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MOLECULAR DYNAMICS ON A PARALLEL COMPUTER

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Abstract

For many years the computing capacity available to research science has grown at a rate of about ten times every five years, a rate which is not expected to diminish for some time yet. The major gain in capacity from now on will come from the use of parallel processors. Such computers are already proving ideal for certain molecular dynamics (and Monte Carlo) problems where the architecture of the computer is especially favourable. The architecture of the DAP is discussed, and it is shown that this favours lattice simulations rather than liquid simulations.

For lattice problems, such as solid-solid transitions, large samples are necessary to avoid finite size effects such as the locking in of metastable phases imposed by the periodic boundary conditions. Experience on a computer with 4096 parallel processors (the DAP) suggests that this is a suitable size. The plastic to crystalline transition in SF_6 will be used as an example.

Recent progress on the analysis of the dynamics of the plastic phase of SF_6 will be reported, followed by results from a simulation of crystalline naphthalene, in which anharmonic properties have been analysed.

Molecular Dynamics

The use of molecular dynamics (MD) as a recognised tool in physics is now well established. Work in the early years (see Rahman, 1978) concentrated on the liquid and gaseous phases, where MD calculations often proved to be the best tool for evaluating quantitative theories of these phases, but now, as our computational resources have become sufficient, it is possible to tackle problems of the solid state which require a MD sample with a very large number of degrees of freedom.

Such calculations will doubtless prove of value in many branches of solid state theory, probing the behaviour of systems for which experimental results are difficult to interpret unambiguously. We are currently using MD to tackle the problems posed by highly anharmonic systems such as plastic crystals and by highly disordered systems such as superionic crystals. In these cases MD calculations are able to determine the nature of the dynamics directly. As for the fluid state, it is possible to use MD calculations to evaluate models of scattering theory, directly testing the validity of approximations and thereby enabling such models to be applied to real systems. In the long term it should also prove possible to use MD to study problems of crystal defects. Furthermore, it is hoped that when real space renormalization methods have been developed further (Swendsen, 1982) it should be possible to apply MD as a tool in the study of phase transitions.

In MD calculations, the computer stores the positions and velocities of a large number of interacting particles, and then calculates all the forces of interaction. With this information and a record of the recent history of each molecule's motion it is possible to calculate the new position and velocity for each molecule after the passage of a small step in time. The molecules are then moved accordingly and the calculational process is repeated.

Modern parallel computers, though still in their infancy, are beginning to widen the MD field, enabling problems requiring enormous calculation to be done.

The Parallel Computer

Characteristic of all MD simulations is the repetitiveness of the calculation steps. The calculations themselves are simple and easily defined, and exactly the same operations are performed on each member molecule of the MD sample. A very large number of identical operations are usually required before the sample develops into a configuration corresponding to thermodynamic equilibrium, and as the sample itself must be large in order to minimise finite size effects, the enormous scale of the

repetitive calculation is immediately apparent.

Much of the gain in computer power over the last two decades has come from the implementation of parallelism in computer design, as argued by Hockney and Jesshope (1981). Thus the modern serial computer utilises pipelined structures, making it very adept at the manipulation of vector data so long as no conditional branching is required, which otherwise disrupts the pipelining. It s architecture is therefore optimised to some extent for the very repetitive calculations such as MD or MC (Monte Carlo), but the use of a fast large serial computer for such work is rapidly losing its cost-effectiveness. The parallelism achieved in a pipelined machine is orders of magnitude less than can be obtained with a massively parallel computer such as the ICL Distributed Array Processor (DAP).

The DAP consists of 4096 processing elements (PE's) joined on a 64 × 64 square array such that each PE is connected to its four nearest neighbours. Those PE's on the boundary of the array are connected to neighbours which conform to the cyclic or periodic boundary conditions. These conditions can be used implicitly in a program, but planar boundary conditions can be chosen at will if required. Any problem which can be mapped onto the PE array is then ideal for this computer, and we will see shortly that the two-dimensionality of the architecture does not lead to any restrictions on the dimensionality of the problem. In MD simulations it is best if one molecule can be identified with one PE, whereupon that PE stores all the information relevant to that particular molecule.

The general class of computers to which the DAP belongs is described as SIMD, meaning Single Instruction Multiple Data. Thus a single instruction is broadcast to all the PE's, which then all obey the instruction making use of their own stored data. The instruction may involve the calculation of the force between one molecule and a neighbour, and then the relevant information from the neighbour can be passed to the PE for the particular molecule, making use of the connectivity of the PE array. Of course, when this operation takes place, all 4096 PE's

simultaneously receive information from the appropriate neighbour defined by the data routing path. Not all problems can make use of this geometrical advantage because the pattern of neighbours may change, but in those problems where diffusion does not take place (or is very rare) the problem maps perfectly onto the computer topology.

