

Thermodynamics of electrolytes on anisotropic lattices

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(Received 6 July 2003; published 18 December 2003)

The phase behavior of ionic fluids on simple cubic and tetragonal (anisotropic) lattices has been studied by grand canonical Monte Carlo simulations. Systems with both the true lattice Coulombic potential and continuous-space $1/r$ electrostatic interactions have been investigated. At all degrees of anisotropy, only coexistence between a disordered low-density phase and an ordered high-density phase with the structure similar to ionic crystal was found, in contrast to recent theoretical predictions. Tricritical parameters were determined to be increasing functions of anisotropy parameters which is consistent with theoretical calculations based on the Debye-Hückel approach. At large anisotropies a two-dimensional-like behavior is observed, from which we estimated the dimensionless tricritical temperature and density for the two-dimensional square lattice electrolyte to be $T_{tri}^* = 0.14$ and $\rho_{tri}^* = 0.70$.

DOI: 10.1103/PhysRevE.68.066110

PACS number(s): 64.60.-i, 02.70.Rr, 05.70.Fh, 64.70.-p

I. INTRODUCTION

After controversial experimental results on the nature of ionic criticality [1–3] the studies of critical phenomena in ionic fluids received a fresh impetus, and over the past decade substantial progress has been made [3,4]. However, a complete thermodynamic description of electrolyte systems is still unavailable.

The simplest and most frequently employed model system for both theoretical and Monte Carlo investigations of Coulombic systems is the restricted primitive model (RPM), which is a gas of equisized hard-sphere ions carrying positive and negative charges of equal magnitude. From the theoretical point of view, a reasonable description of the RPM in the critical region has been obtained at a mean-field level using integral equations approach [6–8] and Debye-Hückel theory [4,5]. While theoretical predictions of the critical parameters [5,8,9] agree reasonably well with those obtained in computer simulations [10,11], recent Monte Carlo investigations of ionic systems indicate a nonclassical Ising-like asymptotic critical behavior [12]. Moreover, predictions of different mean-field theories for charge- and size-asymmetric primitive systems differ significantly from each other [13–17]. In the absence of real experimental data, numerical simulations provide an important criterion for testing different theoretical methods [18–21].

In recent years, a new theoretical approach to study the thermodynamics and criticality of Coulomb systems based on the investigation of corresponding lattice models, has been introduced [15,22–26]. Being obviously less realistic than their continuous-space counterparts, lattice models are much easier to handle analytically, and the information they provide is crucial for understanding the physics of criticality. Moreover, finely discretized lattices with lattice spacing several times smaller than the ion size present substantial com-

putational advantages over continuous space simulations, while producing almost identical critical parameters and phase diagrams [10]. By contrast, when the ionic diameter is equal to the spacing of the underlying lattice, the phase diagram is drastically different. The symmetry of simple cubic or body-centered cubic lattices allows for unequal charge distribution between two identical sublattices, yielding an ordered structure similar to an ionic crystal. The competition between electrostatic interactions of the two charged sublattices and the entropy of charge separation leads then to order-disorder phase transitions and a tricritical point [10,22–24].

A systematic study of the lattice restricted primitive model (LRPM) based on the Debye-Hückel approach has shown that, in accordance with Monte Carlo simulations, a Coulombic-governed gas-liquid phase transitions seen in continuum electrolytes is totally suppressed on simple cubic and body-centered cubic lattices due to the formation of the thermodynamically more stable charge-ordered phase [23]. Ciach and Stell [25] argued that, unlike nonionic fluids, in charged systems the most important are short-range fluctuations. Consequently, they studied a LRPM supplemented with additional short-range interactions between ions and concluded that at some strength of the short-range attraction both the normal critical and tricritical point can become thermodynamically stable [25]. This leads to complex phase diagrams with two distinct phase transitions, one between gas and disordered liquid phase, and another one between disordered liquid and a charge ordered phase. Recent Monte Carlo studies have confirmed qualitatively most of these theoretical predictions but further investigations are required [27].

At low dimensions Coulombic interactions are stronger than in three-dimensional systems, and the possibility for gas-liquid phase transitions increases. This idea has been used recently in the investigation of anisotropic lattice models of electrolytes using Debye-Hückel method [26]. In this study the anisotropy mimicked the lowering of the spatial dimensionality. It has been found that for strongly anisotropic lattices gas-liquid phase coexistence is restored. How-

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ever, this theory neglects an ion clustering phenomena, which are important in charged particles systems [4,5]. Thus these theoretical predictions should be tested by computer simulations.

