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for
MD & MC SIMULATIONS

An Informal Newsletter associated with Collaborative Computational Project No. 5
on Molecular Dynamics and Monte Carlo Simulations of Macroscopic systems.

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Contents

As is now the custom, we begin our third newsletter with a welcome
to our readers and a sincere thank you to the contributors of the
articles presented. Some of the articles appearing are elaborations of
the talks that the authors gave at the CCP5 (UMIST) meeting in September
and we thank them for undertaking the extra effort of writing the
articles for us. As usual, some of the articles contributed give advice
on computational matters. These are always welcome. We should like to
invite our readers to follow the example of our contributors and provide
further articles for the newsletter, we will be very pleased to publish
them.

1.   Readers are reminded that CCP5 supports a growing program library which is available to anyone who is interested in obtaining its programs. All of the programs listed below are available, free of charge, provided the applicant supplies a suitable magnetic tape. Most of the programs have some documentation. Both programs and documents may be obtained from Dr. W. Smith at Daresbury Laboratory.

Program	Author	Purpose
MDATOM	S. Thompson	MD on monatomic liquids
HMDIAT	S. Thompson	MD on homonuclear diatomic liquids
MDLIN	S. Thompson	MD on linear molecules
MDLINQ	S. Thompson	MD on linear molecules with quadrupole
MDTETRA	S. Thompson	MD on tetrahedral molecules
MDPOLY	S. Thompson	MD on polyatomic molecules
MDATOM	D. Fincham	MD on monatomic liquids
MDDIAT	D. Fincham	MD on homonucleo diatomic liquids
MDDIATQ	D. Fincham	As MDDIAT, with quadrupole
MDIONS	D. Fincham & N. Anastasiou	MD on ionic liquids (Ewald Sum)

Note: The D. Fincham and S. Thompson programs generally differ in the use of different integration algorithms. The S. Thompson programs use the Gear algorithm with quaternion orientation parameters. D. Fincham programs use the leapfrog algorithm and constraint dynamics.

    Readers who have other programs, which they would like to contribute (particularly Monte Carlo programs) please contact Dr. W. Smith.

2.   The sixth CCP5 meeting will take place at Royal Holloway College on 29th-30th March, 1982. The topic of interest is "Transport Processes'. Please consult the loose sheet circulated with this newsletter.

3.   Dr. David Fincham is organising a D.A.P. workshop at Royal Holloway College, following on from the March CCP5 meeting. This array processor

is particularly suited to liquid simulation work and interested parties
would be wise to contact Dr. Fincham as soon as possible to secure a
place.   Please see the loose sheet circulated with this letter.

A REVIEW OF THE FOURTH CCP5 MEETING

New Advances of Computer Simulation in Statistical Mechanics held at UMIST, Manchester, between 9-1th September 1981

D.M. Heyes

The aim of the meeting was to present new methods of computer simulation for investigating a wide variety of phenomena in statistical mechanics.

Professor Rahman started the discussion by describing a modification of the usual MD procedure which enables the volume and shape of the MD cell to change in response to an imbalance between an externally applied stress and the internal stress (obtained as usual from the particle positions and velocities). He has used this technique to investigate the effect of pair potential form on preferred crystal structure. For example, Lennard-Jones particles placed on a b.c.c. lattice spontaneously reorganise into the f.c.c. form; whereas the reverse change occurs for a Rb potential. He also gave preliminary results of a similar study on ionic crystals. The application of pressure to a model KC1 crystal induced a change in crystal structure from f.c.c. to the CsCl structure. The mechanism of this process involved some of the ions being co-operatively displaced along the principal axes. In the discussion, Professor Alder said that this programing scheme would tend to favour "global" or homogeneous paths for change in crystal structure, in preference to one involving nucleation.

Dr. Fincham described the applications of the DAP (Distributed Array Processor/ICl 2980 computer system to computer simulation. Computers should be as small as possible because their speed is governed by the rate at which signals can be transmitted. As the packing density is limited by the power dissipation, present computers are nearly as fast as they can be with the available semi-conductor technology. The DAP computer peripheral enables an effective increase in speed by taking advantage of the "parallelism" inherent in many problem solutions, such as an

MD scheme. It gains speed by devolving activity to 4096 processing elements which, although controlled by a master control unit, can work independently. They enable operations applied to each element in an array to be performed simultaneously and not sequentially as in other computers. The DAP FORTRAN is an extremely concise programming language (a typical monatomic MD program needs less than 100 statements). Evidence for the cost effectiveness of this machine was given.

Professor Pawley later gave an example of the use of the DAP computer system applied to a simulation of 4096 model SF_6 molecules at room temperature. He was interested in plastic crystal phase changes. Interestingly, he observed an almost temperature independent rate of rotation of these particles. Good correlations between neighbour reorientations was found.

Professor Cotterill presented some preliminary results of a research programme into the fundamental characteristics of superionic conductivity. He pointed out the irony that although ionicity in a compound is common to all superionic conductors, NaCl does not superconduct. In order to discover the nature of the superconducting sub-lattice, the MD of a model superionic conductor in the vicinity of a split line loose boundary was considered. The presence of a fault was considered to be of interest because of the probable use of such materials in a compressed powdered form in future batteries. It was observed that although disordering of the mobile sublattice increases at the grain boundary, the fault inhibits the disordering of the rest of the lattice. Regions of free volume were followed and it was postulated that the "looseness" of the conducting sub-lattice was a significant parameter. The nature of the liquid state and the concept of ergodicity were thought to be important in its description. Professors Rahman and Berendsen stated that ergodicity in computer experiments was determined by the order of the algorithm for integrating the equations of motion and to a much smaller extent by the round-off errors.

Dr. Schreiner described a novel MC technique which removes some of the computational artefacts of conventional simulations using periodic boundary conditions. The specific example of a two-dimensional system

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was considered in which the particles were confined to occupy the surface of a sphere. The so-called "Double-Distance" convention was used, in which interactions between two particles are considered twice - along both sides of the Great Circle containing them. This has the advantage that for long range forces discontinuities do not arise as with conventional periodic boundary conditions. Here the force goes smoothly to zero as the two particles approach their furthest separation on the spheres. Also this approach enables the N-dependence of the thermodynamic properties to be predicted more easily. This was convincingly shown for LG particles. However, density is not so easily defined in curved space. Also, for the same number of particles "Flat" boundary conditions produce results closer to the thermodynamic limit than those obtained using spherical boundary conditions.

Dr. de Leeuw emphasised his interest in the mechanism of vacancy/ interstitial recombination which takes place after a period of radiation damage of a solid. Model copper near the melting temperature (T ~ 1350 K or $T^* = 0.35$ $\epsilon/k_B T$) was simulated. In order to assess the effect of the chosen ensemble both constant volume and constant pressure calculations were performed from the same starting configuration. Although the dynamical correlation functions agreed at short times, the long time behaviour of the two ensembles was significantly different. This was manifest in a negligibly small rate of diffusion at constant volume but a diffusion coefficient of 1.2×10^{-6} cm^2/s at constant pressure. The MD box size oscillates at a much slower frequency than that typical of interatomic collisions. It was argued that a constant pressure algorithm allows extra freedom for diffusion and consequently this more realistic method should be used for future radiation damage studies. Professor Berendsen suggested that an alternative procedure would be to follow a small volume of material within a larger MD cell at constant volume. Dr. Clarke was surprised at the diffusion constants obtained, as during glass formation by computer simulation constant volume and constant pressure diffusion coefficients have been found to be rather similar. Professor Rahman thought that there was an important difference between the glass forming studies and those of Dr. de Leeuw. In the former work the material was being formed. Dr. Allen suggested that the difference in the diffusion constants could be a computational artefact resulting from the variable

scaled coordinates used as constant pressure.

