

Order-Disorder Transition in the Solid Phase of a Charged Hard Sphere Model

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We investigate the solid phases of the restricted primitive model (RPM). Monte Carlo simulations show the existence of an order-disorder transition from a substitutionally disordered face centered cubic lattice (fcc) to a new ordered fcc structure which is proposed as the ground state of the RPM at the close packing density. Our results suggest that the new phase might turn out in a new triple point in the RPM phase diagram involving three solid phases: CsCl, fcc ordered and fcc disordered structures. The order-disorder transition is also studied using the cell theory. The theory shows good agreement with the simulation results and suggests that the transition is weakly first order.

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All elements and compounds can be solidified under appropriate conditions. The structure of a solid is determined by two main factors: the lattice energy of the crystal and geometric requirements which stem from short range repulsive forces [1]. In addition to this, in ionic systems, the long range Coulombic interaction has an asymmetric character with regard to the ion-ion interactions, and this factor plays an important role in determining the final structure of the solid. Thus, ionic solids consisting of an equimolar mixture of cations and anions may crystallize into structures different from those allowing higher packing fractions. This is, for instance, the case of CsCl and NaCl structures. Nonetheless, it has been shown experimentally in a number of alkali halides that, under pressures of several hundred kilobar [2,3], the crystals might undergo a transformation to more dense structures.

The restricted primitive model (RPM) has played a fundamental role in the study of ionic systems, as it constitutes a natural extension to the hard sphere (HS) model [4]. The RPM consists of an equimolar mixture of charged hard spheres, half carrying positive charge and the rest negative charge. The properties of the RPM in the molten salt regime are well known both from theory and computer simulations (see Ref. [5]). Also, several studies have considered the liquid-vapor equilibrium, discovered almost simultaneously by Vorontsov-Vel'yaminov and Chasovskikh [6] employing Monte Carlo (MC) simulations and by Stell and co-workers using theoretical approaches [7]. Now the existence of liquid-vapor coexistence in the RPM is well established, and computer simulation has allowed its determination [8]. Since these early papers, several others have followed considering different aspects, such as the ionic structure of the vapor phase [9–12] and, very recently, it has been the subject of discussions relevant to the nature of the criticality of ionic fluids [13–15].

With regard to the fluid-solid equilibrium of the RPM, Stillinger and Lovett [16] were the first authors sketching the fluid-solid phase diagram. Later on, Barrat considered the freezing of charged hard spheres using density func-

tional theory [17]. Recently it has been investigated by ourselves [18], both theoretically and by MC simulations and also by Smit *et al.* [19] employing MC simulations. We found that the qualitative view given by Stillinger and Lovett more than thirty years ago was surprisingly accurate. At high temperatures, freezing occurs in a substitutionally disordered face centered cubic solid (fcc), whereas at low temperatures an ordered cesium chloride structure (CsCl) appears. The phase diagram presented two triple points; in one of them the three coexisting phases are vapor, liquid, and solid (CsCl), whereas in the other one the coexistence phases are fluid, solid (CsCl), and solid (fcc disordered).

It is reasonable to think that at $T = 0$ K the crystal might have an ordered phase. Surprisingly, none of the previous studies of the RPM solid phases have considered the possibility of a closed packed structure with an ordered arrangement of ions. In the remainder of the Letter, we investigate this question and the transition between the new ordered phase and the disordered fcc. The model potential for the RPM is defined as

$$u_{\alpha\beta}(r) = \begin{cases} \infty & \text{if } r < \sigma \\ \frac{Z_{\alpha}Z_{\beta}e^2}{4\pi\epsilon_0 r} & \text{if } r \geq \sigma \end{cases}, \quad (1)$$

which results from the sum of a hard sphere repulsion and a long range Coulombic term. In Eq. (1), $Z_{\alpha,\beta} = \pm 1$ are the ionic charges, ϵ_0 represents the dielectric permittivity, e is the electron charge, and σ is the hard sphere diameter. The reduced number density of the system is defined as $\rho^* = N\sigma^3/V$, N being the number of ions enclosed in volume V . The reduced temperature is defined as $T^* = 1/\beta^* = 4\pi\epsilon_0\sigma k_B T/e^2$.

