

DARESBUURY LABORATORY

INFORMATION QUARTERLY

for

COMPUTER SIMULATION OF CONDENSED PHASES

An informal Newsletter associated with Collaborative Computational Project No. 5
on Molecular Dynamics, Monte Carlo and Lattice Simulations of Condensed Phases.

Number 12

MARCH 1984

Contents

Editorial	1
General News	3
Review of the CCP5 Meeting on Phase Transitions Held at Southampton University on 19/20 December 1983. D. M. Heyes	14
Nonequilibrium Molecular Dynamics with Bond Length Constraints. M. P. Allen and G. Maréchal	21
A New Monte Carlo Method to Determine the Absolute Free Energy of Arbitrary Solid Phases. D. Frenkel and T. Ladd.	30
Parallel Computers and Non-Cubic Boundary Conditions. D. Fincham	43
More on Rotational Motion of Linear Molecules. D. Fincham	47
A Three Body Potential Model for Silicon Dioxide. M. Leslie, C. R. A. Catlow, M. Sanders.	49
CCP5 Literature Survey - Addendum W. Smith	54

Editorial.

It is a pleasure once again to thank the contributors to the Newsletter for their efforts on our behalf. David Heyes has again provided us with an excellent review of a CCP5 Meeting, this time for the Meeting that occurred in Southampton on 19 th. and 20 th. December. M. P. Allen and G. Maréchal have provided an interesting article on nonequilibrium molecular dynamics with bondlength constraints which is very much the sort of material that CCP5 is concerned with. D. Frenkel and T. Ladd have written an article on a Monte Carlo method to determine absolute free energy in solid phases. David Fincham has provided further stimulation for those contemplating the use of noncubic simulation cells in molecular dynamics, following the articles published in the previous issues of the newsletter. He also airs his favourite topic of rotational motion, a subject to which he has already contributed some very useful algorithms. Lastly, Maurice Leslie, Richard Catlow and Mick Sanders have presented something of interest to the lattice simulators; a three - body potential model for Silicon dioxide. Many thanks to them all for their contributions !

Contributors:

M. P. Allen Physical Chemistry Laboratory, South Parks Road,
Oxford.

C. R. A. Catlow Department of Chemistry, 20 Gordon Street, London
M. Sanders WC1

D. Fincham D.A.P. Support Unit, Queen Mary College, Mile End
Road, London E1 4NS.

D. Frenkel Fysisch Laboratorium, Rijksuniversiteit Utrecht,
P. O. Box 80000, 3508 TA Utrecht, The Netherlands.

D. M. Heyes Department of Chemistry, Royal Holloway College,
Egham, Surrey TW20 OEX

T. Ladd Department of Applied Science, University of
California at Davis, Davis, California 95616,
U.S.A..

M. Leslie S.E.R.C. Daresbury Laboratory, Daresbury,
Warrington WA4 4AD.

G. Marechal Pool del Physique, Universite Libre de Bruxelles,
Campus del la Plaine CP223, Boulevard du Triomphe,

1050 BRUXELLES.

W. Smith

S.E.R.C. Daresbury Laboratory, Daresbury,
Warrington WA4 4AD.

General News.

a) The next CCP5 Meeting will be entitled 'Potential Models for Computer Simulation' and will take place at University College London from Thursday 20 th. September to Friday 21 st. September 1984. Accommodation will be at Passfield Hall on the nights of the 19 th. and 20 th. September and the cost will be in the region of thirty pounds. A reduced fee will be charged to postgraduate students.

The Meeting will provisionally consist of four sessions:

(i) Quantum Mechanical Potentials. This will last all morning on the 20 th. September until mid-afternoon.

(ii) Potentials in Molecular Beam Studies. This session will occupy the late afternoon of the 20 th. September.

(iii) Effective Potentials. This session will occupy the whole morning of 21 st. September.

(iv) CCP5 Steering Committee Meeting. This will occur on the afternoon of September 21 st.

The speakers who have, at the time of writing, agreed to participate are W. Busing (Oak Ridge), A. Stone and S. Price (Cambridge) and W.C. Mackrodt (I.C.I.).

b) CCP5 participants may not be aware that Professor J. G. Powles has resigned the post of chairman of CCP5 from January of this year. In his place, the CCP5 Executive Committee (set up by the CCP5 Steering Committee last December) has asked Dr. J. H. R. Clarke of the Department of Chemistry, U.M.I.S.T., to be acting chairman until the full Steering Committee Meeting in September 1984 (see above). Dr. Clarke has agreed to take on this responsibility. Anyone wishing to contact the CCP5 Chairman must henceforth get in touch with Dr. Clarke.

We thank Professor Powles for his work on behalf of CCP5 and welcome his continuing interest in the Project.

c) In an attempt to rationalise the membership of the CCP5 Steering Committee, we publish below a list of persons, who may regard themselves as recognised members of the Committee. This means, among other things, that their advice and opinions on all matters related to CCP5 are considered to be representative of the whole

project and thus their presence at CCP5 Steering Committee Meetings is particularly welcomed.

The membership of the Steering Committee is intended to be representative of the simulation groups participating in CCP5, particularly in the U.K. on the basis of one person per institution. We would therefore be pleased to hear from any group not adequately represented. Equally, anyone surprised and dismayed to find themselves on the list and would prefer to withdraw should let us know !

Please send your comments to Dr. W. Smith, S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K..

D. Adams (Southampton)
M. Allen (Oxford)
A. Bellemans (Brussels)
H. Berendsen (Groningen)
B.J. Berne (N.Y.)
K. Binder (Julich)
R. Catlow (U.C.L.)
J. Clarke (UMIST)
M. Evans (Wales)
D. Fincham (Q.M.C.)
J. Finney (Birkbeck)
M. Gillan (Harwell)
K. Gubbins (N.Y.)
D. Heyes (R.H.C.)
R. Hockney (Reading)
G. Jacucci (Trento)
B. Jonssen (Lund)
M. Leslie (Daresbury)
R. Lynden-Bell (Cambridge)
W. Mackrodt (I.C.I.)
I. McDonald (Cambridge)
D. Nicholson (Imperial)
N. Parsonage (Imperial)
S. Pawley (Edinburgh)
J. Powles (Canterbury)
N. Quirk (N.Y.)
J. Rowlinson (Oxford)
J. Ryckaert (Brussels)
K. Singer (R.H.C.)
W. Smith (Daresbury)
D. Tildesley (Southampton)

d) Users of the Rutherford and Appleton Laboratory computing system should note that the Computing Division is about to undertake a

rationalisation of their magnetic tape storage. Owners of magnetic tapes that have not been accessed for five years should inform the tape librarian if they do not wish these tapes to be scrapped.

e) The University of London Computing Centre has just seen the departure of the CDC 6600 and CDC 7600 mainframes, the former after thirteen years service and the latter after ten years service. The surviving system consists of an Amdahl 470/V8, a CDC 6400 and the Cray 1s.

The IBM FORTRAN 77 compiler currently the default on the Amdahl V8 (i.e. VS FORTRAN Version 2.0) will shortly be superseded by Version 3.0. This new version has extended capabilities over Version 2.0; in particular it will permit a symbolic dump at abends. The new version is currently accessible for those bold enough to try it out.

f) The University of Manchester Regional Computer Centre is still in the throes of transferring from the ICL 1904s+1906a / 2*CDC7600 configuration to the new Amdahl 470/V7 - 2* CDC7600 - CDC Cyber 205 configuration. Potential delays in the Loosely Coupled Network degradation tests have been resolved following discussions with CDC to the advantage of UMRCC. As a result of these discussions the UMRCC CDC7600s will be upgraded by 512k words in May 1984, the Cyber 205 will be upgraded by 1m words by April 1985 and the Centre is to receive an additional CDC Cyber 176 by October 1984. Meanwhile both the Amdahl 470/V7 and the Scope Remote Host Facility have completed acceptance trials somewhat late. The good news is that an Amdahl 470/V7 and Cyber 205 service began on March 5 th..

g) Erratum. In the footnote to the article by Professor J.G. Powles on the fast square root method, which appeared in the last issue of 'Information Quarterly', there is a typographical error. On page 41 the expression for the variable Z should be:

$$Z = .25*(Y+X/Y)+X/(Y+X/Y)$$

We are grateful to Professor Powles for pointing out this error. Our apologies go to those readers who found out the hard way.

h) Anyone wishing to make use of the CCP5 Program Library is welcome to do so. Documents and programs are available, free of charge to academic centres upon application to Dr. M. Leslie (*) at Daresbury Laboratory. Listings of programs are available if required but it is recommended that magnetic tapes (to be supplied

by the applicant) be used. Users wishing to send magnetic tapes are requested to write to Dr. Leslie for information before sending the tape. (A list of programs available follows in the next few pages.)
* (Full address: S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.)

