag{8}$$

Equation (7) can be solved via Fourier transformation and it yields the average electrostatic potential $\varphi(\mathbf{r})$ at every point of the lattice.

Note, that in the original lattice Debye–Hückel approach [10, 11, 13] the electrostatic potential at each site was found by averaging over all nearest neighbours. This mean-field assumption provided a reasonable description of thermodynamic properties of lattice electrolytes at low densities of charged particles, however it led to some unphysical predictions at high densities where correlations are important. Here we solve exactly linearized lattice Poisson–Boltzmann equations at all lattice sites and for all possible discretizations. Thus our method provides a consistent thermodynamic description of lattice electrolytes for all ranges of parameters.

The solution of equation (7) then allows one to calculate the average electrostatic potential at the central site due to all ions except the one fixed at the origin,

$$\psi_i = \varphi_i(\mathbf{r}, x^2) - \varphi_i(\mathbf{r}, x^2 = 0), \tag{9}$$

where we introduced a dimensionless parameter $x = \kappa a$. It can be shown that the general expression for ψ_i is given by

$$\psi_i = \frac{4\pi q_i}{D v_0} G(x^2), \tag{10}$$

where the specific functional form of $G(x^2)$ is determined again from equations (3), (5) and (6).

Since the ideal part of the free energy of the lattice model for charged particles is known [10], we only have to calculate the electrostatic contribution. It can be done by utilizing the Debye charging procedure [10, 24],

$$\bar{f}^{\mathrm{el}} = -\frac{1}{k_{\mathrm{B}} T V} \sum_j q_j \int_0^1 \psi_j(\lambda q) \mathrm{d}\lambda,$$

$$-\frac{1}{12 v_0} \int_0^{x^2} G(x^2), \mathrm{d}(x^2). \tag{11}$$

All thermodynamic properties and phase behaviour of the system can be obtained from the free energy through standard calculations [10, 23]. It should also be noted that the Debye–Hückel approach is a mean-field theory and only classical critical behaviour is expected in this case.

3. Lattice electrolytes with different discretization parameters

3.1. Pure DH theory for sc, bcc and fcc lattices with $\zeta = 1$

Let us discuss in more detail the three-dimensional lattices with the smallest value of the discretization parameter, $\zeta = 1$. This corresponds to the situation when each particle occupies one lattice site. Because in this case there are no lattice sites in the exclusion zone, the linearized lattice Poisson–Boltzmann equation (7) can be written in the following form,

$$\Delta \varphi(\mathbf{r}) = \kappa^2 \varphi(\mathbf{r}) - A_0 \delta(\mathbf{r}). \tag{12}$$

The solution of this equation is found via Fourier transformation,

$$\varphi(\mathbf{r}) = A_0 \frac{a^2}{6} \int_k \frac{\exp(\mathrm{i} \mathbf{k} \cdot \mathbf{r})}{(x^2 + 6)/(6 - J(\mathbf{k}))}, \tag{13}$$

where $\int_k \equiv (2\pi)^{-3} \int_{-\pi}^{\pi} \mathrm{d}^3 \mathbf{k}$, and we defined a new lattice function $J(\mathbf{k})$,

$$J(\mathbf{k}) = \frac{1}{c_0} \sum_{nn} \exp(\mathrm{i} \mathbf{k} \cdot \mathbf{r}). \tag{14}$$

The coefficient A_0 can be found with the help of equation (3),

$$\Delta \varphi(\mathbf{r} = (0,0,0)) = -\frac{4\pi q_i}{D v_0} = \kappa^2 \varphi(\mathbf{r} = (0,0,0)) - A_0$$

$$= A_0 \frac{a^2}{6} \int_k \frac{1}{((x^2 + 6)/6 - J(\mathbf{k}))} - A_0. \tag{15}$$

Defining the integrated lattice Green's function as

$$P(z) = \int_k \frac{1}{1 - z J(\mathbf{k})}, \tag{16}$$

we obtain from equation (13)

$$A_0 = \frac{4\pi q_i}{D v_0} \frac{1}{1 - [x^2/(x^2 + 6)] P[6/(x^2 + 6)]}. \tag{17}$$