Current Monte Carlo studies of lattice RPM in $d=3$ dimensions employ the continuous space $1/r$ potential [10,22,27]. However, because of the discrete lattice symmetry, the correct lattice Coulomb potential differs from $1/r$ at short distances and approaches it asymptotically at large distances. This raises the question of how using the correct electrostatic interactions will affect the thermodynamics and critical behavior of ionic systems. Indeed, the lattice correction to $1/r$ potential decays rapidly with distance and thus it can be viewed in a sense as an additional short-range interaction. In order to understand correctly the underlying mechanisms of phase transitions in Coulombic systems, lattice models should be investigated with the corresponding lattice potentials.

In this paper we study the RPM on tetragonal lattices using grand canonical Monte Carlo simulations and histogram reweighting technique [32]. The correct lattice Coulomb potential is used and an Ewald-like summation is utilized to account for the long-range nature of electrostatic interactions. The paper is organized in the following way. In Sec. II the details of the model and simulation method are given. The results and discussions are presented in Sec. III, and summary and conclusions are drawn in Sec. IV. Analytical expressions and the details of lattice potential calculations are given in Appendix A.

II. ANISOTROPIC LATTICE MODEL AND SIMULATIONS METHOD

The system we have studied consists of $2N$ ions, half of them carrying charge q and half $-q$, positioned on a simple tetragonal lattice with lattice parameters ratio (degree of anisotropy) $\alpha=b/a$. The pairwise interaction potential of two ions separated by distance r_{ij} has the form (for details see Appendix A)

$$U_{ij} = \frac{1}{4\pi^2 D b} \int_{-\pi}^{\pi} \frac{e^{i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{k}}{2 + 1/\alpha^2 - (\cos k_1 + \cos k_2 + 1/\alpha^2 \cos k_3)}, \quad (1)$$

where D is the dielectric constant of the structureless solvent. Reduced quantities are obtained by scaling with the energy of the strongest ion-ion interaction in two neighboring xy planes in the continuum limit, $E_0 = q^2/Db$, and the unit cell volume, $v_0 = a^2b$, namely,

$$T^* = \frac{k_B T}{E_0}, \quad \rho^* = \frac{2Na^2b}{V}, \quad (2)$$

where V is the volume of the system.

Since the Coulomb potential is long ranged, one needs to account for interactions with particles in all images of the periodic box used in the simulations. In the case of continuous-space $1/r$ interactions the standard method to achieve this is the Ewald summation (see, e.g., Refs.

[28,29]). However, no similar method is available for the lattice Coulomb potential. Therefore, we propose the following approximate scheme, which is based on the asymptotic properties of the anisotropic lattice potential (1).

It can be shown that the potential (1) for finite α at large distances behaves as

$$U_{ij}(\mathbf{r}=(x,y,z)) \sim \frac{\alpha}{\sqrt{x^2+y^2+\alpha z^2}}. \quad (3)$$

For this potential, an Ewald-like sum can be constructed along the lines of the derivation in Ref. [29], which yields the ‘‘continuum’’ part of the energy of interactions of periodic system of $2N$ particles

$$\begin{aligned} E_1 &= \sum_{all\ space} \frac{1}{|\mathbf{r}'_{ij}|} \\ &= \sum_{i,j=1}^{2N} q_i q_j \left(\sum_{\mathbf{n}'} \frac{\alpha^2 \exp(-\pi^2 |\mathbf{n}'|^2 / \eta^2 + 2\pi i \mathbf{n}' \cdot \mathbf{r}'_{ij})}{2\pi |\mathbf{n}'|^2} \right. \\ &\quad \left. + \frac{1}{2} \sum_{\mathbf{n}'} \frac{\operatorname{erfc}(\eta |\mathbf{r}'_{ij} + \mathbf{n}'|)}{|\mathbf{r}'_{ij} + \mathbf{n}'|} \right) + \sum_{|\mathbf{n}'| \neq 0} \left(\frac{\operatorname{erfc}(\eta |\mathbf{n}'|)}{|\mathbf{n}'|} \right. \\ &\quad \left. + \alpha^2 \frac{\exp(-\pi^2 |\mathbf{n}'|^2 / \eta^2)}{\pi^2 |\mathbf{n}'|^2} \right) - \frac{\eta}{\sqrt{\pi}} \sum_{i=1}^{2N} q_i, \end{aligned} \quad (4)$$

where $r' = (x/\alpha, y/\alpha, z)$, $\mathbf{n}' = (\alpha n_x, \alpha n_y, n_z)$, $0 \leq n_x, n_y, n_z \leq 2\pi$, and $\operatorname{erfc}(x)$ is the complimentary error function. Here conducting boundary conditions have been utilized, which are less sensitive to finite-size effects [19]. As usual, the real-space damping parameter η must be chosen in such a way that all sums in Eq. (4) converge fast. In our simulations we used $\eta=5$, and the Fourier-space sums were restricted to 518 wave vectors.

