

# COMPUTER SIMULATION OF DYNAMICS IN SOLIDS

S. L. CHAPLOT

*Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, India.*

## ABSTRACT

We briefly discuss the "molecular-dynamics" technique of computer simulation of atomic and molecular solids; review some of the recent developments in this area, and also discuss our work on dynamics and reorientational motions in molecular solids.

## INTRODUCTION

**D**YNAMICS of atoms and molecules in solids is usually studied by experiments such as Raman scattering, neutron scattering or absorption of infrared radiation and also by theoretical methods of lattice dynamics. Computer simulation of the motion of atoms at the microscopic level can provide a deeper understanding of the dynamical phenomena. The simulation can also help in suggesting, planning and analysis of the experiments and other theoretical studies.

By computer simulation we mean the computation of a numerical or statistical sample of any physical system or a certain aspect of its behaviour. Such a sample must naturally be the result of certain definite rules although an element of statistical randomness is also introduced. The results are, however, quite fundamental since they usually involve very few and well-defined approximations. Because of the fundamental and statistical nature of the results, they are often termed as results of "computer experiments". On the other hand, they are clearly model-based theoretical results since they are based on a predetermined model of the physical system.

In the context of the study of structure and dynamics of solids at the atomic level one is essentially concerned with two major techniques, namely, the molecular-dynamics (MD) technique<sup>1</sup> and the Monte Carlo technique<sup>2</sup>. In the molecular-dynamics technique, one solves the classical equations of motion for a certain number of atoms  $N$  contained in a box, to

obtain the time dependence of the various coordinates of motion, e.g. the atomic positions. The MD method can thus provide a microscopic picture of complex dynamical phenomena in the system. On the other hand, in the Monte Carlo technique, one has to generate a sample of the large number of possible configurations of the system using statistical methods and based on the energy function. While the average static properties can be easily computed from the sample in the Monte Carlo method, the sequence of the configurations generated can also be used to obtain information about the dynamics as governed by a master equation. In this article we shall consider the MD method only and review some of the recent developments.

The simulation is usually carried out by setting up in the computer a box or "macrocell" consisting of a number of particles. One has the option of applying the periodic boundary conditions around the macrocell in order to remove the surface effects and thus simulate, in effect, an "infinite" system with periodicity of the macrocell. An essential input for the simulation is a suitable potential function to represent the interatomic interactions. While more details of the MD method are given in the next section, we emphasize here that, with the approximation of classical equations of motion, exact simulation can be carried out on a given system for the given potential between particles. The technique is indeed very powerful and versatile in that it allows for the study of several features, e.g. anharmonicity, expli-

cit temperature effects, phase transitions, mixed systems, amorphous systems, diffusion, large rotations and reorientations of molecules. Moreover, the microscopic correlation functions and other quantities relevant to any scattering experiment can be directly calculated with suitable weights of the scattering powers of atoms.

Recently we have been interested in ionic-type rigid-molecular systems<sup>3-5</sup> in which large angle rotations and reorientations are important. The nature of results obtained so far on ammonium halides and  $\text{LiKSO}_4$  will be discussed later in this article.

### MOLECULAR DYNAMICS METHOD

We consider a macrocell as a parallelepiped formed by the vectors  $n_1\mathbf{a}$ ,  $n_2\mathbf{b}$  and  $n_3\mathbf{c}$  where  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  are certain unit cell vectors and  $n_1$ ,  $n_2$  and  $n_3$  are integers. In most of the literature published so far, the number of atoms in the macrocell is usually confined to a few hundred with the usual periodic boundary conditions. This seems to give a fair description of several features like the phonon frequencies, eigenvectors, anharmonicity, rotational dynamics of molecules, diffusion and even certain types of phase transitions. However, a much bigger macrocell is necessary to study many other features like phase transitions involving nucleation and growth and long-range effects. Note that the computation time goes up as something between  $N$  and  $N^2$ .

One needs to identify the coordinates of simulation. For rigid molecular systems the translational motions of molecules are determined by the centre-of-mass coordinates. For the rotational motions, it is advantageous to use the quaternions<sup>6</sup> instead of the Euler angles since they not only provide singularity-free algorithm but also give us a direct understanding of the rotation and the orientation. The orientation of a molecule is represented by the set of quaternions  $(L_1, L_2, L_3, L_4) = (L, L_4) = (L \sin \alpha/2, \cos \alpha/2)$  when the molecule has undergone an anticlockwise rotation

about the axis  $\mathbf{l}$  by an angle  $\alpha$  as compared to the starting orientation. Hence  $\mathbf{l}$  is a unit vector and one has the normalization relation  $L_1^2 + L_2^2 + L_3^2 + L_4^2 = 1$ . With the use of the quaternions, the rotational transformation matrix does not involve any trigonometric functions, thus simplifying the computations.