Thus the average electrostatic potential at the origin is given by

$$\psi_i = \frac{4\pi q_i}{D v_0} \frac{a^2}{6} \left[\frac{1}{1 - [x^2/(x^2 + 6)] P[6/(x^2 + 6)]} \right.$$

$$\left. \times \frac{6}{x^2 + 6} P\left(\frac{6}{x^2 + 6}\right) - P(1) \right], \tag{18}$$

from which, after applying the Debye charging procedure as outlined above, the electrostatic free energy density $\bar{f}^{\mathrm{el}}$ can be easily calculated. The ideal lattice gas contribution to the free energy density is known [10],

$$\bar{f}^{\mathrm{id}} = -\frac{\rho_1^*}{v_0} \ln \rho_1^* - \frac{1 - \rho_1^*}{v_0} \ln(1 - \rho_1^*), \tag{19}$$

where $\rho_1^* = \rho_1 v_0$ is a reduced density of the free ions.

Now we can perform explicit calculations for the ionic systems on sc, bcc and fcc three-dimensional lattices. The lattice functions $J(\mathbf{k})$ are given by [10]

$$J(\mathbf{k}) = \begin{cases} \frac{1}{3}(\cos k_1 + \cos k_2 + \cos k_3) & \text{(sc)}, \\ \cos k_1 \cos k_2 \cos k_3 & \text{(bcc)}, \\ \frac{1}{3}(\cos k_1 \cos k_2 + \cos k_2 \cos k_3 \\ \quad + \cos k_1 \cos k_3) & \text{(fcc)}, \end{cases} \tag{20}$$

with $-\pi \leq k_1, k_2, k_3 \leq \pi$. The corresponding integrated lattice Green's functions can be evaluated numerically exactly by using the fact that they can be expressed in terms of elliptic integrals [10, 25].

The thermodynamic properties and phase behaviour of lattice electrolytes on sc, bcc and fcc lattices are explicitly calculated from equations (1), (18) and (19). The predicted phase coexistence curves are plotted in
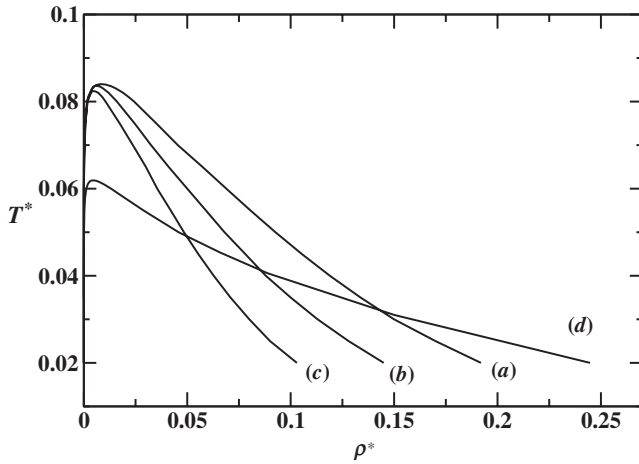
Figure 2. Phase coexistence curves predicted by pure DH theory for lattice electrolytes with $\zeta = 1$: (a) sc, (b) bcc, (c) fcc. The predictions from the continuum model for electrolytes with hard-core interactions [23] are shown in (d).

Table 1. Critical parameters for lattice electrolytes in the pure DH theory. HC corresponds to the predictions from the continuum RPM with hard-core interactions [23].