The difference between the correct lattice potential (1) and its asymptotic limit (3) decays rapidly with distance: see Table I. Therefore, to obtain the total energy of electrostatic interactions, the lattice correction is added for ions in elliptic shells up to certain distance,

$$E_{total} = E_1 + \sum_{|\mathbf{r}'/L| < n_{max}} \left(U_{ij}(r) - \frac{1}{|\mathbf{r}'_{ij}|} \right). \quad (5)$$

We performed grand canonical Monte Carlo simulations on cubic boxes of length L stretched in z direction by a factor of α , under periodic boundary conditions. Distance-biased algorithm was employed for insertions and removals of pairs of unlike ions at each time step in order to facilitate acceptance, following Ref. [31]. To analyze the simulation data and obtain the coexistence curves, multihistogram reweighting techniques [32] have been used.

III. RESULTS AND DISCUSSION

To reduce possible finite-size effects, we used a system size $L^* \equiv L_{x,y}/a = L_z/b = 12$ for the isotropic lattice ($\alpha = 1$) and $\alpha = 1.2$, and $L^* = 16$ for stronger anisotropies.

TABLE I. Dimensionless lattice Coulomb potential $U_{lattice}$ (1) and its asymptotic limit U_{cont} given by Eq. (3).

Crystallographic indexes	$\alpha=1$		$\alpha=4$		$\alpha=10$	
	$U_{lattice}$	U_{cont}	$U_{lattice}$	U_{cont}	$U_{lattice}$	U_{cont}
[1 0 0]	1.0815164	1.0000000	3.192933	4.000000	4.949445	10.00000
[0 0 1]	1.0815164	1.0000000	1.028176	1.000000	1.006922	1.000000
[10 0 0]	0.1002578	0.1000000	0.410816	0.400000	1.066964	1.000000
[0 0 10]	0.1002578	0.1000000	1.000167	0.100000	0.100015	0.100000
[10 10 10]	0.0577029	0.0577350	0.094250	0.094281	0.099021	0.099015
[100 0 0]	0.0100003	0.0100000	0.040009	0.040000	0.100129	0.100000
[0 0 100]	0.0100003	0.0100000	0.010003	0.010000	0.010041	0.010000
[100 100 100]	0.0057736	0.0057733	0.009431	0.009428	0.009924	0.009901

Short initial runs were used to get a rough estimate of the location of the tricritical point. After that, typical runs involved $(1-3) \times 10^7$ Monte Carlo steps for equilibration and $(2-7) \times 10^8$ for production. We did not try to locate the second order transitions Néel line and restricted ourselves with obtaining approximate location of the tricritical point by simple linear extrapolation of the coexistence lines, as expected for $d=3$ tricriticality.

In order to separate the effect of using the correct lattice potential in simulations, we studied first the phase coexistence in LRPM on a simple cubic lattice; see Fig. 1. On a simple cubic lattice, Coulomb gas with $1/r$ potential is known to phase separate, with two coexisting phases being a low-density disordered phase and an ordered high-density ionic crystal-like phase [10,22]. The tricritical parameters estimates for the system size $L^*=12$, obtained by Panagiotopoulos and Kumar [10], are $T_{tri}^*=0.15 \pm 0.01$, $\rho_{tri}^*=0.48$

± 0.02 [10]. For the same system size, taking into account the lattice correction to the potential yields $T_{tri}^*=0.22$, $\rho_{tri}^*=0.48$ with the same accuracy. Thus the tricritical density remains the same within the error limits, but the temperature increases by the factor of 1.5. Qualitatively, the increase in the tricritical temperature should be expected since lattice Coulomb interactions are stronger than $1/r$ at short distances, which leads to a higher stability of dense phases. Nevertheless, the tricritical point is still significantly lower (by 50%) than the predictions of the Debye-Hückel theory of lattice electrolytes $T_{tri}^* \approx 0.365$ [23], but is about 10% higher than the results $T_{tri}^* \approx 0.202$ from the hierarchical reference theory (HRT) of LRPM by Brognara *et al.* [24], who also used the correct form of potential in their calculations. Note, that both of these theories agree on the tricritical density to be $\rho_{tri}^* \approx 0.38$, which is about 20% lower than our simulation results. However, while taking into account Bjerrum pairing of ions into neutral dipoles [33] in Debye-Hückel approach would supposedly produce better results by shifting the phase coexistence to lower temperatures and higher densities, the predictions of the HRT seem to be final.