Dr. Evans defined a non-Newtonian fluid as one whose behaviour at a time is influenced by its recent history. He illustrated the common occurrence of non-Newtonian fluids in everyday life. These include shear thickening fluids which are often (erroneously) called dilating fluids and shear thinning fluids whose viscosity decreases with rate of shear. Thixotropic liquids such as many paints which reversibly change from a gel to a sol on the application of shear enter the latter category. Viscoelastic fluids are also non-Newtonian and they give rise to such unusual behaviour as is evident in the Weisenberg effect (in which a fluid rises up the stirrer and not the walls of the container), self-siphoning, die swelling, the Kay effect and the Bounce effect (drops formed by the pouring of a liquid onto a flat surface eject streams of the fluid later). Dr. Evans then showed the inadequacy of Statistical Mechanics to describe such processes. It is not even able to predict the Newtonian viscosity of argon near the triple point. Problems arise from the divergence of a virial expansion of the Navier-Stokes equation and the related long time tails in the correlation functions used to determine the transport coefficients (which consequently have a cusp in the frequency dependent shear viscosity as frequency tends to zero).

A direct evaluation of the viscosities by MD using the Kubo relationships is 2 or 3 orders of magnitude more slowly converging than those evaluated by non-Equilibrium Molecular Dynamics (NEMD). The non-equilibrium approach involves establishing a velocity gradient in the MD cell. By displacing the image particles discontinuities associated with particles leaving the MD cell are avoided. Extrapolation to zero shear rate for the shear rate dependent viscosity gives a good agreement with argon viscosity near the triple point $(3.1 \ (m\epsilon)^{1/2}\sigma^{-2})$. Dr. Evans showed that for the LJ fluid the viscosity, pressure, internal energy and difference in normal pressure components (in the shear plane) vary as shear rate to the power 1/2, 3/2, 3/2 and 3/2 respectively. This agrees with Mode Coupling theory; although the changes were several orders of magnitude larger than this theory predicts. Dr. Evans interpreted his shear rate dependent pressure and internal energy in terms of Non-Linear Irreversible Thermodynamics. He showed that it is possible to introduce

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a new intensive variable or potential, coupled to the strain rate which affects the thermodynamic state of the liquid. The energy and pressure can be related using a dimensionless dilatency. A shear rate dependent phase diagram was presented. The concepts of vortex viscosity for polyatomics and shear-rate dependent structural changes were introduced. The problem of heating during shear was mentioned in the discussion. Dr. Evans replied that he maintained isothermal conditions by scaling the velocities. However, any artefacts caused by this are eliminated in the limit of zero shear rate as the rate of temperature rise is proportional to the shear rate to the power 1/2, which is lower than the pressure dependence.

Dr. Whittle continued this topic by describing the results of similar calculations on diatomic molecule liquids to determine their non-linear response to applications of shear. A difference in trajectories approach was adopted so as to eliminate irrelevant statistical fluctuations. A series of steps in shear rate were applied to an equilibrium model chlorine system ($\rho^* = 0.55$, $t^* > 0.75$). The stress of an unperturbed trajectory was subtracted from that of a disturbed system starting from the same point in time. The shear viscosities, obtained from the symmetric part of the stress tensor, were in good agreement with previous work. The relaxation time for stress build-up is longer than for monatomics. The anti-symmetric part of the stress tensor gives rise to a transient stress associated with the vortex viscosity. Alignment of molecules with respect to the Covette flow was proved using an orientation correlation function. The relaxation time for this is of the same order as that of the stress rise. Significantly, the model Cl_2 showed little tendency to shear thin.

Professor Powles used a similar difference in trajectories approach to examine the dielectric behaviour of diatomic polar fluids by forced displacement rather than from spontaneous fluctuations. The static dielectric constant for model hydrogen chloride agreed well with experiment over a wide density range to beyond the critical density. However, higher order relaxation times were less well reproducced. This was attributed to an inadequate interaction potential (the second virial coefficient is in poor agreement with experiment). The dipole and quad-

rupole moments of HCl need to be incorporated in future simulations.
Drs. Evans and Adams commented that when simulating polyatomics by a
perturbation and difference technique care must be exercised in adopting
"false plateaus" as limiting behaviour.

Dr. Tenenbaum described a method for establishing a temperature
gradient across an MD cell which is periodically reproduced in two ortho-
gonal directions only. Particles attempting to leave this lamina of in-
finite extent are reintroduced with a velocity selected from a Maxwellian
distribution corresponding to a prescribed wall temperature. This stoch-
astic wall technique creates a flux of thermal energy across the cell and
an associated temperature gradient. The temperature profile showed
rapid changes near the walls but a linear thermal response in the centre.
The obtained liquid thermal conductivities showed little dependence on
the magnitude of the temperature gradient ($\Delta T^* < 0.07 \, \epsilon/k_B T$). The ther-
mal conductivities were noticeably lower than other simulation values by
up to 50%. This was partially accounted for by correcting for the over-
all non-linear temperature profiles. Dr. Heyes wished to know if any
non-uniformity in the density profile perpendicular to the walls had been
observed. Dr. Tenenbaum said that on "8-bin" density profile was meas-
ured and it did show variations which would in future be eliminated by
including images beyond the walls. Professor Alder commented that a
finer resolution would probably reveal oscillations in density typical of
such a confined system. This would undoubtedly affect the conductivity
values.

Two short contributions were made by Drs. Frenkel and Mitra.
Dr. Frenkel presented the results of 3D MD simulations performed with
Dr. J.F. Maguire on hard lines or "needles". This system has the same
statical properties as an ideal gas at the same number density and temp-
erature. However, its dynamical properties show deviations which are
useful in interpreting the results of light scattering experiments on
long thin molecules. Good agreement was obtained with the Doi-Edwards
theory, in which the collision frequency, parallel and perpendicular
diffusion coefficients and reorientational times are related simply to
the number density. Dr. Mitra described a new method for satisfying the
holonomic constraints restriction in MD by maintaining the constrained

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distances rather than their squares as is usual. A gain of 50% in computational speed over the Ryckaert method was obtained.

Professor Berendsen gave the first talk of a series on stochastic dynamics. This is a technique for representing certain degrees of freedom in a system, which are of only secondary importance, in an approximate way so as to reduce computer time. Examples, presented were electrolyte solutions where the behaviour of the solute molecules is of main concern and complex molecules in solution. This method has enabled large molecules such as polymers, proteins, membranes and proteins in water to be investigated. In each case the solvent is represented by frictional and random forces, usually of the Strict Langevin form. This works well for decane. However, for a large polymer it is not easy to decide which degrees of freedom to take out - as the normal modes change with time. Also a more rigorous treatment requires a generalisation in time and space of the friction coefficient, γ. Technical advances of Professor Berendsen's group involve taking the algorithm for integrating the equations of motion to an order which includes the time derivative of the acceleration and being able to accommodate a wide range of $\gamma\Delta t$ (although values of 0.007 to 0.133 are typical). The criterion for the accuracy of the algorithm is not conservation of energy but the number of completed dihedral transitions. A barrier is defined to have been crossed when the next minimum is occupied. Evidence for a correlated sequence of transitions of dihedral angles in n-decane has been observed. Extensions to the investigation of slow events were discussed. It is necessary to define the reaction coordinate and then determine the free energy change along this path as it is affected by the other degrees of freedom.

