PHASE TRANSITIONS IN IONIC CLUSTERS

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ABSTRACT

Molecular dynamics simulations of unconstrained KCl clusters with 8, 64, 216 and 512 ions were carried out using the Born-Mayer-Huggins potential. All the clusters exhibit first-order-like melting and freezing transitions with hysteresis regions. The transitions are detected by sharp variations of the radius of gyration, configurational energy and by the analysis of the radial density functions, mean square displacements and power spectra. The "melting temperature" increases with the number of ions and approaches the melting temperature of the bulk. The radius of gyration turns out to be a good indicator of the transitions and of the sizes of the clusters. Its variation suggests that, for the present length of the simulation runs and temperature range, no evaporation took place. Glass-like transitions were also detected. Snapshots for solid, liquid and glass-like states show the structure of the clusters and some aspects of the nucleation.

INTRODUCTION

The first molecular dynamics simulations of ionic clusters were carried out by Fernandes[1] some years ago. Phase transitions were not detected since the right range of temperatures was not probed. Amini et al.[2-4] have studied the melting of alkali halides crystals with 512 ions, detecting melting and glass transitions, but no recrystalisation. Their potential and method of simulation were, however, different from those used in the present work. Recently, Sakamoto[5] has studied, by Monte Carlo, the behavior of alkali-halide clusters $(MX)_n$ with n=4,8 and 18 using the Born-Mayer potential without dipole-dipole and dipole-quadrupole contributions. He has detected a melting transition, but no information is given on recrystalisation or glassy states. The same kind of potential has been used in the most recent and extensive molecular dynamics calculations of KCl clusters with 8 and 64 ions carried out by Rose et al.[6-8]. They have detected melting and glassy states, but as far as freezing is concerned, they mention that in the 64 ions cluster extensive constant energy and temperature simulations revealed only a single case in which the cluster changed from its high-potential energy liquid-like form back into its low-potential energy solid-like form. In this instance, however, the return stay in the solid-like form was relatively short and moreover, once the cluster eventually transformed back into its liquid-like form it remained liquid-like for the duration of the simulation.

In this article we present constant energy molecular dynamics results for KCl clusters with 8, 64, 216 and 512 ions using the Born-Mayer-Huggins potential[9]. The most representative results are graphically shown mainly for the 64 ions cluster. The differences relatively to the other clusters are explained in the text and eventually complemented with specific figures. The main purpose of the present work is to produce extensive and reliable results for clusters of ions interacting through that potential model and to analyse their phase transitions and stability. These results will be used, in a future work, with the results for the bulk system, to study the artifacts of the simulation process, the importance of the surface in phase transitions and the heating and cooling procedures.

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COMPUTATIONAL DETAILS

For each cluster we have performed three types of calculations: slow heating, slow cooling and instantaneous cooling by adjusting the velocities of the ions accordingly. Each cluster was firstly equilibrated at a very low temperature, about 1K, from a face-centred cubic lattice (so that the coordinates of the ions were between -0.5 and +0.5 in program units) after which the starting configuration for each temperature was taken as the final configuration of the previous run in order to increase or decrease the temperature. A time-step of 0.8×10^{-14}s has been used with the Verlet's leap-frog algorithm[10].

The radius of gyration of the cluster is defined as:

$$RG = < \sum_{i=1}^{N} |\mathbf{r}_i - \mathbf{r}_{cm}| / N >$$

where N is the number of ions, $\mathbf{r}_i$ is the position vector of the ion i and $\mathbf{r}_{cm}$ is the position vector of the centre of mass of the cluster.

The radial density functions were calculated taking as origin the nearest ion to the centre of mass.

Equilibration runs with 10^5-10^6 time-steps were always followed by production runs with 10^6-10^7 time steps.

The calculations were carried out in the CONVEX C3410 and IBM/RISC/550 at the Computing Services of the Faculty of Sciences, University of Lisboa and in the CONVEX C220 at the Foundation for National Scientific Computing (FCCN), Lisboa.

RESULTS AND DISCUSSION

The heating and cooling behaviour of the 64 ions cluster is displayed in the following Figures 1, 2, 3, 4 and 5. Snapshots are in a different section at the end.