The phase coexistence for different degrees of anisotropy α is shown in Fig. 1. At any α , the system shows only order-disorder phase separations and a tricritical point. Thus, the effect of stretching the lattice amounts merely to altering the tricritical point location, without changing qualitatively the topology of the phase diagram. This contrasts with the recent theory based on Debye-Hückel calculations [26] which predicts that at the lattice parameters ratio $b/a \geq 2.6$ a distinct gas-liquid phase coexistence may reappear. However, as was mentioned above, the theoretical approach of Ref. [26] disregards the Bjerrum pairing [33], or, more generally, clustering of ions, which is crucial for the thermodynamics of the gas-liquid transition in electrolytes. Typically, taking into account pairing somewhat diminishes the critical temperature but significantly increases the critical density [4,5,23]. Nevertheless, taking into consideration the ion clustering is unlikely to change the topology of the phase diagram of LRPM on the isotropic lattice. However, since the strength of the electrostatic interactions increases with anisotropy, this may lead to more profound tendency of ions to bind into neutral dipoles/clusters (mostly in xy planes), producing eventually a Kosterlitz-Thouless (KT) transition [34] line at infinite stretching. Stronger pairing then could shift

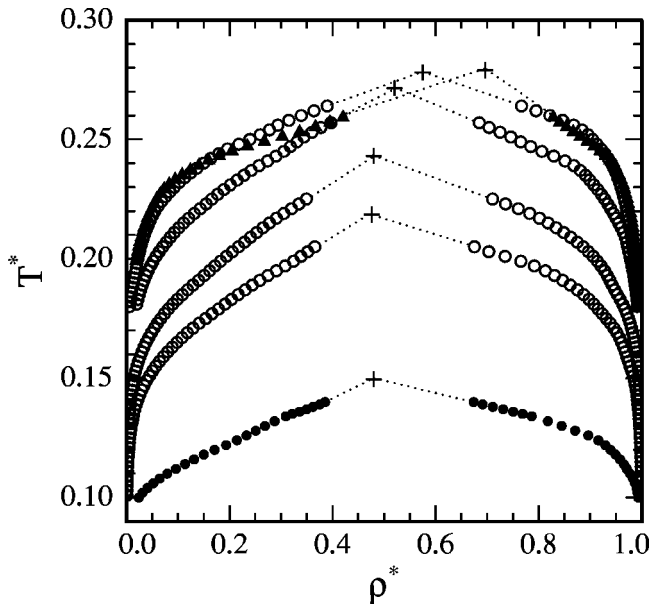


FIG. 1. Phase diagrams in LRPM with correct lattice potential on tetragonal lattices for different degrees of anisotropy (open circles). Open circles from bottom to top $\alpha=1, 1.2, 2, 4$; solid triangles correspond to $\alpha=10$. For reference, phase coexistence in LRPM on cubic lattice with $1/r$ potential [10] is shown in solid circles (see also Fig. 3).