Professor Berne continued this theme of simulating rare events by considering the intramolecular rate process of geometrical isomerization which can take place along a reaction coordinate such as a dihedral angle rotation. The relaxation kinetics were ingeneously cast in terms of a correlation function formalism involving the rate of change of the reaction coordinate or reactive flux. This replaces a Partition Function representation. The concepts of oscillating reactive flux, activation volume, Kramers relation, constraint effects and mode specific chemistry were introduced.

Dr. Lal showed the results of stochastic dynamics simulations of model colloidal particles immersed in a hydrodynamic medium. The colloidal particles have typical diameters of 0.1 to 1 μ. There is a big difference in time scales between these particles and those of the background medium. Ermak's algorithm for diffusive dynamics was used in which interparticle interactions and Brownian motion were incorporated under the DLVO formalism. The motivation for this research was to discover the mechanism of colloidal conglomeration. The evidence being that colloidal particles first form a linear chain and then reorganise into a more compact assembly. For a two particle system he showed the great influence of the depth of the interaction potential on the association time of the particles, which is almost infinity for an interacting well depth of $\sim 9k_BT$.

Dr. Stepto presented an entertaining film illustrating the combined effects of solvent characteristics, chain potentials and flexibility on the average size and shape of polymer chains. The transitions from ellipsoidal envelopes to less compact structures were demonstrated using Monte Carlo techniques.

Dr. Robson outlined the considerable difficulties in using a Monte Carlo scheme to find the preferred conformations of complex biological molecules. Using a combination of MC, energy minimisation and trajectory programming (a constraint method starting from an empirically determined starting structure). These problems have been partially overcome. The MC procedure is performed so that a partly constructed structure can be rejected with confidence before the whole molecule is completed.

Dr. Ryckaert demonstrated the ability of stochastic dynamics applied to a single Lennard-Jones particle to reproduce the single particle dynamical behaviour of the pure fluid. The generalised Langevin equation with a continued fraction representation of the kernal up to the 25th level was needed.

Dr. Jacucci described a Monte Carlo calculation for the exchange part of the radial distribution function of quantum hard spheres at finite temperatures using path integrals with boundary conditions.

Dr. Quirke examined the nature of energy and pressure fluctuations during Metropolis Monte Carlo Simulations of diatomic fluids. It was argued that sub-averages of sufficient duration can be correlated with an effective subaverage temperature different from that imposed by the MC algorithm, using the average configurational energy in the sub-average and the specific heat of the system.

Dr. Goodfellow described the polarisable electropole model of water used in studying water organisation around a protein molecule. The multipole moments vary with configuration and are not a fixed property of the molecule. In formulating the computing scheme use is made of the slowly varying nature of the multipole moments. For the quadrupole moment field gradients need to be calculated.

COMPUTER SIMULATION OF THE PLASTIC TO CRYSTALLINE PHASE
TRANSITIONS IN SF$_6$

G.S. PAWLEY and G.W. THOMAS

Preamble

At the time of the UMIST meeting the result here presented was
locked away on tape, but was legible immediately afterwards.

A simple but realistic model for the condensed phases of SF$_6$ gives a
plastic phase at 80K in a molecular dynamics simulation. Equilibration
of a sample of 4096 molecules at 25K and at zero pressure results in a
transition to a polycrystal. The crystal structure found is triclinic P1,
Z=3, but is pseudo-orthorhombic, a result not inconsistent with recent
spectroscopic measurements. It is suggested that, to avoid bias, a large
sample size is necessary for modelling the plastic to crystalline phase
transition, and that such a result has been achieved for the first time
using the Distributed Array Processor (DAP).

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The realistic modelling of solid state phase transitions with molec-
ular dynamics requires a sample large enough that the nucleating phase is
in no way restricted or determined by the imposed boundary conditions.
With a large enough sample separate grains can grow and complete and each
can be large enough to exhibit the structural pattern of the new phase.
Owing to its extreme anharmonicity the plastic crystalline phase of
matter is difficult to study analytically, and theoretical progress can
best be made through molecular dynamics computer simulations. Ideally
any model for the plastic phase of a system should be capable of repro-
ducing the phase change to the crystalline form, thus furnishing an
excellent tool for the study of such transitions. We here report what
well may be the first realistic example of such a transition found by
this technique, yielding a crystal structure of considerable complexity.

It has been pointed out that the selection of a good potential
function is of central importance to this work[1], and it is argued that
the simple Lennard-Jones F-F atom-atom potential as already used for the

plastic phase simulation of SF_6 has all the requirements to produce a plastic to crystal transition[2]. Molecules are assumed to move as rigid units under interactions with 8 nearest and 6 next-nearest neighbours only. Each intermolecular interaction involves 36 F-F interactions, so that the force field on any one molecule depends on 504 F-F interactions. The dynamical equations followed Beeman's algorithm[3] using the quaternion formulation[4]. The resulting model reproduced the crystallographic result for the plastic phase in which molecules are arranged on average on a body-centred cubic lattice, and perform occasional reorientational jumps as expected in this phase. The temperature of the calcualtion was 80K.

Harmonic lattice dynamical calculation for the body-centred cubic phase gave evidence of a very unstable model, as only the longitudinal acoustic modes had positive eigenvalues[2]. The transverse acoustic modes had negative eigenvalues, indicating that the structure was unstable with respect to any shear, and instability associated with any molecular rotational displacement was similarly shown by the absence of any librational positive definite modes at any point in the Brillouin zone. This was thought to be an attribute for the model as the cubic phase is not a truly crystalline phase.

A sample of 4096 molecules has now been set up on the I.C.L. Distributed Array Processor[5] (DAP) at Queen Mary College, London. This sample uses the total number of parallel processing elements of the DAP, and as these processing elements are hard-wired in a cyclic condition (in fact 64×64), it is very easy to implement cyclic boundary conditions for any desired topology[6]. The sample used in this work was roughly 13×13×13 body-centred unit cells. The calculation of one time step takes 3 seconds on the DAP, making this computer ideal for such problems and effectively competitive with the fastest of modern computers.

In the work on the dynamics of Rb Parrinello and Rahman[7] have reported a crystal to crystal phase transition induced in a molecular dynamics calculation. With the right conditions evidence of a transition was immediate but the transition itself was slow before the rapid move to completion. This result prompted us to run the SF_6 simulation at a low temperature (25K) for a long time (3 hours) in the hope of a similar

event. The temperature of the sample slowly drifted upwards, requiring a continuous extraction of energy from the system. The total potential of the system fell accordingly, and the volume of the constant pressure sample decreased. This behaviour pointed to a gradual ordering process, the geometry of which was quite unknown. No sudden move to completion was observed.

The time step used in this calculation was 0.015 psec. perhaps rather small for a calculation at 25K, but it had been found to be necessary for runs at 150K. An earlier calculation[2] on a sample of 54 molecules was quite stable with a time step of 0.025 psec, but such a time step gave problems with the larger sample, eventually producing a close and catastrophic intermolecular contact. Such events were presumably inhibited in the smaller sample by the artificial constraints of the cyclic boundary conditions. Constant pressure was maintained as follows. The displacement of each molecule was measured from its individual origin, these origins being arranged on a body centred cubic lattice. The size of the lattice spacing was systematically adjusted to maintain zero pressure, but no attempt was made to distort the basic lattice as done by Parrinello and Rahman[7]. Such distortions relieve shear stresses in the sample, but such stresses should be automatically relieved when the structure suffers a transition by the nucleation of a number of crystallites in various different orientations, providing the sample used for modelling such transitions is large enough for the natural development of a mosaic. If this is not the case the possible new structures for the nucleating phase may be arbitrarily constrained. These considerations are not of such importance if the transition structural change is known in advance. In such cases, as with Rb[7], it is possible to have the cyclic boundary conditions so that they are consistent with both phases, and then the onset of the transition will be swift at the moment when one grain dominates and the sample becomes a single crystal.

