Critical behavior of ionic solids

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Phase transitions of lattice models of ionic crystals are studied by computer simulation. The nature of order-disorder transitions on different crystal structures is established and compared with the behavior of related Ising models. It is found that for both, continuous and first order transitions the basic features seem to be similar to those of Ising systems.

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Critical behavior of ionic systems has become in recent times a matter of wide interest [1–5]. The simplest continuous model of ionic solutions or ionic compounds is the restricted primitive model (RPM). The phase diagram or the RPM has been the subject of a number of recent studies using computer simulation [3,5–8]. The results on liquid-vapor equilibrium [5,6] suggest Ising-like criticality, but still some questions regarding the methods of analysis of the simulation results [9,10] seem to be open. Dickman and Stell introduced [2,11] the lattice restricted primitive model (LRPM), where the charges of the system are located on the sites of a regular lattice. More flexible lattice schemes (with different excluded volume criteria) were latter used by Panagiotopoulos and Kumar [12] to link the behavior of continuous and lattice approaches. Lattice models have the advantage of an efficient management of electrostatic interactions.

Bresme, Vega, and Abascal [7] have recently reported the existence of order-disorder transitions on close packing solid phases of the RPM. Lattice models with full occupancy are expected to describe accurately the phase behavior of ionic crystals, where the displacements of ions from their equilibrium positions on the lattice are small. For certain lattices, one can expect to find continuous order-disorder transitions (and critical behavior) due to electrostatic interactions. Moreover, in many cases it is possible to define order parameters that take full advantage of the symmetry of the model in the analysis of results. To our knowledge no systematic studies of the order-disorder transitions of the LRPM at full occupancy have been reported. In this paper we analyze this problem by means of Monte Carlo simulation.

Three cubic lattices have been studied: simple cubic (sc), body centered (bcc), and face centered (fcc), using periodic boundary conditions. The charge of a given site is either $+q$ or $-q$. Electroneutrality is preserved by keeping the constraint $N_+ = N_- = N/2$, where N_+ and N_- are, respectively, the numbers of positive and negative charges and N is the number of sites on the lattice. Ewald techniques [13] were used to write down the potential energy U as a sum of pair interactions [12,14] that depend on the vector $\mathbf{r}_{ij}$ between the two sites,

$$U = \sum_{i \neq j} A(\mathbf{r}_{ij}) s_i s_j , \tag{1}$$

where $s_i = \pm 1$. The values of the function $A(\mathbf{r}_{ij})$ are evaluated with high precision [15] before starting the simulation and kept on tables for latter use. K is defined as the reduced reverse temperature,

$$K = \frac{q^2}{4\pi\epsilon\sigma k_B T}, \tag{2}$$

where σ is the distance between nearest neighbors, k_B is the Boltzmann constant, T is the absolute temperature, and ϵ is the permittivity of the medium. The reduced energy per particle u is given by

$$u = \frac{4\pi\epsilon\sigma U}{Nq^2}. \tag{3}$$

The basic move in the Monte Carlo simulation is the interchange of positions [7] between two charges with opposite signs chosen at random. Two ensembles have been used: NVT ensemble for sc and bcc lattices and a microcanonical ensemble (NVE) on an extended system for fcc lattice. The NVE procedure resembles, to some extent, the so-called Gaussian ensemble techniques [16]. In practice we consider an extended system with a number ν of additional degrees of freedom ($\nu = 3N$ in the current application), which can be thought as ''virtual'' momenta of the particles, and take the form of independent classical harmonic oscillators. The total energy of the extended system E is fixed. Integrating out the contribution of the extra degrees of freedom to the microcanonical partition function, we find that the probability, P_i of a certain configuration with potential energy U_i is given by

$$P_i \propto (E - U_i)^{(\nu-1)/2}. \tag{4}$$

The temperature of the system is related with the mean values of the ''kinetic'' energy as

$$(\nu - 1) k_B T \simeq 2(E - \langle U \rangle). \tag{5}$$

This kind of approach [16] makes easier the identification of weak first order transitions (which exhibit a loop on a $T - E$ plot) and the precise location of the transition temperature.

At conditions close to the order-disorder transition the number of accepted moves is small (1%–6%) (especially for large systems). In order to save computing time we kept tables containing the value of the electric potential on each lattice site. This way, only for accepted steps a full counting

TABLE I. Results for LRPM on a bcc lattice ($K_c=2.077$).

L	$K_c(L)$	$L^{2\beta/\nu}\langle m^2(K_c)\rangle$	$c_v(K_c)L^{3-2/\nu}$	$u(K_c)$
4	2.055(10)	1.727(19)	1.754(18)	−0.7331(11)
5	2.068(7)	1.750(33)	1.94(4)	−0.7210(19)
6	2.071(7)	1.792(30)	2.09(12)	−0.7146(10)
7	2.072(6)	1.760(35)	2.20(6)	−0.7088(14)
8	2.073(3)	1.813(25)	2.30(7)	−0.7064(12)
9	2.074(4)	1.826(26)	2.30(12)	−0.7039(8)
10	2.075(3)	1.889(35)	2.53(13)	−0.7027(14)

of the interactions between the sites that interchanged charges and the rest of the system is required.

