# *MOLECULAR DYNAMICS SIMULATION OF POTASSIUM CHLORIDE MELTING*

## *I. MICROCRYSTAL SIMULATION AND SAMPLE SIZE EFFECT*

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**Abstract** The effect of sample size on the melting parameter of simulated potassium chloride microcrystal is investigated by molecular dynamics simulation. The size of microcrystal is varied from 8 to 4096 ions. The increase in melting temperature with sample size was found to be in good agreement with the theory.

**چکیده :** اثر اندازهٔ نمونه روی پارامترهای ذوب ریز بلور پتاسیم کلرید با روش شبیه‌سازی دینامیک مولکولی مورد بررسی قرار گرفته است. اندازه ریز بلور مورد شبیه‌سازی را از ۸ تا ۴۰۹۶ یون تغییر داده‌ایم . نقطه ذوب بدست آمده در این شبیه‌سازیها با بزرگ شدن اندازهٔ نمونه افزایش یافته و این افزایش توافق خوبی با نظریه دارد .

## INTRODUCTION

Although the structural differences between crystals and liquids are well known, the actual melting process whereby the structure of the crystal is transformed into that of the liquid is not completely understood, even for simple substances. At various times a number of mechanisms have been suggested for this process, but no satisfactory theory of melting exists. From purely thermodynamic considerations, the fundamental theory of melting can be summarised as:

$$T_l; P_l; G_s(P, T) = G_l(P, T).$$

The three conditions correspond to thermal equilibrium, mechanical equilibrium and Gibbs free energy, and must have the same value in the solid phase as in the liquid phase.

Perhaps the oldest and best known melting criterion is that of Lindemann [1]. This assumes that a solid melts when the root mean square amplitude of the vibration of the atoms about their equlibrium positions in the lattice reaches a certain fraction of the interatomic spacing. The Lindemann law was generalized by Ross [2] and when combined with the Lennard-Jones and Devonshire cell model it was successful in predicting the melting properties of rare gases and liquid metals [3, 4]. Another theory of melting due to Born [5] suggests that melting occurs when the rigidity modulus vanishes. Also there has been considerable discussion of a possible connection between melting and the spontaneous generation of dislocations [6]. This theory identifies the melting point with the temperature at which the free energy for thermal generation

of dislocation becomes zero and the crystal becomes saturated with dislocations, giving rise to the liquid structure. The application of these theories is not, however, an easy matter. For example, it is not possible to make an exact calculation even of such a basic parameter as the melting temperature starting from a given interatomic interaction force. In practice there may be further complications because the interactions are known only in terms of a set of effective potentials derived from static properties, and these may not be adequate when thermal motions are involved. For more information about the subject we refer the reader to the book by Ubbelohde [7].

The experimental study of melting is difficult because it is an extremely rapid process so that structural changes cannot easily be followed through the melting transition.

On the other hand the method of molecular dynamics, MD, simulation is very suitable for the study of melting. In this method the crystal is simulated in a computer experiment in which the trajectory of each individual atom is determined from its interactions with the other atoms in the sample. Thus a suitable known interatomic potential can be used and its parameters varied. The structure of the sample can be followed through the transition and experimentally inaccessible ranges of the macroscopic parameters can be used. The disadvantages of the method are that only a limited number of particles can be simulated and the sample must be heated very rapidly compared with physically realisable rates. Much valuable information on the melting transition has been gained from computer simulation, particularly in the range of temperatures and pressures which cannot easily be reached in laboratory experiments.

The method has been applied to hard-sphere by Hoover et al. [8-10]. The melting properties of the Lennard - Jones system have received the most study, for both two and three dimensional systems. In these studies both microcrystal and pseudo-infinite systems (see Sec. 2) are used for computer simulation [6, 11-13].

The melting of ionic systems was also studied by molecular dynamics simulation. Hockney and Goel [14] have conducted an MD simulation of a two dimensional KCl microcrystal. Woodcock et al. [15] applied the method for three dimensional KCl in a triple periodic system. Amini et al. [16-18] simulated several ionic microcrystal systems to understand the effects of various parameters of the interatomic potential on the melting of 512 particles microcrystal.