Model	T_c^*	ρ_c^*
sc	0.084377	0.007978
bcc	0.083793	0.005659
fcc	0.082415	0.004591
HC	0.061912	0.004582

figure 2, while the critical parameters are given in table 1. To analyse the effect of different discretizations we also present in figure 2 and table 1 the phase diagram and critical parameters for the pure DH model of continuum ($\zeta = \infty$) hard-core ionic fluids [23]. It can be seen that the critical temperatures for lattice models are approximately 30% higher than the corresponding continuum value. At the same time the thermodynamic properties and critical parameters of the lattice pure DH models are approaching the continuum model as the number of nearest neighbours grows from $c_0 = 6$ (sc lattice) to $c_0 = 12$ (fcc lattice), as expected. It also should be noted that in the lattice models the predicted phase coexistence curves have a physically reasonable behaviour in the limit of high density and $T \to 0$, in contrast to the original lattice DH theories [10]. This is due to the fact that the presented theoretical method correctly describes the average potential ψ at all densities of charged particles.

3.2. Pure DH theory for sc lattice with $\zeta = 2^{1/2}, 3^{1/2}$ and 2

Now we can examine the lattice models of electrolytes with discretization parameters $\zeta > 1$. Thermodynamic

properties will be expressed in terms of the reduced density and the reduced temperature, namely,

$$\rho_1^* = (a\zeta)^3 \rho_1 \quad \text{and} \quad T^* = \frac{k_B T D a \zeta}{q_0^2}. \qquad (21)$$

Consider first the ionic lattice model with $\zeta = 2^{1/2}$. In this case the exclusion zone around any charged particle consists of the lattice central site, where the charge is located, and 6 nearest-neighbour lattice sites where no other charges can be found due to geometrical constraints: see figure 1. Then the linearized lattice Poisson–Boltzmann equation (7) yields

$$\Delta\varphi(\mathbf{r}) = \kappa^2 \varphi(\mathbf{r}) - A_0 \delta(\mathbf{r}) - A_1 \sum_{nn} \delta(\mathbf{r} - \mathbf{a}_{nn}), \qquad (22)$$

where $\mathbf{a}_{nn}$ describe the position of the lattice sites in the exclusion zone outside the central site. The solution of this equation can be found again using the Fourier transformation and it is given by

$$\varphi(\mathbf{r}) = A_0 \frac{a^2}{6} \int_k \frac{\exp(i\mathbf{k} \cdot \mathbf{r})}{(x^2 + 6)/6 - J(\mathbf{k})}$$

$$+ 6A_1 \frac{a^2}{6} \int_k \frac{J(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r})}{(x^2 + 6)/6 - J(\mathbf{k})}. \qquad (23)$$

The boundary conditions to determine the coefficients A_0 and A_1 are found from equations (3) and (5):

$$-\frac{4\pi q_i}{Dv_0} = \kappa^2 \varphi(\mathbf{r} = (0,0,0)) - A_0,$$

$$0 = \kappa^2 \varphi(\mathbf{r} = (1,0,0)) - A_1. \qquad (24)$$

From equations (23) and (24) we derive

$$A_0 = \frac{4\pi q_i}{Dv_0}$$

$$\times \frac{[(6+x^2)(-1+(1/6)x^2(6+x^2)(-1+P(6/(x^2+6)))]}{-(1+x^2)(6+x^2)+x^2(7+x^2)P(6/(x^2+6))}, \qquad (25)$$

$$A_1 = -\frac{4\pi q_i}{Dv_0}$$

$$\times \frac{[(1/6)x^2(6+x^2)(-1+P(6/(x^2+6)))]}{-(1+x^2)(6+x^2)+x^2(7+x^2)P(6/(x^2+6))}. \qquad (26)$$

Thus the average electrostatic potential at the origin due to all other ions, defined in equation (9), again can

be expressed in terms of the integrated lattice Green's function $P(z)$,

$$\psi_i = \frac{4\pi q_i}{D v_0} \frac{a^2}{6}$$
$$\times \left[A_0' \left(\frac{x^2}{x^2 + 6} P\left(\frac{6}{x^2 + 6} \right) - P(1) \right) \right.$$
$$\left. + 6 A_1' \left(P\left(\frac{6}{x^2 + 6} \right) - P(1) \right) \right], \qquad (27)$$

where $A_j' = (D v_0 / 4\pi q_i) A_j$ for $j = 0$ and 1. After the Debye charging procedure, as described above in equation (11), this equation allows us to calculate the electrostatic contribution to thermodynamic properties.

