MOLECULAR DYNAMICS SIMULATION OF
POTASSIUM CHLORIDE MELTING

II. CONSTANT VOLUME AND CONSTANT PRESSURE SIMULATION
OF FILLED SYSTEM

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Abstract We have used a simple ionic potential to simulate the melting of |KCl|pseudo-infinite crystal. Two MD simulations, one with constant volume and the other with constant pressure condition are performed. These results are compared with the previous micro-sample simulation results. In the |constant|volume simulation the melting temperature increases substantially with increasing pressure. A method for constant pressure MD simulation of melting is discussed.

چکیده :   برای شبیه‌سازی ذوب بلور شبه بینهایت KCl ما از یک پتانسیل یونی ساده استفاده کرده‌ایم . دو شبیه‌سازی دینامیک مولکولی یکی با شرط حجم ثابت و دیگری با فشار ثابت انجام گرفته است . نتایج بدست آمده در این شبیه‌سازیها با نتایج قبلی ریزبلور مقایسه شده است . در شبیه‌ساز با حجم ثابت با افزودن فشار دمای ذوب سیستم افزایش‌قابل ملاحظه‌ای می‌یابد . یک روش برای شبیه‌سازی دینامیک مولکولی ذوب در فشار ثابت مورد بحث قرار گرفته است .

INTRODUCTION

In this part we report two molecular dynamics simulations which were conducted to study the melting of a pseudo-infinite potassium chloride crystal. The aims of this study were (a) to investigate the filled system method for melting simulation and the problems involved, (b) to obtain the melting parameters for an infinite system and (c) to compare the results of microcrystal melting with a constant pressure filled system using the same material and potential.

For present simulations KCl has been chosen as we have investigated different sized microcrystals of it extensively [1, 2]. The interaction potential and its parameters are exactly the same as in part I except here we have filled the whole calculation box with the particles (method A of Sec. 2, part I). Two simulations, one with constant volume and the other with constant pressure have been carried out.

CONSTANT VOLUME SIMULATION

Initially a 512 ion crystal was set-up to form a cube, with 8 ions on each side, with the rocksalt crystal structure in such a way as to fill the whole calculation box. The temperature was held at a constant value of 600° K for the first 200 timesteps. The simulation continued for another 400 timesteps without changing the temperature for the system to equilibrate. The calculation box side has been chosen in such a way that the system stays at zero pressure around this temperature. The crystal was then heated using the cyclic heating procedure [1]. But in this case the

heating cycle increased to 400 steps and HTFAC=1.002. The calculation box length was kept constant throughout the simulation (2.56 nm).

By increasing the temperature both total energy, U, and pressure, P, are raised. The system stayed as a crystal up to a temperature well above the physical melting point of KCl . At a temperature of about 2150°K the crystal started to break down and this point was detected as the melting point of KCl crystal under a very high pressure (constant volume melting). Different features of melting at this point are:

(a) A discontinuity in U/T curves.

(b) A large increase in MSD (diffusion).

(c) A decrease in nearest neighbours' distance.

(d) A sharp decrease in the number of six-fold coordinated ions.

(e) A change in the distribution of bond angles from solid to liquid like.

(f) A change in RDF from the crystal to liquid form.

(g) A plot of the distributions of ions, especially the plane projections, shows an order-disorder change.
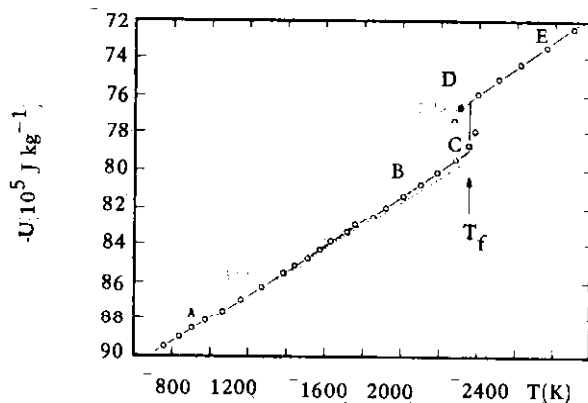
Figure 1 shows the variation of U as a

Figure 1. *Variation of total energy with temperature during the constant volume heating of pseudo-infinite KCl system.*

function of T for this simulation. The solid is heated through A and B to C, it melts from C to D and the liquid is heated from D through E to 2700°K. The circles on this figure show the results obtained after each heating cycle. U and T are averaged over the last 64 time-steps and all the particles in the system. For the solid part of U/T curve two straight lines can be fitted to the results. This shows a slight increase in the specific heat at T $\cong 1200$ K. The following values are obtained for this simulation:

Melting point, T_f=2150 ± 30 K.
Latent heat, L_f=1242 K per ion.
Specific heat of solid below 1200°K, C_V=2.78.
Specific heat of solid above 1200°K, C_V=3.08.
Specific heat of liquid, C_V=3.133.
Entropy of melting, S_f=0.578.