We discuss in Section 2 different methods of melting simulation and in Section 3 the results of some MD simulations of KCl microcrystal are given.

## METHODS OF SIMULATION

The history of molecular dynamics began when Alder and Wainwright [19, 20] reported their computations on hard - sphere fluid. 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 excellent review articles and books have appeared in recent years which describe the MD simulation [21-25] therefore we confine our discussion to those aspects which are related to MD simulation of melting.

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 usually chosen to be zero. Mathematically the model is described by giving 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 equations of motion of particles are integrated numerically [26] and from the positions and the velocities of the particles at each timestep both the static and dynamic properties of the system can be calculated accurately.

The bulk of computational effort in MD simulation is concerned with the calculation of force at each step. If all the interactions of N particles are individually calculated the number of floating-point computer operations in each step is proportional to $N^2$. This limits N to a few hundred even on the fastest computers currently available. However it is possible to use a faster method, like P-P/P-M of Hockney et al. [27], and increase the number of particles in the simulated system to a few thousand. Even with such fast methods the number of particles in a simulated system is far below the number in a real system ($\sim 10^3$ compare with $\sim 10^{23}$). 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. By periodic boundary conditions we mean that the calculation box is surrounded by an 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 or enters through one face of the calculation box an image particle will enter or leave a neighbouring box through the opposite face to balance the move.

The imposition of periodic boundary conditions produces an infinite system of particles, without any surface, which arrange periodically. In a melting simulation we are either interested in the structural change of the crystal while it melts or in the thermodynamical properties such as, melting temperature, latent heat, entropy of melting, volume change due to melting, change in the specific heats, etc. In each case the simulation starts from a crystalline structure, at a temperature below melting point, and subsequently heats the crystal until it melts. For certain measurements the liquid should be heated until it reaches a temperature well above the melting point. The expansion (or pressure) caused by the heating and melting transition makes the melting simulation more difficult than the simulation of liquids or solids at a constant temperature in which the volume of calculation box is fixed.

To overcome the problem of expansion and lack of surface in an infinite system we show, in Figure 1, some alternative methods for initial

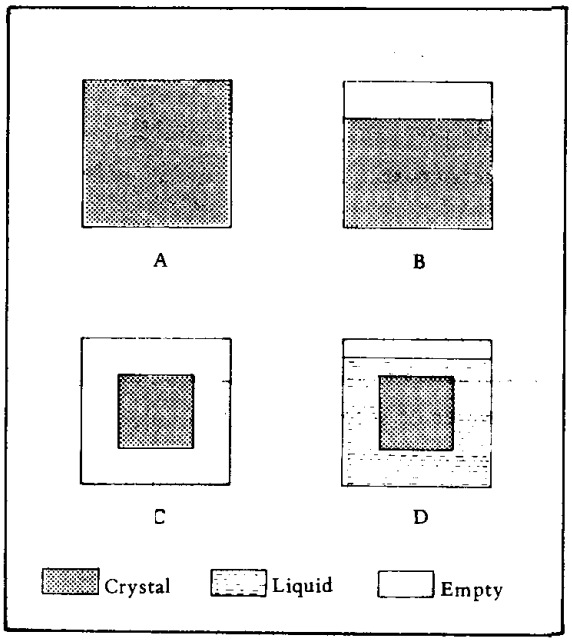


*Figure 1. Schematic illustration of four different ways of filling the two dimensional calculation box with particles.*

filling of the calculation box with the particles. In method A the whole calculation box is filled with particles and the periodic images surrounding the box make the system a pseudo-infinite one. If the box side is kept constant during the simulation, the change in the pressure is enormous, and simulation is a constant volume experiment. In order to simulate the usual physical conditions at constant pressure the box may be expanded with an increase of temperature, as suggested by Berendsen et al. [28], or the alternative way of constant pressure simulation as described in part II may be used. Method B is a partially filled box with periodic images. Compared to A this method has the advantage of containing a surface, which might be important for melting study, but the main problem of pressure still remains. In method C an isolated microcrystal, with free surface all around it, is set up in the centre of the calculation box. The free surface allows the crystal to expand while remaining at zero pressure and no time is spent on adjusting the box length. Although in this case the system has a surface, the ratio of surface particles to the total number of particles is very high compared with any realisable physical system. Finally, in method D a microcrystal is placed in the calculation box surrounded by liquid of the same substance and some space is left in the box to allow for expansion.

