

INVESTIGATION OF MELTING BY MOLECULAR DYNAMICS SIMULATION

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Abstract The melting of a 64 ion microcrystal of KCl was studied by means of a molecular dynamics computer simulation. We used a central pair interaction with an inverse power law repulsion. The thermodynamics, kinetic and structural properties such as melting temperature, latent heat, mean square displacement, diffusion constant, radial distribution function and bond angle distribution are calculated. The simulation indicated that the melting temperature of the microcrystal is lower than the experimental value of the bulk, which is consistent with the Gibbs-Thompson relation. It is shown that all the features of the melting transition which are observed in a bulk system are also exhibited by such a small microcrystal. The simulation is programmed in FORTRAN and run on a PC.

Key Words Molecular Dynamics, Molecular Dynamic Simulation, Melting, Microcrystal, Ionic Salts

چکیده پدیده ذوب در یک ریز بلور کلرور پتاسیم متشکل از ۶۴ ذره با روش دینامیک مولکولی شبیه سازی شده است. پارامترهای ترمودینامیکی، جنبشی و ساختارهای ریز بلور نظیر دمای ذوب، گرمای نهان، میانگین مربع جابجایی، تابع توزیع شعاعی و توزیع زاویه پیوندی محاسبه و در پاره ای موارد با نتایج تجربی مقایسه گردید. دمای ذوب کمتر از مقادیر تجربی سیستم انبوه (bulk) بدست آمد که این نتیجه با رابطه گیبس-تامسون تطابق دارد.

INTRODUCTION

The melting is a process in which at a certain temperature a solid undergoes a phase change to a liquid. This has been the subject of intensive investigation from the theoretical, experimental and the computer simulations points of view during the last few years [1]. One reason for this tendency is that while there is no question about the thermodynamic significance of melting, the mechanism of how the transition occurs is not yet completely understood. According to thermodynamics, at melting temperature the solid and liquid coexist in equilibrium with equal Gibbs free energies. However, it says nothing about the structural arrangements of the atoms and their characteristic motion during melting, *i. e.* although it is generally known that why and when the phase transition occurs,

it is not clear how it takes place. At various times a number of theories have been proposed. An early model, presented by Lindemann [2], treats melting as a vibrational instability. By Lindemann criterion, the melting starts when the mean-square amplitude of vibrations of atoms about their equilibrium position becomes larger than a certain fraction of the lattice spacing. Later it was suggested by Born [3] that the transition arises from the onset of a mechanical instability, manifesting itself in an imaginary phonon frequency. Finally, in the theories of Cahn and others [4], the spontaneous production of intrinsic lattice defects, such as the catastrophic generation of dislocation near the melting point [5], or the presence of thermal vacancies and other point defects [6] are thought to be responsible for melting.

In all of these models only the effects of intrinsic

defects are considered and the role of extrinsic defects such as surfaces, dislocations and grain boundaries are totally ignored. Hence, the extent to which the theories are reliable is still an open question. Specially, in contrast to the assumptions of the above theories, a variety of experimental data indicates the significant role of the extrinsic surface [7-12].

The experimental study of melting is difficult because it is an extremely rapid process and hence structural changes can not easily be followed through the melting transition, particularly in the case of a bulk sample. On the other hand, molecular dynamics simulations as a powerful technique for studying the thermal behavior of matter has become a suitable method for the study of melting.

In this paper, first we discuss the molecular dynamics (MD) simulation and then we report an MD experiment on the melting of potassium chloride crystals with free surfaces. The simulated system is a cubic microcrystal of 64 ions. The study of these small clusters are particularly important because they can provide the intermediate information desired for the transition from small isolated atomic systems to the large scale bulk materials [13-18]. Interesting enough that the major features characterizing physical melting are observed in this small system.

MOLECULAR DYNAMICS SIMULATION

Since the pioneering work of Alder and Wainwright [19, 20] the molecular dynamics method has been used for simulating several different systems: e. g. Lennard-Jones systems [21], liquid metals [22], ionic liquids [23] and molecular liquids [24]. The method has also been used to study melting and glass formation [25-28]. The MD is a computer-based technique for modeling fluids, crystals and glasses at microscopic levels of distance and time. This kind of computer simulation is now well established and many physical results can be obtained from such simulations [29].