Variation of pressure and accumulated MSD (over 375 steps) with temperature are shown in Figures 2 and 3, respectively. In both figures the melting transition is quite clear. The pressure of the liquid at the melting point is about 10 kbar higher than the corresponding pressure of the crystal. Accumulated values of MSD in the solid increase almost linearly up to 200°K below T_f and between this temperature and T_f their increase is slightly more. A sharp increase in MSD at melting specifies the diffusion of particles in the liquid.

Visual observation of the positions of the ions in the system is the most direct method of detecting the melting transition. In Figure 4 the isometric and X-Y projection of all the particles in the system are shown for points A, B and E of the U/T curve. Each projection corresponds to one timestep of the run and the projections on other perpendicular planes are similar to the X-Y projections. As the temperature (and pressure) of the crystal increases
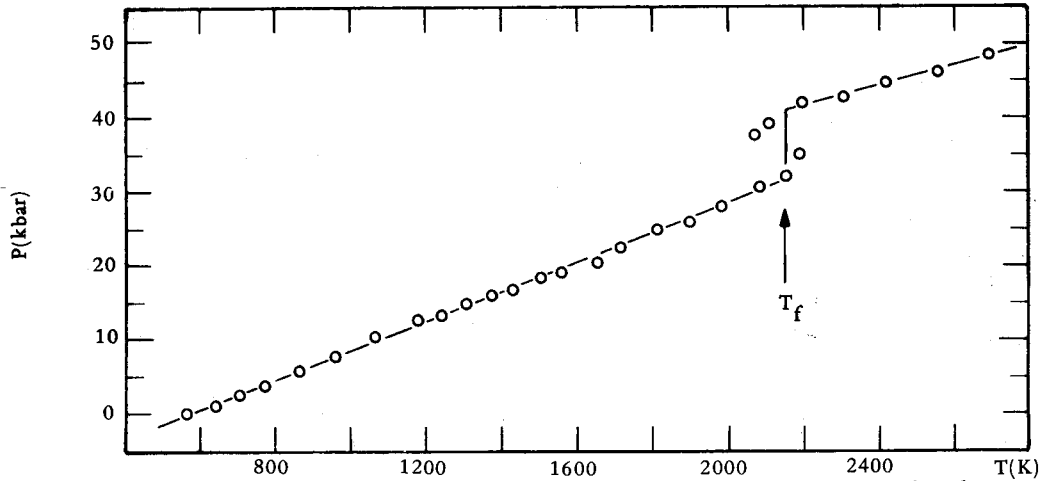
Figure 2. *Variation of pressure with temperature during the heating and melting of KCl system at constant volume.*
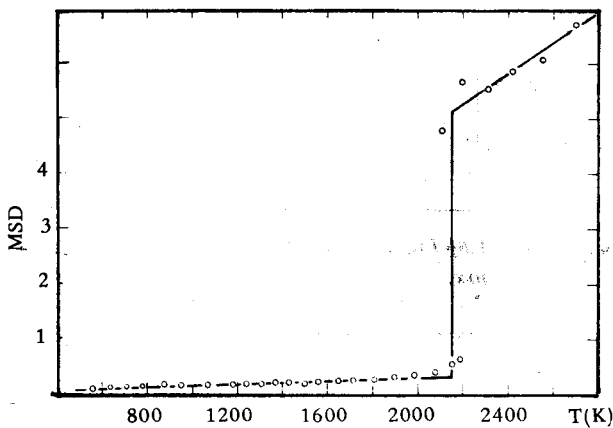

Figure 3. *Variation of the accumulated values of average mean square displacement, over 375 time-steps, with temperature for constant volume melting of KCl system.*

the cubic unit cells are more distorted. Although the average coordination number of the K and Cl ions remained six, even after melting, the percentage of other coordinated ions increases in the solid with increasing temperature. There is a further substantial increase on melting. In Figure 5 variation of six-fold coordinated ions with temperature is shown. If all the unit cells remain as a perfect cube then all the ions in the system should be six coordinated. But the figure shows that with increasing temperature the six-fold coordinated ions decrease i.e., the cubic unit cells are increasingly distorted. Interestingly, at a temperature T $\cong 1200$ K the slope of the curve

in Figure 5 has changed and this is the temperature at which we observed an increase in specific heat of the solid.