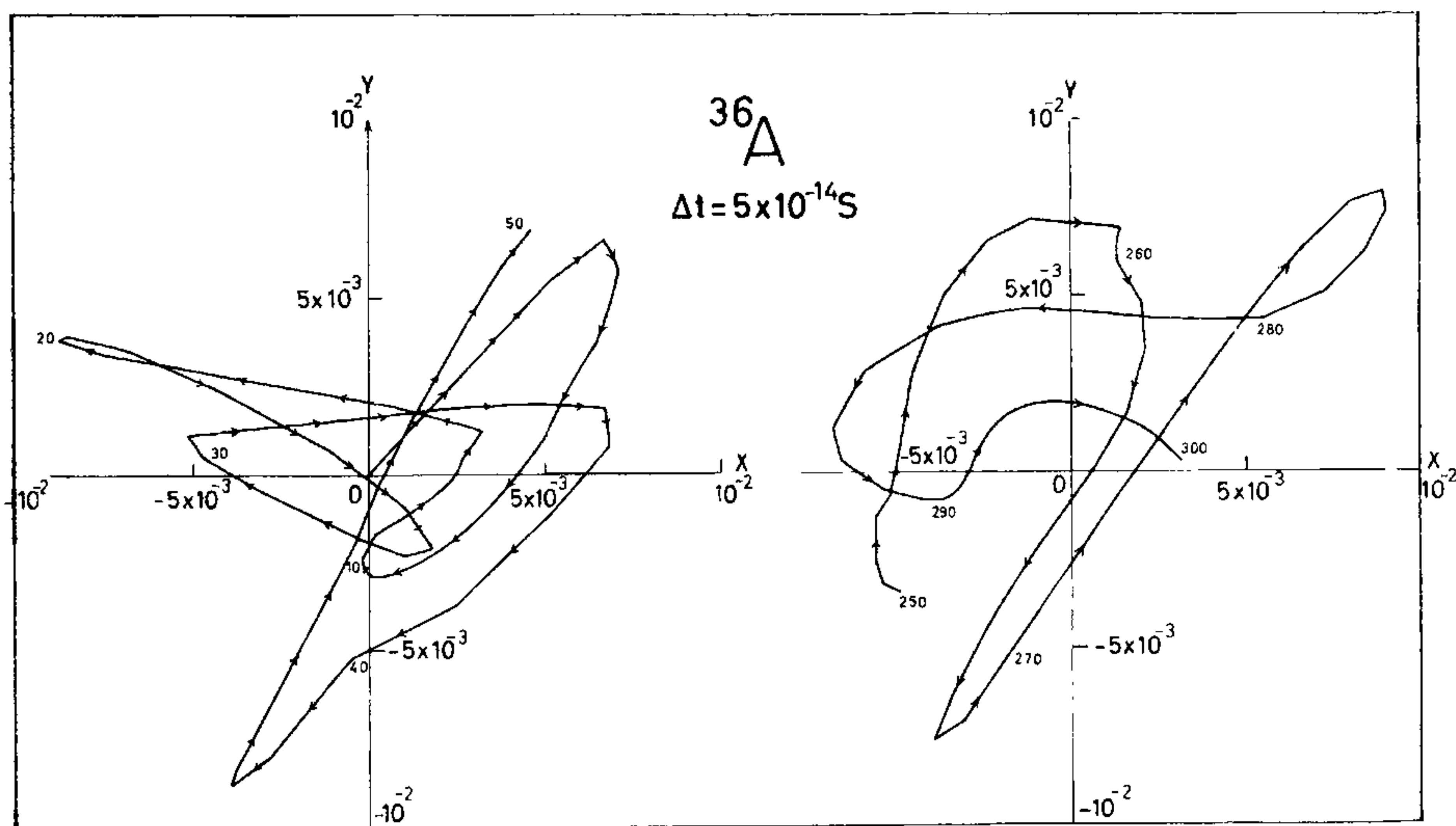
We initialize the system with atoms located at their equilibrium positions which are usually known from experiments, although any other starting position can also be used. The atoms are also provided with some initial random velocities which may be scaled to the square-root of the desired temperature of the simulation.

Time evolution of the system is calculated at steps of suitable time intervals. One has to compute the net force and torque on every molecule for the known configuration at the given time  $t$  and obtain the values of various co-ordinates at time  $t + \delta$  by using a suitable computer-algorithm for solving the equations of motion, namely, the Newton-Euler equations for the translational and rotational motions. A typical algorithm is

$$r(t + \delta) = -r(t - \delta) + 2r(t) + a(t)\delta^2,$$

where  $r(t)$  and  $a(t)$  are the position and acceleration at time  $t$ . Several such algorithms have been discussed earlier<sup>1</sup>. The time-step  $\delta$  should be about a tenth of the minimum vibrational period of any of the coordinates in the system, (which is the inverse of the maximum phonon-frequency), or a little lower if necessary for ensuring total-energy stability. An important criterion for choosing the time-step and the algorithm should be the requirement of total energy stability within say 1 in  $10^4$ . We display in figure 1 the time dependence of an argon atom in solid argon for a small interval of time as obtained from the MD simulation.