In an MD study, a system of N particles is placed within a box, generally a fixed volume cube, called the "calculation box". A set of velocities is assigned in such a way that the average kinetic energy of the particles in the system gives the desired temperature, while the net linear momentum is chosen to be zero. Mathematically the model is described by applying the law of force between each pair of particles and stating that the particles move according to Newton's laws of motion under these forces. The force on a particle, i , with mass m_i , position \mathbf{r}_i and velocity \mathbf{v}_i due to particle j is $\mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ and the equations of motion are simply

$$\dot{\mathbf{r}}_i = \mathbf{v}_i \quad (1a)$$

$$m_i \ddot{\mathbf{r}}_i = \sum_j \mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j) \quad (1b)$$

Where, $i = 1, 2, \dots, N$. This is a system of $6N$ ordinary differential equations, which can be solved numerically. From the positions and velocities of the particles at each timestep both the static and dynamic properties of the system can be calculated accurately.

MD simulations have a number of valuable features such as: the possibility of direct monitoring of individual atomic motions, access to practically non-obtainable laboratory conditions, and the ability to study the rapid processes. Another aspect of MD studies is that they can provide the possibility for investigating the reliability of theoretical models by comparing their results with quasi-experimental data obtained by simulation with similar preconditions.

However, the technique has some limitations related to the approximate nature of the interatomic potentials, finite system size and duration of the simulation which can be explained as follows:

(i) In a simulated system the particles interact according to some prescribed force law. This has the great advantage of testing and improving the theories, but it puts the results of the simulation in doubt

because of uncertainty in the form of the force law.

(ii) To solve the equations of motion numerically, the continuous differential equations 1a and 1b are replaced by finite difference equations which give values of \mathbf{r} and \mathbf{v} at discrete time intervals. The length of the timestep, which comes into such calculations, depends on a number of factors [30]: the temperature, the density, the mass of the particles, and the nature of the force law. A typical timestep is of the order of 10^{-14} seconds. This small timestep makes the simulation of even one second of physical time totally impossible, so that although MD can examine very short time-scale effects, it cannot model at experimentally observable time-scale.

(iii) The bulk of computational effort in MD simulation is concerned with the calculation of force at each step (rhs of Equation 1b). If all the interactions of N particles are individually calculated, the number of floating-point computer operations in each step is proportional to square of N . This limits N to a few hundred or thousand even on the fastest computers currently available. Therefore, the number of particles in a simulated system is far below the number in a real system ($\approx 10^3$ compare with $\approx 10^{23}$). This makes the model much smaller than any physical system which can be studied in the laboratory. To simulate the properties of a bulk system more closely, periodic boundary conditions are usually imposed [29, 30] in which the cubic box is replicated throughout space to form an infinite lattice, *i. e.* the calculation box is surrounded by infinite number of images. Each image is a box, exactly as the calculation box, containing N particles with the same relative positions. When a particle leaves the central box, one of the images will enter through the opposite face to balance the move.

SIMULATION DETAILS

In this paper, we report the result of simulation for a system of 64 particles (32 Cl^- and 32 K^+). The ions

were placed in the calculation box in the form of a cubic microcrystal with the rocksalt crystal structure. This is an alternative to the usual technique in which the calculation box is filled with particles, and the periodic boundary condition creates a pseudo-infinite system. The choice of isolated microcrystal is motivated by at least three factors: Firstly, the advantage of having free surfaces which allows the crystal to expand during the heating while remaining at zero pressure, Secondly, the significant role of the surfaces on melting, and finally the complicating effect on the generation of dislocations due to the imposition of periodic boundary condition.

Here, we have used a simple central pair interaction with an inverse power law repulsion [25-27]. The force of interaction between a pair of ions i and j , at separation \mathbf{r} is

$$\mathbf{F}_{ij}(\mathbf{r}) = \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r^2} (\pm 1 + (S_i + S_j)/r^n) \quad (2)$$

The sign of the first (Coulombic) term is positive for similar ions and negative for others. The parameter s is proportional to the ionic radius, and n determines the hardness of the repulsion (in this simulation $n = 8$.) The value of s_+/s_- was taken from Pauling [31] and we chose the value of $s_+ + s_-$ in such a way to reproduce approximately the observed lattice spacing for the crystal ($s_+ = 0.10971$, $s_- = 0.150289$ nm).