The exact expressions for the free energy contributions for the lattice models with $\zeta > 1$ including hard cores are not known, but for low-densities expression (19) is still approximately valid. In addition, the continuum DH calculations [23] suggest that putting more real hard-core free energy terms does not change significantly the thermodynamic and critical properties of the electrolytes. Then the thermodynamic properties and phase behaviour of the system can be calculated in a similar way as was done for $\zeta = 1$ lattices. The critical parameters for the sc lattice model of electrolytes with $\zeta = 2^{1/2}$ are $T_c^* = 0.069$ and $\rho_c^* = 0.0054$.

For the system of charged particles on the lattice with the discretization parameter $\zeta = 3^{1/2}$ the exclusion zone around any arbitrary ion consists of 19 lattice sites: 1 central site, 6 nearest-neighbour sites and 12 next-nearest-neighbour sites. For this model the general linearized lattice Poisson–Boltzmann equation (7) has the following form:

$$\Delta\varphi(\mathbf{r}) = \kappa^2 \varphi(\mathbf{r}) - A_0 \delta(\mathbf{r}) - A_1 \sum_{nn} \delta(\mathbf{r} - \mathbf{a}_{nn})$$
$$- A_2 \sum_{nnn} \delta(\mathbf{r} - \mathbf{a}_{nnn}), \qquad (28)$$

with $\mathbf{a}_{nnn}$ defining the positions of next-nearest-neighbour lattice sites. As before, we can determine the coefficients A_0, A_1 and A_2 with the help of equations (3) and (5),

$$-\frac{4\pi q_i}{D v_0} = \kappa^2 \varphi(\mathbf{r} = (0,0,0)) - A_0,$$
$$0 = \kappa^2 \varphi(\mathbf{r} = (1,0,0)) - A_1,$$
$$0 = \kappa^2 \varphi(\mathbf{r} = (1,1,0)) - A_2. \qquad (29)$$

Unfortunately, for the lattice models with $\zeta > 2^{1/2}$ the electrostatic part of the reduced free energy cannot be expressed only in terms of the integrated lattice

Green's function. However, for explicit numeric evaluations of the thermodynamic properties the following equality can be used [22, 26]

$$\int_k \frac{\exp[i\mathbf{k} \cdot (lx, my, nz)]}{\alpha - J(\mathbf{k})}$$
$$= 3 \int_0^\infty dt \, \exp(-3\alpha t) I_l(t) I_m(t) I_n(t), \qquad (30)$$

where $I_k(t)$ is a modified Bessel function of the first kind. Then the thermodynamic calculations indicate that the critical parameters for the system of charged particles on the lattice with $\zeta = 3^{1/2}$ are given by $T_c^* = 0.063$ and $\rho_c^* = 0.0047$.

A similar procedure can be performed for the lattice model of electrolytes with the discretization parameter $\zeta = 2$. The schematic picture for this model is shown in figure 1. In this case there are 27 lattice sites in the exclusion zone. The general linearized lattice Poisson–Boltzmann equation (7) can be written as

$$\Delta\varphi(\mathbf{r}) = \kappa^2 \varphi(\mathbf{r}) - A_0 \delta(\mathbf{r}) - A_1 \sum_{nn} \delta(\mathbf{r} - \mathbf{a}_{nn})$$
$$- A_2 \sum_{nnn} \delta(\mathbf{r} - \mathbf{a}_{nnn}) - A_3 \sum_{nnn} \delta(\mathbf{r} - \mathbf{a}_{nnn}). \qquad (31)$$

The solution of this equation leads to the determination of the average electrostatic potential, which allows one to obtain the electrostatic contribution to the free energy density. The resulting thermodynamic calculations yield the following values of the critical parameters for this model: $T_c^* = 0.066$ and $\rho_c^* = 0.0060$.