List of Programs in the CCP5 Program Library.

MDATOM by S. M. Thompson.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones potential function and fifth order Gear integration algorithm. Calculates system average configuration energy, kinetic energy, virial, mean square force and the associated R.M.S. deviations and also system pressure, temperature, constant volume specific heat, mean square displacement, quantum corrections and radial distribution function.

HMDIAT by S. M. Thompson.

M.D. simulation of diatomic molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. Calculates system average configuration energy, kinetic energy, virial, mean square force, mean square torque and the associated R.M.S. deviations and also system pressure, temperature, constant volume specific heat, mean square displacement and quantum corrections.

MDLIN by S. M. Thompson.

M.D. simulation of linear molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

MDLINQ by S. M. Thompson.

M.D. simulation of linear molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions plus a point electrostatic quadrupole. Uses a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

MDTETRA by S. M. Thompson.

M.D. simulation of tetrahedral molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

MDPOLY by S. M. Thompson.

M.D. simulation of polyatomic molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and a fifth order Gear algorithm for centre - of - mass motion. Angular motion is calculated by fourth order Gear algorithm with quaternion orientation parameters. List of calculated properties is the same as HMDIAT.

ADMIXT by W. Smith.

M.D. simulation of monatomic molecule mixtures. Uses 12/6 Lennard - Jones atom - atom potential functions and a Verlet leapfrog algorithm for centre - of - mass motion. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution functions.

MDMIXT by W. Smith.

M.D. simulation of polyatomic molecule mixtures. Uses 12/6 Lennard - Jones site - site potential functions and a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure and temperature.

MDMULP by W. Smith.

M.D. simulation of polyatomic molecule mixtures. Uses 12/6 Lennard - Jones site - site potential functions and point electrostatic multipoles (charge, dipole and quadrupole). Long range electrostatic effects are calculated using the Ewald summation method. Uses a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and

associated R.M.S. deviations and also pressure and temperature.

MDMPOL by W. Smith & D. Fincham.

M.D. simulation of polyatomic molecule mixtures. Uses 12/6 Lennard - Jones site - site potential functions and fractional charges to represent electrostatic multipoles. Long range electrostatic effects are calculated using the Ewald summation method. Uses a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure and temperature.

DENCOR by W. Smith.

Calculation of density correlation functions. Processes atomic M.D. data to produce the Fourier transform of the particle density, the intermediate scattering functions and the dynamic structure factors.

CURDEN by W. Smith.

Calculation of current density correlation functions. Processes atomic M.D. data to produce the Fourier transform of the current density, the current density correlation functions and their temporal Fourier transforms.

HLJ1 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ2 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements, radial

distribution function and velocity autocorrelation function.

HLJ3 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. The link - cell method is employed to enable large simulations. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ4 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre - of - mass motion. The algorithm allows either the temperature or the pressure to be constrained. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ5 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site shifted potential function and a Verlet leapfrog algorithm for centre - of - mass motion. This method removes the discontinuities at the potential cutoff radius. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ6 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site shifted potential function and the Toxvaerd algorithm for centre - of - mass motion. This algorithm is more accurate than the Verlet algorithm. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

MCRPM by D. M. Heyes.

M.C. simulation of electrolytes. Monte Carlo program using restricted primitive model of an electrolyte. The potential is regarded as infinite for $r < d$ and Coulombic for $r > d$. The properties calculated are the average configuration energy and its R.M.S. deviation, the pair radial distribution function and the melting factor.

SURF by D. M. Heyes.

M.D. simulation of model alkali halide lamina. Molecular dynamics simulation for ionic laminae using the Tosi-Fumi / Born-Mayer-Huggins potential and the Evjen method for evaluating the lattice sums. The integration algorithm used is the Verlet method. The program calculates the system potential and kinetic energies, the pressure and the final averages and R.M.S. fluctuations. The program also calculates density profiles such as number density, temperature, energy and pressure.

HSTOCH by W. F. van Gunsteren & D. M. Heyes.

S.D. or M.D. simulation of molecules in vacuo or in a rectangular cell with solvent or lattice atoms (i.e. Langevin or Brownian dynamics of large molecules).

MDATOM by D. Fincham.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones potential function and Verlet leapfrog integration algorithm. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature, mean square displacement and radial distribution function.

MDDIAT by D. Fincham.

M.D. simulation of diatomic molecule fluids. Uses 12/6 Lennard - Jones site - site potential functions and the Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated using the constraint algorithm. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature and mean square displacement.

MDDIATQ by D. Fincham.

M.D. simulation of diatomic fluids. Uses 12/6 Lennard - Jones site - site potential functions and a point quadrupole electrostatic term. Employs the Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated using the constraint algorithm. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature and mean square displacement.

MDIONS by D. Fincham & N. Anastasiou.

M.D. simulation of electrolytes. Uses exp/6/8 potential function and the Coulomb electrostatic potential. Long range interactions are calculated using the Ewald summation method. Uses the Verlet leapfrog algorithm for particle motion. Calculates system average configuration energy, kinetic energy, virial and the associated R.M.S. deviations and also system pressure, temperature, radial distribution functions, static structure factors and mean square displacements.

MDMANY by D. Fincham & W. Smith.

M.D. simulation of polyatomic molecules. Uses 12/6 Lennard - Jones site - site potential functions and fractional charges to represent electrostatic multipoles. Long range electrostatic effects are calculated using the Ewald summation method. Uses a Verlet leapfrog algorithm for centre - of - mass motion. Angular motion is calculated by the Fincham leapfrog algorithm using quaternion orientation parameters. Calculates system average configuration energy, kinetic energy and virial and associated R.M.S. deviations and also pressure and temperature. FORTRAN 77 standard program.

CARLOS by B. Jonsson & S. Romano.

M.C. simulation of a polyatomic solute molecule in an aqueous cluster. (i.e. a molecule surrounded by water molecules). The water - water potential is calculated using an analytical fit to an ab initio potential energy surface due to Matsuoka et al. The solute-solvent potential is optional. The program provides an energy and coordinate 'history' of the M.C. simulation. An analysis program CARLAN for processing the data produced by CARLOS is also available.

MCN by N. Corbin.

M.C. simulation of atomic fluids. Standard (Metropolis) Monte Carlo

program for atomic fluids.

SCN by N. Corbin.

M.C. simulation of atomic fluids. Standard (Rosky, Friedman and Doll) Monte Carlo program for atomic fluids.

SMF by N. Corbin.

M.C. simulation of atomic fluids. Standard (path integral method) Monte Carlo program for atomic fluids.

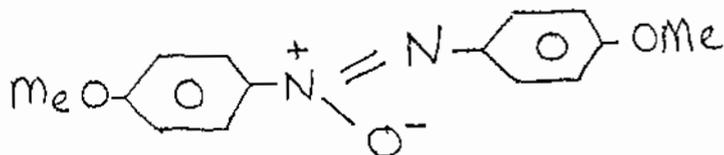
REVIEW OF THE CCP5 MEETING ON PHASE TRANSITIONS
HELD AT SOUTHAMPTON UNIVERSITY ON 19/20 DECEMBER 1983.

By D. M. Heyes

Yet another successful CCP5 conference was held recently at Southampton University. The organisers, Drs. D. J. Adams and D. J. Tildesley are to be congratulated on the smoothness with which the proceedings took place. There were over 70 participants which included visitors from Italy, France, W. Germany, U. S. A. and Canada.

The timely entry of the Lattice Simulation group into CCP5 has coincided with increased interest in the application of MD to solids, spurred by the development of the Parrinello and Rahman technique which enables a time varying MD cell shape to be incorporated in the model. Their contribution has provided a welcome stimulus and I look forward to continued collaboration between these groups in the future.