The time integration of Newton's laws of motion was conducted by the "leapfrog" algorithm [30] in which the position \mathbf{r}^n and the velocity $\mathbf{v}^{n+\frac{1}{2}}$ of a particle at timesteps n and $n+\frac{1}{2}$ are defined alternatively:

$$\mathbf{v}^{n+\frac{1}{2}} = \mathbf{v}^{n-\frac{1}{2}} + (\mathbf{F}^n/m) DT \quad (3a)$$

$$\mathbf{r}^{n+1} = \mathbf{r}^n + \mathbf{v}^{n+\frac{1}{2}} DT \quad (3b)$$

Here \mathbf{F}^n is the total force on particle i (of mass m) at step n . The timestep DT was chosen to be about one-sixteenth of the period of oscillation of a typical ion

in the crystal (here we used $DT = 0.75E-14$ s). As the positions are calculated at each timestep but the velocities are known at each half time-level, the kinetic energy of the system, K^n , at timestep n (average values of the kinetic energies of all particles in the system at step n), was calculated [32, 33] from:

$$K^n = (K^{n-1/2} + K^{n+1/2})/2 + (P^{n+1} + P^{n-1} - 2P^n)/8 \quad (4)$$

where P^n is the potential energy of the system at step n .

For this simulation the ions were given initially a velocity distribution corresponding to a temperature of 200 K, and the temperature was held at this value by scaling the velocities in each timestep for 800 steps. This was followed by 800 timesteps in which the velocities were not scaled. The microcrystal was then subjected to cyclic heating with a period of 300 timesteps. At each of the first 25 steps the system was heated by multiplying each velocity by the factor $HTFAC = 1.001$. It was then allowed to equilibrate for the remaining 275 steps of the cycle. The kinetic energy, potential energy, total energy and the temperature of the system were averaged over the last 64 steps of the cycle, and the mean square displacements of the ions in the system were accumulated over the last 275 steps of the cycle.

In order to measure the melting point and the thermodynamic properties of the solid and liquid, the simulation must start well below the melting point and continue to a temperature above it. Since the computer time required for this kind of simulation is substantial, it limited us to 64 particles.

RESULTS AND DISCUSSION

Figure 1 shows the graph of total energy against temperature of simulated system. Each point represents the result after a heating cycle. The crystal is heated from A through B to C, melts between C to

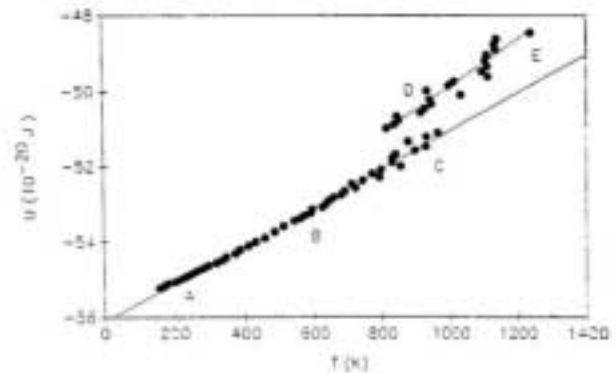


Figure 1. Variation of internal energy per particle (U) with temperature during the heating of 64 ions system. The labels A-E represent the selected points which are studied in detail.

D, and the liquid is heated from D to E. A clear first order phase change occurs between the points C and D from which the melting point, $T_f = T(C \text{ or } D)$, and the latent heat, $L_f = U(D) - U(C)$, can also be obtained. The specific heat of solid and liquid can be obtained from the slopes of the lines AC and DE.

The melting temperature and the latent heat obtained from our simulation are 950 ± 50 K and $1.1E-20$ J/particle respectively, and the corresponding experimental values for the bulk are 1045 K and $2.18E-20$ J/particle [26]. It is clearly seen that the simulated melting point and latent heat of the cluster are lower than the experimental values for the bulk. It is believed that the difference in the surface-to-volume ratio leads to the depression of the melting temperature in microcrystals as predicted by the Gibbs-Thompson relation [34]. This thermodynamics equation predicts a temperature reduction inversely proportionate to the diameter of the cluster. The lowering of the melting temperature with decreasing size of the cluster has also been observed by experiments [35].