Critical parameters for lattice models of ionic systems with different discretizations, obtained in pure DH theory, are shown in figure 3 as a function of $1/\zeta^2$. This scaling is based on heuristic arguments as discussed in [15, 18]. It can be seen that the increase in the discretization parameter ζ generally lowers the values of critical temperature and density, although the dependence is non-monotonic. This noisy behaviour of critical parameters, especially for non-integer ζ, has also been observed in Monte Carlo computer simulations of lattice models with large $\zeta \geq 5$ [15].

3.3. *Bjerrum ion pairing for lattices with $\zeta = 1$*

It is known that the pure Debye–Hückel theory, which takes into account only free ions, is not successful for the description of thermodynamic properties of electrolytes at low temperatures [10, 23]. At these conditions the positive and negative particles have a tendency to stick together in ion pairs. The framework of the lattice description of ionic systems is very convenient for complete analysis of the process of ion pairing, and it
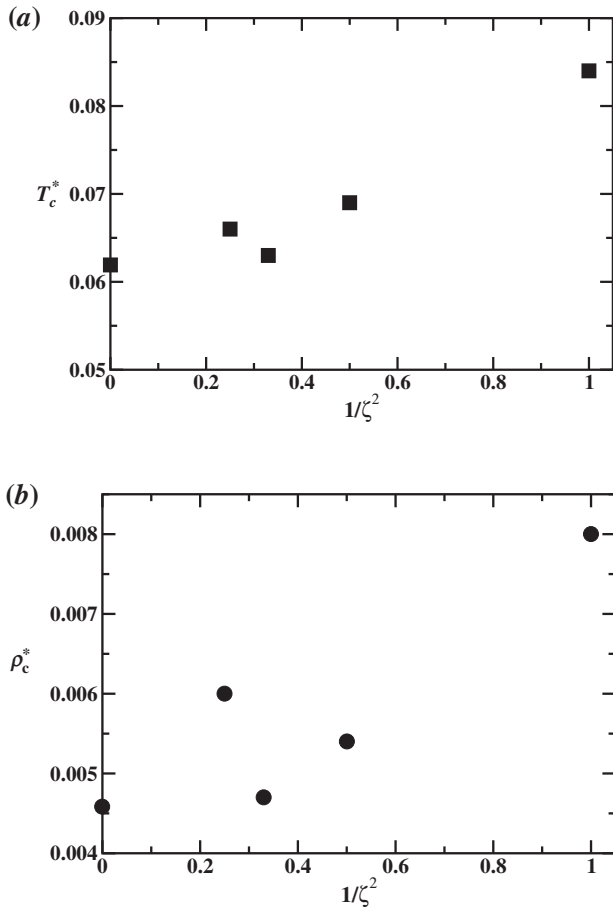
(a)

(b)

Figure 3. Critical parameters for lattice models of electrolytes for pure DH theory as a function of inverse squared lattice discretization parameters ζ for simple cubic lattices: (a) critical temperatures and (b) critical densities.

avoids the problem encountered in the continuum models of electrolytes [10, 23].

Here we consider the pairing as a reversible chemical reaction of the association of positive and negative ions and the production of neutral pairs. This process is controlled by equilibrium constant $K(T)$, which can be determined from the densities of different species. Ion pairs are specified by a density ρ_2 and a chemical potential μ_2. In the simplest Debye–Hückel–Bjerrum (DHBj) approximation we neglect the Coulombic interactions between ion pairs and free charged particles [10, 23].