We start our discussion by considering the structure of minimum energy at $T = 0$ K and at the close packing density, $\rho^* = \sqrt{2}$. We have considered several arrangements for the cations and anions in two close packed structures of hard spheres, face centered cubic and hexagonal close packing (hcp). It is usual to describe fcc and hcp structures

in terms of the close packing planes, namely, those parallel to the bases in hcp and the planes with Miller indices $hkl = 111$ in fcc. The similarity between hcp and fcc is due to the fact that the only difference between them consists in the different stacking of these layers which are arranged as $ABAB\dots$ in the former and $ABCABC\dots$ in the latter. A very simple structure is obtained when all the atoms in the same layer have the same charge and the sign of the successive layers is alternating. As every ion is surrounded by six ions of the same type and another six with opposite charge, the Madelung constant for this arrangement—calculated using the Ewald summation method [20]—is quite low; $M = 1.235$ for both fcc and hcp structures. On the other hand, it is not possible to devise a structure in which every particle is surrounded by 12 ions with opposite charge. We have investigated different arrangements, and we have found that some of them result in an appreciable electrostatic energy which enables the stabilization of the crystal. In all of them, 8 out of the 12 nearest neighbors of any ion are unlike charged particles. Thus, the Coulombic energy of an ion with the nearest neighbors is -4 . In particular, we have considered a simple fcc structure in which the cations are located at the vertices and in two parallel faces of the cubic cell while the anions are placed in the remainder four faces [see Fig. 1(a)]. This structure has four ions per unit cell and its Madelung constant is $M = 1.594$. The fcc structure is of the same kind observed in alloys [21] such as AuCu which exhibit order-disorder transitions. The corresponding hcp structure, i.e., that is made up with identical layers but stacked in an hcp arrangement, is a ferroelectric crystal with $M = 1.564$. It is interesting to note that the fcc and hexagonal structures show very similar lattice energies, though the fcc one is slightly more stable. This is in agreement with the results obtained for neutral models [22], and our results suggest that this trend is also followed by hard core ionic models.

The analysis at zero temperature indicates that there are ordered fcc structures which must be more stable than the substitutionally disordered crystal. We have performed Monte Carlo simulations of the fcc solid at the close packing density for a wide range of temperatures in order to confirm this point and to calculate the temperature of the order-disorder transition. At this density, any displacement of the ions off the lattice positions results in an overlap, and therefore they are constrained to remain at the lattice positions. Thus we did not consider the movement of the ions but only the change in their charge. One MC step consists of an attempt to swap the charge of one cation with one anion. The step is accepted according to the Metropolis criterion (see, for instance, [23]). We considered samples of $N = 256$ ions. The runs started with the ions distributed randomly in the lattice at infinite temperature which was then reduced along the close packing isochore. The simulations involved 2×10^6 steps for the equilibration and $(5-10) \times 10^6$ for the production. Figure 2 shows the dependence of the energy with temperature. The energy does not vary continuously but exhibits a “jump,” which would indicate an increase in the constant volume heat capacity of the system, and therefore the existence of a transition. This behavior resembles the Λ type transformations [21] observed in alloys, as in AuCu₃, which undergo order-disorder transitions. Further reduction of the temperature beyond $T^* = 0.296$ does not modify the electrostatic energy which is $U/Nk_B = -0.818$ ($M = 1.636$), i.e., more stable than any of the structures previously considered. This new RPM structure consists of one unit cell of eight ions, with every particle also being surrounded by eight ions of opposite charge and four of the same charge [see Fig. 1(b)]. The dipole moment of this cell is zero. This structure is one of the main findings in this Letter, and we propose it as the fundamental state of the RPM at high pressures and low temperatures. The space group of the cell is $I\bar{4}m2$ (tetragonal) when the substitutional order is

