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Characterization of the order-disorder transition of a charged hard-sphere model

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Monte Carlo simulations at constant pressure are used to characterize the structure of the restricted primitive model in the tetragonal-ordered solid phase. A method to estimate the location of the order-disorder transition and the densities of the coexistence phases is discussed. The results support the weakly first-order character of the transition.

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A fruitful approach to the understanding of the structure of matter is the investigation of simple models that incorporate the essential features of real systems. The so-called restricted primitive model (RPM) has recently received great attention in relation to the behavior of ionic systems [1–10]. It consists of a mixture of hard spheres, half being positively charged and the other half being negatively charged. The absolute value of the charges, as well as the particle diameters, are the same for both species. Despite its apparent simplicity, the structural properties of the RPM model show a complex behavior which is reflected in its phase diagram. The existence of a vapor-liquid phase transition in this model was demonstrated in the 1970's by means of Monte Carlo computer simulations [11]. However, the systematic study of the solid phases has only recently been undertaken. Barrat [12] used density functional theory in the description of the freezing of the RPM model. Simulation results for the fluid-solid equilibrium of the model were presented by Smit *et al.* [6] and by Vega *et al.* [13]. Both studies indicated that the stable structure at low temperatures is the same as that of solid cesium chloride, while at high temperatures the RPM solid exhibits a face centered cubic (fcc) structure with a random allocation of cations and anions. Later on, Bresme *et al.* [7] found that the substitutionally disordered fcc structure may undergo an order-disorder transition. The unit cell of this new phase may be obtained from the replication of two fcc unit cells along the c direction and contains eight particles. According to the fcc packing, every particle is surrounded by 12 nearest neighbors but, unlike the usual case in simple ionic solids, not all the surrounding ions are of the same type. In this case, eight particles carry opposite charge to that of the central ion and four carry the same charge [see Fig. 1]. Despite the positional fcc symmetry, the symmetry of the unit cell is tetragonal when substitutional order is considered. Moreover, every ion is surrounded by four particles with opposite charge in the XY plane whereas only two nearest neighbors in the planes XZ and YZ carry different charge (see Fig. 1). This means that the interactions along the Z axis are less attractive, therefore it is expected that the corresponding cell parameter c will be larger than the other cell parameters a and b, which should be identical.

In a previous Letter we reported a preliminary phase diagram of the RPM [7] including the tetragonal solid. The calculations were based on Monte Carlo simulations in the NVT ensemble assuming $c=2a$ (see Fig. 1). Very recently, we have recalculated the RPM phase diagram [14] using the NpT ensemble [15] which allows the explicit incorporation of the tetragonal symmetry in the simulation box. The coexistence lines were determined by integration of the Clapeyron equation following a similar procedure to that first proposed by Kofke [16]. The technique requires knowledge of an initial coexistence point. This was calculated by means of the Einstein crystal methodology [17]. Unfortunately, this procedure cannot be used for the tetragonal-disordered fcc solid coexistence for two reasons. First, the disordered fcc

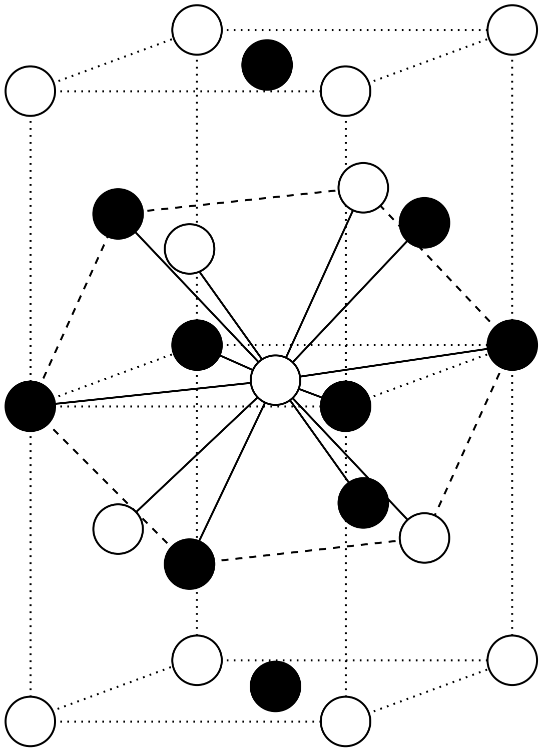

FIG. 1. Unit cell of the RPM ordered solid stable at high pressures and low temperatures. The cell is tetragonal $I\overline{4}m2$. The equivalent unit cell lengths are $a=b$ and the other unit cell length is c. The cell corresponds to a fcc structure if the substitutional order is not taken into account (in such a case $c=2a$).

solid has no definite unit cell because the crystal consists of many different disordered cells with considerably different electrostatic energies. Hence, the application of the Einstein crystal technique is not possible for this phase. Besides, the order-disorder transition is likely a weakly first-order one [7,8,13] and, therefore, both phases have very similar densities. In these conditions, the integration of the Clapeyron equation introduces unacceptably large errors. In this work we tackle this problem using an alternative methodology that is explained below.