The structure of the natural crystalline phase of SF_6 is not yet known, though recent spectroscopic measurements[8] lead to a conjecture that the phase is orthorhombic. The transition from the plastic phase takes place at 92K for the natural system, so a temperature of 25K is reasonable for a long calculation to search for a crystalline phase. As

mentioned above, ordering of the sample took place slowly, and when it appeared that most of the transition was accomplished, about one quarter of the sample was drawn out in layers by the computer, the molecules being represented by octahedra. The layers contain molecules on cubic (100) planes, close molecules therefore being next-nearest neighbours. Part of one typical layer is reproduced in figure 1, where the ordering is clearly apparent. In this figure there are two major crystal grains, both with ordering along the diagonal lines parallel to AB. The three molecules nearest B on AB have an orientation (orientation 1) which is not repeated until three rows distant. The intervening two rows contain molecules of orientation 2. Molecules of orientation 1 occupy symmetry inversion centres, utilising the centrosymmetry of the octahedral molecules. Molecules of orientation 2 do not use the molecular symmetry, but are related in pairs about inversion centres. A primitive unit cell thus comprises one molecule of orientation 1 and two of orientation 2, and is triclinic, P1 (Z=3). This result is consistent with the instability with respect to shear in the cubic phase. A unit cell is outlined in figure 1, where the circles denote inversion centres; the upper part of the cell is related to the layer of nearest neighbours above that of figure 1, and the inversion centres relating these two layers are also shown.

A more convenient centred unit cell can be chosen as follows. The shortest axis on figure 1, that between layers, has a vector c = (d/2, d/2, d/2) expressed in terms of the underlying cubic grid of spacing d. Two other axes can be chosen which are orthogonal in the true cubic arrangement, b = (d, -d, 0) and a = (d, d, -2d). A typical cell of these dimensions has been chosen from the middle of a large grain and is shown projected down a in figure 2. As this is a 'snapshot', the symmetry related molecules do not appear exactly identical. The molecules labelled + and - are at c/3 and -c/3. The unit cell is

a; b; c = 14.1; 7.7; 4.70 Å
α; β; γ = 89.4; 91.9; 88.1°

and is pseudo C face centred orthorhombic. This is quite consistent with recent spectroscopic measurements on the natural material[8].

It has been suggested[9] that structural complexity is likely to characterise plastic crystals in their ordered phases. The developing triclinic cell can nucleate in any of 48 possible oreintations, thus giving a large entropy contribution at the transition. Furthermore the choice of origin of the unit cell introduces a further factor of three as there are three molecules in the unit cell, and it is therefore not surprising that ordering in the simulation is not abrupt. However, the fundamental ordering in each grain has been found to be identical.

The annealing of grains will be considerably frustrated by twinning which is likely to occur in a number of ways. The layer of figure 1 has been chosen because it displays twinning, as can be seen by careful observation. Of the seven molecules in the row AB, the 4th and 5th are related by a two-fold axis perpendicular to the diagram. This twin axis relates a large number of molecules in the two ordered grains, both in the plane of the diagram and on several parallel planes.

A count of the number of molecules in the larger grains gives a value of about 300, indicating a correlation length of roughly 8 nearest-neighbour distances. As this is well short of the cyclic repeat distance, it is clear that the observed transition is not driven by cyclic boundary constraints.

Further work is planned both to solve the natural structure experimentally and to study the simulation phase transition in depth. To monitor the sample on cooling we can follow Parrinello and Rahman[7] and scan the radial distribution function. Figure 3 shows the first peak in the S-S radial distribution function at 25K; if this were in the cubic phase there would be only one peak centred at 4.77 Å. For observing the transition on warming, the triclinic angles α, β, γ for a single crystal can be used as order parameters. It is amusing to note that a single crystal sample will require a multiple of 3 (therefore 4095) molecules, and careful programming will be necessary to discard just one molecule[5]!

We believe that the large size of the molecular dynamics cell has made it possible, for the first time, to model a realistic transition from the plastic to the crystalline phase. Many other systems are within

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the power of the DAP, and it should soon be possible to perform a comprehensive unifying analysis of the wide variety of experimental data available for many of these systems. Furthermore such simulations should stimulate experimental work - the present result clearly indicates the point in the Brillouin zone of the cubic phase which should show evidence of the transition through X-ray diffuse scattering; that is, if the simulation has developed the true natural structure.

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Figure Captions

1. A part of one (100) layer of the polycrystalline SF_6 at 25K. Order occurs along rows parallel to AB, repeating every three rows. The primitive triclinic cell is shown near B, where the open circles denote centres of symmetry. These lie in the plane of the diagram and in two parallel planes, the upper of which is in the next plane of molecules. Twinning occurs as seen by the existence of a local two-fold axis perpendicular to the plane of the diagram, situated between molecules 4 and 5 on the line AB.

2. A pseudo C-face centred orthorhombic cell extracted from a large crystal grain. The axes below show the definition of the triclinic cell. The molecules at + and − are approximately at + $1/3\underline{c}$ and − $1/3\underline{c}$, the other molecules (orientation 1) being in the plane of the diagram.

3. The nearest neighbour molecular centre-centre (S-S) radial distribution function in the sample at 25K. If this sample were in the plastic phase there would be only one peak, at 4.77 Å.
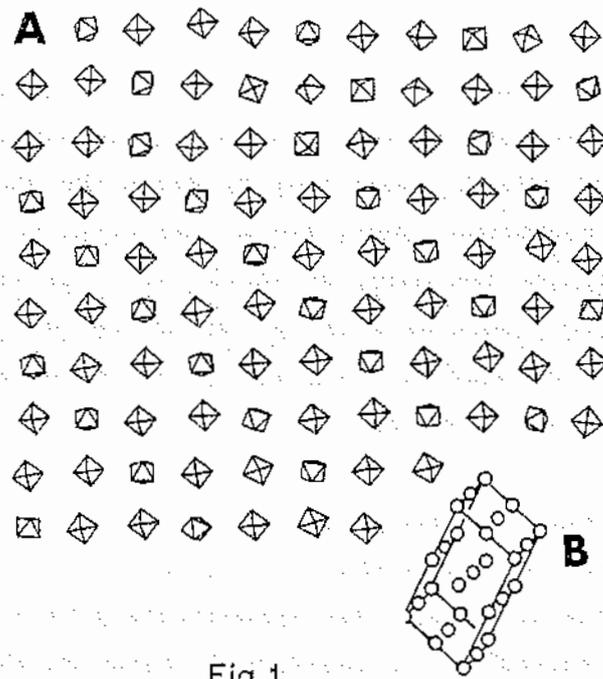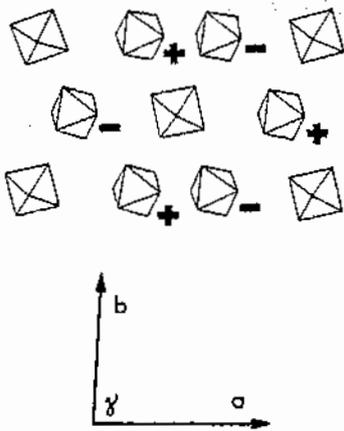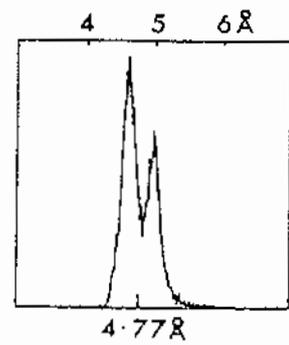
Fig.1

Fig.2

Fig.3

MOLECULAR DYNAMICS STUDY OF INFINITELY THIN HARD RODS. COMPUTER
EXPERIMENTS ON DYNAMICAL SCALING.