Sample mapping

The DAP computer is a bit-serial machine, and is ideal for logical problems such as pattern recognition. Logical arrays of single bits can be treated in a high level language as masks, and these can be used to implement sample geometries of almost any kind, as outlined by Pawley and Thomas (1982,b). Detailed discussion of this aspect of the work is out of place here, but it is instructive to see how one very simple mapping may be achieved.

The software for the DAP (and, we presume, for any future computer of similar architecture) allows the 4096 PE's to be treated as a one-dimensional cyclic vector array. Given such a vector we will see that it is possible to develop a two-dimensional sample, and the procedure for stepping from one to two dimensions can be repeated *ad lib* to develop a sample of general dimensionality.

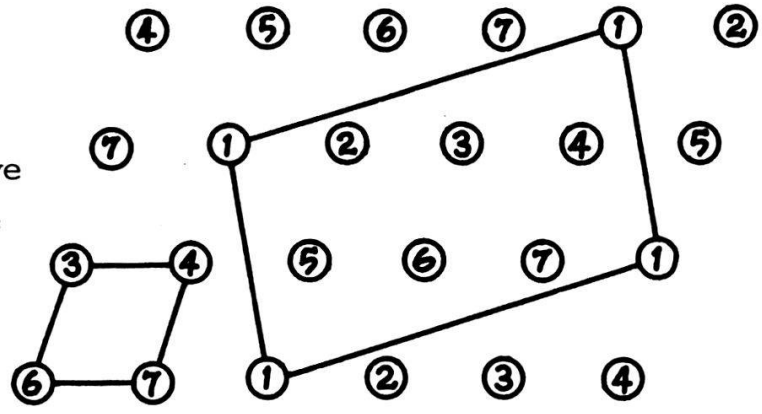


Figure 1
Folding of a cyclic linear vector of 7 elements to give a two-dimensional MD sample (large cell) of 7 unit cells (small cell)

Consider a ring of 7 calculators. This can be arranged to represent a MD sample as in figure 1. The bottom left part of the figure shows a unit cell of the 'crystal', whereas the larger parallelogram, joining repetitions of the first element, encompasses the MD sample. The relative index for a neighbour from any given molecule is the same (modulo 7) for all molecules,

and the computer only needs to know the shape of the crystal unit cell to set up a local origin for each PE, from which each molecule's displacement is determined.

The two-dimensional sample thus produced can be overlaid with copies to give a three-dimensional sample though of course, in the spirit of the use of cyclic boundary conditions, no actual copies have to be made. In the true crystal and plastic crystal examples to be discussed later the thermal motion of the molecules is insufficient to disturb the relative placing of neighbours, but in liquids this does occur and different techniques are then needed.

Liquid simulations

The customary procedure for simulating a liquid on a serial machine is to produce a list of neighbours and to update this index list as the molecules diffuse throughout the system. This is inappropriate for parallel computers, as it requires the random access of information between PE's. There are software algorithms which allow such computers to do this task, but as they are time-consuming their usefulness is much restricted.

The best method of using a parallel computer for a diffusive system is to divide the MD sample space into a fixed lattice of identical cells, and allow the molecules to move through these cells. Each cell is assigned to one PE, and the volume of the cell is chosen so that there is not room for more than one molecule in each. In fact it is necessary to reduce the cell volume somewhat so that there is a considerable number of empty cells. When a molecule wishes to leave one cell, it is allowed to move into an empty cell and its relevant information is transmitted between the old and new PE's. Decisions as to whether a molecule may move or not are easily reduced to logical operations, whereupon the bit-serial computer becomes very efficient indeed.

The most obvious partitioning of space is not the most efficient. Figure 2(a) shows a cube as the basic cell, and the fact that eight cubes meet at a vertex makes the problem of determining a new cell for a molecule rather difficult. Much the

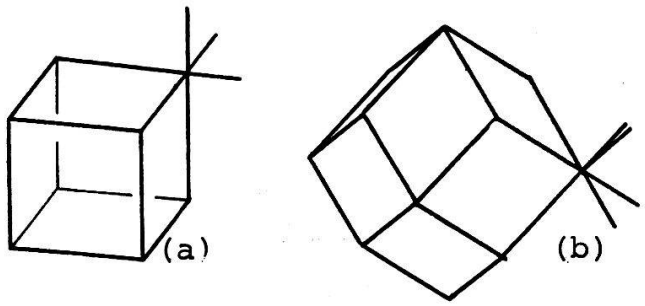


Figure 2
(a) elementary cube and
(b) rhombic dodecahedron
to be used as basic cells
for liquid MD simulations.
The arrangement about one
vertex is suggested.

easiest choice is the rhombic dodecahedron of figure 2(b) where at the sharp vertices only six cells meet. Only four meet at the blunt vertices. Thus the Wigner-Seitz cell for the cubic close-packed structure, the densest packing of spheres, is the best for this work, and gives rise to simpler algorithms than would the primitive cubic structure.