In Figure 6 the radial distribution functions, RDF, at three selected points, A, B and E, are shown. The effect of temperature (or pressure) on the RDF of the solid is to depress the peaks. At point B the second peaks on the like-like distributions have almost disappeared. Each distribution is normalized to unity for an infinite system. The accumulated values of the RDF are also displayed on the graphs and show that the average coordination number of Cl remains near six in both the crystal and high pressure liquid.

We also show in Figure 7 the distribution of the coordination numbers and the bond angle at the three selected points on the U/T curve. The main difference between the distributions of the bond angle for the liquid and crystal is that in the liquid there is a peak (here $\cong 80$ degrees which monotonically decays to zero at 180 degrees which for the crystal there are always two peaks at about 90 and 180 degrees (at higher temperature the second peak moves to an angle less than 180 degrees) which is characteristic of the rocksalt crystal structure. What is interesting here is that at point B, with less than 80% of ions six-fold
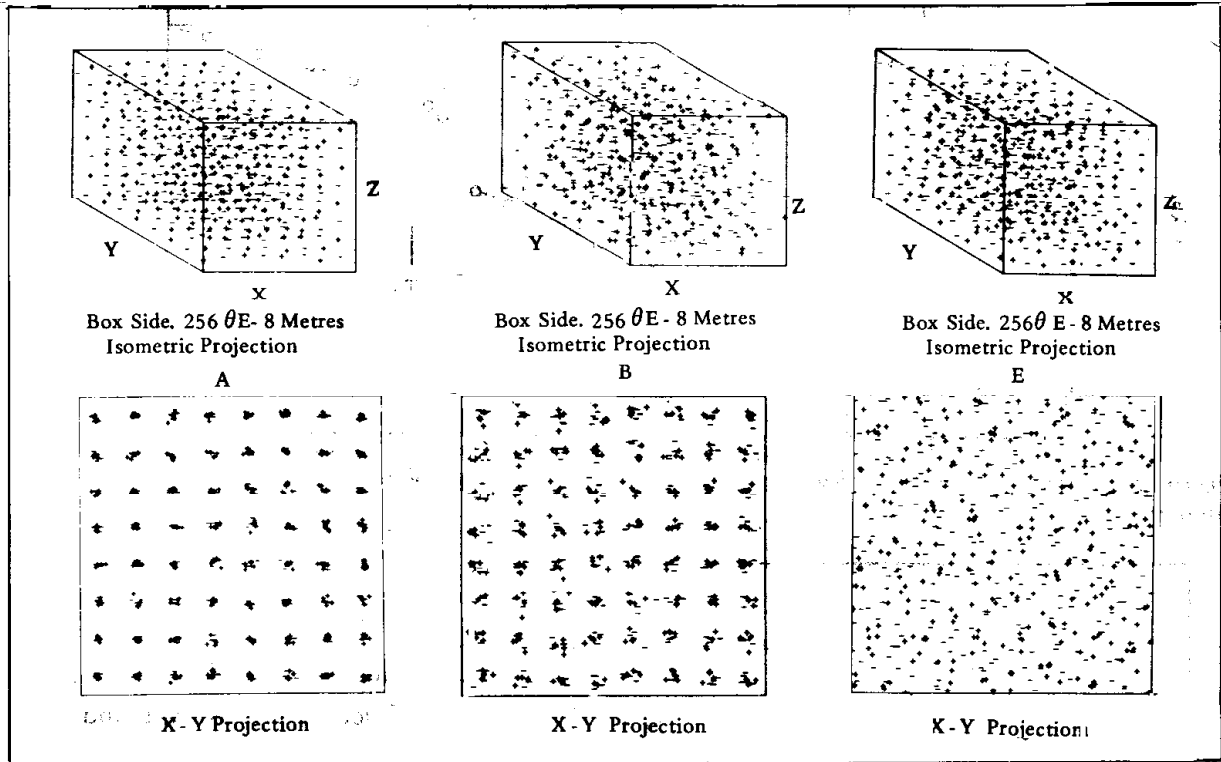
Figure 4. Distribution of ions in the system for three selected points of Figure 1. Positive ions are marked with a (+) and negative ions with a (−). The box delineates the calculation box.
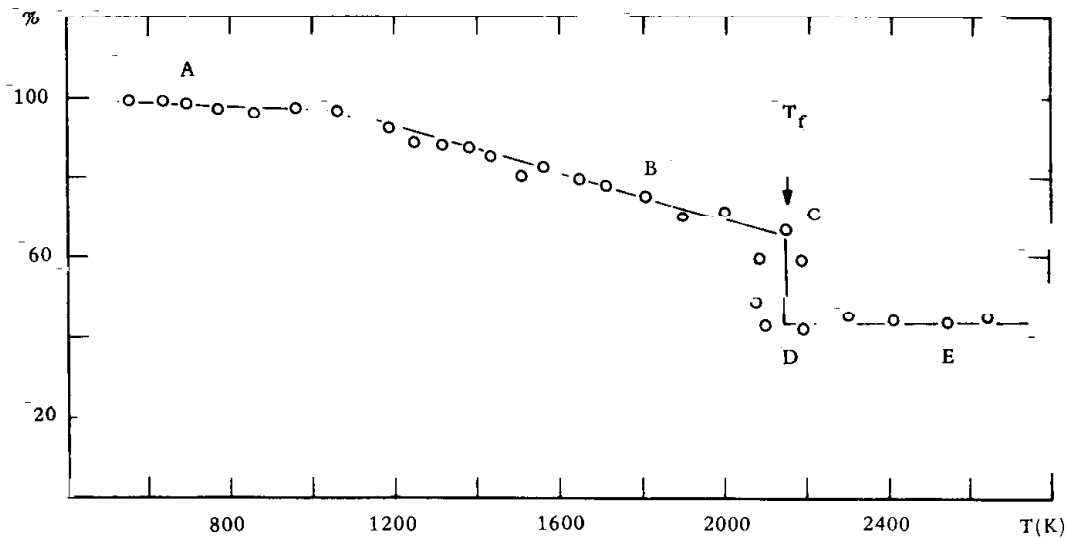