The condition for chemical equilibrium between the ion pairs and free ions means that $\mu_2 = \mu_+ + \mu_- = \mu_1$. Let us introduce thermodynamic activities of the particles in the system:

$$z_1 = 2z_+ = 2z_-, \quad z_1 = \frac{2\theta_1}{\Lambda_1^3} e^{\overline{\mu}_1}, \quad z_2 = \frac{\theta_2}{\Lambda_2^6} e^{\overline{\mu}_2}, \quad (32)$$

where Λ_i denotes the de Broglie wavelengths and $\Lambda_+ = \Lambda_- = \Lambda_1 = \Lambda_2$; the parameters θ_i define the appropriate internal configurational partition functions [10, 23]. The chemical equilibrium condition can be expressed in the form of the mass-action law, $z_2 = (1/4)Kz_1^2$, which yields for equilibrium constant $K(T)$,

$$K(T) = \theta_2(T) = \sum_{nn} \exp[-\beta q_0 \varphi(\mathbf{a}_{nn})]$$

$$= c_0 \exp[-\beta q_0 \varphi(\mathbf{a}_{nn})]. \quad (33)$$

With the help of Widom's potential-distribution theorem [10, 27], the chemical potential for free ions is given by

$$\overline{\mu}_1 = \ln\left(\frac{\rho_1^*}{1 - \rho_1^* - 2\rho_2^*}\right) + \ln\left(\frac{\Lambda_1^3}{\theta_1}\right) + \overline{\mu}_1^{el}. \quad (34)$$

To obtain the corresponding expression for the chemical potential of ion pairs we use the Bethe approximation [10, 13, 28]. In this case it yields

$$z_2 = \frac{(2\rho_2^*/c_0)[1 - (2\rho_2^*/c_0)]}{(1 - \rho_1^* - 2\rho_2^*)^2}, \quad (35)$$

and, finally,

$$\overline{\mu}_2 = \ln\left(\frac{(2\rho_2^*/c_0)[1 - (2\rho_2^*/c_0)]}{(1 - \rho_1^* - 2\rho_2^*)^2}\right) + \ln\left(\frac{\Lambda_2^6}{\theta_2}\right). \quad (36)$$

Using the expression for the mass-action law and equations (32), (34) and (36), we obtain

$$\rho_2^* = \frac{c_0}{4}\left[1 - \left(1 - c_0(\rho_1^*)^2\right.\right.$$

$$\left.\left.\times \exp\left\{\frac{2\pi a^3}{3T^* v_0}\left[\frac{P(6/(x^2+6))-1}{(1-(x^2)/(x^2+6))P(6/(x^2+6))}\right]\right\}\right)^{1/2}\right].$$

$$(37)$$

This expression specifies the density of ion pairs in terms of densities of free charged particles.

Because the ion pairs are neutral, in the DHBj approximation they do not contribute to the electrostatic free energy. Thus,

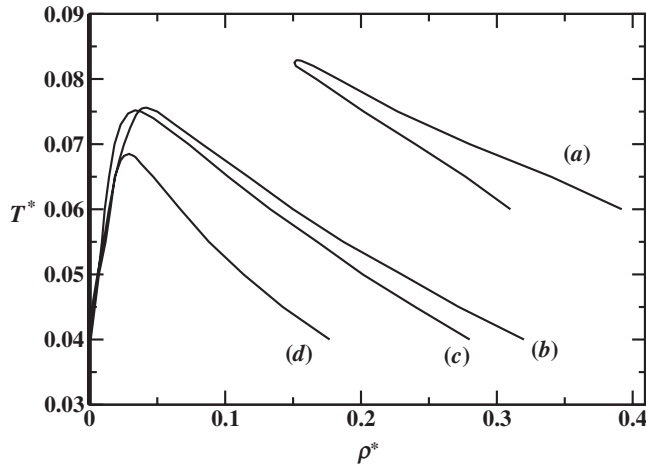$$\bar{f} = \bar{f}^{id}(\rho_1^*, \rho_2^*) + \bar{f}^{el}(\rho_1^*), \quad (38)$$

Figure 4. Phase coexistence curves of ionic systems calculated for (*a*) sc lattice in the DHBj approximation; and using the full DHBjDI approach for (*b*) sc, (*c*) bcc and (*d*) fcc lattices.