The plastic crystal transition

The intermolecular potential which determines the structure of systems of molecules for which Coulomb interactions are not important has a short-range repulsive and a medium-range van der Waals attractive part, and can well be represented by a Lennard-Jones potential. A sample of 4096 SF_6 molecules has recently been set up on the DAP computer at Queen Mary College, London by Pawley and Thomas (1982,a). The system at 150 K showed the characteristics of a plastic phase, in which molecules occasionally performed rotational jumps, a phenomenon described as rotational diffusion.

The simulation was mounted using the quaternion formulation for orientational motion (Evans, 1977) and the Beeman (1976) time-stepping algorithm. Orientational jumps were found by monitoring the quaternions (Pawley, 1981). On cooling the sample to 25 K the MD sample contracted as the pressure was adjusted to zero, but it took a long time before thermal equilibrium was achieved. This was thought to be indicative of a phase transition, and so the low temperature sample was analysed for crystallinity.

The fundamental difficulty in this analysis was that the crystalline structure was unknown, but this was overcome by

drawing out the planes of the MD sample, as in figure 3, and looking for crystallinity. This was immediately apparent as the crystallites formed with molecules arranged in two different orientations, two of one orientation and one of the other. The figure shows the division of the sample into crystallites, and it is this phenomenon which gives the method its success. The molecules are assumed to lie on a body-centred cubic lattice which can change its size but not its shape. In order to accommodate a lower symmetry structure — triclinic in this case — the sample must break up into crystallites, otherwise the effect of the cyclic boundaries would be so severe that the transition would be prevented. For this to occur the sample size of 4096 molecules would seem to be ideal, giving crystallites of a few hundred molecules — the total size of many another MD study. For such work therefore, a sufficient sample size is imperative.

The plastic phase

The MD plastic phase itself has recently been studied in more detail (Dove and Pawley, 1983), using single-molecule

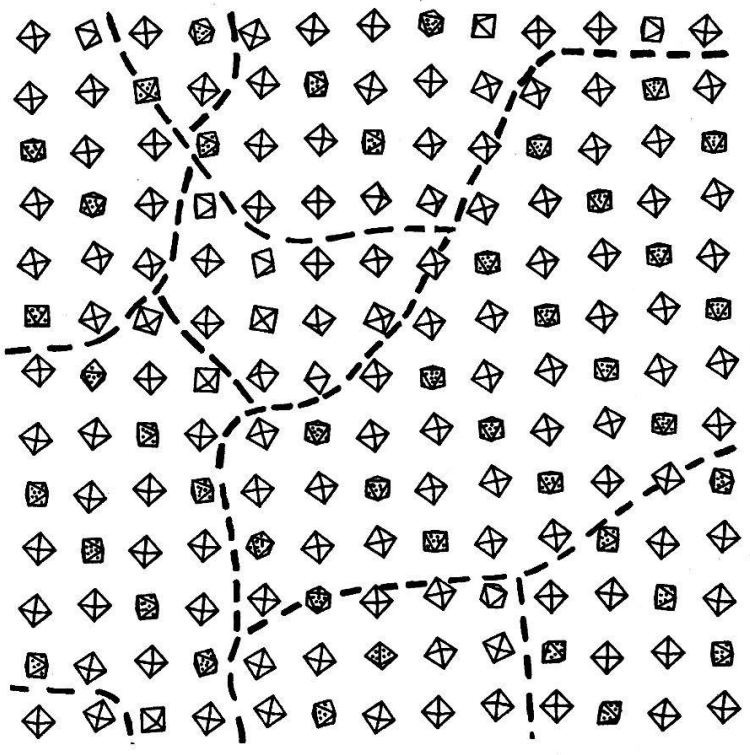


Figure 3
Mosaic structure in the crystalline phase, with crystallites outlined by dashed lines. There are two molecular orientations, and the molecules of one of the orientations have been marked with a stipple.