Daan Frenkel and John F. Maguire

Molecular Dynamics (MD) calculations are widely used to study the
structural and dynamical properties of atomic and molecular fluids.
Often, such calculations provide the only tool to test predictions of
statistical-mechanical theories of transport phenomena in dense fluids on
a microscopic scale. Many of the recent developments in liquid state
theory have been inspired by the results of computer simulations (see
e.g. ref.1). Among the systems studied, the hard-sphere system has
played a special role[2,3]. The reason is twofold: computer simulations on
the hard-sphere system could be used to test existing theories of the
liquid state such as the Percus-Yevick equation (equilibrium properties)
and the Enskog expressions for transport properties. Such tests, and the
discrepancies they revealed (e.g. Alders test of the Enskog theory of
molecular diffusion) form the starting point for many of the modern
theories of dense fluids. A second reason why the hard-sphere system has
played a special role is that, once its properties were known, it could
be used as a reference system for fluids with continuous intermolecular
potentials. This approach has resulted in very successful perturbation
theories for dense fluids[4,5].

In view of the important role that the hard sphere system has play-
ed, it is somewhat surprising that virtually no work has been done on the
dynamics of non-spherical molecules with impulsive interactions. In
fact, the work of Rebertus and Sando on the dynamics of hard sphero-
cylinders is, to our knowledge, the only published MD study of "hard",
non-spherical molecules[6] (see, however, ref.7). Admittedly, the rough-
sphere fluid has been studied in detail by MD[8], but rough-spheres are not
really typical for non-spherical molecules. There are however other
"hard" systems which, in their simplicity, are comparable to the
hard-sphere fluid. One such system, a fluid consisting of infinitely
thin, hard rods of length L ("hard-lines") is the subject of the present
letter. In this letter, we present the results of MD simulations on a

system of hard-lines, over a range of densities. We compare the results of these simulations with theoretical predictions for the density dependence of transport properties. Although we will briefly indicate the nature of these theoretical predictions, we must refer the reader to a subsequent publication[9] for a more detailed discussion. Similarly, only certain features of the computational method that we used will be mentioned here; ref.9 will contain a detailed discussion.

The hard-line fluid is remarkable in that all of its structural properties are those of an ideal gas, whereas all of its transport properties are non-ideal, and strongly dependent on density. The absence of structural correlations is a direct consequence of the fact that the hard-line system has zero excluded-volume; at any density, any molecular position and orientation (but for a set of measure zero) is equally likely. Obviously, as the configurational part of the partition function equals $V^N/N!$, the pressure of a hard-line fluid must follow the ideal gas law and no thermodynamic phase transitions are possible in this system. In contrast, the dynamics of hard-lines is very sensitive to the presence of other lines. Theoretical predictions can be made about the dynamics of hard-lines (in particular about translational and rotational diffusion), using two very different approaches. The first is the well-known Enskog method for computing transport properties (we use the word "Enskog-theory" in the sense explained in refs.10 and 8). Due to the absence of structural correlations in the hard-line system, the following, very simple expressions result for the diffusion constant D, and the angular momentum correlation time τ_J[9]:

$$D = 2.303 \ldots / \rho^* \tag{1}$$

and

$$\tau_J = 1.705 \ldots / \rho^* \tag{2}$$

In the above expressions, reduced units have been used: $\rho^* = \rho L^3$, where ρ is the number density and L the length of the line. We define L to be the unit of length, m (the mass of the line) to be the unit of mass, and kT to be the unit of energy. I, the moment of intertia of the rods, is chosen to be equal to 1/12, which corresponds to a uniform mass distribution. Other choices for I are possible; they result in other numerical

constants in eqns.1-2 (and 3), below). The collision frequency in a hard-line fluid can be calculated exactly:

$$\Gamma = 1.23766 \ldots \rho^* \tag{3}$$

Eq.3 is valid in the thermodynamic limit; the explicit N-dependence of Γ can be worked out[9]. It is important to note that eq.3 is _exact_; it provides our most important, non-trivial check on the MD results to be presented below.

At high densities eq.3 is still valid, but the Enskog expressions (eqns.1-2) may fail. However, it is precisely at high densities ($\rho^* \gg 1$) that theoretical predictions can be made about rotational and translational diffusion, using scaling arguments similar to those presented by Doi and Edwards[11] (henceforth referred to as DE). These authors have developed a theory of Brownian dynamics of rod-like macromolecules in concentrated solutions. One of the central predictions of the DE theory is that for thin, flexible rods the following relation should hold between the rotational diffusion constant D_r and the longitudinal translational diffusion constant $D_{\parallel}$ (i.e. along the rod axis):

$$D_r \sim D_{\parallel}/\rho^{*2} \tag{4}$$

The basic idea behind this expression is that the reorientation of the rods is constrained by the presence of other rods. Only when one of the constraining rods diffuses away (typically, in a time $1/D_{\parallel}$), can the constrained molecule perform an angular jump of order $\theta \approx \rho^{*-1}$. Several attempts have been made to test the DE theory experimentally[12,13], using light-scattering to study the rotational dynamics of long, rod-like viruses. There are however some discrepancies between theory and experiment, and it is not obvious at present whether these discrepancies are due to deficiencies of the DE theory or to the fact that real viruses are actually not completely rigid, nor infinitely thin. MD simulations on a hard-line system should provide a more direct test of the DE theory. It should be noted, however, that the DE theory was derived for rods performing Brownian motion in a viscous fluid. For smooth, hard-lines, eq.4 has to be modified slightly[9], and reads:

$$D_r \sim 1/\rho^{*2} \tag{4a}$$

(The original eq.4 should hold for _rough_ hard lines). The high-density behaviour of $D_{\parallel}$ can be predicted by extending the scaling arguments used by Doi and Edwards. One arrives at a remarkable prediction, namely that $D_{\parallel}$ should _diverge_ at high densities:

$$\lim_{\rho^* \to \infty} D_{\parallel} \sim \rho^{*1/2} \tag{5}$$

The reason for this unexpected behaviour is that, during a collision, only forces perpendicular to the molecular axis act on a smooth hard-line. As a simple approximation for the rate of change of the correlation function of the longitudinal velocity, $C_{\parallel}(t) \equiv \langle v_{\parallel}(0)v_{\parallel}(t)\rangle$, we may write:

$$\dot{C}_{\parallel}(t) = -\gamma\langle\sin^2\theta(t)\rangle \, C_{\parallel}(t) \tag{6}$$

where the "friction constant" γ is proportional to the collision frequency, $C_{\parallel}(t) \sim \exp(-\gamma\langle\omega^2\rangle t^3/3)$, where $\langle\omega^2\rangle$ is the mean square rotation frequency of the rods. In the rotational diffusion regime ($\Gamma^{-1} \ll t \ll D_r^{-1}$), $C_{\parallel}(t)$ decays as $\exp(-2\gamma D_r t^2)$, and for $t \gg D_r^{-1}$, it should decay as $\exp(-2/3\,\gamma t)$. At high densities the correlation function should become predominantly Gaussian, and hence $D_{\parallel} \approx (\pi/2\gamma D_r)^{1/2} \sim \rho^{*1/2}$ (eq.5). Unlike $D_{\parallel}$, $D_{\perp}$ should decrease with increasing ρ^*, but somewhat faster than predicted by eq.1:

$$\lim_{\rho^* \to \infty} (D_{\perp}/D_{Enskog}) = 2/3 \tag{7}$$

No amolous behaviour is predicted for τ_J; this, in itself, has interesting consequences because combination of eqns.2 and 4 yields:

$$\lim_{\rho \to \infty} \tau_J \, D_r^{-1} \sim \rho^* \tag{8}$$

which implies that the Hubbard relation ($\tau_J/D_r = $ constant)[14] fails at

high ρ^*.