Figure 5. Percentage of six-fold coordianted ions as a function of temperature during the constant volume heating and melting.

coordinated, the crystal structure is still present and the temperature rises another 350°K before melting occurs. At the point that the crystal under high pressure melts (point C of Figure 1) there is only 65% of the ions perfectly six-coordinated.

CONSTANT PRESSURE SIMULATION

In a system in which the whole calculation box is filled with the particles, and the periodic images make it a pseudo-infinite system, there are two possibilities of keeping the pressure
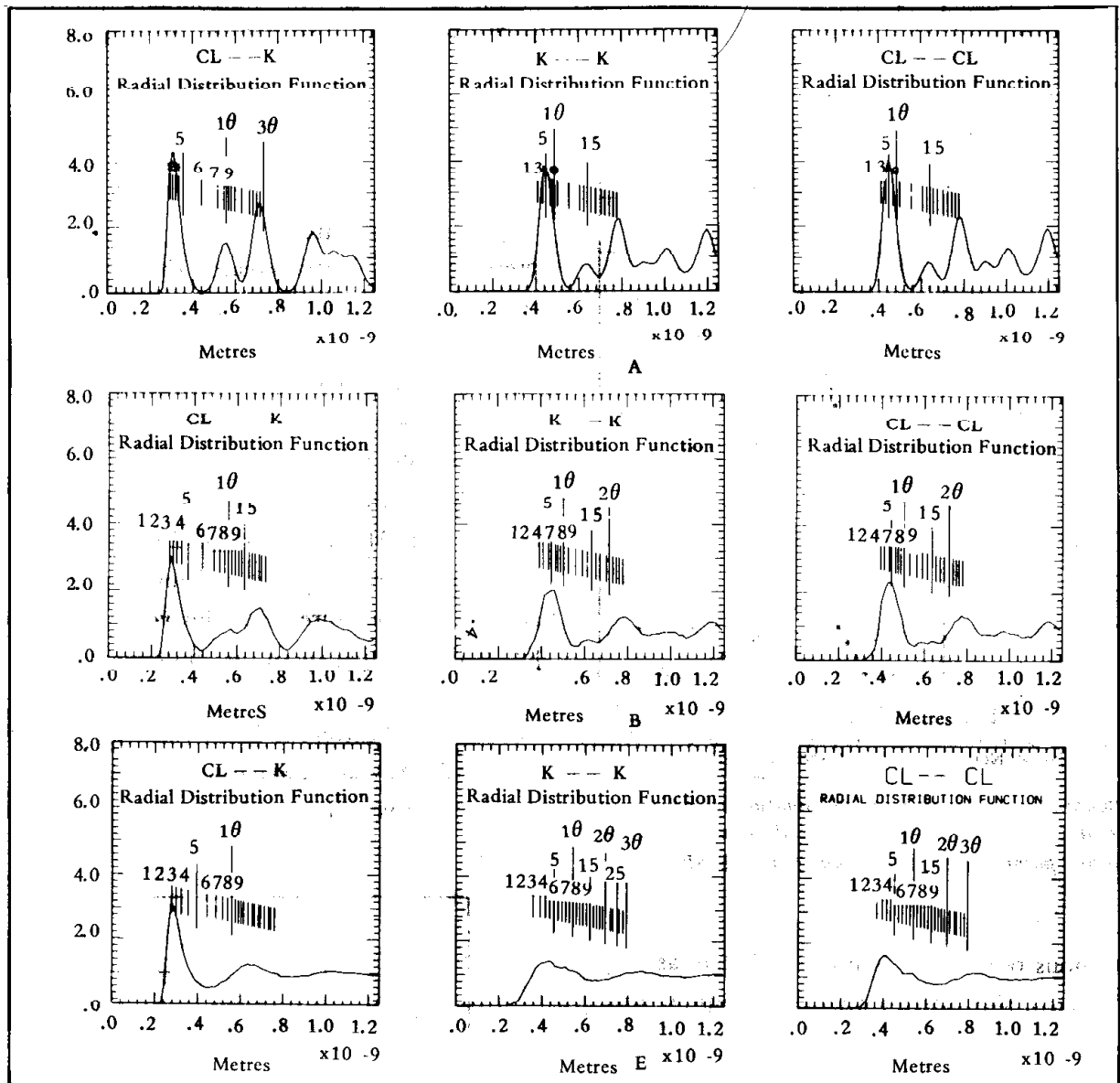
Figure 6. The radial distribution functions of the three selected points of KCl constant volume simulation.