Apart from the U-T curve, there are several other quantities which can be used to detect the melting. To study the diffusion of the particles we determined the mean square displacement (MSD) of the ions. The plots of MSD versus time for five selected point: A,

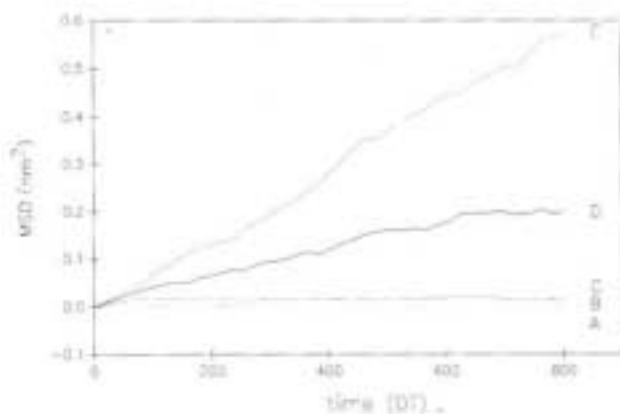


Figure 2. Plot of mean square displacement of the ions as a function of time at the five selected points. The points are as shown in Figure 1, with corresponding temperatures: A = 200 K, B = 455 K, C = 930 K, D = 920 K and E = 1240 K.

B, C (crystal), D and E (liquid) are shown in figure 2. The MSD values for K^+ are slightly higher than Cl^- 's. This can be attributed to larger ionic radius of Cl^- compared to K^+ ions [36]. For simplicity the average value of MSD for all 64 particles are used in this figure. The diffusion constant can be calculated from the slope of the MSD-time curve. In the solid, the MSD increases for a few steps and then stays nearly constant, which is the characteristic behavior of vibrational motion. In the liquid, the MSD increases almost linearly with time, indicating diffusion. A useful indication of the amount of diffusion is the final MSD of the ions from their starting position at the end of each heating cycle. This quantity is shown as a function of temperature in Figure 3. The labels A to E on this figure represent the selected points which are studied in detail. The sudden increase of the accumulated value of MSD at T_f gives a good indication of the melting transition.

Figure 4 is the plots of total energy, temperature and MSD obtained in this simulation as a function of time. This kind of presentation may help one to find out more about the melting mechanism and convey the actual feeling of the simulation. In order to save the computer time, at the beginning we heated the crystal more rapidly and the rate of heating was then

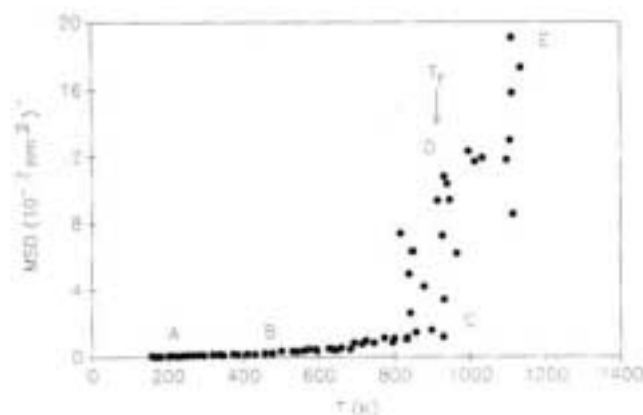


Figure 3. Accumulated values of mean square displacement of the ions over the last 275 timestep of each cycle as a function of temperature.

decreased. The change at point distinct at time 45 is caused by the change in HTFAC from 1.002 to 1.001. These figures show that, although during the melting T drops slightly (due to transferring part of kinetic energy to the potential), the total energy

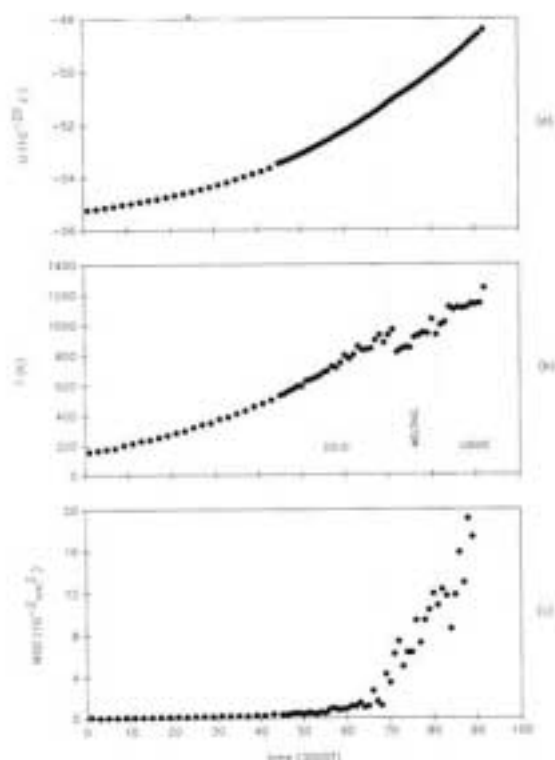


Figure 4. Variation of some thermodynamics properties of the system with time during the simulation: (a) internal energy, (b) temperature, (c) mean square displacement.