In the next section we report the results of melting simulations using method C (microcrystal melting), and in part II the melting of KCl crystal is discussed when method A of initial setting is used.

## MELTING OF MICROCRYSTAL AND SAMPLE SIZE EFFECTS

To determine the effect of microcrystal size on the melting parameters we have performed three KCl simulations with 8, 64 and 4096 ions respectively. The interaction pair-force in these simulations is exactly the same as the previous simulation with 512 ions [16]. It contains two terms, coulombic and inverse power repulsion. The force of interaction between a pair of ions at separation $r_{ij}$ is:

$$F_{ij}(r)=\left(\frac{e}{4\pi\epsilon_0}\right)\frac{1}{r^2}\left[\pm 1+\left(\frac{s_i+s_j}{\quad}\right)^8\right. \qquad (1)$$

Where i, j = +, −. The sign of the first (coulombic) term is positive for like ions and negative for unlike ions. The parameter s is proportional to the ionic radius. This form of potential has the advantage of being scalable and simple to analyse theoretically, while

**Table 1. Values of the initial parameters for three different sized KCl microcrystal simulations.**

| PARAMETERS | I | II | II | UNITS |
|---|---|---|---|---|
| number of particles, N | 8 | 64 | 4096 | |
| timestep, DT | 7.5 | 7.5 | 7.5 | fs |
| radius ratio, $s_+/s_-$ | 0.73 | 0.73 | 0.73 | |
| heating cycle, NS8 | 600 | 400 | 200 | DT |
| averaging over, NS9 | 96 | 64 | 32 | DT |
| initial temperature, TDKO | 100 | 100 | 400 | K |
| heating factor, HTFAC | 1.001 | 1.001 | 1.002 | |

retaining the essential features of a condensed ionic system. In the present simulations all the parameters of the potential are the same as previous one [16], but the number of particles are varied. These are summarised in Table 1.

The calculation box is a cube and in each case a cubic N particles (N/2 cation and N/2 anions) microcrystal with the Sodium chloride crystal structure was placed in the middle of the box.

The time integration of Newton's laws of motion was conducted by using the leapfrog scheme [26]. The timestep, DT, was chosen to be about one-sixteenth of the period of oscillation of a typical ion in the crystal.

In each simulation the ions were initially given a Maxwellian velocity distribution corresponding to an initial temperature, TDKO, and the temperature was held at this value by scaling the velocities in each timestep for 200 steps. This was followed by 800 timesteps in which the velocities were not scaled. The microcrystal was then subject to cyclic heating with a period of NS8 timesteps. At each of the first 25 steps the system was heated by multiplying each velocity by a factor, HTFAC. The system was then allowed to equilibrate for the remaining steps of the cycle. The total energy and the temperature of the system were averaged over all particles and the last NS9 steps of the cycle.

All three simulations, including 8 ions system which is the smallest cubic microcrystal which can be set-up with a rocksalt structure, show the features of melting quite clearly. After heating the cubic microcrystals they were melted to form roughly spherical liquid droplets. The melting was characterised by:

(a) Discontinuity in the total energy at the melting point and an increase in the specific heat after melting.

(b) A loss of long-range order on melting, and a decrease in the coordination number from six to about four.

(c) Thermal expansion of the crystal before melting and a decrease in the density on melting.

(d) The onset of diffusion at the surface of the crystal slightly below the melting temperature and throughout the system at the melting temperature (except for 8 ion system which all particles are on the surface of the microcrystal).