The talks were of a very high standard and were started by PROFESSOR G. R. LUCKHURST (Southampton University) who talked about liquid crystals. These contain shaped molecules which show many liquid properties but can order orientationally over long distances. An electric field will constrain the molecules to align along a particular direction so that they are technologically useful in displays which use the resulting birefringence properties of the orientationally ordered liquid. He revealed in an entertaining manner the types of liquid crystals available. All anisotropic molecules, it was revealed, should exhibit liquid crystal behaviour (a degree of rotational and perhaps translational order) just prior to freezing. But in fact most liquids freeze too readily so that this phase is of little importance. However, long thin needle-like molecules form easily into a stable phase which has long range orientational order; being only slightly disturbed by some librational motion about the preferred direction (called the director). This as discussed already can be fixed by an externally imposed field. Such a nematic phase is formed by, for example, the molecule.



These exhibit translational disorder which is shown in the centre of mass pair radial distribution function. There are classes of liquid

crystal which also have varying degrees of translational order. They are called smectic phases and come in a variety of forms which are distinguished by letter appendages ranging from A to H (so far!). Disc and rodlike molecules produce these phases.

Analysis of the melting of liquid crystals show them to have blurred transitions, exhibiting only small changes in thermodynamic quantities such as volume and entropy. Pre-transition effects are prevalent. The 2nd order Legendre polynomial of the absolute molecular orientation with respect to some space fixed direction is a convenient means of characterising the orientational changes which take place on melting. In contrast, this shows a sharp drop from about 0.3 to 0 at the phase transition. Interestingly many at first sight disparate molecules which form liquid crystals can be fitted on to a universal curve of the order parameter when plotted against a reduced temperature: $T^* = T/T_{NI}$ where T_{NI} is an experimentally determined temperature at which the nematic to isotropic phase change takes place. This suggests that a well defined but simple potential could account for the main features of liquid crystal behaviour. There have been approximately 20 papers on the computer simulation of liquid crystals which have looked at such properties as surface tension, effect of solutes and field effects. They have not been very successful because of the slow relaxation times and strong size dependencies inherent in these systems. These show up in hysteresis effects. There is little difficulty in producing a "mono-domain" as the inherent correlation length is much larger than a typical simulation cell size. The direction of the director within a MD cell is obtained from the diagonalisation of an order parameter tensor called the q tensor, an eigenvalue of which gives the order parameter. As in any simulation much thought must be expended in choosing the pair potential. Although real liquid crystals are described by quite complex potential surfaces it is believed that the features which confer liquid crystal behaviour on many dissimilar molecules are found in quite simple shapes. The BPK potential was chosen by the speaker's group in an attempt to produce liquid crystal behaviour. This is a Lennard-Jones potential with an orientation dependent sigma and well-depth. It was discovered that any initial ordering eventually disappears and was therefore found not to produce a stable nematic phase. This led to even further simplifications in the model for which analytic approximate solutions are also available. A cubic lattice model which had a $20 \times 20 \times 20$ array of model molecules was established. Nearest neighbour interactions were only allowed. The order parameter and potential energy show strong changes at the phase transition. The entropy change at this point is small and agrees approximately with the prediction of Mean Field Theory. The constant pressure specific heat diverges on the approach of the phase transition. The potential energy can be obtained from the short range order parameter, which the Mean Field Theory unfortunately underestimates. The speaker expressed his opinion that the days of this lattice model are coming to an end and thought that improved pair potentials are needed in order to restart a full dynamical MD programme.

Another system for which liquid crystal behaviour was sought was discussed by Dr. S. DE LEEUW (University of Oxford) who presented results of Monte Carlo simulations of hard ellipsoidal systems. Both oblate and prolate spheroids were considered. He summarised the developments in this area which go back about 10 years. Two dimensional calculations of hard ellipses were carried out early on but suffered from the disadvantage that the pressure was not calculated, due to a lack of an available expression for this quantity. The speaker solved this problem and presented an expression for the pressure which was derived from the partition function and which looked similar to the comparable hard sphere formula written in terms of the pair radial distribution function at contact of the spheres. The Monte Carlo method performed, on 256 spheroids, involved solving a quintic equation. Two different eccentricities were considered. Small eccentricities produced no evidence of orientational order throughout the fluid range. The pressure was inbetween those of hard spheres with diameters equal to the maximum and minimum dimensions of the spheroids. The pair radial distribution function has a first peak which is less sharp than that of the hard sphere at the comparable state point. As the spheroids are anisotropic, harmonic components of the pair radial distribution function can be calculated. The $g_{200}(r)$ function was mostly negative at the point of closest contact. Used with $g_{220}(r)$ (which tends to be more positive) evidence for parallel and "T" packing at short and long range was given. Calculations at a higher elongation were made on 288 spheroids. Again no orientational order was discovered up to a reduced density of 0.7. However the order parameter rose markedly at $\rho^* = 0.9$, but was then found to decrease with length of the computation, leaving the existence of a nematic phase again in some dispute. Under all circumstances long range orientational order dies away within a few spheroid diameters. There was postulated the existence of an orientational order/disorder transition in the solid phase.

In keeping with a strong emphasis on second order solid-solid phase changes at the conference, Dr. D. McCONNELL (University of Cambridge) discussed the characterisation of incommensurate structures in insulators such as NaNO_2 . Incommensurate structures exist as modulations of component species on a wavelength which is not that of the overall periodicity, i. e. is incommensurate with that of the basic lattice repeat distance. Incommensurate phases can be observed by diffraction techniques in which they produce side spots close to the usual Bragg maxima. The origins of these sub-structures in insulators are obscure and cannot be attributed to electron-phonon interactions as for metals. It appears that the two interweaving incommensurate structures collaborate to produce a phase change. Symmetry analysis in terms of space group theory is useful in characterising these structures, which are mapped on to a sine or cosine wave so that structural resonance is possible with both coexisting. Shear properties and enthalpy changes are influential factors in determining the position of the phase change. Systems exhibiting such behaviour are Cu-Fe-S and $\text{K}_2\text{CuPN}_2\text{O}_6$. In the following discussion Dr. Lynden-Bell asked if theory could be used to predict when the phase

change will occur. Dr. McConnell said that our understanding was not so far developed but it could give a reasonable estimate. Solid-solid phase changes were also discussed by Dr. S. C. PARKER (University of Cambridge). He talked about phase changes in minerals from the point of view of the energy required for them to take place. In particular Alumino/Magnesium Silicate was considered which can exist as olivine, which has a hexagonal structure and spinel, which exists in a cubic close packed form. This phase transition is very important as it is thought to power the plate movements in the earth. The choice of potential used to model this phase change was discussed in some detail. The parameters were taken from MgO, alumina and quartz (SiO_2) work. In the latter case a Saunders 3-body potential, which gives good agreement with the experimental phonon spectrum in a Lattice Dynamics calculation, was used. A variable ionic charge and a Morse potential were also used to include covalency in the model. The PV term in the enthalpy was found to be the most important factor in driving the phase change; for which the bulk moduli were needed from the model. The energy change between these two solid forms is only about 20 kJ mol^{-1} . There are a number of intermediate phases such as β -olivine which is cubic close packed; α and γ phases also exist and are separated by approximately 3 kJ mol^{-1} from one another.

These static lattice calculations are now being supplemented by full dynamical treatments of solid-solid phase changes. Dr. M. L. KLEIN (N. R. C. C. Canada) introduced the Parrinello-Rahman technique which allows changes in crystallographic form determined by the thermodynamic state and the interaction potential surface, to be followed.

The symmetry and dimensions of the MD cell are allowed to change in line with these internal demands. As an application he looked at 96 atoms of model He^4 in the GPa pressure range and observed phase transitions between bcc and fcc close to the melting line which are similar to those previously assigned. NH_3 also has a very complicated solid phase diagram. In addition to HCP, and FCC phases a BCC structure was also generated for which there is no experimental evidence. He commented on the need for better potentials, an oft-repeated remark at the conference. Dr. R. W. IMPEY (N. R. C. C., Canada) continued this theme by reporting results from a very general program, which he applied to KCN, here represented by a four site charge model. KCN is believed to exhibit a plastic crystal phase (i. e. one which has translational order but rotational disorder). The FCC crystal was heated and expanded with temperature (a natural result from a constant pressure scheme). Unfortunately it exhibits hysteresis effects in molar volume on cooling so that the original density is never recovered i. e. an "orientation glass" was perhaps formed. Elastic moduli and compliances were evaluated and showed anomalous effects near the plastic phase change; in that some increased and some decreased. The calculations were performed for about 45,000 time steps. Dr. G. S. PAWLEY (University of Edinburgh) reported the results of constant pressure MD calculations of the plastic phase of SF_6 . A 2 Mbyte DAP computer was used and

described. A 3 dimensional lattice was mapped on to the 4096^3 1 bit grid in the DAP. His results agreed with others in the conference who showed that the energy differences between orientationally ordered and random phases are small. In particular solid SF_6 finds it difficult to accommodate the relative molecular orientations so that two S-F bonds on adjacent molecules are not pointing towards each other. He showed some very informative models to illustrate his ideas. His group is now working on butane, which is believed to have three coexisting solid phases.