where the ideal contribution to free energy is given by [10]

$$\bar{f}^{id}(\rho_1^*, \rho_2^*) = \rho_1^* \ln \rho_1^* - (1 - \rho_1^* - 2\rho_2^*) \ln (1 - \rho_1^* - 2\rho_2^*)$$
$$- \rho_2^* \ln \rho_2^* - (\rho_2^* - 3) \ln (1 - 2\rho_2^*/c_0). \quad (39)$$

The phase coexistence curve for the sc lattice in the DHBj approximation is shown in figure 4. The critical temperature is slightly lower, while the critical density is much larger than in the pure DH approximation. However, it also has an unphysical banana-like shape, and this is is due to the neglect of electrostatic interactions of ion pairs with free charged particles, as explained for continuum and lattice models of electrolytes [10, 23].

3.4. Dipole–ion interactions for lattices with $\zeta = 1$

Clearly unphysical phase behaviour in the DHBj approximation is due to the fact that the properties of ion pairs as dipoles are not taken into account. As was shown earlier [10, 23], for the realistic description of ionic fluids it is important to consider the ion pairs as dipoles that interact with residual free charged particles. These solvation effects eliminate the unphysical phase behaviour and provide a better agreement between the calculated critical parameters and the parameters estimated from the computer simulations [10, 23].

Let us consider an arbitrary dipole particle that occupies 2 neighbouring lattice sites. Let us assume that the positive charge of the particle is at site $(0, 0, 0)$, while the negative charge is at $(1, 0, 0)$. The linearized lattice

Poisson–Boltzmann equation (7) in this case can be written in the following form,

$$\Delta\varphi(\mathbf{r}) = \kappa^2\varphi(\mathbf{r}) - A_0\delta(\mathbf{r}) - A_1\delta(\mathbf{r} - (1, 0, 0)). \quad (40)$$

Comparing with equation (12), we note that the last 2 terms in this expression reflect the fact that the particle is a dipole, consisting of two opposite charges. Equation (40) can be solved as before,

$$\varphi(\mathbf{r}) = \frac{a^2}{6} \int_k \frac{A_0 + A_1 \exp[i\mathbf{k} \cdot (-1, 0, 0)]}{(x^2 + 6)/(6 - J(\mathbf{k}))} \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (41)$$

with coefficients A_0 and A_1 determined from the following conditions:

$$\Delta\varphi(\mathbf{r} = (0, 0, 0)) = -\frac{4\pi q_+}{Dv_0} = \kappa^2\varphi(\mathbf{r} = (0, 0, 0)) - A_0,$$
$$(42)$$

and

$$\Delta\varphi(\mathbf{r} = (1, 0, 0)) = -\frac{4\pi q_-}{Dv_0} = \kappa^2\varphi(\mathbf{r} = (1, 0, 0)) - A_1.$$
$$(43)$$

These equations lead to the expression for the average electrostatic potential ψ_i^{DI} due to all ions except the positive ion fixed at $(0, 0, 0)$ and negative ion fixed at $(1, 0, 0)$,

$$\psi_i^{DI} = \frac{4\pi q_i}{Dv_0} \frac{a^2}{6} \left[\frac{x^2(1 - P(6/(x^2 + 6)))}{6 - x^2 + (x^4/(x^2 + 6))P(6/(x^2 + 6))} \right]$$
$$= \frac{4\pi q_i}{Dv_0} \frac{a^2}{6} G(x^2), \quad (44)$$

where we defined an auxiliary function $G(x^2)$,

$$G(x^2) = \frac{x^2(1 - P(6/(x^2 + 6)))}{6 - x^2 + (x^4/(x^2 + 6))P(6/(x^2 + 6))}. \quad (45)$$

The contribution to the free energy density due to the interactions between dipoles and free ions can be calculated from

$$\bar{f}^{DI} = -\frac{2\pi\rho_2^*}{3T^*v_0} \frac{1}{x^2} \int_0^{x^2} G(x^2) \, dx^2. \quad (46)$$

The overall free energy density of the system can be written as

$$\bar{f} = \bar{f}^{id}(\rho_1^*, \rho_2^*) + \bar{f}^{el}(\rho_1^*) + \bar{f}^{DI}, \quad (47)$$

Table 2. Critical parameters from the full DHBjDI theory for lattice and continuum electrolytes. For comparison, the estimates of Monte Carlo computer simulations are also shown.