Figure 2 shows the graph of total energy against temperature of 4096 particle simulation. The crystal is heated from point A to B, melts between B and C, and the liquid is heated from C to D. The values shown in this figure are the results obtained at the end of each heating cycle. A clear first order phase change occurs between the point B and C from which the melting point, $T_f$=T(B or C), and latent heat, $L_f$=U(C)−U(B), are obtained. The specific heats for solid and liquid are obtained from the slope of the lines AB and

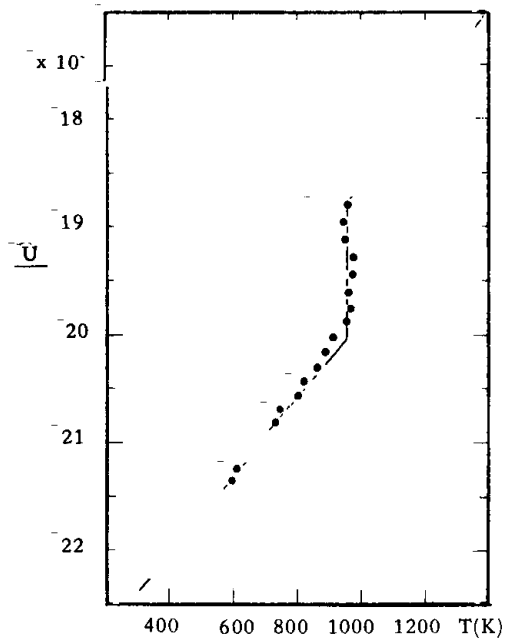


*Figure 2. Variation of internal energy per particle, U, with temperature, for 4096 ions system, showing a first order transition at $T_f$. The origin of U is arbitrary.*

CD. Values of melting temperatures, latent heats and specific heats are given in Table 2 together with the physical values for the bulk stystem.

The accumulated values of the average mean square displacements (MSD), for 4096 ion system, for the last 100 timesteps of the heating cycle, are shown in Figure 3. Each point represents the result obtained at the end of a heating cycle. Although for practical reasons the number of timesteps in which the MSD is accumulated is limited to 100, the variation of MSD with T for the solid and the liquid is a smooth curve clearly showing the melting transition. The accumulated MSD's averaged separately over each kind of ions show that the values for the Cl ions (larger) are about four percent lower than for K ions. To study the diffusion of the system we examined the plot of MSD's versus timestep for the last 100 steps of each cycle. In the solid the MSD increases for a few steps and then stays constant, this behaviour being characteristic of vibrational motion. In the liquid the MSD increases linearly with time indicating diffusion. A careful examination of Figure 3 shows that the accumulated MSD increases noticeably at a temperature some 90°K below the melting point. By examining the neighbours of all the ions, from the time of initial setting of the microcrystal till the end of melting, we found that at this point the ions at the surface of the microcrystal began to change their neighbours (diffuse).

The radial distribution functions, RDF, for like and unlike ions were also obtained at the end of each heating cycle. For this the average is taken over the last 10 steps of the heating cycle and only the ions in a middle cube are taken as centre (see Figure 4). From these distributions the nearest neighbour's distance (position of the first peak of unlike ions RDF) and the coordination number (number of ions surrounding an ion out to a cutoff radius which is chosen close to the first minimum of RDF) are measured. At melting the average coordination number of the system suddenly drops from six to about four and the nearest neighbor's distance also decreases.

The density of the system was measured from the accumulated values of RDF up to a distance r. By using this method we are including all the particles in spheres with radius r and centres inside the middle cube. This method is more accurate than time

**Table 2. Scaled results of melting parameters for four KCl microcrystal simulations.**

| N | 8 | 64 | 512 | 4096 | Physical |
|---|---|---|---|---|---|
| $r_0$(nm) | 0.260 | 0.260 | 0.260 | 0.260 | |
| $T_f$(K) | 753 | 816 | 950 | 990 | 1045 |
| $L_f$(K) | 620 | 1032 | 1240 | 1342 | 1580 |
| $C_p$ solid | 3.40 | 3.35 | 3.24 | 3.15 | 3.03 |
| $C_p$ liquid | 3.45 | 3.64 | 4.14 | 4.20 | 4.03 |
| $S_f$ | 0.82 | 1.27 | 1.31 | 1.35 | 1.51 |