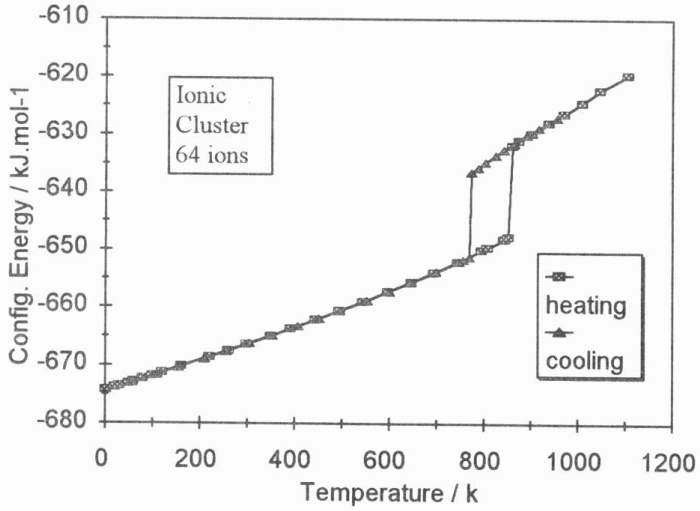


Figure 1. Configurational energy versus temperature

The curves were obtained by slow heating and cooling the cluster. The evolution of the radius of gyration, in Figure 2, suggests that no evaporation took place in that range of temperatures, since the initial positions of the ions were between -0.5 and +0.5 in box units.

The behaviour of the energy and radius of gyration for the 8 ions cluster is very similar to those of the 64 ions cluster, although it shows a much smaller hysteresis region. The radial density functions (Figures 3 and 4) and the Snapshots 1 and 2 show, clearly, solid and liquid-like structures. Those structures are stable for the duration of the simulation. The power spectra, not shown here, obtained by Fourier transforming the velocity autocorrelation functions also confirm the existence of those structures.

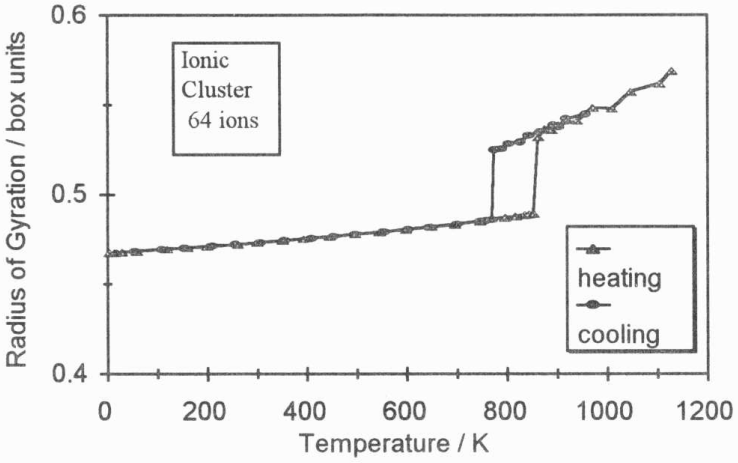


Figure 2. Radius of gyration versus temperature

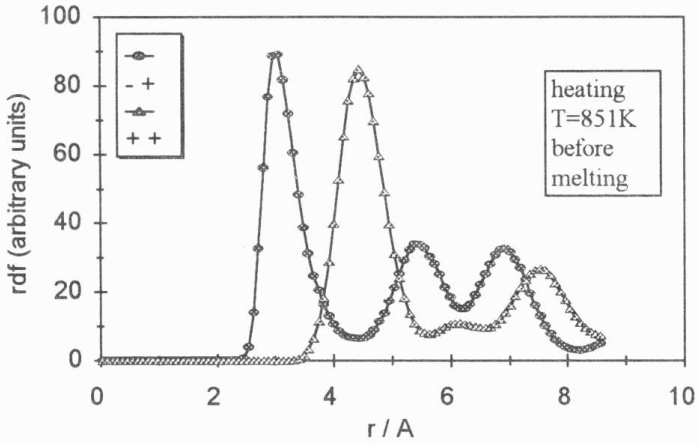


Figure 3. Radial density functions before melting (64 ions)

All the clusters have recrystalised by slowly cooling the liquid. Figure 5 display the mean square displacements just before and after the freezing and Snapshot 3 show the structure after cooling slowly until 2K. Evidently the cluster has recrystalised in its perfect original cubic lattice.