We are also interested in the characterization of the structural changes along the transition. From a structural point of view, our interest is to investigate to what extent the symmetry of the system is reflected in the cell parameters. The disordered fcc solid has a cubic lattice so the unit cell length is determined once the density is known. This is no longer true for the tetragonal solid since it has two independent cell lengths. The difference between the c parameter and the $a=b$ cell lengths is an indication of the departure from the cubic symmetry induced by the ionic interactions. An inspection of the tetragonal unit cell (cf. Fig. 1) shows that the ratio $c/(2a)$ should be equal to 1 if the mean value of the components of the interaction potential were the same along the three coordinate axes. Hence, the deviation from unity of the ratio $c/(2a)$ is a significant structural parameter. Regarding the thermodynamic properties, the transition is characterized by a relatively large change in the internal energy and a very small density change. As mentioned above, one of the goals of this work is the accurate determination of the coexistence densities.

The restricted primitive model is an equimolar-equisized mixture of anions and cations which interact via the potential

$$u(r)=u_{HS}\pm q^2/(\epsilon r), \tag{1}$$

where u_{HS} is the hard-sphere potential, q is the ionic charge, ϵ is the dielectric constant of the medium, and σ is the hard-sphere diameter. In Eq. (1) the plus and minus signs apply to interactions between ions of the same or opposite charge, respectively. The reduced number density of the system is defined in terms of σ as $\rho^*=\rho\sigma^3=(N/V)\sigma^3$ with N being the total number of ions filling a volume V and ρ the number density. Similarly, the reduced temperature is defined as $T^*=1/\beta^*=kT\epsilon\sigma/q^2$, with k being the Boltzmann constant and T the temperature. Finally, the reduced pressure is $p^*=p\epsilon\sigma^4/q^2$.

In Table I NpT simulation results for the tetragonal structure at $T^*=0.10$ are presented. For the computation of the Coulombic interactions, the Ewald summation method [18,19] is employed with a parameter $\alpha=0.863/\sigma$. Interactions in real space are truncated at 2.7σ. The reciprocal space sum is restricted to the vectors $\vec{h}$ with modulus $|\vec{h}|^2<27$. The simulations were performed with runs of 2×10^5 cycles for a sample size of 256 ions. Each cycle consists of a trial move per particle plus an attempt to change the volume of the system. In these simulations the tetragonal symmetry of the cell box is enforced, i.e., the axes are orthogonal and $a=b$. Then, the cell parameters a and c are allowed to change independently in the NpT simulations. Table I shows that $c>2a$ for all the thermodynamic states considered in this work. This is because ions with opposite charge tend to be closer to a given ion than those with the same charge. The ratio $c/(2a)$ increases as pressure—or density—decreases but it is always relatively close to unity. It is to be pointed out that for lower pressures ($p<1.66$) the stable phase has a CsCl-type structure [14].

TABLE I. Thermodynamic and structural results along the $T^*=0.1$ isotherm as obtained from anisotropic NpT simulations for the solid structure of Fig. 1.

p^*	ρ^*	$U/(Nk)$	$c/(2a)$
3.0	1.2573	−0.7901	1.007
2.7	1.2453	−0.7874	1.008
2.5	1.2287	−0.7847	1.013
2.2	1.2111	−0.7812	1.016
2.0	1.1967	−0.7791	1.022
1.8	1.1777	−0.7741	1.019
1.6	1.1605	−0.7709	1.024

As commented above, it is not possible to estimate the order-disorder coexistence line using the Einstein methodology to calculate the solid free energies. In the previous work [7] we estimated the coexistence temperature from the jump in the internal energy when going from the ordered to the disordered structure. A related approach has also been used in this work. It consists in the monitoring of a substitutional order parameter. For the calculation of the order parameter, every lattice site is assigned a value $+1$ if the ion in that site has the same charge than the ion in the starting configuration, and -1 otherwise. The final sum over the sites is normalized so that the order parameter is 1 when all of the particles oscillate around their initial lattice positions. For randomly disordered lattices, the order parameter fluctuates around 0. Notice that it is possible to eventually obtain an ordered lattice with all of the ion charges carrying opposite sign to those in the starting configuration in which case the order parameter is -1. Although the definition of the order parameter is not completely independent of the initial configuration it has proven to be a useful way to detect the transition to another phase.