constant while increasing the temperature: (a) reducing the size of ions in the force law, or (b) increasing the calculation box-length. We have used the second method in this simulation which corresponds to physical experiments of melting.

This simulation was carried out with a 512 ion KCl crystal with all the parameters, except the box-length (BL), the same as the constant volume case. In this case when we start with an equilibrated system (T_1, V_1,

P_1, U_1) and change only the value of BL the resulting system with thermodynamic parameters T_2, V_2, P_2, and U_2 is not in equilibrium . Therefore while we are changing the volume of the system to produce the right pressure the velocities should also be scaled to reach the desired temperature. After such a change the simulation must continue for some time for the system to reach a new equilibrium. So the new state can no longer be regarded as the natural continuation of the
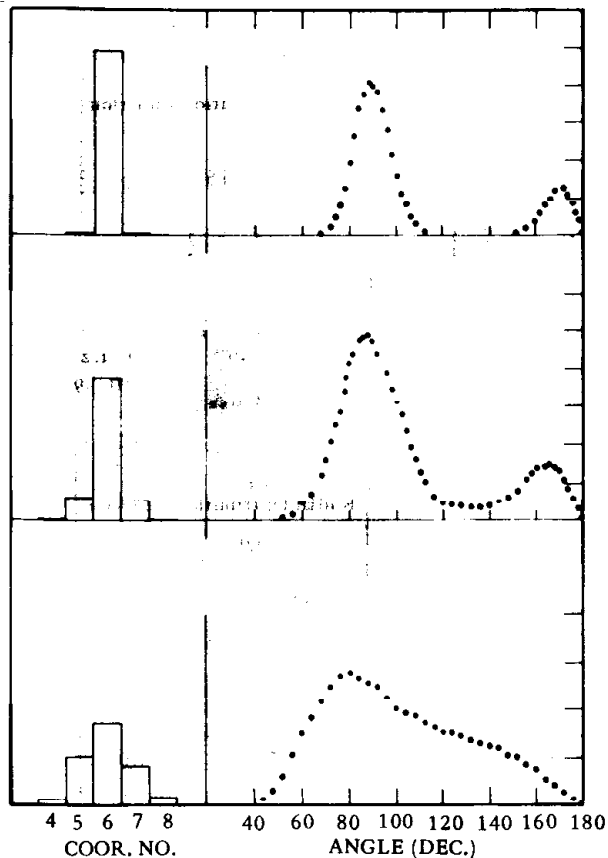
Figure 7. *Distribution of coordination numbers and bond angles of the three selected points: point A (top), point B (middle) and point E (bottom).*

4 5 6 7 8
COOR. NO.

40 60 80 100 120 140 160 180
ANGLE (DEC.)