In order to solve the equations of motion one needs a potential function, that is, the potential energy as a function of nuclear positions and also positions of electronic shells if a shell model is used. Such a potential



**Figure 1.** The XY projection of the positions of an argon atom at 10K as a function of time in a MD computer simulation. The axes are marked in angstrom units.

function is not restricted to the case of small-amplitude vibrations of atoms and therefore can allow for the anharmonicity of vibrations. The potential may be obtained by different methods, either directly from the first principles or empirically using cohesive energy, equilibrium crystal structures, phonon frequencies etc<sup>3</sup>. One uses the conventional Lennard-Jones or 6-exponential type potentials for van der Waals systems and also for the nonbonded interactions in nonionic type molecular systems. For ionic interactions, the Coulomb potential is also used and the long-range summations are obtained using the Ewald-technique. Covalent or hydrogen-bond interactions are represented by the Morse function or the Lippincott-Schroeder functions. Note, however, that the H-bonds may break or form with time when large displacements are involved. For interaction between molecules one usually sums over all the interactions between pairs of atoms belonging to the two different molecules. The potential function may be tested by comparison of the

predicted structure and lattice dynamics with that of a suitable ordered crystalline phase at low temperatures before use in simulation under other conditions<sup>3</sup>.

An idea as to what extent the parameters of the potential function are important can be obtained<sup>7</sup> from a revealing study on  $\alpha$ -AgI. The superionic  $\alpha$ -phase is obtained only for a certain range of the values of a certain parameter, namely the ratio of the Coulomb potential to the short-range potential between close iodine-iodine pairs. For the right ratio, the iodines form an ordered lattice and the silvers form a disordered structure with peaks at the tetrahedral sites as experimentally obtained; and the transition temperature of about 400 K is close to the experimental value. It is clearly important that the potential must be properly chosen.

#### DYNAMICS OF IONIC MOLECULAR SOLIDS

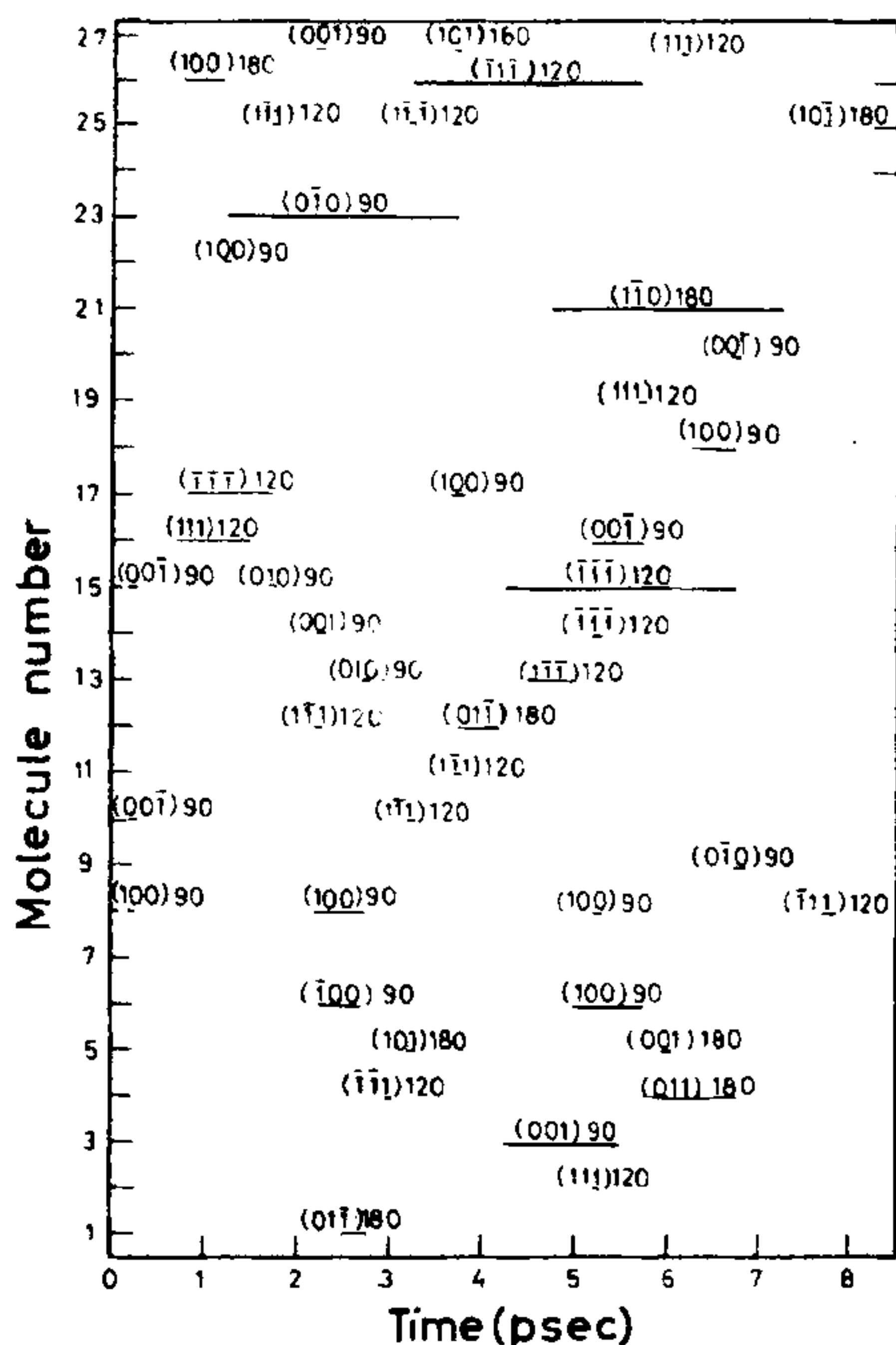
We have developed a general purpose software for the computer simulation of translational