Finite size effects are observed when one approaches the coexistence line. In such conditions, and for a small number of particles in the simulation box (250), the internal energy fluctuations and the order parameter indicated that the system eventually changed to a different state. However, the inverse process also took place so it was impossible to determine the stable phase. The problem may be avoided by increasing the number of particles and, therefore, reducing the fluctuations. In particular, for a sample size of 864 ions the systems never showed oscillations between both phases (see Fig. 2). As the disordering process is highly cooperative, more simulation cycles are needed to detect the transition from the ordered to the disordered state, but once the phase change takes place it never reverses. The only drawback is the possibility of metastable conditions as the system may

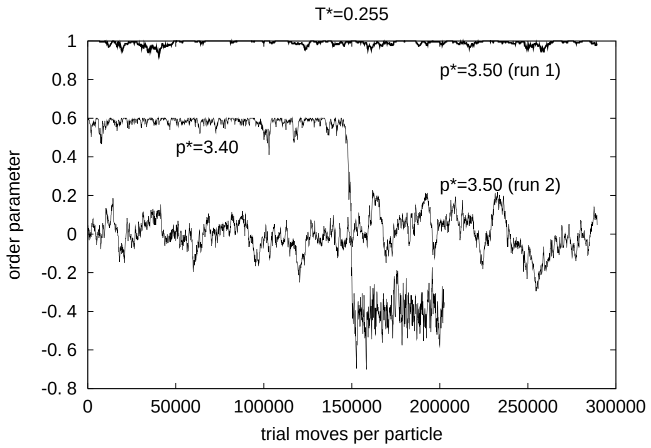

FIG. 2. The substitutional order parameter for three simulation runs at $T^* = 0.255$. Pressures are labeled within the plot. The results of run at $p^* = 3.40$, which have been shifted for clarity, indicate that the solid undergoes an order-disorder phase transition. Run 1 at $p^* = 3.50$ was started from a tetragonal solid while run 2 was initialized with the final (disordered) configuration of run at $p^* = 3.40$. At $p^* = 3.50$ the tetragonal solid remains in its initial state irrespective of the starting configuration.

TABLE II. Properties along the coexistence line. p^*_{lower} and p^*_{upper} are the lower and upper values of the pressure coexistence interval (see the text for details). ρ^*_{ord} and ρ^*_{disord} are the densities of the ordered and disordered solid, respectively.

T^*	p^*_{lower}	p^*_{upper}	$c/(2a)$	ρ^*_{ord}	ρ^*_{disord}
0.25	3.0	3.125	1.017	1.083	1.074
0.255	3.4	3.5	1.017	1.105	1.094
0.26	3.9	4.03	1.012	1.125	1.119
0.265	4.4	4.5	1.010	1.149	1.147
0.27	5.67	5.94	1.013	1.192	1.194
0.275	6.3	6.5	1.008	1.2097	1.2085
0.28	7.56	7.84	1.006	1.240	1.235
0.285	9.5	10.0	1.002	1.2654	1.2645
0.29	15.14	15.95	1.001	1.3154	1.3153

remain in the initial ordered/disordered state for a long time. This possibility is far less likely if the number of cycles increases significantly so that the system can properly explore the phase space. We have used up to 10^6 cycles—about 8×10^8 trial moves—to ensure as much as possible that the final state corresponds to a genuine stable phase. A new type of trial move, which consists in the swapping of the ionic charge of two random particles, is required in these simulations. As commented above, once the 864 particles systems eventually becomes disordered they never return to the ordered phase.

For the determination of the coexistence point at a given temperature we move along the corresponding isotherm starting at a low enough pressure such that the starting configuration, an ordered system, is unstable. Then, several runs at increasing pressures are carried out with a relatively small number of trial moves (about 4×10^4 cycles). In these runs the starting configuration is the ordered solid. The highest pressure at which the solid disorders and the lowest pressure at which the system remains ordered provides an initial rough interval for the coexistence pressure. More simulations within the pressure interval (with a large number of trial moves) allow the procedure to be refined until the interval is reduced to the desired accuracy. Note that the lower value of the pressure interval is a bound for the coexistence pressure but the opposite does not hold true for the higher pressure. It could be possible that extremely long simulations would show that the system also disorders under these conditions. An idea of the accuracy of the procedure is given by the number of cycles required to disorder the solid as one approaches the transition. For instance, at $T^* = 0.29$ the ordered systems at $p^* = 8.7, 10.15, 11.6, 13.05, 14.5, 15.14$ disordered at cycle 12 000, 25 000, 250 000, 350 000, 20 000 and 500 000, respectively (at $p^* = 15.95$ the solid remained along ordered along a 1 000 000 cycles simulation). The coexistence pressure interval for each isotherm is given in Table II (for these calculations, the real space cutoff radius was set to 3σ). We have covered the temperatures between $T^* = 0.25$ at which the tetragonal solid melts [14] and $T^* = 0.29$ close to the transition temperature at close packing. Despite the narrow range of temperatures involved, the coexistence pressures show a wide range of values. This is because at the close packing density, $\rho^* = \sqrt{2}$, the coexistence pressure goes to infinity. Our results reflect this trend. It should be noted that the coexistence pressures change slowly for lower temperatures and increase sharply for the higher isotherms.