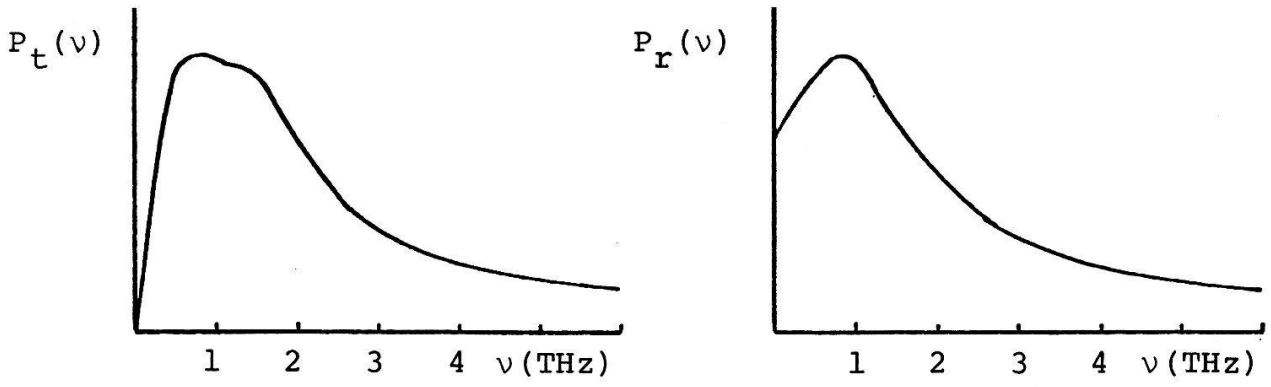


Figure 4. Power spectra (a) $P_t(\nu)$ and (b) $P_r(\nu)$ for translational and rotational motions respectively, (arbitrary units).

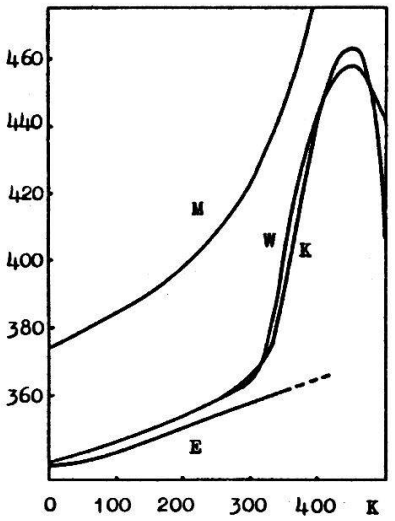
velocity autocorrelation functions and their associated power spectra, as was done for $CC\ell_4$ by MacDonald, Bounds and Klein (1982). The power spectra at 150 K are shown in figure 4. For translational motion (fig. 4a) the spectrum shows no zero frequency component, indicating that diffusion of the molecules does not occur, whereas rotational diffusion is indicated by the zero frequency component in the angular motion power spectrum (fig. 4b). An analysis for phonon motion shows that a phonon description is appropriate for translational motion but not for rotational motion, and further calculations are in progress aimed at elucidating the nature of the cooperative excitations of this system. The MD studies have also revealed the form of the orientational distribution function for the SF_6 molecules and have demonstrated the existence of coupling between the rotational and translational motions, features that are difficult to determine experimentally. This highlights the value of MD simulations. Moreover, it has been possible in these studies to relate the behaviour of the molecules in the plastic phase to the form of the inter-molecular potential, (Dove and Pawley, 1983).

Crystal dynamics

Given any intermolecular interaction potential it is possible to calculate the lattice dynamics of a system in the harmonic approximation, as was done for naphthalene by Pawley (1967, 1972). Temperature cannot be included in these calculations in any

satisfactory way, except that now it is possible to simulate a system of 4096 naphthalene molecules. Each molecule interacts with 16 neighbours through atom-atom pair potentials, requiring 18 × 18 interactions (18 atoms per molecule) for each molecule pair. Recent calculations (Della Valle and Pawley, 1983) have shown that simple atom-atom potentials give rise to anharmonic effects which are closely matched in nature (see Baharie and Pawley, 1982) for such measurements as the temperature variation

Figure 5
Variation of the unit cell volume ($Å^3$) with temperature at zero pressure for naphthalene. The experimental variation is labelled E, and K, W and M correspond to the potential functions of Kitaigorodskii, Williams and Mackenzie et al. respectively. A computational artefact appears in the melting region (broken line).



of the unit cell volume, as shown in figure 5. This study used the potentials of Kitaigorodskii (1973), Williams (1967) and Mackenzie, Pawley and Dietrich (1977), denoted K, W and M respectively in the figure. K and W very closely fit the experimental measurements and show peculiarities indicative of melting close to the melting temperature.

This result supports the usefullness of such simple interaction potentials, and shows that we will soon be able to test more sophisticated potentials and compare with a wider range of experimental data as our computers continue to increase in power.

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