coordinates of the constant volume experiment at T=600°K (Sec. 2) and the T and BL are suddenly reduced to 400 °K and 2.528 nm respectively. This value of BL was estimated by considering the thermal expansion of the crystal. After running the system for 400 steps to equilibrate it was found that the pressure was slightly greater than zero. At this stage the volume was not changed again but the pressure was made zero by reducing the temperature with the cyclic heating procedure. At T=390 °K the pressure stayed at zero. Another point was obtained in the same way by starting from an 800 °K crystal of Sec. 2 and BL expanded to 2.60 nm. The temperature in which the system remained at almost zero pressure with this volume is 790 °K. A line joining these two points in the V-T plane has been used as a guide to guess the values of V at different T. As the temperature was raised the volume expansion increased and the V-T curve was no longer a straight line, (Figure 8).
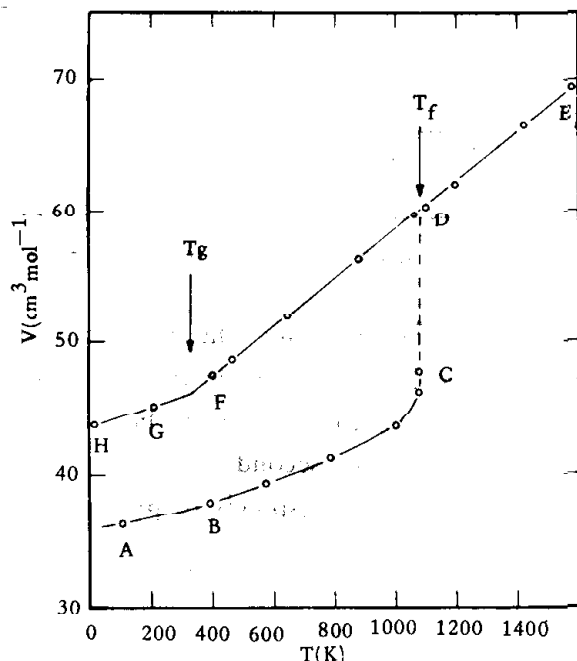
previous one. This is not a problem as long as we are simulating a crystal or a liquid. But it can be a problem when we want to simulate the melting and the aim is to measure the melting temperature or follow the system throughout the melting.

The procedure which we have adopted to conduct a filled system constant pressure simulation ($|P| < 0.5$ kbar) will be explained below. With this technique we have been able to measure the melting parameters, including the melting point. But for the reasons mentioned above we are not able to follow the structural change of the system throughout the melting.

For the solid we started from the crystal

Figure 8. *Variation of volume with temperature during the constant pressure simulation of KCL filled system.*

The above procedure is not able to deter^ melting point of the system accurately for the following reasons:

(a) A small over-expanding of the crystal close to the melting point will result in a liquid structure, while underexpanding of the system will give a high pressure crystal again.

(b) As each volume change creates a non-equilibrium system, the disturbance caused by the expansion procedure may force the system to melt at a lower temperature than true T.

To measure the melting point of an isobaric filled system we carried out a set of constant volume melting with different V. Each run started from an equilibrated crystal with volume V_i and temperature T_i, a few hundred degrees below the estimated melting temperature for V_i. Then the system was heated
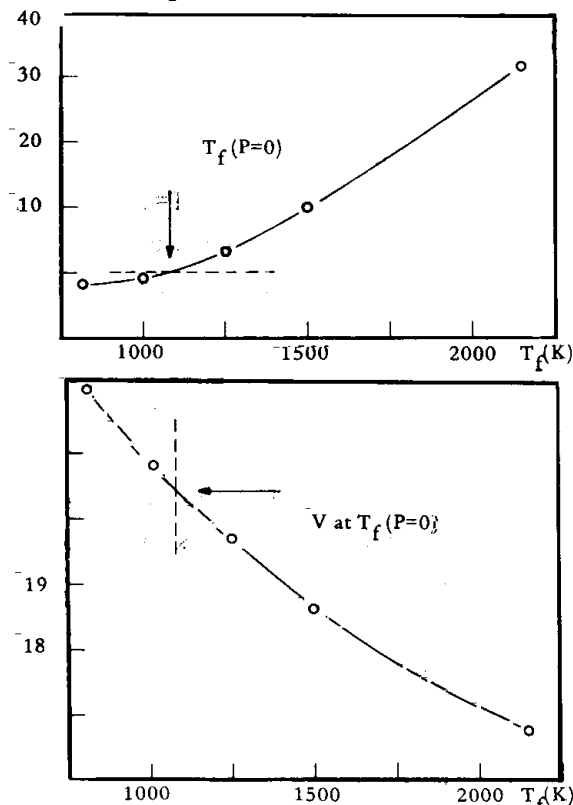

Figure 9. Top figure is plot of the pressure, of the constant volume simulations when the systems start to melt, as a function of T_f bottom plot is their corresponding volume vs. T_f
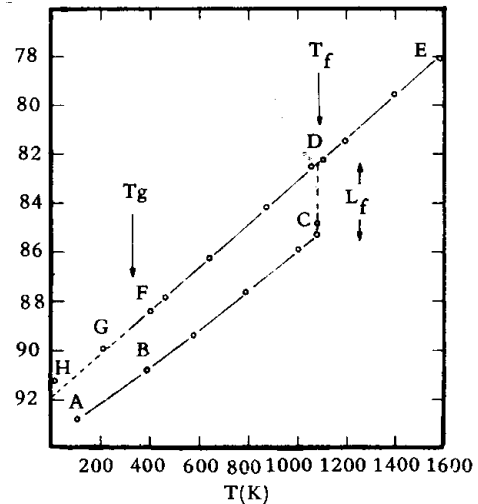