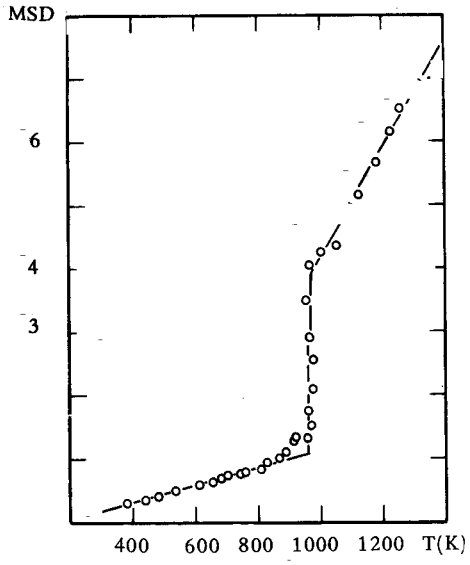


*Figure 3. Average mean square displacement after 100 timesteps as a function of temperature for 4096 ion KCl.*

averaging the number of particles in the middle cube, because more particles are taken into account for the calculation, but more weight is given to the central particles. The results are more accurate for larger r, but r must not exceed a maximum value $r_m = (l_s - l_m)/2$. In which $l_s$ and $l_m$ are the sides of the system and the middle cube. In Figure 4 a schematic picture of this method is shown in two dimensions and it is obvious that if a particle near the surface of the middle cube is chosen as a centre with radius $r > r_m$ the total volume of this sphere is not filled with particles. For 4096 ion simulation $r_m$ is almost 1.5 nm, so the plot of number density calculated in this way for values of r equal to 0.8, 1.2 and 1.4 nm as a function of temperature are shown in Figure 5. All these plots show a decrease in number density with increasing temperature and a sudden drop on melting. The liquid part of these plots gives almost the same variation of density with temperature but for the solid the measurement with r=1.4 nm gives the lowest density which might be due to the spacing of the ions in the microcrystal and the choice of r. The reduction in number densities in the melting

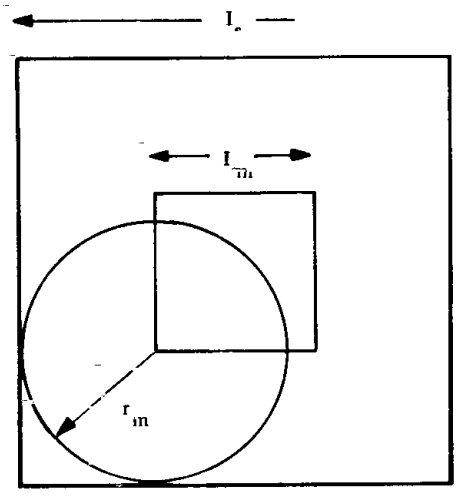


*Figure 4. Schematic method of density measurement from the accumulated values of RDF in two dimensions.*

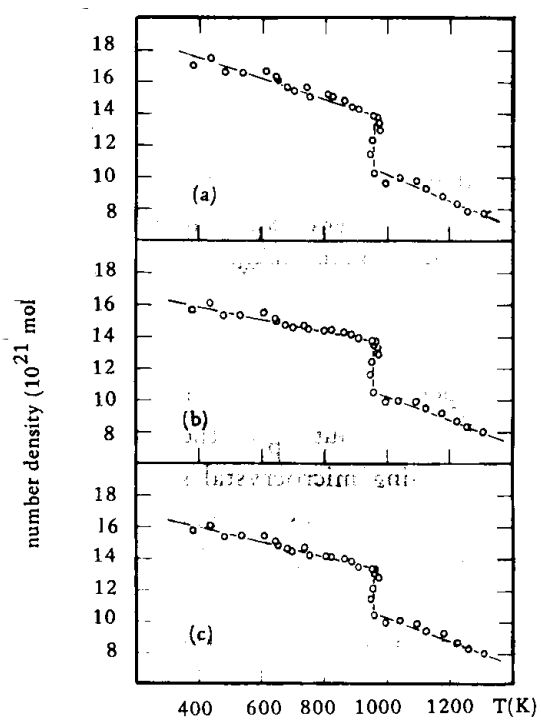


*Figure 5. Plots of number density as a function of temperature obtained from the accumulated values of RDF up to (a) 0.8 nm, (b) 1.2 nm and (c) 1.4 nm.*

([d(solid)-d(liquid)]/d(solid)) obtained from these plots are 0.30, 0.29 and 0.26 for r equal 0.8, 1.2 and 1.4 nm respectively. The values are within the physical values measured for alkali halides but they are about 1.5 times higher than the physical values for KCl.