and rotational motions in a system of atomic and molecular ions. The simulation is based on the molecular dynamics technique and it uses the Ewald sums to handle the long-range ionic interactions. The program does calculations for about 10 time-steps per minute for a macrocell of about 200 atoms on ND/560 computer. The temperature and pressure can be altered during the simulation. The program also calculates the auto-correlation function of linear and angular velocities, their Fourier-transforms, the radial distribution functions, structure factor, dynamical structure-factor  $S(Q, \omega)$  and its

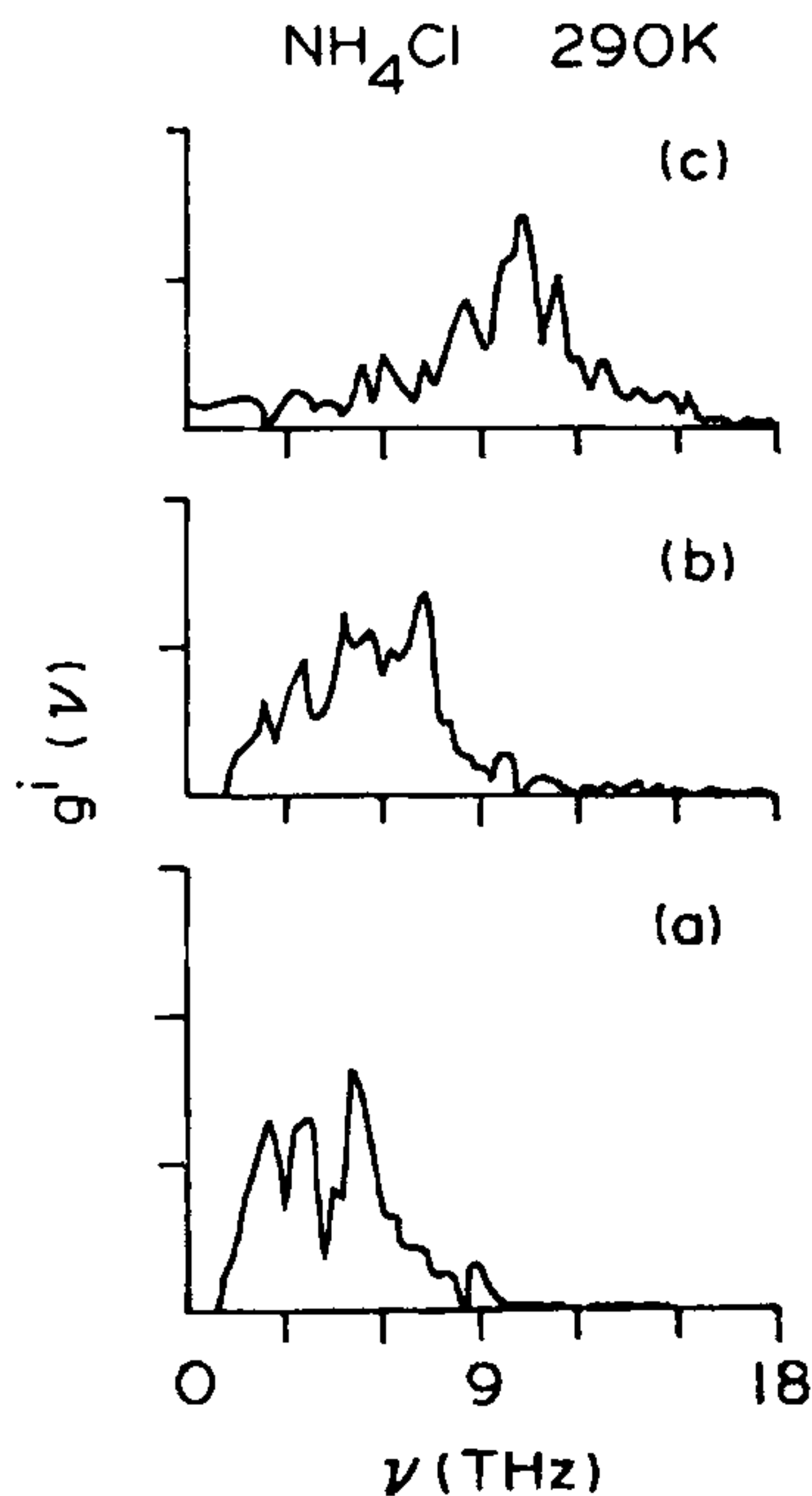
one-phonon approximation, mean-square displacements etc. There are separate routines for monitoring diffusion, hopping and reorientational motions of individual particles.