Simulations on the NVT ensemble were carried out for several system sizes. For sc lattice ($N=L^3$), with $L=$ 4, 6, 8, 10, and 12 and for bcc lattice ($N=2L^3$), with $L=$ 4, 5, 6, 7, 8, 9, and 10. After some preliminary short runs to locate approximately the critical points K_c we have run long trajectories (5×10^6 attempts of interchange per site) for a number of values of K around K_c (15 points in the range [2.04,2.18] for the bcc lattice and 16 points in the range [1.90,2.05] for the sc lattice). The properties were evaluated over the second half of each trajectory. On sc and bcc lattices an accurate order parameter, m, to follow the transition is that of the antiferromagnetic Ising-1/2 models [2]. In both cases the order-disorder transition is continuous. Finite-size scaling (FSS) methods have been used to locate and analyze the nature of the transition. A parameter G [17], closely related with the fourth order cumulant introduced by Binder [18], is defined as

$$G=\frac{1}{2}\left[3-\frac{\langle m^4\rangle}{\langle m^2\rangle^2}\right]. \tag{6}$$

The value of G in the thermodynamic limit is expected to be equal to zero (disordered phase) or to 1 (ordered phase), except at the critical point where it takes a nontrivial value G_c, which is expected to be invariant (except for small corrections to scaling) with the system size [19]. As a first step to locate the critical point we have used the simulation results to interpolate the values of K where the curves $G(K,L)$ for two different values of L cross. For the bcc lattice, considering systems with $L\geqslant5$ the crosses occur in ranges: $2.074<K<2.083$; $0.70\leqslant G\leqslant0.75$. For the sc lattice the results are: $1.939\leqslant K\leqslant1.951$; $0.69\leqslant G\leqslant0.74$. Both ranges of G are close to the estimation of G_c for the three-dimensional 3D-Ising universality class in periodic systems with cubic symmetry [20] $G_c^I\approx0.698$. The deviations of the crossing values of G with respect to G_c^I are about the same order that those found in simulation of Ising systems with similar sizes [20]. The corresponding value for classical critical behavior (i.e., that of one component systems with long-range interactions [21,22]) is $G_c^{MF}\approx0.406$ [21,23]. In what follows, Ising-like behavior (i.e., $G_c\simeq0.698$, and critical exponents: $\beta\simeq0.326$, $\theta\simeq0.52$, $\nu\simeq0.630$ [20]) will be assumed. Apparent critical coupling constants for finite-size systems [19], $K_c(L)$, can be evaluated by the interpolating on the simulation results to fulfill: $G(K_c(L),L)=G_c$. The results are shown in Tables I and II. These values are expected to scale [19] as

$$K_c-K_c(L)\propto L^{-(1+\theta)/\nu}. \tag{7}$$

The values of K_c were estimated using last equation,

$$\begin{aligned} K_c^{sc}&=1.942\pm0.005\\ K_c^{bcc}&=2.077\pm0.003. \end{aligned} \tag{8}$$

At the apparent critical points, $K_c(L)$, the order parameter distribution function is expected to be universal [19,24] (for L not too small). The results for two cases on the bcc lattice ($L=6$ and $L=8$) are compared in Fig. 1 with the distribution at the scaling limit for the 3D-Ising class [24]. A good agreement is observed (better for $L=8$, as expected). A further check of the previous estimations of K_c can be carried out by using the values of the order parameter $\langle m^2\rangle$ for $K>K_c$ to extrapolate K_c. This was performed taking only the values of K where $\langle m^2(L)\rangle$ converge within error bars for the two largest values of L on each lattice. The critical point is estimated by fitting the results [10] to

$$\langle m^2\rangle^{1/2}=(K-K_c)^{\beta}[A+B(K-K_c)^{\theta}], \tag{9}$$

TABLE II. Results for LRPM on a sc lattice ($K_c=1.942$).

L	$K_c(L)$	$L^{2\beta/\nu}\langle m^2(K_c)\rangle$	$c_vL^{3-2/\nu}$	$u(K_c)$
4	1.913(18)	1.885(21)	1.094(9)	−0.7353(11)
6	1.932(9)	2.10(4)	1.450(21)	−0.7131(12)
8	1.938(7)	2.15(4)	1.606(29)	−0.7031(8)
10	1.940(6)	2.22(9)	1.72(4)	−0.6988(11)
12	1.940(5)	2.28(10)	1.87(10)	−0.6960(20)

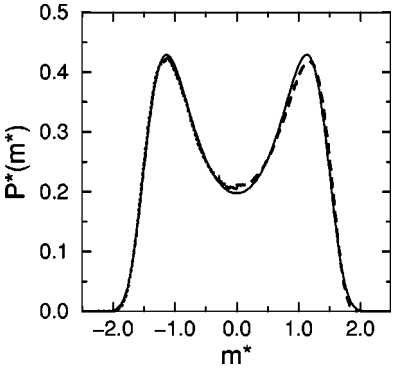

FIG. 1. Critical order parameter distributions. Continuous line: Limiting Ising distribution from Ref. [24]. Dashed line (on the right side): bcc lattice with $L=6$. Dotted line (on the left): bcc lattice with $L=8$. The value of m is reduced to get distributions with unit variance.