There were a number of talks on the solid-liquid transition. Professor R. M. J. COTTERILL (Technical University of Denmark) reported work performed with Dr. J. U. Madsen on the Molecular Dynamics Simulation of the isochoric liquid-glass and melting transitions. An analysis of experimental data was made which revealed a linear relationship between entropy and fractional volume change on melting. He reviewed the semi-empirical theories of melting such as one which postulates that melting takes place when 50% of the solid molecules can jump into interstitial vacancies. A 336 LJ particle system was heated well above the estimated melting temperature from other work of $T^* = 0.64$ but which eventually did melt. Emphasis was then changed to consider the effect of cooling a liquid through the glass transition. The trend observed was that the entropy of the liquid and crystal tend to the same value at low enough temperature. He also introduced the fascinating concept of a crystal melting directly into a glass. Dr. Clarke was reassuring in stating that in his experience the entropy of the glass can approach that of the crystal. Dr. N. QUIRKE (Cornell University U. S. A.) discussed the melting transition of microcrystals in a hard sphere cavity; work supported by EXXON. Small clusters of order 15 LJ atoms were melted over 2.5 million attempted MC moves in the temperature range $T^* = 0.3$ to 0.5 . The phase transition also showed in a peak in the constant pressure specific heat. Evaporation was found to be a problem, which was reduced by the cluster being embedded in a spherical cavity. The solid-liquid transition was found to be a function of the number of particles. Triangles of atoms were found to be particularly prominent in the melting transition to form, in one case, a defective icosahedron. The crystal structure is not that of the bulk for small systems. For systems of over 200 particles the melting transition is sharp. Professor K. SINGER (Royal Holloway College) reported the results of calculations performed with Drs. N. Anastasiou, K. F. Carter and D. Fincham into the mechanism of crystal dissolution in water. He revealed that the mechanism depends strongly on the equilibration procedure. When crystal and water are equilibrated separately and then positioned adjacent to each other the Na^+ come off into the water, the water penetrates to the third crystal layer and the crystal film splits in two - all within 2 psec. (which requires about 9 hours of CRAY time). In contrast, if the crystal and water are equilibrated in close proximity but separated by an impenetrable barrier for molecule crossings then a quite different result was obtained. The Cl^- dissolved first and the water showed little sign of penetration within the simulation

time. A velocity scaling scheme was employed in this latter calculation to suppress the large temperature rises in the interface (but with the result that the centre of the crystal approaches OK for a period, as an unwanted side-effect). Pressure adjustment, by altering the dimension of the cell in the direction perpendicular to the surfaces, was made in order to keep the density of the water furthest from the crystal at a realistic value. Nevertheless the water next to the crystal had a density which was fifty percent greater than in the bulk. The water molecules were also strongly orientated with respect to the surface. These manipulations delay but do not prevent crystal splitting. The ease with which the crystal splits was rationalised in terms of the small difference in potential energy between a surface and bulk ion, (only about 4%) which was established by Parry. Dr. Parsonage gave a plausible explanation for the reason for crystal splitting. He said that the build-up of water on the crystal necessarily produced a negative pressure in the bulk region spanned by the periodic boundary conditions on either side of the crystal and which consequently pulled the crystal apart.

There were two stimulating talks on the methodology for fixing phase boundaries. Dr. D. FRENKEL (University of Utrecht, The Netherlands) developed in cooperation with Dr. A. J. C. Ladd (University of California, at Davis, U. S. A.) a new method designed to compute absolute free energies of arbitrary solid phases. These are needed to determine the temperatures of solid-solid and solid-liquid phase boundaries. To obtain the absolute free energy a reference state of known absolute free energy is needed, such as the ideal gas or the "Hoover-Ree" lattice gas. A path from the gas to the solid is then undergone with simulations carried out at intermediate points. These tend to be expensive calculations and there can be complications due to a second or even first order phase transition taking place at the point where the self-confinement of the crystal lattice takes over from the artificial imposed lattice containment. The Frenkel/Ladd method is claimed to be more computationally efficient and involves going from the Einstein crystal (whose absolute free energy is known) to the desired crystal using a switching function to 'turn-on' the desired potential. The change in free energy during this process can apparently be related simply to the mean square amplitudes of vibration at points in this process.

Dr. S. NOSE (N. R. C. C. , Canada) described a new method for producing a canonical ensemble in MD simulations. Although there have been a number of constant temperature schemes proposed (e. g. those by Andersen, Hoover, Evans and Haile and Gupta), none (except that of Andersen) claims with proof to generate a canonical ensemble. The Andersen method is very severe on the dynamics of selected molecules. Dr. Nose has made a valuable contribution to this field by providing a link between essentially mechanical methods for maintaining constant kinetic energy and the true canonical ensemble which is ideally required. Dr. Nose's method bears some resemblances to Andersen's constant

pressure method. There is a "piston mass" which drives a kinetic energy acceleration. If the piston is too heavy it produces long periods of semi-microcanonical ensemble behaviour. He claimed that the thermodynamic (but possibly not dynamical) properties produced by this method are those of a canonical ensemble. The talk produced much lively discussion. Professor Powles warned against the indiscriminate use of momentum scaling as a means of producing constant kinetic energy dynamics. He said that each application should be considered carefully to determine if the perturbations to the dynamics are seriously going to affect the property of interest.

Gases adsorbed on solid surfaces undergo phase transitions which are being increasingly investigated by computer simulation. Quasi-two-dimensional models are revealing that there is a disappointingly large number and time dependence associated with these phase changes which make it a dangerous area to be working in with limited computer resources. Professor D. LANDAU (University of Georgia, U. S. A) introduced this area by discussing critical behaviour in a triangular lattice gas Ising model. The pattern of adsorbed gases on graphite can be "mapped" on to a triangular lattice. The critical behaviour of these systems was discussed for periodic finite systems using finite scaling analysis. He introduced the concept of a "critical surface" which has a so-called tricritical point of special interest. These dimensional systems such as ethanol-carbon dioxide water mixtures have a tricritical point. Symmetry appears to influence strongly the characteristics of these phase changes. Dr. M. ALLEN (University of Oxford) considered a lattice of linear quadrupoles on a triangular lattice. This is a simple model of, for example, nitrogen on graphite. Calculations performed with 16,000 quadrupoles using the DAP produced contiguous domains of similar quadrupole orientations which were charmingly described as forming a "herring-bone" pattern. Phase changes were observed to coincide with peaks in the specific heat with temperature (the potential energy per molecule was in contrast more smoothly changing). The changes in orientation can be correlated with alternations in symmetry between C_{3V} to D_6 . These domain fluctuations were on a time-scale of the same order as the simulation itself, so the speaker warned against making any definite conclusions at the present.

Dr. T. J. SLUCKIN (University of Southampton) spoke on behalf of his fellow authors, Drs. H. Evans and D. J. Tildesley, on the subject of boundary effects on the orientational ordering of nitrogen adsorbed on graphite. Simulations were conducted to elucidate the role of ledges and walls in a stepped surface on the adsorption characteristics. Nitrogen molecules were found to adsorb preferentially along the bottom of a wall, presumably to maximise the number of close carbon neighbours. Order parameters again showed the sharpest change near phase transitions.

A recurring theme of the conference was the desire for better or at least better substantiated potentials. Professor S. ROMANO

(University of Pavia, Italy) examined a number of pair potentials for nitrogen from the view point of assigning the solid-liquid phase transition. Somewhat surprisingly he argued that the more recent potentials which include a quadrupole and dispersion terms are not an improvement on the older ones without these terms.