Figure 10. Variation of total energy as a function of temperature for the KCl filled system at P=0, showing a first order transition at T_f.

up (cyclic heating) without changing the volume until melting was detected. It was found that for values of BL less than or equal to 2.7 nm the values of the pressure of the crystal when it starts to melt, P_f, are greater than zero. While the crystals with BL greater or equal 2.8 nm start to melt when their pressure is negative.

A plot of P_f versus T_f (Figure 9a) suggests that for a temperature $T_f \cong 1080$ K the crystal should start to melt while its pressure is zero. The corresponding volume for this temperature can be obtained from the T_f/V plot (Figure 9b) which is $20.4*10^{-21}$ cm^3. This is the volume of the crystal at the melting point for a pseudo-infinite KCl crystal melting at constant pressure.

The simulation was continued to obtain some points for isobaric heating of the liquid by adjusting the volume and temperature to make the pressure zero. In this case a liquid configuration of one of the melted systems has been taken and its volume expanded. The system was then run for long enough to equilibrate and then the zero pressure point obtained by changing the temperature by cyclic heating or cooling. In the case of the
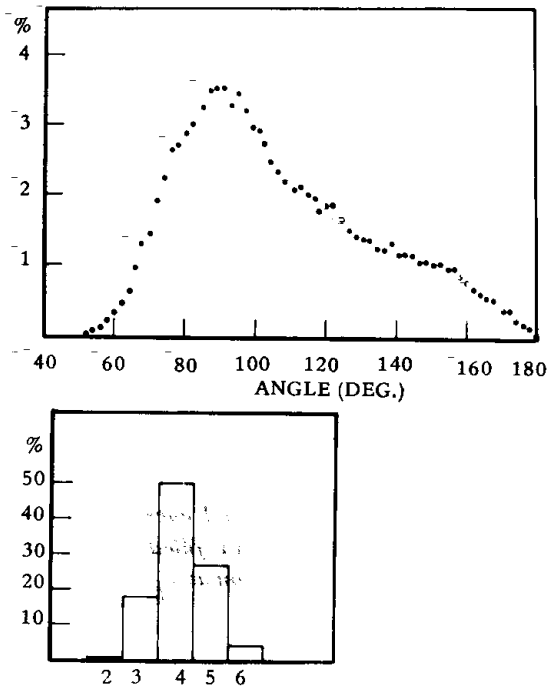
Figure 11. Distribution of Cl-K-Cl bond angle (top) and K coordination number (bottom) in KCl liquid at T=1200°K and P=0.

liquid the time needed for equilibration is longer than the crystal (1000 steps or more compared to 200-400 timesteps for crystal). The equilibrium was defined as the point at which without any change in the velocities the total energy and temperature remain almost constant.

The results of the constant pressure experiment for the volume and energy are shown in Figures 8 and 10. In these figures A to C represents the solid, from C to D the system melts and the line DE shows the liquid part of the simulation. The system is cooled down from D through G to H which represents a supercooled liquid and a glass. These will be discussed in a future publication.

From Figure 7 one can calculate the volume expansion of the system due to melting which is 25.98%, this is 8.67% higher than the physical value of 17.31% for KCl [3]. However it is almost equal to the value we measured for 4096 ion microcrystal by cal-

culating density from the accumulated RDF up to 1.4 nm [1].

From the U/T curve of Figure 10 we measure the specific heats of solid at room temperature and liquid from the slope of the lines AB and DE. The latent heat is obtained from the energy gap between the crystal and liquid structure at T_f which is shown in Figure 10. This may indicate an overestimate of L_f compared to U_D-U_C, but we believe the lack of surface in the system and the generation of defects will raise the energy of the crystal without melting. This also creates a superheated crystal and it raises the melting temperature. The parameters of melting for this simulation are listed below with the corresponding physical values in brackets.

Melting point, T_f=1080 (1045)°K.

C_p of solid at room temp.=3.15 (3.03).

C_p of liquid=3.98 (4.03).

Latent heat, L_f=1410 (1580)°K.

Entropy of melting, S_f=1.32 (1.51).