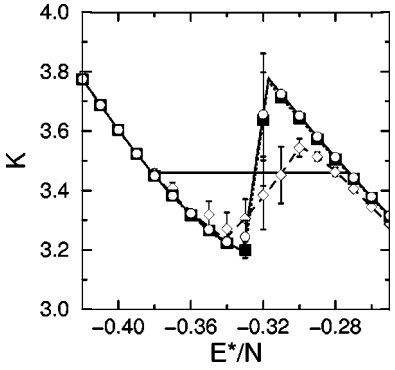

FIG. 2. Results of simulations of the fcc lattice for three different system sizes. K is the inverse of the reduced temperature, E^*/N is the total energy per particle (see the text for details). Diamonds and dashed line represent results for $L=4$. Filled squares and dotted line ($L=6$). Opaque circles and continuous line ($L=8$). Horizontal continuous line marks the value of K_c for $L=8$

where β and θ are fixed parameters. In both cases eight points were used: $K\in[2.11,2.18]$ for bcc lattice and $K\in[1.98,2.05]$ for the sc lattice. The results are shown in Table III. The estimated values of K_c agree within error bars with those given in Eq. (8). According to FSS statements, at the critical point K_c, the following scaling behavior [19,20,24] is expected for the order parameter and the heat capacity per particle c_v:

$$\langle m^2(K_c)\rangle \propto L^{-2\beta/\nu}, \tag{10}$$

$$c_v(K_c,L)\propto L^{-3+2/\nu}. \tag{11}$$

In Tables I and II the quantities $L^{2\beta/\nu}\langle m^2(K_c)\rangle$ and $c_v(K_c,L)L^{3-2/\nu}$ (which are expected to be invariant for large values of L) are reported for both lattices and different sizes. It seems clear that the scaling invariance has not been reached within the system sizes considered. Similar trends have been found in systems with short range interactions [19,20]. In addition we have estimated the value of the potential energy at the critical point u_c using the previous estimations of K_c [Eq. 8] and the scaling relation [19],

$$u_c - u(K_c,L)\propto L^{-3+1/\nu}. \tag{12}$$

The results for u_c are

$$u_c^{sc} = -0.685\pm 0.011,$$
$$u_c^{bcc} = -0.691\pm 0.008. \tag{13}$$

TABLE III. Fitting of the order parameter [Eq. (9)] as a function of K for sc and bcc lattices.

Lattice	K_c	A	B
sc	1.946(10)	2.05	−1.28
bcc	2.077(13)	2.06	−1.19

The values of $u(K_c,L)$ (collected in Tables I and II) are consistent (within error bars) with the scaling relation given in Eq. (12).

The results shown for ionic lattices with a continuous order-disorder transition seem to assess the likelihood of an Ising-like critical behavior and the reliability of the estimations of critical temperatures and energies.

Simulations of the LRPM on fcc lattice using NVT ensemble showed hysteresis effects, specially for large sizes. Therefore, the transition is likely to be first order. This scenario was pointed out as one of the possibilities in Ref [7]. In order to clarify this point and to locate precisely the transition, simulations on the extended NVE ensemble were performed for three system sizes: $L=$ 4, 6, and 8 (with $N=4L^3$). After preliminary short runs to locate the transition, a sequence of simulations from $E^*/N=-0.25$ to $E^*/N=-0.42$ (18 points) were carried out for each system size. The reverse sequences of states were also simulated to discard hysteresis effects. Each simulation run implied $\sim 5\times 10^5$ moves per particle. The transition was found to be discontinuous. The value of K at the transition K_c was evaluated by performing a Maxwell construction over the plot of $\langle K\rangle$ versus E (See Fig 2). Numerical results are reported in Table IV.

These results on fcc lattices can be related with the behavior of the fcc Ising antiferromagnet with nearest-neighbor and next-nearest neighbor pair interactions [25]. In fact the

TABLE IV. Results of the LRPM on a fcc lattice for different system sizes. K_c is the estimated reverse temperature at the transition, u_d and u_o are, respectively, the reduced potential energies per particle of disordered and ordered phases at the transition. Δu is the reduced latent heat per particle of the transition at $K=K_c$.

L	K_c	u_d	u_o	Δu
4	3.391(17)	−0.710(1)	−0.813(1)	0.103(1)
6	3.450(17)	−0.706(1)	−0.815(1)	0.108(1)
8	3.459(12)	−0.706(1)	−0.815(1)	0.109(1)

order-disorder transition in the LRPM is completely analogous to that of the type-III fcc antiferromagnets [25] that is also discontinuous and has the same ground state structure.

From the results presented here we can conclude that the critical behavior of the fully occupied LRPM seems to be similar to that of systems with short range interactions. Nevertheless, larger systems must be considered to reach definitive conclusions.

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