The conference finished with an excellent talk by Dr. O. BEYER (Ruhr-Universitat Bochum, W. Germany) who with C. Hoheisel simulated the glass-transition of binary metallic mixtures; adopting a MD model and Lennard-Jones 12:6 potentials. In order to create a reproducible glass the calculations were performed at high pressure and temperature of $T^* \approx 1$ and $\rho^* = 1.4$. A system of 2048 particles was considered. A nickel/boron mixture was simulated and the partial pair radial distribution functions were evaluated. The first peak in the BB pair radial distribution function was greater than the B atomic diameter so that Boron-Boron contact was largely eliminated within the Ni "lattice". The general features of experimental and calculated structure factors were in agreement. In the discussion Professor Powles said he was not surprised at this as he was doubtful about the relevance of a "humped" metal effective potential in determining liquid structure.

NONEQUILIBRIUM MOLECULAR DYNAMICS OF MOLECULES WITH BOND LENGTH CONSTRAINTS

M.P. Allen and G. Maréchal

Nonequilibrium methods of simulating transport coefficients have become very popular in recent years, due to the potential statistical advantages in measuring the response of a system to an applied perturbation over the conventional route via equilibrium time correlation functions. The shear viscosities of atomic liquids, and liquids of small rigid molecules, for example, have been investigated in this way. The extension of the technique to large, possibly flexible, polyatomic molecules brings up one or two interesting questions. Should the perturbation be applied to individual atoms, to the centres of mass of entire molecules, or to molecular fragments of intermediate size? Does this choice affect the technical difficulty of the simulation? Can we handle, for example, bond length constraints in a polyatomic molecule, in a way consistent with applying a perturbation? This last question is important, since both time-dependent perturbations and the application of bond length constraints seem to involve a degree of 'meddling' with the equations of motion; it is quite conceivable that some of the techniques currently employed might be incompatible with each other.

In this paper, we describe a technique developed at a CECAM workshop last summer [1] to simulate homogeneous shear flows in molecular liquids. The aim was to develop a program which would handle the fixed bond lengths in a system of polyatomic molecules, using the method of constraints [2,3], together with modified equations of motion to generate a time-dependent shear [4,5,6], without introducing any clash between the two techniques. This turned out to be easily achieved, using equations of motion in which the applied velocity gradient appears explicitly [4] (rather than an approach which involves least-squares fitting of velocities to the desired profile) and by using a constraint method built around an algorithm in which the velocities appear [3]. We tested the program, using a small system of diatomic molecules, and, as well as demonstrating the feasibility of the approach, we compared the consequences of applying a time-dependent shear to the molecular centres of mass, with an atomic perturbation.

The modified equations of motion for atoms in an imposed, time-

dependent, homogeneous shear flow $\dot{\epsilon} = (\partial v^x / \partial y)$ may be written [7]

$$\begin{aligned} \dot{q}_{ia}^x &= p_{ia}^x / m_{ia} + \dot{\epsilon} q_{ia}^y & \dot{q}_{ia}^y &= p_{ia}^y / m_{ia} & \dot{q}_{ia}^z &= p_{ia}^z / m_{ia} \\ \dot{p}_{ia}^x &= f_{ia}^x - \dot{\epsilon} p_{ia}^y & \dot{p}_{ia}^y &= f_{ia}^y & \dot{p}_{ia}^z &= f_{ia}^z \end{aligned} \quad (1)$$

Here we are using a double index ia (atom a in molecule i) to identify the atoms; m_{ia} is the atomic mass, f_{ia}^x etc. are the force components due to all interatomic interactions, p_{ia}^x etc. the momenta and q_{ia}^x etc. the coordinates. These equations are almost, but not quite, the equations resulting from a qp-(Doll's)-tensor perturbation to the equilibrium Hamiltonian [4]; the distinction is discussed elsewhere [7]. Equation (1) is particularly convenient for us, since the momenta may be eliminated to yield

$$\ddot{q}_{ia}^x = f_{ia}^x / m_{ia} + \dot{\epsilon} \ddot{q}_{ia}^y \quad \ddot{q}_{ia}^y = f_{ia}^y / m_{ia} \quad \ddot{q}_{ia}^z = f_{ia}^z / m_{ia} \quad (2)$$

Thus, if we concentrate on q_{ia} , \dot{q}_{ia} and \ddot{q}_{ia} , the perturbation simply appears as an extra force $m_{ia} \dot{\epsilon} \ddot{q}_{ia}^y$ dependent explicitly on coordinates q and the time, through $\dot{\epsilon}$. These equations would be implemented in conjunction with modified periodic boundary conditions [8]; for steady shear, apart from an initial kick, the modified boundaries alone will be sufficient, since $\ddot{\epsilon} = 0$.

The momenta p_{ia} need not appear in the integration procedure, but may be calculated from equation (1), and are useful, since off-diagonal elements of the pressure tensor

$$p_{yx}^{atv} = \sum_{ia} p_{ia}^y p_{ia}^x / m_{ia} + \sum_{iajb} q_{iajb}^y f_{iajb}^x \quad (3)$$

and the energy

$$E = \sum_{ia} p_{ia}^2 / 2m_{ia} + U(q) \quad (4)$$

will be of interest to us. Here, $q_{iajb} = q_{ia} - q_{jb}$, f_{iajb} is the force on atom ia due to atom jb , with the sum being over distinct pairs of atoms, and $U(q)$ is the potential energy. A key check on the correctness of the simulation algorithm, and the size of the time step employed, is that the first law of thermodynamics shall be obeyed

$$\dot{E} = - \dot{\epsilon} P_{yx}^{at} V \quad (5)$$

This follows from (1) - (4). Because the momenta are needed, it is most convenient to use an integration algorithm which uses \dot{q}_{ia} as well as q_{ia} and \ddot{q}_{ia} .

Equations (1) - (4) have their counterparts in the molecular representation. We may write a different set of equations of motion [7]

$$\begin{aligned} \dot{q}_{ia}^x &= p_{ia}^x / m_{ia} + \dot{\epsilon} q_i^y & \dot{q}_{ia}^y &= p_{ia}^y / m_{ia} & \dot{q}_{ia}^z &= p_{ia}^z / m_{ia} \\ \dot{p}_{ia}^x &= f_{ia}^x - \frac{m_{ia}}{m_i} \dot{\epsilon} p_i^y & \dot{p}_{ia}^y &= f_{ia}^y & \dot{p}_{ia}^z &= f_{ia}^z \end{aligned} \quad (6)$$

or

$$\ddot{q}_{ia}^x = f_{ia}^x / m_{ia} + \ddot{\epsilon} q_i^y \quad \ddot{q}_{ia}^y = f_{ia}^y \quad \ddot{q}_{ia}^z = f_{ia}^z \quad (7)$$

where $q_i^y = m_i^{-1} \sum_a m_{ia} q_{ia}^y$, $p_i^y = \sum_a p_{ia}^y$. Now every atom in molecule i is subjected to the same extra acceleration, i.e. to a force proportional to m_{ia} , based on the value of the centre-of-mass coordinate q_i^y . In place of (3) we have

$$P_{yx}^{mol} V = \sum_i p_i^y p_i^x / m_i + \sum_{ij} q_{ij}^y f_{ij}^x \quad (8)$$

where $f_{ij} = \sum_{ab} f_{iajb}$ and $q_{ij} = q_i - q_j$. The energy is still defined through (4), but note that the momenta are now given by (6); the energy conservation law (5) again follows directly, with P_{yx}^{mol} in place of P_{yx}^{at} .

Now we are ready to describe the simulation program, and the algorithm used to solve the equations of motion (2) or (7). It will become apparent that the addition of bond length constraints does not introduce any further complications.