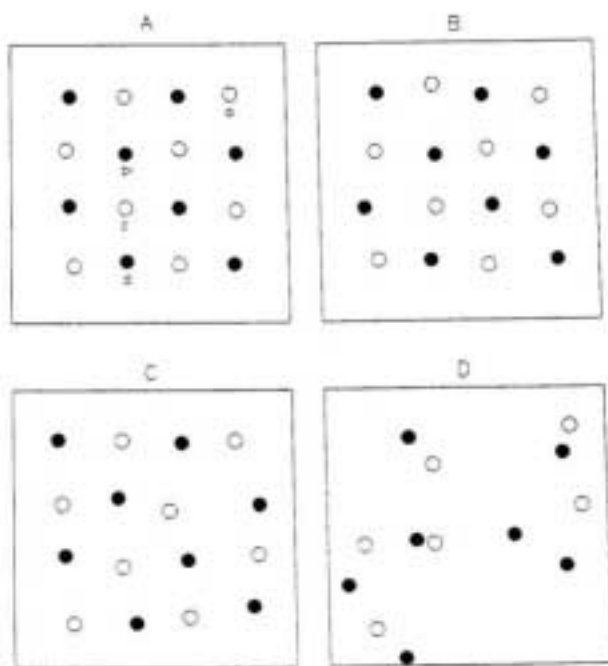


Figure 5. Instantaneous position of 16 ions originally located in a layer obtained by a hypothetical atomic camera at the selected temperature: three for solids (A, B and C) and one for liquid (D). The filled circles are Cl^- and the open circles represent K^+ .

increases at the same rate as before the melting. Figure 4(c) is possibly the best means of detecting the melting point, in which the value of MSD increases abruptly, due to the diffusing of the ions.

Figure 5 show the instantaneous plane position of the particles, on one layer only, obtained by a hypothetical atomic camera at the five selected temperatures. On the figure the filled circles are Cl^- and the open circles represent K^+ . As mentioned earlier the original microcrystal is composed of 4 layers, each containing 16 ions. It is clearly seen that at low temperature, the ions are located on an order array. By increasing the temperature the regulation diminishes and finally above the melting temperature (plot D) the ions are distributed without any observable order. A similar result can be obtained by plotting the one dimensional position of the particles on a period of time. This is shown in Figure 6 for four selected ions in the system and at four different temperature. The ions are selected in such a way to be a good