We would like to stress that our interest is not just a precise determination of the coexistence pressures but the characterization of the transition. In particular, we are interested in estimating the density change between the ordered solid and the coexisting disordered phase. Previous work suggests that the coexistence is weakly first order [7,8]. In this work, we have estimated the coexistence densities through the following procedure. We have already seen in Fig. 2 that when a simulation begins with a disordered solid it is not possible to obtain an ordered solid even if it is in a thermodynamic state where the ordered phase is stable (and we are in the vicinity of the coexistence curve). Thus, two different runs with different initial configurations—ordered and disordered, respectively—at the same thermodynamic state remain ordered and the disordred, respectively. To estimate the densities of both phases, it suffices to calculate the densities for both the ordered and the disordered solid at the same temperature and pressure (for the latter we have arbitrarily selected p^*_{upper}). An accurate estimation of the coexistence densities is thus possible provided that the coexistence pressure intervals are limited to a narrow range. Coexistence densities are shown in Table II. As expected, both phases have very similar densities; the differences between them are of the order of 1% at the lower temperatures and become negligible as we approach the close packing density. This result is consistent with the temperature dependence of the coexistence pressures. According to the Clapeyron equation, the p-T slope is inversely proportional to the volume change. Thus, in agreement with our previous

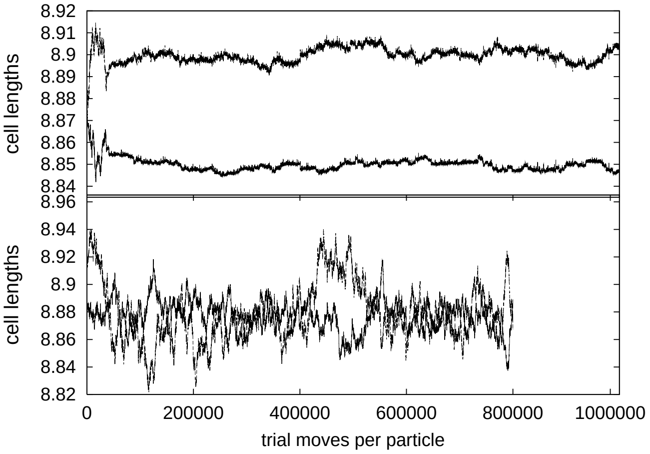

FIG. 3. Evolution of the cell lengths (in reduced units) along NpT simulation runs at the coexistence point $T^*=0.28$, $p^*=7.84$. Upper and lower plots are for the ordered and the disordered solid, respectively. The simulation box consists in a $6\times6\times3$ replication of the unit cell depicted in Fig. 1. The tetragonal symmetry is enforced in both Rahman-Parrinello simulations.

findings, the slope should dramatically increase when approaching the close packing transition temperature. As the coexistence pressure and densities have been obtained independently in our simulations, the consistency between these two properties gives additional support to the validity of the procedure used in this work.

The evolution of the cell lengths along two NpT simulation runs (corresponding to the ordered and disordered systems coexisting at $T^*=0.28$) is depicted in Fig. 3. For the ordered solid, the cell lengths are clearly distinct—$c/2$ being always larger than a, ≈ 8.90 versus 8.85—despite the small difference between them [the mean value of the ratio $c/(2a)$ is only 1.006]. The fluctuations associated to the cell lengths are small—about 0.1% of their values. Therefore, the difference between the cell parameter mean values is significant. In the disordered solid, the fluctuations are much larger but, as expected, the mean values of the three cell lengths are identical given the statistical noise. Table II shows the ratio $c/(2a)$ for the tetragonal solid at the coexistence points. At densities below that of close packing, the tetragonal symmetry of the system is reflected in the axes lengths, i.e., $c/(2a)\neq 1$. Departures from unity are, nevertheless, quite small (the maximum difference is about 2%) and become negligible as we approach the close packing density.

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