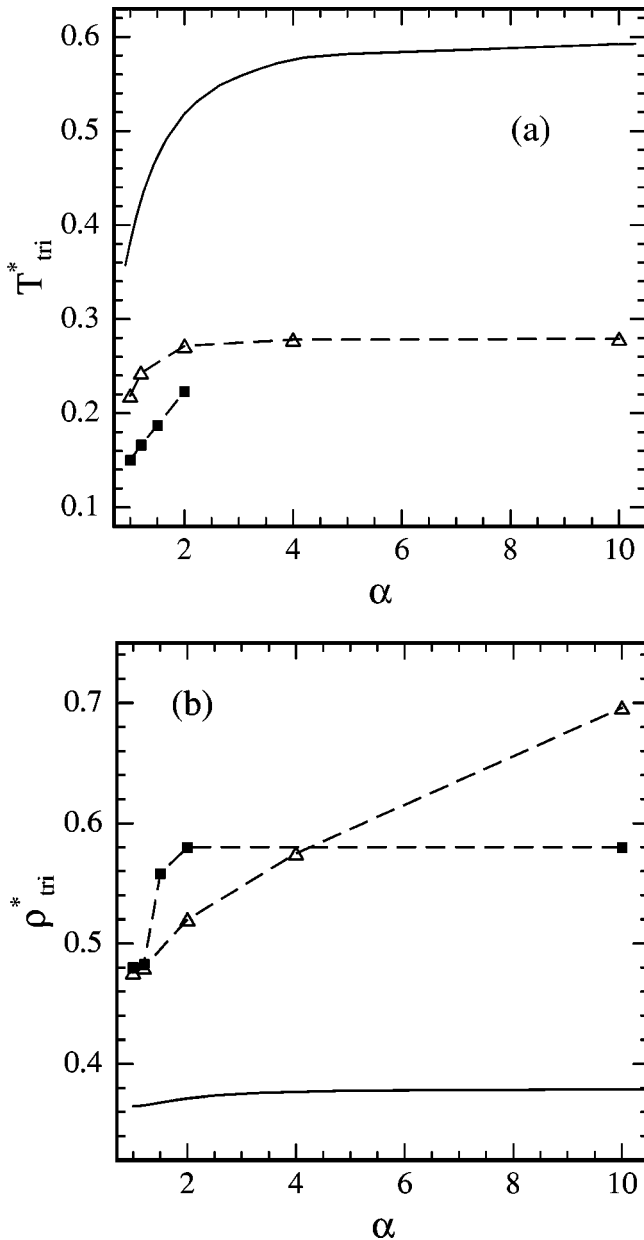


FIG. 2. Reduced tricritical parameters as a function of the lattice spacing ratio. (a) Tricritical temperature; (b) Tricritical density. Open triangles correspond to the correct lattice potential; squares are for the continuous space potential $1/r$. Dashed lines are merely guides to the eye. The analytical theory predictions are shown in solid lines [26].

the gas-liquid coexistence curve much further than in the isotropic case, again putting it completely inside the order-disorder phase envelope. It should be noted that simulations of the two-dimensional lattice Coulomb gas [35] also reveal no normal first order gas-liquid transition, but only an order-disorder phase separations [35].

Tricritical temperature and density as functions of the lattice parameters ratio α are presented in Fig. 2. As anisotropy increases, both tricritical temperature and density increase. Physical account of this behavior follows from the properties of the lattice Coulomb potential. Indeed, in z direction lattice

potential (1) behaves almost as $1/z$ (see Table I). However, in crystallographic directions different from $[001]$, the anisotropic lattice potential is much stronger than $1/r$ and decays slower. While the interactions in z direction almost do not change with α , stronger anisotropy brings stronger interactions inside the xy layers. This becomes especially important at large densities, where the average distance between ions is of the order of the lattice spacing. Therefore, the average energy per particle increases with anisotropy. As a consequence, higher temperatures are required for fluctuations to achieve a critical level, and the tricritical temperature grows. At the same time, more intensive interactions between ions lead to more active clustering. The free charges density, and hence the electrostatic part of the free energy diminishes significantly. However, the entropic part of the energy remains the same. Therefore, electrostatic interactions of two charged sublattices become comparable with the entropy of charge separation at higher overall densities, and the coexistence shifts to denser phases.

The trend for tricritical temperature and density to increase with anisotropy is correctly reproduced by the Debye-Hückel treatment of anisotropic lattices [26]: see Fig. 2. However, the quantitative agreement between theoretical predictions and simulations is not very good. While the theory predicts only a few percent increase in density at large lattice stretching, our simulations showed more significant growth. For the tricritical temperature, on the contrary, simulations yield a somewhat smaller slope.

At large stretching, increasing interactions inside xy planes result in lesser relative importance of interactions between ions with different z coordinates. At some point, interactions with ions in the same layer start dominating, and the 3D system becomes quasi-2D. Since different layers become uncoupled, due to its probabilistic nature phase separation in each of them takes place at different values of the chemical potential, and one may have configurations with gas phase in some of the layers and high-density ordered phase in the others, which prevents reliable sampling of the system. At $\alpha=10$, it turned to be impossible to obtain a reliable phase separation in a periodic system of more than one layer in z direction: at high densities the system would not equilibrate after more than 10^9 Monte Carlo steps.

To this end, for $\alpha=10$ we carried out simulations of the system consisting of only *one* plane, that is, square box with $L_x^* = L_y^* = 32$ periodic in x and y directions, with the potential (1). Using only one layer in simulations yielded a highly asymmetric phase coexistence very similar to that obtained by Teitel for Coulomb gas on two-dimensional square lattice [35], with the tricritical point located at $T_{tri}^* = 0.28$, $\rho_{tri}^* = 0.70$; see Fig. 1. But in two dimensions, the coefficient in the Laplace equation (A1) is not 4π but 2π . Since all our simulations were done with three-dimensional potential, the temperature at large anisotropies must be divided by 2 to obtain the correct 2D limit, while the density should remain intact. This yields $T_{2D}^* = 0.14$, $\rho_{2D}^* = 0.70$ which exactly coincides with the values obtained by Teitel.