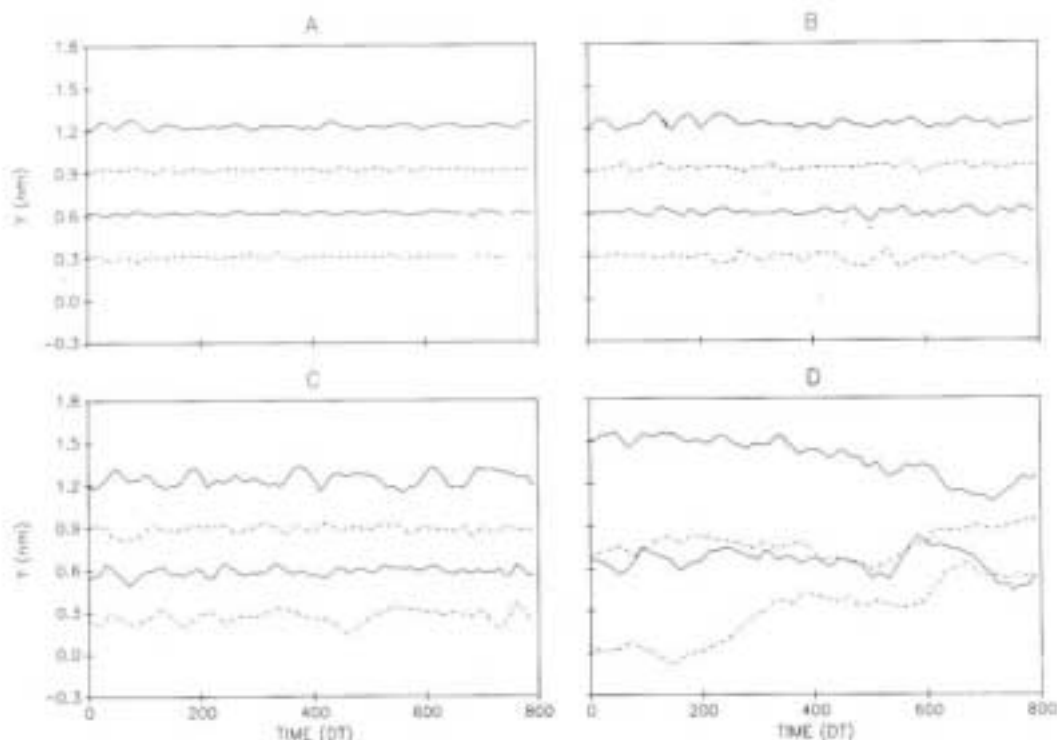


Figure 6. One dimensional position features of some selected ions with respect to time at the selected temperature: three for solids (A, B and C) and one for liquid (D). The selected ions are marked on figure 5-A (a, b, c, d).

representation of all the ions, among them there are two K^+ and two Cl^- which are chosen from the corner (a), middle (b and c) and edge (d) of the layer (see Figure 5-A). As expected by warming up the system, the fluctuation of the ions increases.

Another feature which can be observed during the simulation is the plot of trajectories of some selected particles in the system over a considerable number of timesteps. This is shown in Figure 7 for 4 ions which originally located in outer layer of the system the selected ions are the same as in Figure 6 (a, b, c and d). Again it can be seen clearly that at low temperature, the ions of the crystal are vibrating around their original positions with a small amplitude. By increasing the temperature of the crystal the amplitude of vibration has increased. Around the melting point (point C of Figure 1) some ions start to diffuse. Finally in the liquid case, the ions move around without any observable order.

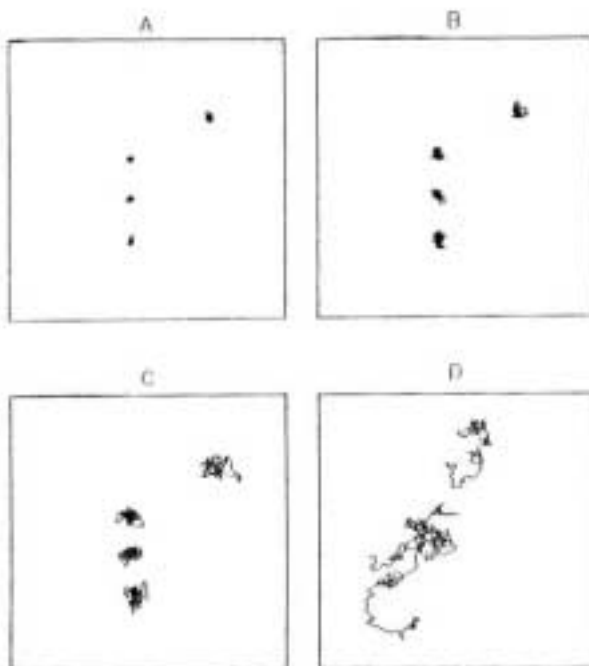


Figure 7. Projection of the trajectories of selected ions on the x-y plane over 800 steps, at the selected temperatures: three for solids (A, B and C) and one for liquid (D). The selected ions are marked on Figure 5-A (a, b, c, d).

In order to study the structural changes of the system under melting, we have plotted Figures 8 and 9. The $K-Cl$ radial distribution function (RDF) of crystal ($T=230\text{ K}$) and liquid ($T=1240\text{ K}$) are compared in Figure 8. The figure shows that, for crystal there are 4 distinct peaks. The first neighbor peak at around 0.32 nm shows the lattice separation of the simulated system is equal to the physical value of the bulk. As the system melts (Figure 8-b), the first peak moves slightly inward, and the other peaks diminish indicating loosing of long range order. The $Cl-K-Cl$ bond angle distributions (BAD) for the crystal and the liquid states of the system are compared in Figure 9. In the case of the crystal (Figure 9-a) there are two sharp peaks at 90° and 180° , which is expected from rocksalt crystal structure. When the system melts (Figure 9-b), the $Cl-K-Cl$ angles range from about 60° to 180° clearly showing the liquid structure.