The algorithm to solve the equations of motion for the hard-line fluid is rather different from most conventional MD procedures. To find the time t_c at which two moving, rotating lines (i and j) are due to collide, the program searches for the roots of the following equation:

$$F(t) \equiv \vec{r}_{ij}(t) \cdot \vec{u}_i(t) \wedge \vec{u}_j(t) = 0 \tag{9}$$

Here $\vec{r}_{ij}$ is the distance between the centres of mass of rods i and j; $\vec{u}_i(\vec{u}_j)$ is the orientation vector along the molecular axis. A ncessary (but not sufficient) condition for a collision is: $F(t_c) = 0$, which implies that $\vec{r}_{ij}$, $\vec{u}_i$ and $\vec{u}_j$ are all in one plane. next, one has to test whether the coplanar lines do actually intersect. If not, the program searches for the next zero of $F(t)$ and repeats the test. We took great care to ensure that no roots of $F(t)$, and hence no collisions, were overlooked. In practice, the routine that searches for the next collision is written in such a way that the number of computations of $F(t)$ (which are rather time-consuming) is kept to a minimum. More details about the program are given in ref.9. The collision dynamics is completely determined by the condition that energy, angular momentum and liner momentum are conserved, plus the assumption that the impulsive force between two colliding lines $(\vec{f}_{ij})$ is perpendicular to both lines (the condition of "smoothness"). This latter condition guarantees that smooth hard-lines obey the ideal gas-law; the virial vanishes identically, because $\vec{f}_{ij} \cdot \vec{r}_{ij} = 0$.

Several tests were performed to check whether the program was functioning properly. It was found that energy and momentum were conserved to better than 1 in 10^{10}, the average rotational and translational temperatures were equal (within the noise), the dynamics was reversible for at least 1000 collisions and, most importantly, the density dependence of the collision frequency was found to obey eq.3. Computing time was long, but not excessive: on a CYBER 170-750 computer, 20,000 collisions in a 500 particle system (with periodic boundary conditions), at a density of $\rho^* \sim 16$, took about 2800 CPU seconds. In a conventional MD simulation, a production run is preceded by an equilibration run. In hard-line simula-

tions, the equilibration step can be eliminated, provided that the initial molecular positions and orientations are carefully randomized, while the initial velocities and angular momenta are distributed according to the Maxwell-Boltzmann law.

Runs were done on a 100-particle system at densities $\rho^* = 1, 2, 4, 6$ and 8, and on a 500-particle system for $"^* = 16, 24, 32$ and 48. Compared to typical runs on a hard-sphere system, the runs were quite short (20,000 collisions). Consequently, we could only study single particle properties; the estimated noise in the computed correlation functions is 1-2%. (ACF's) of the molecular centre of mass velocity $\langle \vec{v}(\tau).\vec{v}(t+\tau)\rangle$ (decomposed into components parallel and perpendicular to the molecular orientation at time τ) were computed, as well as the ACF's of the molecular angular momentum $(C_{J(}t) \equiv \langle \vec{J}(0).\vec{J}(t)\rangle)$. In addition, we computed the orientational correlation functions $\langle P_1(\vec{u}(0).\vec{u}(t))\rangle \equiv C_1(t)$ and $\langle P_2(\vec{u}(0).\vec{u}(t))\rangle \equiv C_2(t)$, were $\vec{u}(t)$ is the molecular orientation at time t and $P_1(P_2)$ the 1st (2nd) Legendre polynomial. All correlations were studied out to 25 collision times.

At low densities ($\rho^* < 8$), the velocity and angular momentum ACF's decay exponentially with a slope that agrees well with the Enskog predictions. At these densities, the orientational correlation functions $C_1(t)$ and $C_2(t)$ closely follow the behaviour predicted by the J-diffusion model (with a "collision frequency" equal to $1/\tau_J^{Enskog})$.[14,16,9] At high densities, all correlation functions show marked deviations from the Enskog (c.q. J-diffusion) predictions. With increasing density, the decay of $C_{J(}t)$ and $\langle v_\perp(0)v_\perp(t)\rangle$ becomes faster than exponential, and for $\rho^* > 30$ both ACF's develop a negative minimum after about 5 collision times. $C_1(t)$ and $C_2(t)$ decay exponentially at high ρ^*; from the slopes of these exponential correlation functions we determined the effective rotational diffusion constant D_r, using the relation:

$$\frac{d}{dt} \ln C_\ell(t) = -\ell(\ell+1)D_r \quad (\ell = 1,2). \tag{10}$$

Fig.1 shows a plot of D_r^{-1} vs. ρ^{*2}. Clearly, at densities $\rho^* > 8$, the (modified) Doi-Edwards prediction (eq.4a) is in good agreement with the

observed density dependence of D_r. Fig.2 shows the time dependence of log $\langle v_\parallel (0) v_\parallel (t) \rangle$ ($\equiv \log(C_\parallel (t))$). Several points should be noted. First of all, the initial slope of $\log(C_\parallel, t))$ (out to ~ 2 collision times) is very flat; in fact, it follows the predicted t^3-dependence. One should also note the dramatic positive departures from the Enskog predictions; for $\rho^* > 24$, $v_\parallel$ persist much longer than 25 collision times. The criteria formulated below eq.6 predict predominantly Gaussian behaviour of $C_\parallel (t)$ for $\Gamma^{-1} \ll t \ll D_r^{-1}$. For densities $\rho^* = 32$ and 48, $D_r^{-1} > 25$ collision times. At these densities one might therefore hope to observe Gaussian decay of $C_\parallel (t)$ in fig.2. Inspection of fig.2 suggests that the decay of $C_\parallel (t)$ is, in fact, simply exponential. But when $\log(C_\parallel (t))$ is plotted vs. t^2, it is found that the high density data fit equally well to a Gaussian. On basis of the present results we are unable to eliminate either possibility. The diffusion coefficients $D_\perp$ and $D_\parallel$ were obtained from the integrals of the transverse and longitudinal velocity ACF's. In order to perform the integrals of $C_\parallel (t)$, for $\rho > 24$, we had to extrapolate $C_\parallel (t)$ for times longer than 25 collision times. Both Gaussian and exponential extrapolations were used. It is seen in fig.3 that, irrespective of the nature of the extrapolation, $D_\parallel$ increases with increasing ρ^* for $\rho^* > 24$. The corresponding Enskog predictions are shown for the sake of comparison. The results shown in fig.3 strongly suggest that $D_\parallel$ diverges as $\rho^* \to \infty$. On basis of the present data we are, however, unable to confirm or reject the $\rho^{* 1/2}$-dependence predicted by eq.5. Table I contains a summary of the transport properties obtained from the MD simulations. Tabulated are: the collision frequency (Γ), the diffusion constants $D_\parallel$ and $D_\perp$, the decay time of $C_J(t)$ (τ_J) and the orientational correlation times τ_1 and τ_2.