The clusters with 216 and 512 ions show a similar behaviour, although some differences should be noted. Firstly, the respective hysteresis regions are greater than those presented by the 8 and 64 ions clusters as observed in Figure 6 . Secondly, the slow cooling curve in the solid part does not coincide with the corresponding slow heating curve, being systematically (~ 4kJ) higher in energy. This reflects an imperfect growth of the crystal as can

be observed in Snapshot 4, taken at the end of the slow cooling process. The structure has a surface energy higher than the perfect crystal.

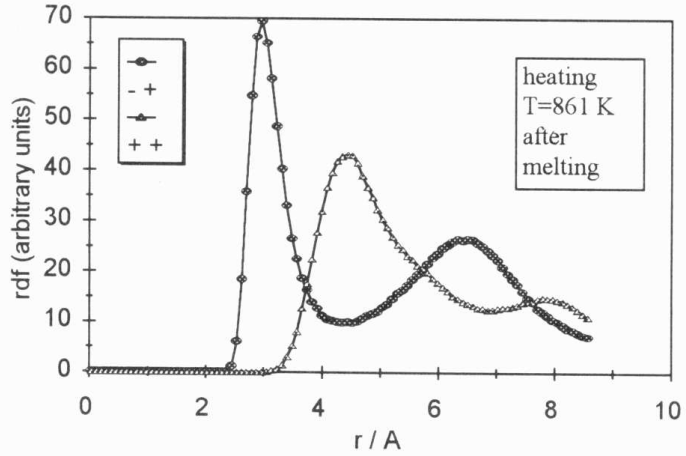


Figure 4. Radial density functions after melting (64 ions)

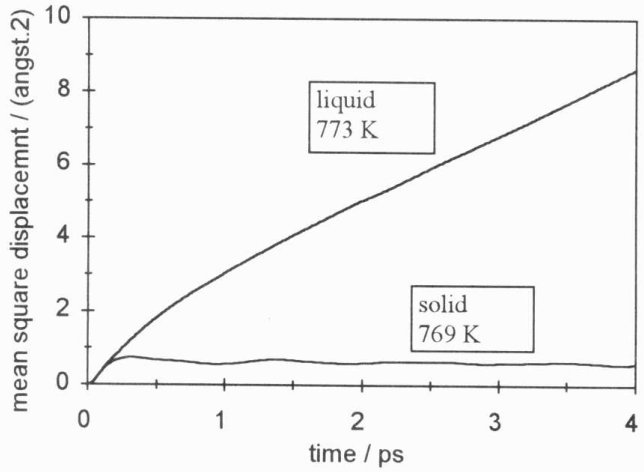


Figure 5. Mean square displacements before and after freezing (64 ions)

The melting points of the clusters have been estimated by taking the arithmetic mean of the apparent melting and freezing temperatures and the following values were found: 696K (8 ions), 817K (64 ions), 890K (216 ions) and 906K (512 ions).

Finally, the fast cooling curve in Figure 6 was obtained by instantaneously cooling the liquid at 0.75 , 0.5 , 0.35 , 0.25 and 0.1 T_m where T_m is the estimated melting temperature. At about 0.3 T_m a glass-like transition is detected by a slight change in the slope of the enthalpy curve and a marked decrease in the mean square displacements. This behaviour is similar to the one reported for the bulk system[11,12]. Snapshot 5 show the structure of the cluster at 0.1 T_m .