Model	T_c^*	ρ_c^*
sc	0.0756	0.0422
bcc	0.0752	0.0336
fcc	0.0686	0.0292
Continuum [23]	0.0522–0.0554	0.0244–0.0259
Simulations [7, 15, 29]	0.049	0.06–0.08

where $\bar{f}^{id}(\rho_1^*, \rho_2^*)$ is given by equation (38). From these equations all thermodynamic properties can be obtained.

The resulting phase coexistence curves and the critical parameters for sc, bcc and fcc lattices estimated using the full DHBjDI approach are presented in figure 4 and table 2, respectively. The predicted critical temperatures are decreasing as the number of nearest neighbours goes up, but they are still 25–30% higher than the corresponding values for the continuum DHBjDI theory [23] and for the Monte carlo simulations [7, 15, 29]. At the same time, the critical densities are approaching the predictions of continuum RPM calculations, while deviating significantly from the computer simulation estimates [7, 23, 29].

4. Summary and conclusions

A theoretical investigation of ionic systems on lattices with different discretizations is presented. A general lattice theory, based on the Debye–Hückel approach, is developed for lattices with any discretization parameter. The theory is applied for explicit calculations of thermodynamic properties, phase behaviour and critical parameters for several lattice models of electrolytes.

The simplest version of general lattice theory, the pure Debye–Hückel theory that takes into account only the free ions, is utilized for obtaining the thermodynamic properties of sc, bcc and fcc lattices for the discretization parameter $\zeta = 1$, and for sc lattices with $\zeta = 2^{1/2}$, $3^{1/2}$ and 2. All considered cases exhibit the low-density gas–liquid phase transitions. As expected, with the increase in the lattice discretization parameter ζ the critical parameters, generally, are decreasing and approaching the values obtained in the continuum RPM treatment of ionic fluids [23] which corresponds to the $\zeta = \infty$ case. The behaviour of the critical parameters is non-monotonic, especially for non-integer ζ, in agreement with observations from the latest Monte Carlo computer simulations for large discretization parameters ($\zeta \geq 5$) [15].

For ionic fluids on the sc, bcc and fcc lattices with $\zeta = 1$, a more realistic theoretical description, which takes into account the creation of ion pairs and the ion–dipole interactions, is developed. The consideration of ion pairs as neutral species (the DHBj approach) slightly lowers the critical temperature and significantly increases the critical density, while the overall phase coexistence curves have unphysical banana-like shapes. This unphysical behaviour is cured when the ion pairs are treated as dipoles that interact with the residual free charged particles. The resulting critical temperatures decrease even more, while the values for critical densities are also lower. The critical temperatures for the lattice electrolytes are slightly higher than the continuum RPM values and the computer simulation estimates. The predicted critical densities for the lattice models are essentially the same as in the corresponding continuum models for electrolytes. However, they are much lower than the critical densities from Monte Carlo simulations. This behaviour is typical for lattice models.

Our theoretical approach allows us to calculate the thermodynamic properties of ionic systems at low densities. However, at higher densities the sublattice ordering becomes very important in sc and bcc lattice models of electrolytes [8, 10]. The original lattice Debye–Hückel approach [10] was able to capture the ordering processes. It was predicted that the sublattice ordering would suppress the gas–liquid phase coexistence and the tricritical point would appear, in accord with recent lattice computer simulations [22]. The predicted tricritical density was in agreement with the estimates from Monte Carlo computer simulations [22], while the critical temperature was overestimated. We plan to investigate the sublattice ordering using the modified lattice DH method, developed in this paper, in the near future. In addition, our theoretical method might be used to investigate many other problems related to ionic fluids, such as the effect of additional short-range interactions, the size asymmetry and charge asymmetry, and the multi-component mixtures.

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