Assume that $q_{ia}(0)$ and $\dot{q}_{ia}(0)$ are available at time $t = 0$. The forces f are calculated in a quite standard FORCE subroutine, except for the modified periodic boundary conditions which affect the calculation of minimum image separations. In (hopefully) an obvious notation, this can be accomplished by statements of the kind:

```
DX=RX(ATOMA,MOLECI)-RX(ATOMB,MOLECI)
DY=RY(ATOMA,MOLECI)-RY(ATOMB,MOLECI)
DZ=RZ(ATOMA,MOLECI)-RZ(ATOMB,MOLECI)
DX=DX-AINT(DY/BOX+SIGN(0.5,DY))*OFFSET
DX=DX-AINT(DX/BOX+SIGN(0.5,DX))*BOX
DY=DY-AINT(DY/BOX+SIGN(0.5,DY))*BOX
DZ=DZ-AINT(DZ/BOX+SIGN(0.5,DZ))*BOX
```

where OFFSET is the current value of the strain ϵ multiplied by the boxlength BOX. (Note that we are not sticking to the FORTRAN initial letter convention!). The additional force, due to the perturbation, is calculated in a separate routine FEXTRA, and within this routine a switch, ATOMIC, selects an atomic or molecular type of perturbation:

```
IF (ATOMIC) THEN

DO 100 MOLECI=1,NMOLEC
DO 100 ATOMA =1,NATOM
    ACCN=EPSDD*RY(ATOMA,MOLECI)
    FX(ATOMA,MOLECI)=FX(ATOMA,MOLECI)+ACCN*MASS(ATOMA)
100 CONTINUE

ELSE

DO 200 MOLECI=1,NMOLEC
    RYCM=0.

    DO 150 ATOMA=1,NATOM
        RYCM=RYCM+MASS(ATOMA)*RY(ATOMA,MOLECI)
150 CONTINUE

    RYCM=RYCM/TMASS
    ACCN=EPSDD*RYCM

    DO 160 ATOMA=1,NATOM
        FX(ATOMA,MOLECI)=FX(ATOMA,MOLECI)+ACCN*MASS(ATOMA)
160 CONTINUE

200 CONTINUE

ENDIF
```

Here EPSDD is ϵ , and TMASS is the total molecular mass m_i .

These routines are called at the start of a simulation, after q_{ia} and \dot{q}_{ia} have been read in. In practice, we find it most convenient to start (and end) each simulation with a condition of zero strain, so that the molecular coordinates are consistent with normal periodic boundaries. For an oscillatory strain $\epsilon(t) = A \sin \omega t$ this means that, for convenience one oscillation period, $2\pi/\omega$, should be an integral

number of time steps, and the full simulation run should consist of many (perhaps several hundred) complete cycles. In principle, whenever the strain rate $\dot{\epsilon}$ is changed abruptly (for example, when starting a series of runs at a new frequency) the particle velocities should be instantaneously adjusted, according to eqns. (2),(7). In practice, we found this unnecessary, since, in any case, several (10-20) cycles are allotted for 'equilibration' of the system, before accumulating averages, whenever the conditions are altered. Memory of the change is expected to be lost in this time.

With a properly initialized system, we are ready to implement the integration algorithm. We adopted the RATTLE constraint method [3], which is built around a velocity version of the Verlet algorithm, a two-part process. The first part can be written

$$\begin{aligned} q_{ia}(h) &= q_{ia}(0) + h\dot{q}_{ia}(0) + \frac{1}{2}h^2\ddot{q}_{ia}(0) \\ \dot{q}_{ia}(\frac{1}{2}h) &= \dot{q}_{ia}(0) + \frac{1}{2}h\ddot{q}_{ia}(0) \end{aligned} \quad (9)$$

where h is the time-step. The accelerations \ddot{q}_{ia} include the normal forces $f_{ia}^c(0)/m$ and the extra terms in (2),(7).

In our program, this move takes place in a subroutine MOVEA, which is quite standard. For each molecule, after making the move, the new and old coordinates of all the atoms in that molecule are fed into the first part of the constraint procedure, a routine RATLA. This routine calculates from these coordinates and the molecular geometry, as described by Andersen [3], a set of constraint forces $f_{ia}^c(0)$, and hence accelerations $\ddot{q}_{ia}^c(0) = f_{ia}^c(0)/m_{ia}$, needed to guarantee that the new coordinates $q_{ia}(h)$ satisfy the bond length constraints. The details of the routine obviously depend on the molecules under study; the forces consist of individual components directed along the bonds $q_{iaib}(0)$. These forces are retrospectively included in equation (9), i.e. $q_{ia}(h)$ is replaced by $q_{ia}(h) + \frac{1}{2}h^2\ddot{q}_{ia}^c(0)$ and $\dot{q}_{ia}(\frac{1}{2}h)$ is replaced by $\dot{q}_{ia}(\frac{1}{2}h) + \frac{1}{2}h\ddot{q}_{ia}^c(0)$.

Now the forces $f_{ia}(h)$ are calculated in FORCE, and the additional perturbation forces are computed in FEXTRA. The second part of the algorithm is now implemented. This is written

$$\dot{q}_{ia}(h) = \dot{q}_{ia}\left(\frac{1}{2}h\right) + \frac{1}{2}h \ddot{q}_{ia}(h) \quad (10)$$

This is carried out in subroutine MOVEB. Once again, there is a constraint correction to make, this time to guarantee that the time derivatives of the constrained bond lengths are zero. The second constraint routine, RATLB, takes the values of $q_{ia}(h)$ and $\dot{q}_{ia}(h)$, together with the molecular geometry information, and returns a set of constraint forces $f_{ia}^{c'}$ (h), with components directed along the bonds $q_{iaib}(h)$. Hence the additional accelerations $\ddot{q}_{ia}^{c'}$ (h) are computed, and added into equation (10).

Finally, we come to the calculation of properties of interest, before looping around to MOVEA once more. The calculation of configurational properties is carried out in the normal way: the potential energy and potential contributions to the pressure tensor are calculated in the inner loop of FORCE. Either equation (3) or (8) can be used for the atomic or molecular pressure tensor as desired; in practice, if atom-atom intermolecular forces are used, it is easiest to calculate the atomic pressure tensor within the force loop, and then apply a correction of the form [9]

$$p_{yx}^{mol}(pot) = p_{yx}^{at}(pot) - \sum_{ia} (q_{ia}^y - q_i^y) f_{ia}^x \quad (11)$$

Note that the perturbation forces do not appear in equations (3) and (8); they are externally applied, and do not contribute to the pressure tensor. The intramolecular constraint forces, however, do contribute. Their contribution to p_{yx}^{at} , (and to the hydrostatic pressure) may be calculated in RATLA or in RATLB, where they are evaluated; remember that $f_{ia}^{c'}$ (h) in RATLB, and f_{ia}^c (h) calculated in the following call to RATLA, are both approximations to the same quantity.

For the kinetic contributions to the energy and the pressure tensor, different expressions again apply for atomic- and molecular-based quantities, because of the different definitions of momenta. These quantities are evaluated in a separate routine KINET, which contains the code

```
DO 100 MOLECI=1,NMOLEC
DO 100 ATOMA=1,NATOM
  PX=MASS(ATOMA)*(VX(ATOMA,MOLECI)-EPSD*RY(ATOMA,MOLECI))
  PY=MASS(ATOMA)*VY(ATOMA,MOLECI)
  PZ=MASS(ATOMA)*VZ(ATOMA,MOLECI)
  EKATOM=EKATOM+(PX**2+PY**2+PZ**2)/MASS(ATOMA)/2.
  PKATOM=PKATOM+PY*PX/MASS(ATOMA)
100 CONTINUE

DO 200 MOLECI=1,NMOLEC
  RYCM=0.
  PXCM=0.
  PYCM=0.

DO 150 ATOMA=1,NATOM
  RYCM=RYCM+MASS(ATOMA)*RY(ATOMA,MOLECI)
  PXCM=PXCM+MASS(ATOMA)*VX(ATOMA,MOLECI)
  PYCM=PYCM+MASS(ATOMA)*VY(ATOMA,MOLECI)
150 CONTINUE

  RYCM=RYCM/TMASS

DO 160 ATOMA=1,NATOM
  PX=MASS(ATOMA)*(VX(ATOMA,MOLECI)-EPSD*RYCM)
  PY=MASS(ATOMA)*VY(ATOMA,MOLECI)
  PZ=MASS(ATOMA)*VZ(ATOMA,MOLECI)
  EKMOL=EKMOL+(PX**2+PY**2+PZ**2)/MASS(ATOMA)/2.
160 CONTINUE

  PXCM=PXCM-TMASS*EPSD*RYCM
  PKMOL=PKMOL+PYCM*PXCM/TMASS
200 CONTINUE
```

Here, EPSD is $\dot{\epsilon}$, the strain rate, EKATOM and EKMOL are the atomic and molecular kinetic energies, and PKATOM and PKMOL are atomic and molecular pressure tensor components. In checking the energy conservation relation, eqn. (5), the kinetic energy and pressure tensor appropriate to the chosen perturbation are, of course, selected. In the course of a simulation, energy is abstracted from the system to prevent continual heating. This may be carried out by a further modification of the equations of motion, but in our case we simply scale the momenta at the end of each oscillation cycle, to yield the desired (fixed) total energy. Note, again, that it is the momenta which appear here; in the scaling routine, they must be calculated from the velocities, scaled, and then used to recalculate the velocities. The magnitude of heating effects in these oscillatory simulations may be kept down by restricting the amplitude of the shear strain (maximum strains of 10-15% are typical). To summarise, the basic organization of the main loop of the program is

↓
MOVEA (RATLA)
FORCE
FEXTRA
MOVEB (RATLB)
KINET

with momentum scaling to fix the energy at the end of each complete oscillation of the applied shear.