Table I: Density dependence of computed collision frequency (Γ), longitudinal and transverse diffusion constants ($D_\parallel$ and $D_\perp$), and the decay times of the correlation functions of angular momentum (τ_J), $C_1(t)$ (τ_1) and $C_2(t)$ (τ_2).

ρ^*	Γ	$D_\parallel$	$D_\perp$	τ_J	τ_1	τ_2
1	1.24	2.59	2.30	1.69	0.12	0.49
2	2.44	1.37	1.05	0.93	0.14	0.30
4	4.89	0.82	0.51	0.44	0.21	0.22
6	7.24	0.60	0.36	0.31	0.25	0.17
8	9.99	0.53	0.25	0.20	0.30	0.18
16	19.8	0.50	0.11	0.088	0.51	0.23
24	30.2	0.49	0.073	0.058	0.73	0.36
32	40.0	0.50	0.049	0.039	0.93	0.36
48	61.5	0.76	0.021	0.021	1.54	0.56

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Figure Captions

Fig.1 Inverse rotational diffusion constant (D_r^{-1}) vs. the square of the reduced density (ρ^{*2}). D_r was obtained using eq.7 on $C_1(t)$ (0) and on $C_2(t)$ (*). The dashed line is a best fit to the high density points.

Fig.2 Log $C_{\parallel}(t)$ vs. t. t is expressed in mean collision times. (*): $\rho^* = 1$, (●): $\rho^* = 8$, (∇): $\rho^* = 16$, (▼): $\rho^* = 24$, (0): $\rho^* = 32$, (▲): $\rho^* = 48$.

Fig.3 $D_{\parallel}$ (●), $D_{\perp}$ (■) and Tr $D = (2D_{\perp} + D_{\parallel})/3$ (*) vs. reduced density. For $\rho^* = 32$ and 48, 2 values for $D_{\parallel}$ are shown; the lower value is based on a Gaussian extrapolation, the higher one on an exponential extrapolation (see text). The solid curve is the Enskog prediction (eq.1).
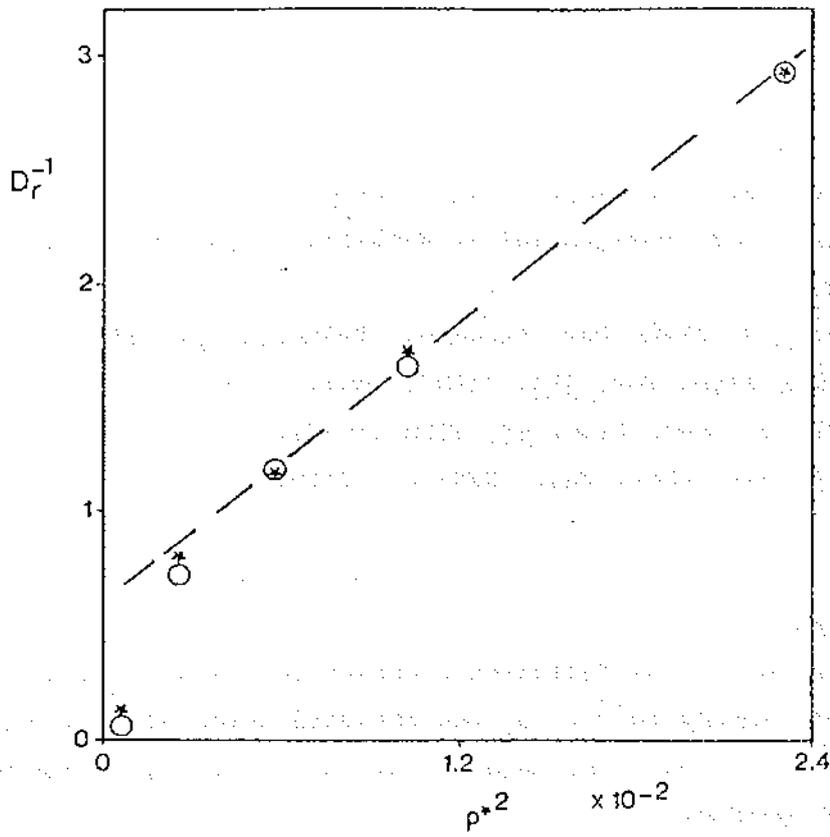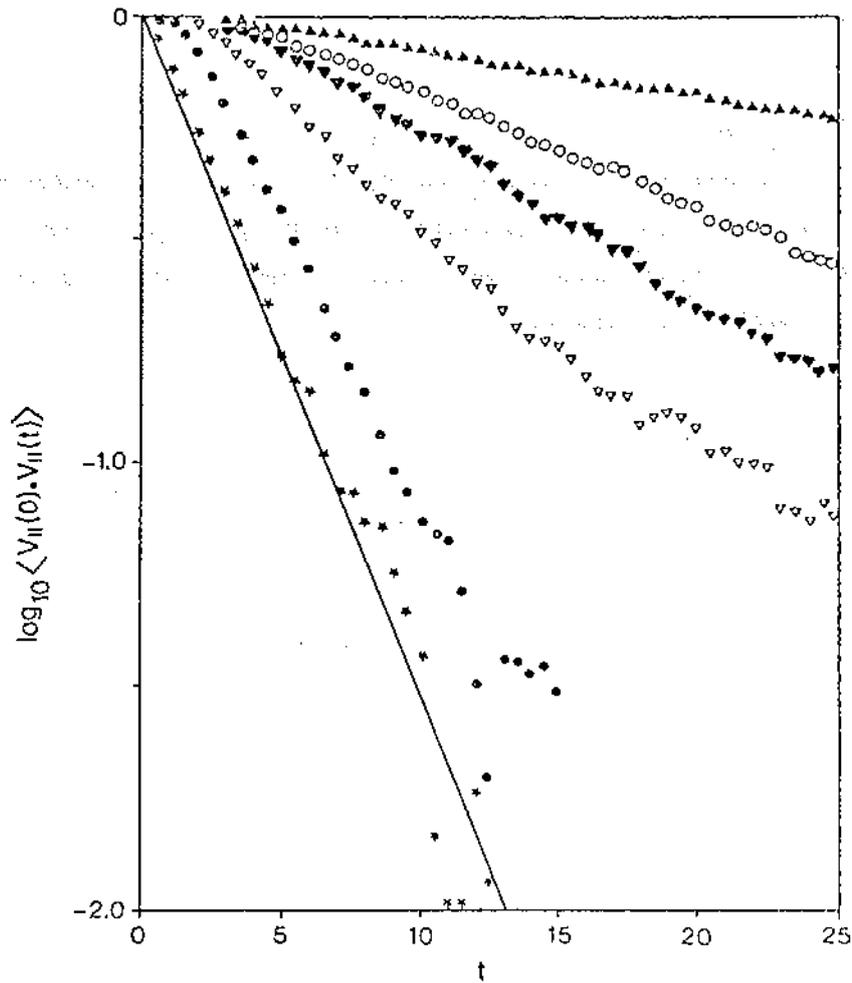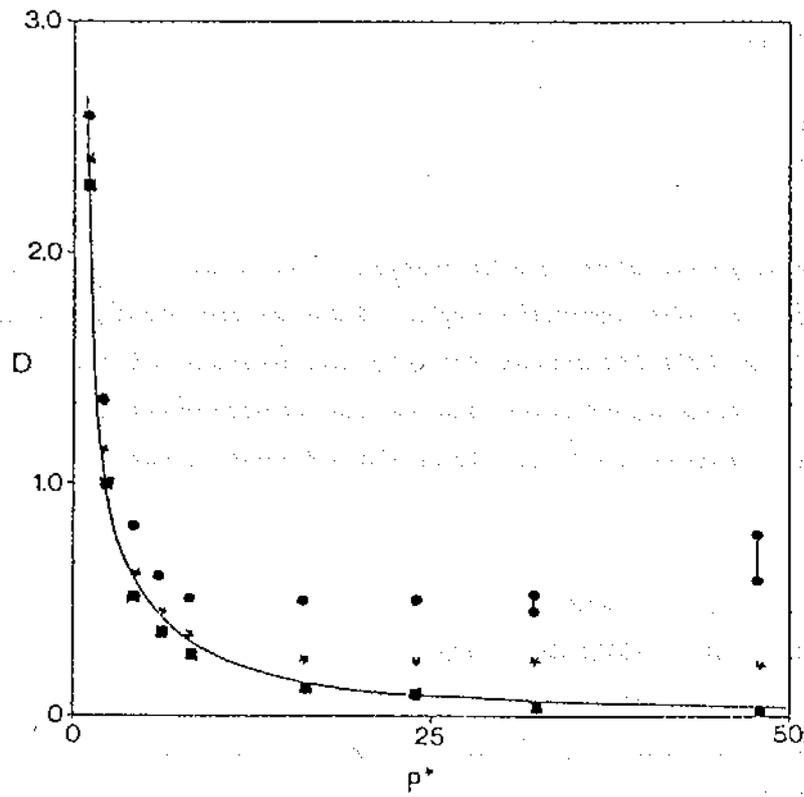
637ABU