It should be also noted that parts of the coexistence curve for $\alpha=10$ at intermediate densities lay below the corre-

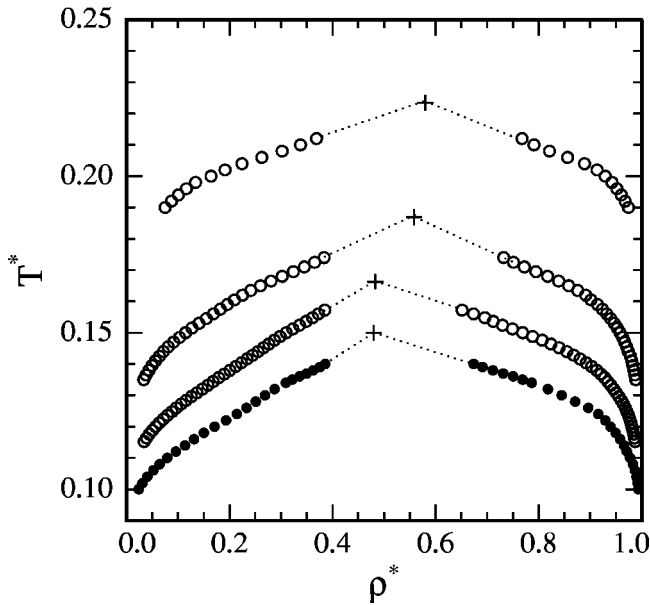


FIG. 3. Phase diagrams of LRPM with continuous-space $1/r$ Coulomb potential. From bottom to top, $\alpha=1,1.2,1.5,2$. Reduced temperature is defined by Eq. (2).

sponding curve for $\alpha=4$. However, for the latter case in contrast to $\alpha=10$, the interactions between layers are still very important and add significantly to the total free energy of the system: simulations of periodic system of only one layer produce much lower coexistence curve. Therefore, although at equal densities the energy of ions interactions inside a single layer for $\alpha=4$ is less than for $\alpha=10$, the total energy density may be higher because of the interactions between layers, and hence the temperature of phase separations would also be higher. However, this is not essential at very low or high densities where the interactions inside layers dominate anyway. Taking into account the influence of layers on each other at $\alpha=10$ probably would eliminate this intersection of the coexistence curves. Nevertheless, this hardly would change our estimate for the tricritical point location in the limit of infinite stretching, which, as it has been mentioned, coincides with the results by Teitel for two-dimensional square lattice.

To gain further insight on the behavior of LRPM on anisotropic lattices we also performed simulations with the continuous space Coulomb potential. The corresponding phase diagrams for box size $L^*=16$ and $\alpha \leq 2$ are presented in Fig. 3. At any fixed lattice stretching, the phase coexistence is very similar to the case of the true lattice potential. No normal gas-liquid phase transition is found, and the phase coexistence is between a disordered low-density phase and ordered high-density phase. The tricritical temperature shows the same trend as for the correct lattice potential, increasing with the inter-layer distance. However, since for small α the interactions are weaker now, the tricritical temperatures are lower. Nevertheless, at further increasing of anisotropy, the reduced tricritical temperature diverges.

This is directly related to the choice of the temperature units. The scaling of the temperature T with $E_0=q^2/Db$ has been maintained so far in this paper to allow comparisons

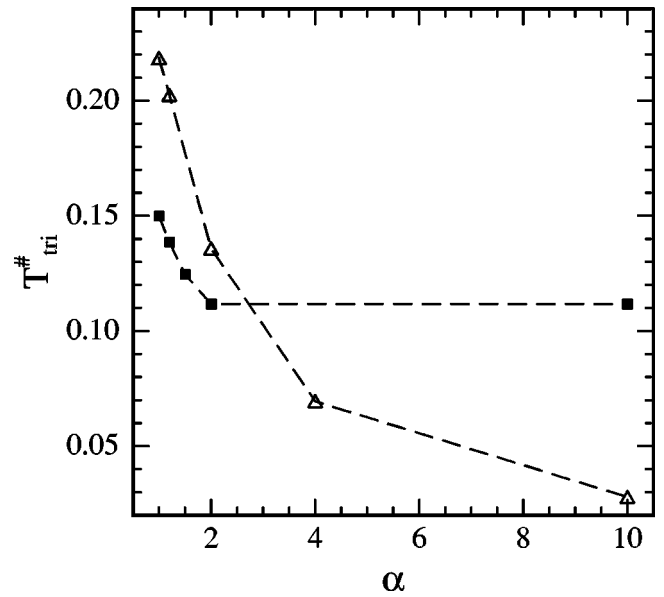


FIG. 4. Reduced tricritical temperature $T^\# = kTDa/q^2$ for the system with continuum $1/r$ Coulomb potential (solid symbols) and true lattice potential (open symbols) as a function of the anisotropy.

with earlier theoretical results. Another possible scaling is defined by the interaction energy of the two ions in the same plane, $E_0^\# = q^2/Da$ (where D is the three-dimensional dielectric constant, appropriate for the $1/r$ potential). Calculations with the temperature normalized by this energy, $T^\# = kTDa/q^2$, are shown in Fig. 4. With this scaling, the tricritical point behavior as a function of anisotropy is drastically different: the tricritical temperature for $1/r$ potential *decreases* with anisotropy, converging to $T^\# = 0.11$, which physically is more sensible. The tricritical temperature for the correct lattice potential, however, now decays to zero at high anisotropy.