We show in Figure 11 the distribution of coordination number of K ions and Cl-K-Cl, bond angle for the liquid at T=1200°K. The cut-off radius which has been used to obtain the figure is 0.435 nm and the result is an average value over 50 timesteps. The results for the coordination number of Cl and K-Cl-K bond angle are very similar to the K one. A comparison between the distribution of coordination number and bond angle of this simulation and the previous micro-samples [1, 2] shows remarkable similarity. This indicates that even a 512 particle droplet in the centre has the same structure as an infinite system with P ≅ 0. However a similar comparison between the present results and the results of the liquid under a high pressure (Figure 7-E) shows that the structure of these two liquids is completely different. In the high pressure liquid, the maximum of bond

angle is at 80 degrees (rather than 90 here) and the six coordinated ions are in majority (compared to 4-fold coordinated at P=0).

DISCUSSION

The main purposes of a molecular dynamics simulation of melting are:

(a) To obtain the melting point of an infinite system at P=0 and hence test a potential.

(b) To get the microscopic features of the melting and study the melting mechanism.

(c) To study the melting of a system under unreachable physical conditions (e.g. constant V, very high or low P and the melting of a very small cluster).

The other thermodynamic and structural measurements of a solid and a liquid (latent heat, specific heats, RDF etc.), which are obtained in a melting simulation, can be measured by simulating the solid or liquid phase separately. Therefore the most interesting case in a melting study is the constant P simulation. This will give a melting point comparable to the one usually measured in the laboratory, and hence test the accuracy of the potential. Further accessible microscopic data of the simulated system provide an opportunity to study the melting mechanism and test various theories of melting.

It was shown that an accurate measurement of melting point of a pseudo-infinite system is difficult, although we suggested here a method of doing it. In addition the lack of surface in a filled system makes the measurement unphysical and the melting temperature will possibly be an overestimate.

Comparison of our results with the results for 4096 ion microcrystal [1] suggests that the middle part of a micro-system has the same structure as an infinite system in both the liquid and solid phases. We examine this by comparing the positions of the first two peaks in RDF, coordination numbers and densities of two systems. The only disadvantage of a microcrystal simulation is that the surface particle should be excluded when obtaining information about the structure of the system and this makes the statistics poor.

From our results (Figure 1) we see that the melting temperature increases significantly with increasing pressure. This increase is not linear (Figure 9a) and it is higher for higher values of P. From Figure 9a, if we calculate dT_f/dP for values of T=1180 and 1250 $\overset{o}{K}$, the calculated value $\cong 23$ K/kbar is in good agreement with the measured value of $\cong 25$ K/kbar [4].

In our constant volume simulation, even under high pressure, no transition from NaCl to CsCl crystal structure was observed (as happens in experiment under P=20 kbar at room temperature). But a transition which was associated with the creation of many defects in the crystal at T $\cong 1200$ $\overset{o}{K}$ and P $\cong$ 13 kbar was observed. At this point we detected an increase in C_V and a decrease in the number of six-fold coordinated ions. This might be interpreted as an attempt for the system to go to the CsCl structure but the simulation time is not long enough to permit such a transition.

In the constant pressure simulation it was noticed that although the volume of the crystal at room temperature is equal to the physical value, the volumes of the solid and the liquid at the melting point are higher than the measured experimental values. The discrepancies are much greater for the liquid than for the solid. As our potential is scalable [5], it is possible to scale any of these volumes to the physical value. But with a fixed set of parameters for the potential we cannot reproduce the correct volume over a wide

range of T for solid and liquid. This is a feature of our potential and in fact has been pointed out [6] that even the Huggins-Mayer potential does not give the correct volume for the solid and liquid at different temperatures. Two of the features which remain unchanged on scaling are the shape of the RDF curves and the coordination numbers. The coordination number for the liquid at T=1200°K and P=0 is 4.2. This value is lower than 5.5 obtained in previous simulation [7] but it is in better agreement with experiment (3.5-3.7, see Ref. [8] page 376).

REFERENCES

1. See part I.
2. M. Amini and R. W. Hockney, *J. Non-Crystalline Solids*, 31, 447 (1979).
3. "American Inst. Phys. Handbook", McGraw-Hill, New York (1972).
4. K. F. Herzfeld and M. Goeppert-Mayer, *Phys. Rev.*, 46, 995 (1934).
5. R. W. Hockney and J. W. Eastwood, "Computer Simulation Using Particles", McGraw—Hill (1981).
6. D. J. Adams and I. R. McDonald, *J. Phys. C: Solid St. Phys.*, 7, 2761 (1974).
7. L. V. Woodcock and K. Singer, *Trans. Faraday Sos.*, 67, 12 (1971).
8. G. J. Janz, "Molten Salts Handbook", Academic Press, New York (1967).