To test the program, we ran oscillatory shear calculations on a small system of 27 diatomic molecules. Intermolecular interactions were atom-atom Lennard-Jones 12-6 potentials $u(r) = 4\epsilon((\sigma/r)^{12} - (\sigma/r)^6)$, truncated at the well-bottom and shifted up so that both potential and force vanish at the cutoff. The bond length was fixed at σ . We chose a reduced atomic density $\rho\sigma^3 = 0.6$ and a reduced energy per atom $E/N\epsilon = 2$. This corresponds to a reduced temperature $k_B T/\epsilon \approx 1.3$. Simulations using atomic and molecular perturbations were carried out, and in each case the atomic and molecular stress responses, and other microscopic quantities, were measured. With a reduced time-step $h/\tau = \pi/1000$ ($\tau^2 = m\sigma^2/\epsilon$) the energy conservation law was obeyed to roughly 1 part in 10^{-3} . For low frequencies $\omega\tau \lesssim 5$ the stress responses followed the expected $\omega^{1/2}$ law. The differences between atomic and molecular stress responses in each kind of experiment were small at low frequency, less than 6% for $\omega\tau \lesssim 5$, and so within the typical statistical errors for the absolute values of these quantities. Detailed results of these simulations will be published elsewhere.

The main result of this article has been to show that a program combining time-dependent shear perturbations with molecular constraint dynamics may be written, and that this program performs satisfactorily. The simplicity of the program rests on the fact that the shear perturbation takes the form of an additional force term in the chosen modified equations of motion, and that the method of constraints also involves the calculation of force terms; no inconsistencies between the two techniques need arise. It makes no difference, in terms of technical difficulty, whether the perturbation is applied to atoms or molecular centres of mass: this is a purely physical choice, i.e. the decision should be based on what is thought to happen in the case of a real-life perturbation, if comparison with a real experiment is contemplated. The program was tested on a diatomic system, but there is no reason why a more complex system should not be investigated; the

simulation of a liquid of flexible chains is currently contemplated.

In the lengthy discussions of nonequilibrium simulation techniques which preceded the development of this program, we greatly benefitted from the advice of Dr. A.J.C. Ladd, Dr. D. Frenkel, Dr. J.P. Ryckaert and Professor H.C. Andersen. We are also grateful to the CECAM Workshop Organiser, Professor A. Bellemans, and to Professor C. Moser for his hospitality at CECAM.

References

- [1] CECAM Workshop on 'Dynamics of Molecular Liquids and Other Complex Systems Under External Constraints', June 19 - July 13 1983, Paris.
- [2] Ryckaert, J.P., Ciccotti, G., and Berendsen, H.J.C., J. Comput. Phys. 23 327 (1977).
- [3] Andersen, H.C., J. Comput. Phys. 52 24 (1983).
- [4] Hoover, W., Evans, D.J., Hickman, R.B., Ladd, A.J.C., Ashurst, W.T., and Moran, B., Phys. Rev. A22 1690 (1980).
- [5] Evans, D.J., Molec. Phys. 37 1745 (1979) ; Phys. Lett. A74 229 (1979) ; Phys. Rev. A23 1988 (1981).
- [6] Singer, K., Singer, J.V.L., and Fincham, D., Molec. Phys. 40 515 (1980).
- [7] Ladd, A.J.C., in ref. [1] and preprint.
- [8] Lees, A.W., and Edwards, S.F., J. Phys. C5 1921 (1972).
- [9] Singer, K., Taylor, A., and Singer, J.V.L., Molec. Phys. 33 1757 (1977).

NEW MONTE CARLO METHOD TO DETERMINE THE ABSOLUTE FREE ENERGY OF
ARBITRARY SOLID PHASES

Daan Frenkel and Tony Ladd

In this paper we present a computer simulation method to determine the domain of thermodynamic stability of solid phases in model systems. The recent development by Parrinello and Rahman (1) of a new Molecular Dynamics simulation technique has greatly stimulated the use of computer simulations in investigating solid-solid phase transitions in model systems. The basic idea upon which the Parrinello-Rahman method is based is that the fixed Periodic Boundary Conditions (PBC's) employed in conventional MD simulations all but exclude the direct observation of solid-solid phase transitions, as boundary conditions chosen to be compatible with the solid phase are, in general, incompatible with the other. Hence fixed PBC's tend to stabilize one solid phase well beyond its range of thermodynamic stability. Simulations involving fixed PBC's may easily overlook the existence of other, more stable phases altogether. In the Parrinello-Rahman method the shape of the periodic box is no longer fixed; shape and size of the periodic box are expressed in terms of variables which play the role of generalized coordinates in an extended Hamiltonian. The resulting equations of motion describe the "natural" time evolution of the shape and size of the periodic box under constant applied external pressure and zero applied stress. Note that if only the size of the box is treated as a variable the Parrinello-Rahman method reduces to Andersen's constant pressure MD (2). The P-R method provides a "reaction path" from one solid phase to the other as the boundary conditions adjust themselves to the favoured solid structure. For this reason the P-R method is now being used to map phase diagrams involving several solid phases (3). It should be noted, however, that the P-R method does not provide a reversible route from one phase to the other; the solid-solid phase transformation takes place when the initial solid phase becomes mechanically unstable. The actual thermodynamic phase transition is bracketed by the width of the hysteresis region. In order to locate the thermodynamic phase transition one needs information on the free energy of both solid phases.

Two methods have traditionally been used to obtain such information. Both methods rely on constructing a reversible path from a state of known

free energy to the solid phase under consideration. The first method is the Single Occupancy Cell (SOC) method introduced by Hoover & Ree (4). In this method one starts with a lattice gas with one particle per lattice cell. At high densities the centres of the lattice cells coincide with the average atomic positions in the unconstrained solid. Expanding this lattice uniformly one approaches a dilute gas which has the same pressure as an ideal gas at the same density, and a free energy that can be evaluated exactly. The free energy of the lattice gas at high densities coincides with the free energy of the corresponding unconstrained solid, if the density is sufficiently high to ensure that the artificial cell walls have negligible effect on the particle displacements. The free energy of the solid is then obtained by computing:

$$F_{\text{solid}}(V_2) - F_{\text{lattice gas}}(V_1) = - \int_{V_1}^{V_2} P(V) dV \quad (1)$$

at constant temperature.

This method was used by Hoover & Ree to obtain the free energy of the hard-sphere and 2D hard-disk solid (5,4). The actual numerical integration of eqn.(1) may require evaluating the pressure at many state points because lattice gas isotherms exhibit a cusp at the point where nearest-neighbour interactions take over from the cell walls in constraining the particles. There is even some evidence that a weak first order transition takes place at this point (6), in which case the supposedly reversible path linking the solid to the dilute lattice gas may, after all, be not quite reversible.

A second method to compute the free energy of a solid phase is to start from the low-temperature harmonic solid, the free energy of which can be computed exactly. This method was first used by Hoover, Gray & Johnson (7). There are two factors limiting the applicability of the latter method. The first is that it only works for solids that are harmonic at low temperatures (and/or high densities). This excludes all systems with discontinuous intermolecular forces, e.g. the hard-sphere solid. Moreover, solid phases that are mechanically unstable at low temperatures cannot be investigated by this method. A practical problem with the harmonic-lattice method is that for anything but the simplest solids, and in particular for molecular solids, evaluating the harmonic lattice free energy involves some

non-trivial computation.