We have carried out simulations on some ammonium halides and  $\text{LiKSO}_4$  at various temperatures. The potential functions have been determined from lattice statics and dynamics<sup>4,5,8</sup>.

In  $\text{NH}_4\text{Cl}$  we have studied<sup>5</sup> the order-disorder transition and for the first time determined using molecular dynamics simulations the nature of rotational dynamics of the ammonium tetrahedra in the disordered CsCl-type

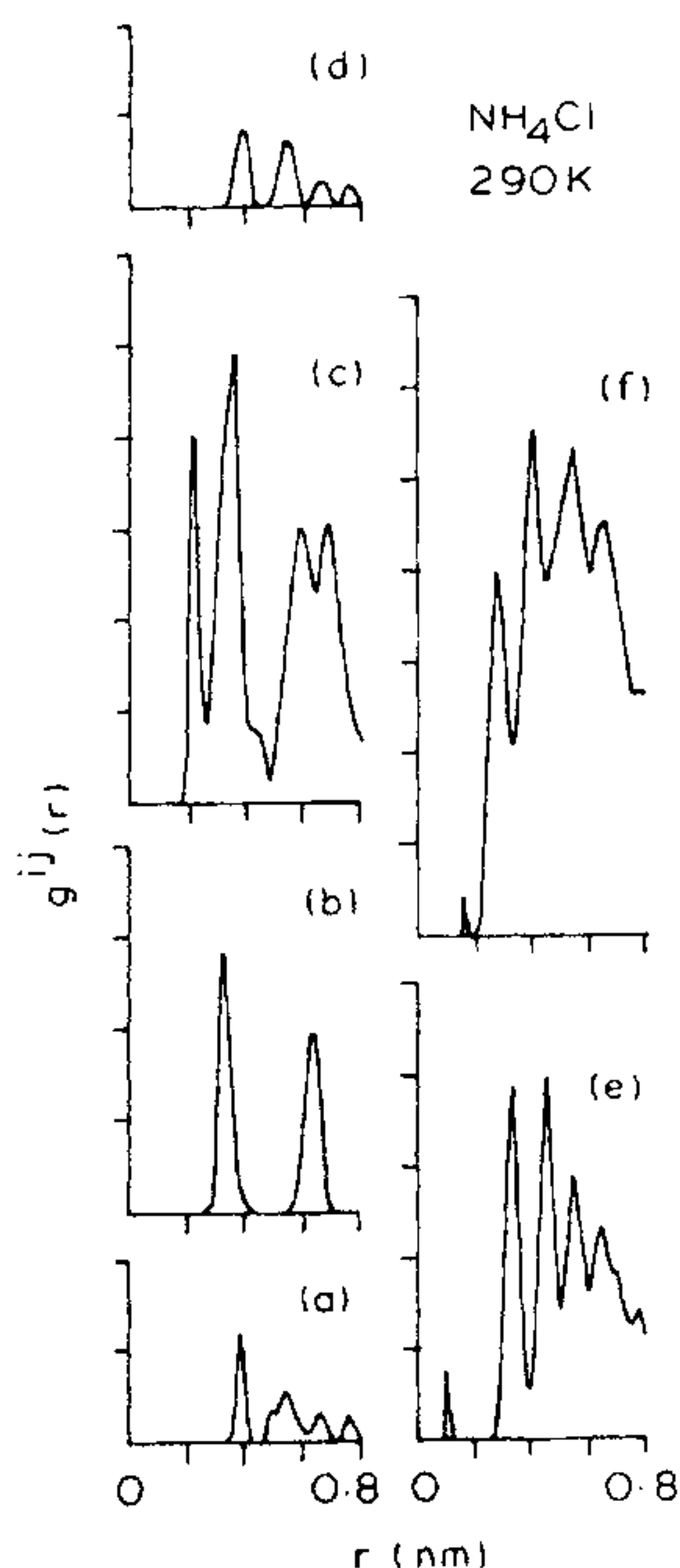


**Figure 2.** The rotational jumps observed in a molecular-dynamics computer simulation of  $\text{NH}_4\text{Cl}$  at 290 K. Each row represents the jumps of one of the molecules as a function of time. The jump about an effective axis  $\{hkl\}$  by an angle of  $\alpha$  degrees is denoted as  $\{hkl\}\alpha$ . The length of the line denotes the flight time.



**Figure 3.** Results from a molecular-dynamics computer simulation of  $\text{NH}_4\text{Cl}$  in its disordered CsCl phase at 290 K. Density of states corresponding to the translational degree of freedom of (a) chlorines and (b) ammoniums, and (c) the rotational degrees of freedom of ammoniums.

phase. A jump diagram is shown in figure 2. We observe reorientational jumps about  $\langle 111 \rangle$  axes by  $120^\circ$ , about  $\langle 001 \rangle$  axes by  $90^\circ$ , about  $\langle 001 \rangle$  axes by  $180^\circ$  and about  $\langle 110 \rangle$  axes by  $180^\circ$  whereas previously<sup>9, 10</sup> only the first two types of jumps were believed to be significant and the experimental data from incoherent quasielastic neutron scattering<sup>9</sup> had been analyzed on the basis of this assumption. We find that the earlier experimental data are not sufficient to obtain the reorientation rates about all the axes. Therefore more experiments are required to understand the rotational dynamics of the ammonium tetrahedra in the disordered phase. Figures 3 and 4 illustrate the nature of some results one may obtain from



**Figure 4.** Results from a molecular-dynamics computer simulation of  $\text{NH}_4\text{Cl}$  in its disordered CsCl phase at 290 K. The pair correlation function corresponding to the various pairs of atoms (a) Cl-Cl, (b) Cl-N, (c) Cl-H, (d) N-N, (e) N-H and (f) H-H.

MD simulations, namely, the partial density of states corresponding to various degrees of freedom and the pair-correlation function of various pairs of atoms.