Although it may seem at first sight to be a mere numerical rescaling of the temperature, $T^\# = T^*/\alpha$, actually it is not, since it reflects the difference in the appropriate energy scales for lattice and continuum potentials. From purely simulational point of view the choice of the energy (and temperature) scale is arbitrary. However, physical reasoning must be taken into account. With the correct lattice potential, increasing anisotropy leads to a qualitative change of the potential. In the limit of infinite layer separation, the in-plane potential becomes asymptotically logarithmic, which means that the in-plane interactions become stronger with increasing α . Becoming logarithmic, it also becomes independent of the in-plane length scale. These two arguments require that for the correct lattice potential the energy must be scaled with $E_0 = q^2/Db$ [see Eq. (1)], and scaling with $E_0^\# = q^2/Da$ yields unphysical zero tricritical temperature in the 2D limit. On the other hand, while for the correct lattice potential the “natural” anisotropy-independent scale of energy is set by layer-layer interactions, it is not appropriate for the discretized continuum Coulomb potential. Indeed, from the physical point of view, for $1/r$ potential increasing anisotropy is not accompanied by stronger interactions between ions. On the contrary, while interactions inside the xy planes

remain the same, due to a weaker coupling of the layers effective energy per particle diminishes, and so must the tricritical temperature. The correct scale is then obviously given by the energy of the ion-ion interactions at contact *inside* a layer, $E_0^\# = q^2/Da$. The decay of the tricritical temperature is rather fast and the temperature saturates already at the lattice parameters ratio $\alpha \approx 2$. Detailed studies of ions configurations showed that at $\alpha \geq 2$ different xy planes become totally independent of each other, and the system behaves as a quasi-2D liquid. Similarly to the true lattice potential case, to obtain phase coexistence for the limit of infinite stretching ($\alpha \geq 2$), simulations of periodic system of only one plane were carried out with box size $L=32$ and $L=48$.

The tricritical density gradually increases from $\rho_{iri}^* \approx 0.48$ for isotropic lattice to $\rho_{iri}^* \approx 0.58$ at strong anisotropy, following the trend shown by the system with correct lattice interactions; see Fig. 2(b) and Fig. 3. This again reflects the relative importance of clustering when one approaches the two-dimensional limit of infinite stretching. However, since the potential is now weaker, the limiting density is lower than in true lattice 2D systems. Also, since for $1/r$ potential the transition to the quasi-2D behavior occurs at lower degrees of anisotropy, the tricritical density saturates earlier than for true lattice system.

IV. CONCLUSIONS

In this study, grand canonical Monte Carlo simulations and histogram reweighting techniques have been used to investigate phase behavior of the restricted primitive model with correct lattice Coulomb potential on simple cubic and tetragonal lattices. Our results show that, at all degrees of anisotropy, only order-disorder phase separations and a tricritical point exist. For isotropic cubic lattice, the effect of using the correct lattice potential shows only in the value of the tricritical temperature. As anisotropy increases, both the tricritical temperature and density increase. At large anisotropy the system undergoes a qualitative shift from a three-dimensional to two-dimensional behavior. This shift only alters the tricritical parameters, with no change in the phase diagram topology. To study in detail the transition from 3D to 2D behavior, further investigations are needed. In particular, its location may depend on the system size and boundary conditions used in Ewald summation. For continuous $1/r$ potential, the properly defined reduced tricritical temperature displays an opposite trend and decreases with the anisotropy. Although exact values of the tricritical temperature and density can be influenced by finite size effects, an issue totally omitted in this study, their qualitative behavior seems physically plausible. It would be also useful to develop another procedure for Ewald-like summation for lattice potential, which will not rely on its asymptotic behavior.

The only existing theoretical treatment of Coulomb gas on anisotropic lattices based on the Debye-Hückel approach captures correctly the trend of the tricritical temperature and density behavior with anisotropy [26]. However, the absence of the anticipated normal gas-liquid transition suggests that with increasing anisotropy, stability of both ordered and dis-

ordered dense phases increases in a similar way, and the formation of an ordered structure remains thermodynamically more favorable than possible gas-liquid phase coexistence. Taking explicitly into account the ion clustering will provide a better theoretical description of thermodynamics of ionic systems on anisotropic lattices.

ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund (Grants No. 37867-G6 to A.B.K. and 38165-AC9 to A.Z.P.) for support of this research. A.B.K. also acknowledges the support of the Camille and Henry Dreyfus New Faculty Awards Program (Grant No. NF-00-056). A.Z.P. acknowledges the support of the Department of Energy, Office of Basic Energy Sciences (grant DE-FG0201ER15121). The authors would like to thank Professor M.E. Fisher for critical comments and useful suggestions.

APPENDIX A: LATTICE COULOMB POTENTIAL: EXACT REPRESENTATION AND FAST CALCULATION

Due to the discrete symmetry, the correct lattice Coulomb potential differs from continuous $1/r$. The analytical expression for this potential follows from the lattice version of the Poisson equation [23],

$$\Delta \varphi(\mathbf{r}) = -\frac{4\pi}{Dv_0} \delta(\mathbf{r}), \quad (\text{A1})$$

where the exact form of the lattice Laplacian depends on the geometry of the lattice, D is the dielectric constant of the media, and v_0 is the unit cell volume. For simple tetragonal lattice with lattice spacings a in x and y directions and b in z direction one has

$$\Delta \varphi = \Delta_x \varphi + \Delta_y \varphi + \Delta_z \varphi, \quad (\text{A2})$$

with

$$\Delta_i \varphi(\mathbf{r}) = 1/a_i^2 [\varphi(\mathbf{r} - a_i \mathbf{e}_i) - 2\varphi(\mathbf{r}) + \varphi(\mathbf{r} + a_i \mathbf{e}_i)], \quad (\text{A3})$$

where $i = x, y, z$; $a_x = a_y = a$, $a_z = b$ and \mathbf{e}_i are the unit vectors along the corresponding lattice directions. After introducing the anisotropy parameter $\alpha = b/a$, the solution of the Poisson equation has the following form:

$$\varphi(\mathbf{r}) = \frac{1}{4\pi^2 D b} \times \int_{-\pi}^{\pi} \frac{e^{i\mathbf{k} \cdot \mathbf{r}} d^3 \mathbf{k}}{-\pi^2 + 1/\alpha^2 - (\cos k_1 + \cos k_2 + 1/\alpha^2 \cos k_3)}. \quad (\text{A4})$$

However, the potential in the form of a triple integral of a periodic function is not convenient for numerical calculations. More practical expression for this integral has been obtained by Maradudin *et al.* [36],

$$\varphi(\mathbf{r} \equiv (l, m, n)) = \frac{2\pi}{Db} \int_0^\infty \exp[-(2 + 1/\alpha^2)t] \\ \times I_l(t) I_m(t) I_n(t/\alpha^2) dt, \quad (\text{A5})$$

where I_l denotes a modified Bessel function of the first kind.

To enhance calculations of the lattice potential for the whole lattice, an error-free propagating algorithm, similar to that proposed by Friedberg and Martin [30] for isotropic lattice, has been used. First, we compute lattice potentials in planes $\langle x0z \rangle$ and $\langle x1z \rangle$ using Eq. (A5). Now, for a given lattice cite (l, m, n) , the anisotropic lattice potential satisfies the gradient equations

$$\frac{\varphi(l+1, m, n) - \varphi(l-1, m, n)}{l} \\ = \frac{\varphi(l, m+1, n) - \varphi(l, m-1, n)}{m} \\ = \alpha^2 \frac{\varphi(l, m, n+1) - \varphi(l, m, n-1)}{n}, \quad (\text{A6})$$

which follow from Eq. (A4). At fixed n , potential at any point (l, m, n) can be obtained recursively from two lines, $m=0$ and $m=1$. For $l=0$ it would be indeterminate, but this is not important since due to the symmetry $\varphi(0, m, n) = \varphi(m, 0, n)$. As Friedberg and Martin showed [30], this recursion does not lead to increase of the initial possible rounding error at $m=0$ and $m=1$ lines as long as $|l| \leq |m|$. For $|l| > |m|$ the symmetry $\varphi(l, m, n) = \varphi(m, l, n)$ can be employed.

Note that similar considerations can be done for initial $\langle x0z \rangle$ and $\langle x1z \rangle$ planes in attempt to generate the potentials from two lines, using the second equation in Eq. (A6). In these planes the potential is not symmetric, and therefore two sectors, $|l| \leq \alpha^2 |n|$ and $|l| \geq \alpha^2 |n|$ need to be calculated separately, starting from the corresponding axes and then “stitched” together at the $|l| = \alpha^2 |n|$ line. However, since all potentials and interactions are computed only once at the beginning of simulations and then fast look-up algorithm is used, this gives us a relatively small advantage in the overall computational time.

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