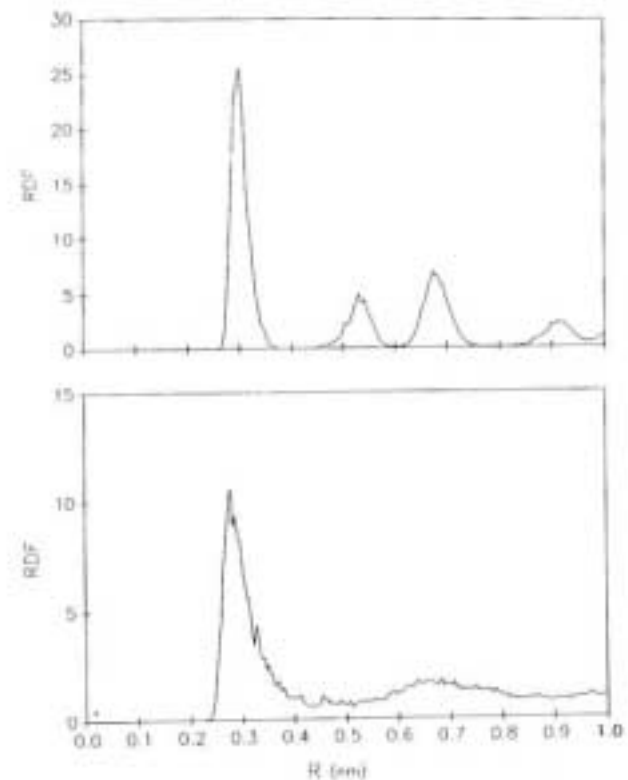


Figure 8. The $K-Cl$ radial distribution function (RDF) of crystal at $T=230\text{ K}$ (a), and liquid at $T=1240\text{ K}$ (b).

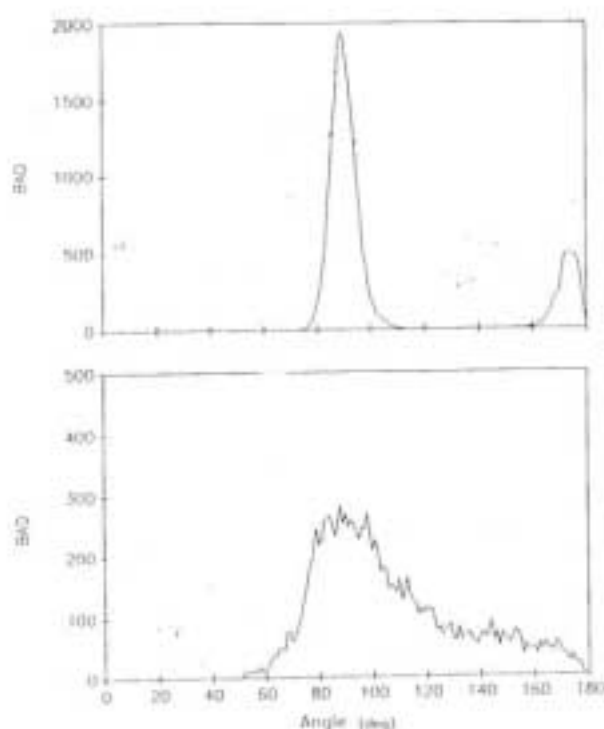


Figure 9. The Cl-K-Cl bond angle distributions (BAD) for the (a) crystal at T=230K and (b) the liquid at T=1240K.

CONCLUSIONS

In the present paper we have shown that a molecular dynamics simulation of a small KCl microcrystal of 64 ions exhibits most of the features of the melting transition which are observed in a bulk system. It is also shown that easily accessible micro-computers can be successfully used to perform scientific experiments. For present simulation, a run of 22000 timesteps, corresponding to 85 hours CPU time on IBM-PC was needed. In this calculation, the required computer time for trial runs and additional analysis are not included. The requirement of computer time limited us to a system of 64 particles, although there are many interest in the simulation of small cluster itself. It was possible to obtain the thermodynamics, kinetic and structural properties of the system and compare them with the corresponding values for the bulk. It was shown that all the features of the melting

transition which are observed in a bulk system are also exhibited by such a small microcrystal. Finally one should keep in mind that the significance of the simulation results is always limited by the reality of the interatomic potential used.

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