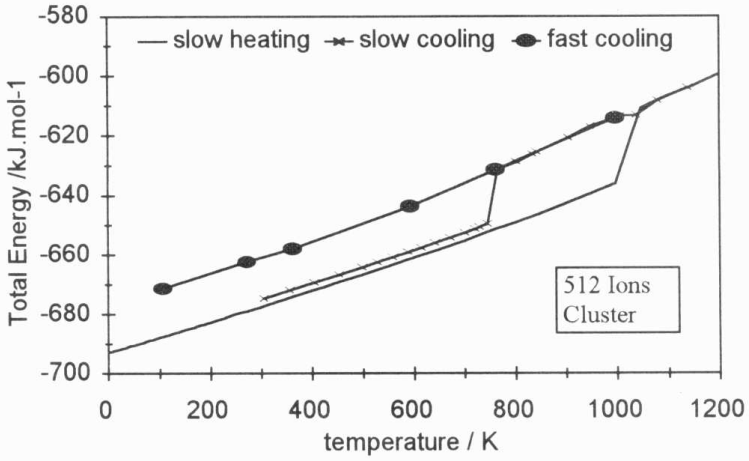
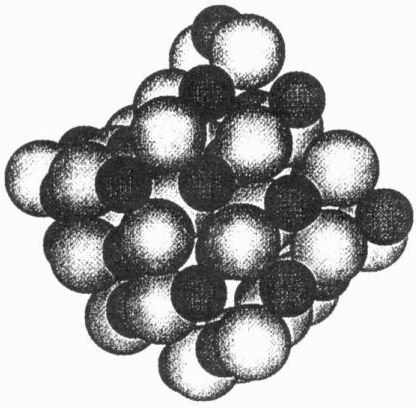
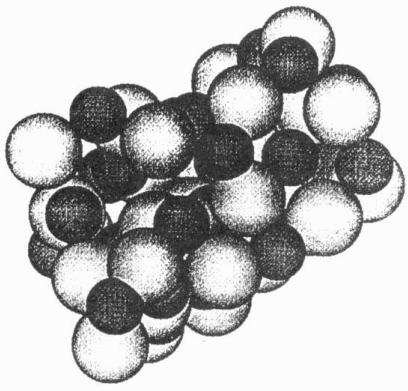


Figure 6. Total energy versus temperature

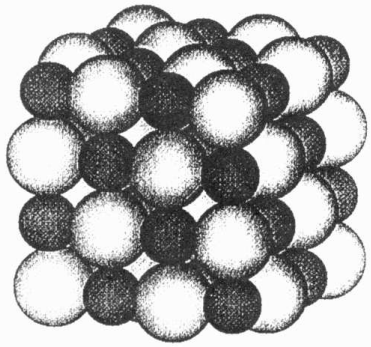
SNAPSHOTS



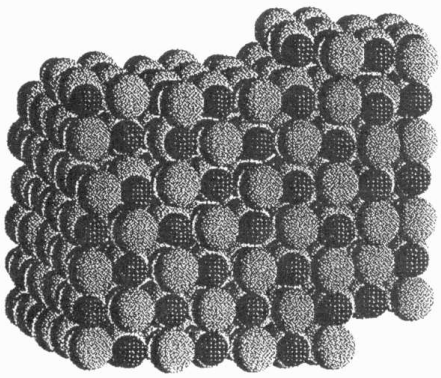
Snap. 1. Before melting, 851K (64 ions)



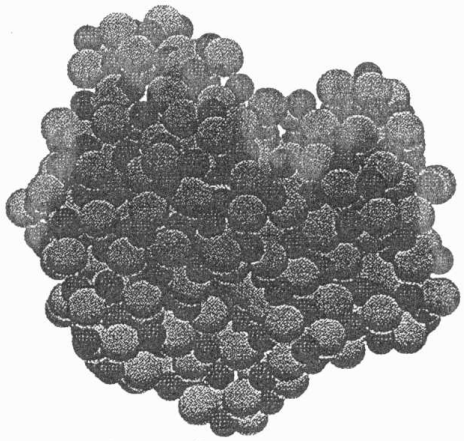
Snap. 2. After melting, 861K (64 ions)



Snap. 3. After slow cooling, 2K (64 ions)



Snap. 4. After slow cooling, 100K (512 ions)



Snap. 5. After fast cooling, ~100K (0.1 T_m ; 512 ions)

FINAL COMMENTS

Our results show that all the clusters exhibit first-order-like melting and freezing transitions. Glass-like transitions are also detected by instantaneously cooling the liquid. The structures before and after the transitions are stable for the duration of the simulation runs. The freezing of the 216 and 512 ions clusters leads to imperfect crystals. The estimated melting temperature increases with the number of ions and approaches the melting temperature of the corresponding bulk system (~ 1000K).

Chokappa and Clancy[13], in their extensive study on the melting and freezing of the Lennard-Jones system, suggest that the superheating and supercooling of the system are not an artifact of the simulation, but are probably related to the lack of a surface in the bulk simulated system and the tendency of the boundary conditions to suppress the long-range fluctuations. The unconstrained clusters of the present work, however, have surfaces and no boundary conditions. Even so, they present superheating and supercooling with hysteresis regions increasing with the number of ions and approaching the hysteresis observed in the bulk model system for KCl[14].The 512 ions cluster, for example, superheats about 14% above the estimated melting temperature as in the corresponding bulk system. This is, also, the value reported by Chokappa and Clancy. These questions are presently being investigated.

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