Using the simulation<sup>11</sup> of  $\text{ND}_4\text{I}$  in the plastic phase with the NaCl-type structure, we calculated the structure factor for incoherent neutron diffraction which shows diffuse scattering arising from the rotational motion characteristic of the plastic phase and agrees reasonably well with the results from the powder neutron diffraction<sup>12</sup> experiment carried out at Trombay.

Simulations of a complex solid  $\text{LiKSO}_4$ , in which the dynamics of sulphate rotations and its coupling with lithium translations is interesting, have been carried out<sup>4</sup> using a macrocell of 36 formula units at several temperatures. At room temperature the favourable axis of rotation is found to be the hexagonal c-axis. This suggests that the transition between the space groups  $P6_3$  and  $P31c$  would be achieved predominantly by nearly  $60^\circ$  rotations about the c-axis rather than through the larger rotations of  $110^\circ$  about a perpendicular axis. In the ionic-conductor phase above 700 K, the diffusion of the lithium ions is not found to be appreciable as might be expected from the known small ionic conductivity. However, at 1000 K it is observed that the lithium ions move to interstitial positions and vibrate there for fairly long times of a few pico-seconds and then some of them return to their lattice positions. This phenomenon of lithium movement appears to be closely related to the orientations of the neighbouring sulphate tetrahedra which are found to rotate and reorient by large angles of up to  $180^\circ$  degrees.

#### PHASE TRANSITION STUDIES

Study of phase transitions using MD computer simulation as a function of temperature and stress is very valuable in spite of the approximations of the simulation technique. Such studies can provide insight into the mechanism

of the transition process and would also give information about the details of the dynamics close to the transition point. Present-day simulations, however, would not give detailed information on slow behaviours which take longer than a nanosecond, e.g. the phenomena of the critical slowing down near a second-order phase transition.