## DISCUSSION

As the interaction force of Equation 1 is scalable [23] all the results obtained in these simulations are scaled in such a way that $r_0 = S_+ + S_- =$ 0.260 nm. This value of $r_0$ gives the correct physical lattice separation for the crystal at room temperature. The scaled values are given in Table 2. To make the comparison easier the results of the 512 ion simulation [16] and the physical bulk system values for KCl also are given.

The results show by increasing the size of the simulated system the melting temperature, latent heat and entropy of melting increase.

The increments are towards the physical values of the bulk system. The melting temperature and latent heat depression of two and three dimensional microcrystals have been observed in several MD simulations [14, 29]. Also there are several experimental and theoretical results which show that the melting temperature decreases with decreasing radius [30-36].

The specific heat of liquid is higher for a larger droplet. But $C_p$ of the solid decreases with increasing microcrystal size. This is to be expected as a smaller microcrystal has a relatively higher number of surface particles and the surface ions, lacking a full set of neighbours; are in a sense, already partly melted. The specific heat of a microcrystal is expected to lie between the physical large-crystal and the liquid values and decreases with increasing microcrystal size. This is also observed (Table 2).

To show the effect of sample size on the melting temperature of simulated microcrystal we plot our results in Figure 6. In this figure the values of $T_f$ for four different sized KCl microcrystal versus number of ions on each side of the cubic microcrystal are plotted. Couchman [36] in his calculation, based on the Lindemann hypothesis of melting, relates the melting temperature of a microcrystal ($T_f$) with the bulk system melting point ($T_f 0$) by the following formula:

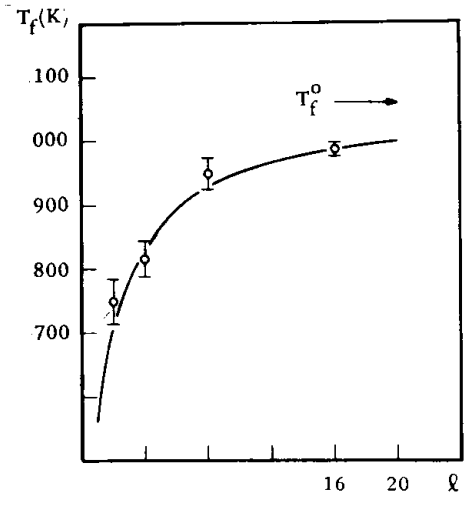


*Figure 6. Variation of melting temperature of four KCl microcrystals as a function of number of particles on each side of the cubic microcrystal, l. The theoretical formula, Eq. (3), is shown as a continuous line.*

$$T_f/T_f0 = \frac{1+(\pi/6)^{1/3}/8v^{1/3}*(S/V)}{1+(\pi/6)^{1/3}/8v^{1/3}*(S/V)} \quad 2)$$

In which v is the volume per particle and S and V are the surface and volume of the microcrystal respectively. For a cubic microcrystal with l particles on each side and the lattice separation a, we have $v^{1/3}=a$, $S=6(la)^2$ and $V=(la)^3$. Therefore Equation 2 becomes

$$T_f/T_f0 = \frac{+6/8*(\pi/6)^{1/3}/}{+6/8*(\pi/6)} \quad (3$$

To compare our simulation results with Couchman's theory, Equation 3 is plotted in Figure 6 in such a way to pass through the 4096 ion melting point. The agreement between the theory and simulation results seems very good although no extra care is taken in the theory to include the line or point effects arising from the cubic shape of the system. Melting temperature of the bulk system calculated from Equation 3 by using $T_f$ of 4096 ion system gives $T_f 0=1063+11$ K which is higher by a small amount from the physical value of 1045 K measured for KCl.