Fig.1

Fig.2

Fig. 3

MORE ON NEIGHBOURHOOD TABLES

David Adams

Like everybody else, so it seems, I have used coordinates scaled from -1 to +1 in the periodic cell. This is not necessary in order to use the INT or AINT functions for the calculation of the nearest image, and I find it more convenient now to use coordinates from -1/2 to +1/2 so that the cell volume is one. Then the nearest image transformation becomes:

```
DX = X(I) - X(J)
DX = DX - AINT(DX + DX)
```

on the CRAY. On other machines the DX + DX may be written as 2.0 * DX equally well[1].

In the calculation of a neighbourhood table only the distance to the nearest image is needed and there is a more elaborate but considerably faster method for that. It will work for any cell length, but the -1 to +1 version goes as follows:

In the outer loop:
```
    XI = X(I)
    IF(XI.GT.0.0) XI = XI - 2.0
    XI = XI + 1.0
```
and similarly for Y and Z.

In the inner loop:
```
 |R2 = ((1.0 - ABS(X(J) - XI))**2+
1|       ((1.0 - ABS(Y(J) - YI))**2+
2|       ((1.0 - ABS(Z(J) - ZI))**2
```

where R2 is the square of the smallest distance between particles I and J. Should the coordinates used go from 0 to 1 then the code is slightly different:

In the outer loop:

```
XI = XI + 0.5
IF(XI.GT.1.0) XI = XI - 1.0
and similarly for Y and Z
```

In the inner loop:

```
R2 = ((0.5 - ABS(X(I) - A))**2 + (0.5 - ABS(Y(I) - B))**2
1      + ((0.5 - ABS(Z(I) - C))**2
```

Obviously the method can be very useful in Monte Carlo also. I have found that for hard sphere potential Monte Carlo on the 7600 it is roughly twice as fast as any other method.

David Heyes in his article suggested Verlet's method[3] of calculating the neighbourhood tables very tenth step. For the cautious there is a safer method which has been around for a long time but has only recently appeared in print[1]. When the neighbourhood table is constructed a copy is kept of the particle coordinates at that time. Then at every step the displacement of every particle is checked. When any one has moved more than $1/2(r_2-r_c)$, where r_c is the cut off radius and r_2 the maximum distance at which a pair of particles goes into the neighbourhood table, then the table is reconstructed. There is a slight variation of this which makes the reconstruction slightly less frequent. The two largest displacements are found instead of just the largest. Only when the sum of these two is greater than r_2-r_c does the table need recalculating.

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AN EFFICIENT ALGORITHM FOR CONSTRAINT DYNAMICS

M.K. Memon, R.W. Hockney and S.K. Mitra

In constraint dynamics one solves the Newton equations of motion of the particles along with the holonomic constraints on a given set of particles. The holonomic constraints are generally of the form

$$(\vec{r}_i - \vec{r}_j)^2 - d_{ij}^2 = 0 \tag{1}$$

where $\vec{r}_i$ and $\vec{r}_j$ are the positions of particle i and j of the given set and d_{ij} is the preassigned bond length between these particles constituting the molecule.

The numerical technique used in constraint dynamics is:

1. First to solve the unconstrained Newton equations using some convenient algorithm, e.g. Verlet or leapfrog and thereby obtain the unconstrained positions from the initial constrained positions;

2. Then to use these unconstrained positions in eq.(1) to find constrained positions, the difference in unconstrained and constrained positions are used to calculate the velocities of the constrained particles from the unconstrained velocities. The details of the numerical procedure is given in ref.1 and 2.

Basically, if the unconstrained positions are $\vec{r}_i\,'$ and $\vec{r}_j\,'$ and the corresponding constrained positions are $\vec{r}_i$ and $\vec{r}_j$ such that

$$\vec{r}_i\,' = \vec{r}_i + \delta\vec{r}_i$$

and $\vec{r}_j\,' = \vec{r}_j + \delta\vec{r}_j$

then one has to solve

$$((\vec{r}_i\,' - \delta\vec{r}_i) - (\vec{r}_j\,' - \delta\vec{r}_j))^2 - d_{ij}^2 = c_k = 0 \tag{2}$$

In fact there will be a set of simultaneous equations of the above type, each constraining a pair of particles in the molecule.

An approximate solution of these equations can be obtained by using an iterative method of root finding (Newton iteration). It is well known that the convergence of such an iterative method depends very much on the curvature of hyper-surface given by eqn.(2).

Another form of holonomic constraint which can lead to a faster convergence than eqn.(1) is

$$|\vec{r}_i - \vec{r}_j| - d_{ij} = 0 \tag{3}$$

The simultaneous equations corresponding to eqn.(2), for this constraint are

$$|(\vec{r}_i^{\,\prime} - \delta\vec{r}_i) - (\vec{r}_j^{\,\prime} - \delta\vec{r}_j)| - d_{ij} = c_k = 0 \tag{4}$$

Faster convergence in this case is possible because the hypersurface given by eqn.(4) is much flatter than the former.

In fact in the iterative calculation of eqn.(4) one need not calculate the first derivative of c_k at each and every iteration. Considerable computational time can be saved by using the initial value of this derivative calculated at the beginning of the iteration for negligibly small sacrifice of convergence.

These constraints (eqn.(2) and eqn.(4)) are used to simulate a system of water molecules ($2H^+$ and O^{2-}) at very high temperature. Typically first method (eqn.(2)) requires 10 iterations as compared to 5 iterations by second method (eqn.(4)) to achieve 10^{-7}% accuracy in the position.

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