Temperature is monitored during the MD simulation through the total kinetic energy in the macrocell and therefore can be changed by suitably scaling the velocities. One can carry out MD simulation at constant isotropic pressure or at a given stress by allowing for dynamical variation of the size and shape of the macrocell. For the case of constant pressure this has been done in an elegant manner by Perrinello and Rahman<sup>13</sup> who obtain the MD equations of motion through a Lagrangian of the macrocell. The dynamical coordinates in their simulation technique are the fractional coordinates of atoms with respect to the unit cell axes and the three cell vectors of the unit cell. While the equation of motion for the fractional co-ordinates is similar to the usual Newton's equation involving forces on atoms, the equation of motion for the cell vectors involves difference between the internal stress and the externally applied pressure. The technique has been applied to study the phase transitions in such different systems as AgI<sup>14</sup>, molecular solid nitrogen<sup>15</sup> and lithium metal<sup>16</sup>. In AgI the phase transition between the normal phase to the superionic conducting phase was simulated in both the heating and cooling directions by variation of temperature. A pair potential involving the Coulomb and short range interactions and a macrocell containing 500 ions were used in that study. The phase transition was monitored by studying the partial pair-correlation functions. In the molecular solid nitrogen the transition between the space groups Pm3n and R3c was simulated at 70 kbar and 140 K using a macrocell of 64 molecules. In lithium metal the phase diagram of the bcc-fcc transition was simulated in the range of 300–600 K and 0–12 GPa.

There are obvious limitations on the nature of the phase transition and also on the size of the macrocell and complexity of the potential function with the presently available computational resources. Transitions which involve nucleation or lattice defects etc can only be studied with a fairly large macrocell in which no restriction is placed on the structure within the macrocell. In a simulation on SF<sub>6</sub> using distributed-array-processors which allow simultaneous calculation on 4096 molecules in a macrocell, Pawley and Thomas<sup>17</sup> were able to spot the nucleation of a triclinic ordered structure and found several grains in different orientations.

#### SIMULATION OF SUPERIONIC CONDUCTION

Simulation studies have been carried out on various superionic conductors like  $\alpha$ -AgI, CaF<sub>2</sub>, SrCl<sub>2</sub>, etc. Gillan and Dixon<sup>18</sup> simulated SrCl<sub>2</sub> using a macrocell of 324 ions at a few temperatures and found the transition temperature of about 1200 K which is 20% higher than the experimental value. A pair potential comprising of Coulomb and short-range terms was used. From the separate pair-correlation functions for the pairs Sr–Sr, Cl–Cl and Sr–Cl, it was found that while the Sr<sup>++</sup> ions form an ordered lattice, the Cl<sup>-</sup> ions show discrete jumps between regular lattice sites with a residence time (= 7 psec) of nearly 10 times the flight time (0.6 psec). Therefore the anions do not stay at any transit positions for a long time and so the density of point defects (vacancies) was only about 3% of that of the regular sites. The diffusion coefficient for Cl<sup>-</sup> ions was determined to be about  $3 \times 10^{-5}$  cm<sup>2</sup>/sec from the variation of the mean square displacement with time. One uses the equation  $\langle r^2(t) \rangle = B + 6Dt$  even though the dynamics is not of continuous diffusion type as in liquids. The ionic conductivity thus obtained is about  $1 \Omega^{-1} \text{ cm}^{-1}$ . The simulation also demonstrated that even at low temperature the vibrations of the Cl<sup>-</sup> ions are highly anharmonic.

## AMORPHOUS SYSTEMS

Computer simulations of the structure and dynamics of glasses or amorphous systems are of current interest. Grest *et al*<sup>19</sup> simulated a monatomic Lennard-Jones glass by quenching a macrocell of 100–500 particles from a well equilibrated liquid state. The quenched system showed no diffusion, its pair-correlation function  $g(r)$  had a split second-peak and its structure factor did not show any Bragg singularities. The simulation thus provides a structure of the model glass. Its phonon spectrum can be calculated either from the standard harmonic lattice dynamics or, when this is difficult for a large macrocell due to limited computer memory, from simulation itself using the quench-echo technique<sup>20</sup> or the calculated dynamical structure factor and analogous quantities. The calculated “phonon dispersion relation” shows very interesting properties with similarities and differences with the results for a polycrystalline system. The dispersion curve for the longitudinal excitations is very similar to that of the polycrystalline sample with a minimum at the wavevector where the static structure factor  $S(Q)$  has the first peak which is the second zone-centre in the crystal. However, for transverse excitations the dispersion curve for the glass does not show any such sign of a pseudo zone-boundary unlike as in the case of a polycrystal. Experimental results from neutron inelastic scattering on longitudinal excitations in metallic glasses<sup>21</sup> have been obtained recently and compared with results from computer simulations.

## SUMMARY

In this article we have briefly discussed the computer simulations based on the molecular-dynamics technique. The problems of phase transitions, rotations and reorientations of molecules in molecular solids, the diffusion of ions in fast-ionic conductors and the structure and dynamics in glasses were given as some

examples of particular interest in which simulation studies have been valuable. It should be emphasized that several microscopic properties like static and dynamical structure factors, which are observed in scattering experiments can be predicted from simulations directly, while they are difficult to obtain from other theories.

## ACKNOWLEDGEMENT

The author would like to thank Dr K. R. Rao for useful discussion.