## REFERENCES


1. F. A. Lindemann, *Z. Physik.*, 11, 609 (1910).
2. M. Ross, *Phys. Rev.*, 184, 233 (1969).
3. W. G. Hoover and M. Ross, *Contemp. Phys.*, 12, 339 (1971).
4. K. Ishizaki, P. Bolsaitis and I. L. Spain, *Solid St. Commun.*, 15, 1591 (1974).

5. M. Born, *J. Chem. Phys.*, 7, 591 (1939).
6. R. M. J. Cotteril, E. J. Jensen, W. D. Kristensen, R. Paetsch and P. O. Esbjorn, *J. Phys. (Paris)*, 36, C2 (1975).
7. A. R. Ubbelohde, *"The Molten State of Matter"*, Wiley, New York, (1978).
8. W. G. Hoover and F. H. Ree, *J. Chem. Phys.*, 49, 3609 (1968).
9. W. G. Hoover, M. Ross, K. W. Johnson, D. Henderson, J. A. Barker and B. C. Brown, *J. Chem. Phys.*, 52, 4931 (1970).
10. W. G. Hoover, S. G. Gray and K. W. Johnson, *J. Chem. Phys.*, 55, 1128 (1971).
11. R. M. J. Cotterill and L. B. Pedersen, *Solid State Commun.*, 10, 439 (1972).
12. R. M. J. Cotteril, W. D. Kristensen, J. W. Martin, L. B. Pedersen and E. J. Jensen, *Computer Phys. Commun.*, 5, 28 (1973).
13. C. L. Briant and J. J. Burton, *J. Chem. Phys.*, 63, 2045 (1975).
14. R. W. Hockney and S. P. Goel, *Chem, Phys.*, 35, 500 (1975).
15. L. V. Woodcock, *Proc. R. Soc.* London, A348, 187 (1976).
16. M. Amini and R. W. Hockney, *J. Non-Crystalline Solids*, 31, 447 (1979).
17. M. Amini, D. Fincham and R. W. Hockney, *J. Phys. C*, 12, 4707 (1979).
18. M. Amini, D. Fincham and R. W. Hockney, *J. Phys. C*, 13, L221 (1980).
19. B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 27, 1208 (1957).
20. B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 31, 459 (1959).
21. J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, 48, 587 (1976).
22. D. Fincham, in *"Dynamical Processes in Condensed Matter"* ed. M. W. Evans, John Wiley & Sons, 493-575 (1985).
23. R. W. Hockney and J. W. Eastwood, *"Computer Simulation Using Particles"*, McGraw-Hill (1981).
24. G. Ciccotti and W. G. Hoover (eds.), *"Molecular Dynamics Simulation of Statistical-Mechanical Systems"*, proceedings of the international school of physics, North-Holland (1986).
25. M. P. Allen and D. J. Tildesley, *"Computer Simulation of Liquids"*, Clarendon Press, Oxford (1987).
26. M. Amini, J. W. Eastwood and R. W. Hockney, *Computer Phys. Commun.*, 44, 83 (1987).
27. J. W. Eastwood, R. W. Hockney and D. Lawrence, *Computer Phys. Commun.*, 19, 215 (1980).
28. H. J. Berendsen, J. P. M. Postma, W. F. Van. Gunsteren, A. Di. Nola, and J. R. Haak, *J. Chem. Phys.*, 81, 3684 (1984).
29. W. Damgaard Kristensen, E. J. Jensen and R. M. J. Cotterill, *J. Chem. Phys.*, 60, 4161 (1974).
30. J. R. Sambles, *Proc. R. Soc. London*, A324, 339 (1971).
31. S. J. Peppiatt and J. R. Sambles, *Proc. R. Soc. London*, A345, 387 (1975).
32. P. H. Buffat and J. P. Borel, *Phys. Rev.*, A13, 2287 (1976).
33. C. J. Coombes, *J. Phys.* F, 2, 441 (1972).
34. P. R. Couchman and W. A. Jesser, *Phil. Mag.*, 35, 787 (1977).
35. P. R. Couchman and W. A. Jesser, *Nature*, 269, 481 (1977).
36. P. R. Couchman, *Phil. Mag. A*, 40, 637 (1979).