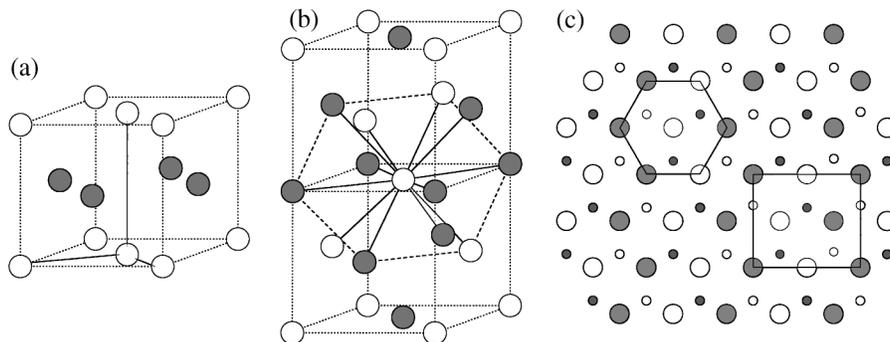


FIG. 1. Representation of the unit cell of the solid phases of the RPM. (a) A cell with a Madelung constant, $M = 1.594$ (see the text). The space group is $P4/mmm$ (tetragonal). Solid lines indicate the translational vectors of the primitive tetragonal cell. (b) Minimum energy structure of the RPM at close packing and low temperatures ($M = 1.636$). The space group is $I\bar{4}m2$ (tetragonal). The layers corresponding to planes with Miller indices $hkl = 111$ in the originating fcc cell are indicated by the dashed hexagon and are identical to those represented for the next structure. The solid lines connect the central ion with its twelve nearest neighbors. (c) A projection of the hexagonal counterpart of the previous structure ($M = 1.632$). The small circles give the positions of the ions in the layers above (and below) the plane containing the ions represented by the big circles.

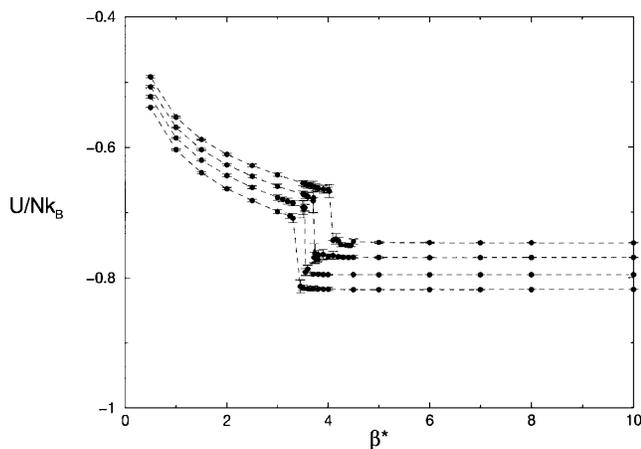


FIG. 2. Dependence of the energy with temperature. Lines connect points at the same density. The isochores are, from bottom to top, $\rho^* = \sqrt{2}$ (close packing density), 1.3, 1.2, and 1.1. The discontinuity signals the location of an order-disorder transition.

considered but it would remain as fcc if no distinction is made between the ions. Thus, for simplicity, we will refer to it as *fcc ordered structure*. Taking into account the Madelung constant of the CsCl structure ($M = 1.7627$), it seems clear that Coulombic forces favor it with respect to the fcc ordered. Nevertheless, an increase in pressure should induce the transition from the former to the latter. The hexagonal analog of the fcc ordered, depicted in Fig. 1(c), is slightly less stable ($U/Nk_B = -0.816$, $M = 1.632$) in agreement with the trends noted above. In contrast with the hcp previously considered, the new ordered hcp structure is not ferroelectric.

The analysis by Monte Carlo simulation of the energy for different isochores of the RPM also shows the existence of an order-disorder transition (Fig. 2). In this case, in addition to the swapping of ion identities we allowed the ions to move out of the lattice positions. The Metropolis method was adopted also here and details of the simulations can be found in our previous paper [18]. The transition temperature decreases with density (see Fig. 2), a similar behavior as that observed in previous studies of the LRPM fluid. The LRPM is just a RPM but with the ions fixed at the lattice positions. In fact, the model has been recently used by different authors [15,24] for the investigation of the fluid phase. Stell and Dickman [15] predicted the existence of an order-disorder transition for the LRPM in the fluid phase (i.e., when not all of the lattice positions are occupied by ions). One can establish certain parallelism between these transitions and the well-known order-disorder transition observed in lattice models such as Ising [25–28] or related models and also in Heisenberg solids [29].