7 March 1986; Revised 11 June 1986

1. Rao, K. R. and Chaplot, S. L., In: *Current trends in lattice dynamics*, Proc. of IPA seminar, 1978, (ed.) K. R. Rao, Indian Physics Association, Bombay, 1979, p.589 and references therein.
2. Binder, K., (ed.) *Monte Carlo methods in statistical physics*, Springer Verlag, Berlin, 1979. Mouritsen, O. G., *Computer studies of phase transitions and critical phenomena*, Springer Verlag, Berlin, 1984.
3. Chaplot, S. L., *Nucl. Phys. Solid State Phys. (India)*, 1983, **A26**, 356.
4. Chaplot, S. L. and Rao K. R., *Bull. Mater. Sci.*, 1985, **7**, 31.
5. Chaplot, S. L. and Rao, K. R., *Phys. Rev.*, 1986, **B33**, 4327.
6. Evans, D. J., *Mol. Phys.*, 1977, **34**, 317; Pawley, G. S., *Mol. Phys.*, 1981, **43**, 1321.
7. Fukumoto, A., Ueda, A. and Hiwatari, Y., *J. Phys. Soc. Jpn*, 1982, **51**, 3966.
8. Chaplot, S. L., Rao, K. R. and Roy, A. P., *Phys. Rev.*, 1984, **B29**, 4747.
9. Töpler, J. M., Richter, D. R. and Springer, T., *J. Chem. Phys.*, 1978, **69**, 3170.
10. Gerling, R. W. and Hüller, A., *J. Chem. Phys.*, 1983, **78**, 446.
11. Chaplot, S. L., Rao, K. R. and Mukhopadhyay, R., *Solid State Phys. (India)*, 1984, **C27**, 130.
12. Mukhopadhyay, R. and Rao, K. R., (unpublished).
13. Parrinello, M. and Rahman, A., *Phys. Rev. Lett.*, 1980, **45**, 1196.
14. Parrinello, M., Rahman, A. and Vashishta, P., *Phys. Rev. Lett.*, 1983, **50**, 1073.

15. Nosé, S. and Klein, M. L., *Phys. Rev. Lett.*, 1983, **50**, 1207.
16. Munro, R. G. and Mountain, R. D., *Phys. Rev.*, 1983, **B28**, 2261.
17. Pawley, G. S. and Thomas, G. W., *Phys. Rev. Lett.*, 1982, **48**, 410.
18. Gillan, M. J. and Dixon, M., *J. Phys.*, 1980, **C13**, 1901; Dixon, M. and Gillan, M. J., *J. Phys.*, 1980, **C13**, 1919.
19. Grest, G. S., Nagel, S. R. and Rahman, A., *Phys. Rev. Lett.*, 1982, **49**, 1271.
20. Nagel, S. R., Rahman, A. and Grest, G. S., *Phys. Rev. Lett.*, 1981, **47**, 1665.
21. Suck, J. B., Rudin, H., Güntherodt, H. J. and Beck, H., *Phys. Rev. Lett.*, 1983, **50**, 49.

---

## ANNOUNCEMENT

---

### SEVENTY-FOURTH SESSION OF THE INDIAN SCIENCE CONGRESS

The Seventy-fourth session of the Indian Science Congress will be held at Bangalore from January 3 to 8, 1987 under the auspices of the Bangalore University. Prof. (Mrs) Archana Sharma will preside over the Session.

The focal theme of the Congress will be "Resources and human well-being—inputs from science and technology". The scientific programme is organized under thirteen sections, each presided over by a Sectional President. Meetings of each section will be held every day, where original research papers/posters are presented.

Two endowment lectures, the G. P. Chatterjee Memorial Lecture on "Some aspects of man and science" and the B. C. Guha Memorial Lecture on "Some relevance to the science of nutrition particularly vitamins", will be delivered during the session. A series of special lectures on various scientific subjects will be delivered at different sections.

An exhibition of scientific instruments and books

etc will be organized during the session, in addition to exhibits related to the focal theme.

Further details may be had from the Local Secretaries: Prof. G. K. Narayana Reddy, Head, Department of Chemistry, Central College, Bangalore 560 001; Prof. M. P. Chowdiah, Head, Department of Mechanical Engineering, University Visveswaraya College of Engineering, Bangalore 560 001.

As usual *Current Science* will publish the scientific activities of the Annual Session of the Science Congress.

Members of the Council for 1986–87 of the 74th Indian Science Congress include: General President: Prof. (Mrs) Archana Sharma; Past General President: Dr T. N. Khoshoo; General President Elect: Prof. C. N. R. Rao; General Secretaries—Prof. D. K. Sinha and Dr (Miss) S. P. Arya; Treasurer: Dr S. C. Pakrashi and 52 Members.