In addition to the order-disorder transition, we have investigated the solid-solid equilibrium between the new phase, fcc ordered, and the CsCl lattice. These calculations involve the computation of the free energy of the

fcc ordered crystal. The latter was obtained by thermodynamic integration using as a reference the values previously reported for the fcc disordered phase [18]. This procedure involves the integration of the energy through the order-disorder transition. As this is weakly first order (or even second order), this can be done accurately, and we have checked the consistency of the calculation by evaluating the change in free energy over a thermodynamic cycle involving four thermodynamic states, $(\beta^*, \rho^*) = (2, 1.1)$, $(2, 1.2)$, $(5, 1.2)$, and $(5, 1.1)$, which we denote as states A, B, C, and D. The change in free energy $\Delta A_{AB}/Nk_B T + \Delta A_{BC}/Nk_B T + \Delta A_{CD}/Nk_B T + \Delta A_{DA}/Nk_B T$ should be zero as in any other thermodynamic cycle. We obtained ΔA_{AB} and ΔA_{CD} from the integration of the equation of state, whereas the other two free energy differences corresponding to the isochores were obtained by integration of the internal energy. Our values for the differences expressed above are $1.37 - 2.10 - 1.27 + 1.99$ which is -0.01 within the uncertainty of the calculations. This fact gave us confidence to use the procedure described above to calculate the free energies of the fcc ordered phases. Our results suggest the existence of a new triple point in the RPM phase diagram, which would involve the three solid phases. Nevertheless, given the proximity of the triple point fluid-CsCl-fcc disordered, and the order-disorder transition, we cannot rule out a change in the scenario, though we propose the one depicted in Fig. 3 as the most likely one.

We have also studied the order-disorder transition of the RPM employing the cell theory [30]. We have already shown [18] that the cell theory is very accurate in predicting the fluid-solid equilibrium of the RPM. With regard to its implementation to study the RPM, we refer the reader

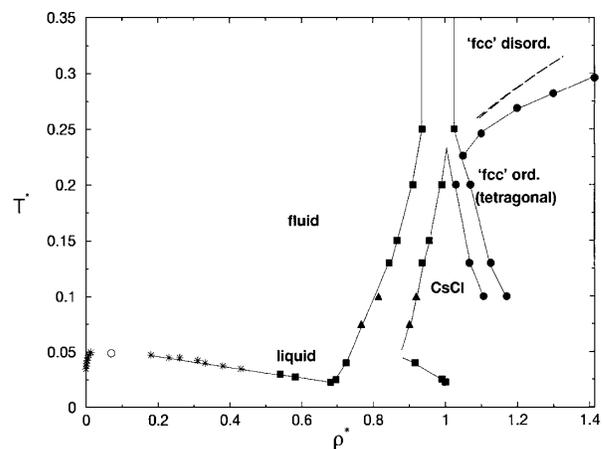


FIG. 3. Phase diagram of the RPM. Points are simulation data: black circles are the results of this work, squares are taken from Ref. [18], triangles from Ref. [19], stars from Ref. [8], and the white circle represents a recent estimate of the critical point of the RPM (Ref. [31]) (full lines are a guide to the eye). Dashed lines are the predictions from the cell theory for the order-disorder transition (both sides are depicted though the change in density is not distinguishable at the scale of the figure).

to our previous paper [18]. The novelty of the theory in this paper is the consideration of a new RPM phase, the fcc ordered structure. The cell theory predicts (cf. Fig. 3) rather accurately the location of the order-disorder transitions.

Stell [15] has recently pointed out that the order-disorder transition observed in the fluid LRPM, because of the loss of charge-charge screening, signals the onset of long range ordering, and therefore this line would be a signature of crystallization. Stell further notes that this could not be realized in the RPM fluid but in a solid, along a phase boundary separating two solid phases of different symmetry. Our simulation results and the cell theory confirm this hypothesis as the transition involves a change from cubic to tetragonal symmetry. The cell theory shows the existence of a weak first order phase transition between the fcc disordered phase and fcc ordered phase. The possibility that the transition between the disordered and the ordered phases is of Λ type (second order) cannot be ruled out. The absence of hysteresis in the simulations suggests that this could be the case. Also, the small change in density predicted by the cell theory might be a consequence of the theoretical approximations. In any case, this fact will not alter our conclusions regarding the existence of an order-disorder phase transition.

On the whole, we can conclude that the RPM is far from being a simple model. As we have seen, it shows a complex phase behavior in the solid phase. We have seen in this Letter that at low temperatures and very high pressures a new fcc structure appears. We propose this structure as the ground state of the RPM at close packing density. This new phase is ordered and at high temperatures undergoes an order-disorder transition to a substitutionally disordered fcc lattice. In addition, our study suggests that the existence of this phase results in a new triple point in the RPM phase diagram which involves simultaneous equilibrium of this phase with the CsCl and the disordered fcc lattice.

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