Below we present a method to compute the free energy of an arbitrary solid in a way that we believe is easy, reliable and efficient. Our approach is once again based on the construction of a reversible path to a state of known free energy. In this case the reference state is an Einstein crystal with the same structure as the solid under consideration. This reference state can be reached from the real solid by slowly switching on harmonic springs which bind the atoms to their lattice sites. As the Einstein solid is structurally identical to the initial solid, it is very likely that such a path will be free of phase transitions and then reversible. The simplest way to transform a solid to an Einstein crystal is to add a term λV to the unperturbed Hamiltonian H_0 , such that

$$H(\lambda) = H_0 + \lambda V = H_0 + \lambda \sum_{i=1}^N (\vec{r}_i - \vec{r}_i^0)^2, \quad (2)$$

where \vec{r}_i^0 is the lattice position of particle i . The derivative of the free energy of this system with respect to the coupling constant λ is given by:

$$\frac{\partial F}{\partial \lambda} = -kT \frac{\partial}{\partial \lambda} \ln \left(\int \dots \int \exp(-\beta(H_0 + \lambda V)) d\vec{q}^{3N} \right) = \langle V \rangle_{\lambda}, \quad (3)$$

from which it follows that the free energy of the real crystal is related to the free energy of a crystal with spring constant λ by:

$$F(\lambda=0) = F(\lambda) - \int_0^{\lambda} \langle V \rangle_{\lambda'} d\lambda'. \quad (4)$$

At sufficiently high λ the free energy of the system reduces to that of an Einstein crystal:

$$F(\lambda) = \phi_0 - kT \ln \left(\frac{\pi kT}{\lambda} \right)^{(3/2)N} + C(T) + O(1/\lambda), \quad (5)$$

where ϕ_0 is the potential energy of a system with all atoms at their lattice sites. $C(T)$ is the kinetic contribution to the free energy which depends only on the temperature. Of course, a rather high value of λ may be required before the terms of order $O(1/\lambda)$ in eqn.(5) become negligible. In practice there is no need to go to very high values of λ as it is rather

simple to evaluate the leading corrections to the free energy at finite λ . In some cases these corrections can be evaluated analytically (as in the case of hard spheres, to be discussed below), but in the most general case the free energy difference between the ideal Einstein crystal and the Einstein crystal with intermolecular interactions can be found numerically by performing a Monte Carlo simulation on the ideal Einstein crystal, and deriving the free energy of the interacting Einstein crystal by umbrella sampling (8).

In order to investigate the usefulness of the method described above, we used it to compute the free energy of the hard sphere solid. We chose this particular system because reliable numerical results on the Hard-Sphere (HS) solid are available (5), yet the calculations on which these results are based are by no means trivial (it involves computing a complete isotherm of the single-occupancy cell system). Of course, for hard spheres the harmonic approximation cannot be used. In the present study we computed the free energy of the hard sphere solid at the fluid-solid coexistence point (reduced density $\rho/\rho_0 = .736$). The simulation consisted of 10 runs, each of 10^4 sweeps (i.e. 10^4 attempted moves/particle) excluding equilibration (typically 10^3 sweeps). Each run was carried out for a different value of the spring constant λ . The values of λ at which the different runs were performed were chosen as follows. For $\lambda > 600$ the free energy of the interacting Einstein crystal could be accurately approximated by an analytical expression based on a "virial" expansion to be described below. Hence the numerical simulations were limited to the interval $0 \leq \lambda < 600$. At high values of λ , $\langle r^2 \rangle \sim 1/\lambda$ whereas $\langle r^2 \rangle \rightarrow c$ as $\lambda \rightarrow 0$, where c is the mean-square displacement of an atom around its lattice site in the normal hard-sphere solid. In the simulation we have kept the centre of mass of the system fixed; we correct for the effect of this constraint on the free energy. Clearly then the function $(\lambda+c)\langle r^2 \rangle_\lambda$ varies little over the interval $0 \leq \lambda < 600$. Hence to compute the desired free energy difference we evaluated the integral:

$$\Delta F = - \int_0^{\lambda_{\max}} \langle r^2 \rangle_\lambda (\lambda+c) \frac{d\lambda}{(\lambda+c)} = - \int_{\ln c}^{\ln(\lambda_{\max}+c)} \langle r^2 \rangle_\lambda (\lambda+c) d \ln(\lambda+c) \quad (6)$$

Here the integrand is a very smooth function of λ , and the integral could be evaluated using a 10-point Gauss-Legendre quadrature. Later tests indi-

cated that no dignificant loss of accuracy resulted if a 5-point quadrature was used. Each simulation took about 2 minutes on the IBM 192 computer.

The free energy of the interacting Einstein crystal at λ_{\max} was evaluated in the following way. The configurational part of the partition function of the interacting Einstein crystal is of the following form:

$$Q(T; \lambda) = \int \dots \int \exp(-\beta \lambda \sum_i (\Delta r_i^0)^2) \exp(-\beta \sum_{i < j} U(r_{ij})) dr^N, \quad (7)$$

where $\Delta r_i^0 = \vec{r}_i - \vec{r}_i^0$ (\vec{r}_i^0 is the lattice site of particle i), $\beta = 1/kT$ and $U(r_{ij})$ is the value of the pair potential of particles i and j . Eqn.(7) can be rewritten as:

$$Q(T; \lambda) = Q_E(T; \lambda) \left(\int \dots \int \exp(-\beta \lambda \sum_i (\Delta r_i^0)^2) \exp(-\beta \sum_{i < j} U(r_{ij})) dr^N / Q_E(T; \lambda) \right), \quad (8)$$

where $Q_E(T)$ is the partition function of the non-interacting Einstein crystal. Hence:

$$Q(r; \lambda) = Q_E(T; \lambda) \langle \exp(-\beta \sum_{i < j} U(r_{ij})) \rangle_E \quad (9)$$

Here the subscript E stands for averaging over all configurations of the non-interacting Einstein crystal. This average can of course be carried out by Monte Carlo (umbrella sampling) but in the present case we use an expansion in cluster functions $f_{ij} = \exp(-\beta U(r_{ij})) - 1$,

$$\langle \exp(-\beta \sum_{i < j} U(r_{ij})) \rangle_E = \langle 1 + \sum_{i < j} f_{ij} + \sum_{i < j} \sum_{k < l} f_{ij} f_{kl} + \dots \rangle_E \quad (10)$$

Note that $\langle f_{ij} \rangle_E = \langle p^{ij} \rangle_{\text{overlap}}$, the probability that particles i and j in the non-interacting Einstein crystal are separated by a distance $|r_{ij}| < \sigma$. At high values of λ all $\langle f_{ij} \rangle$ for i and j not nearest neighbours become negligible, while $|\langle f_{ij} \rangle^{n.n.}| \ll 1$ (n.n. stands for "nearest neighbour"). In this limit we approximate eqn.(7) by:

$$\langle \exp(-\beta \sum_{i < j} U(r_{ij})) \rangle_E \approx (1 + \langle f_{ij} \rangle^{n.n.})^{Nn/2}. \quad (11)$$

In eqn.(11) n stands for the number of nearest neighbours of a particle i

(in the present case: $n=12$). To the same level of approximation, $\langle f_{ij} \rangle^{n.n.}$ can be evaluated by computing the probability of overlap of 2 isolated, harmonically bound penetrating spheres at an average separation $a = |\vec{r}_1^0 - \vec{r}_i^0|$. This probability can be evaluated analytically; the result is:

$$\langle P_{\text{overlap}}^{n.n.} \rangle = \frac{1}{2} \left[\text{erf}\left(\left(\frac{\beta\lambda}{2}\right)^{1/2}(\sigma+a)\right) + \text{erf}\left(\left(\frac{\beta\lambda}{2}\right)^{1/2}(\sigma-a)\right) \right] - \left(e^{-(\beta\lambda/2)(\sigma-a)^2} - e^{-(\beta\lambda/2)(\sigma+a)^2} \right) / \left((2\pi\beta\lambda)^{1/2} a \right) \quad (12)$$

The expression for the free energy of the interacting Einstein crystal then becomes:

$$F(T; \lambda) = F_E(T; \lambda) - \frac{Nn}{2} kT \ln(1 - \langle P_{\text{overlap}}^{n.n.} \rangle_\lambda) \quad (13)$$

From this expression for $F(T, \lambda)$ we can obtain an estimate for $\langle r^2 \rangle_\lambda = \frac{-1 \partial F}{N \partial \lambda}$, viz.:

$$\langle r^2 \rangle_\lambda = - \frac{\partial \ln Q_E}{\partial \beta \lambda} - \frac{n}{2} \frac{\left[\left(e^{-(\beta\lambda/2)(a-\sigma)^2} (\sigma(a-\sigma) - 1/\lambda) + e^{-(\beta\lambda/2)(a+\sigma)^2} (\sigma(a+\sigma) - 1/\lambda) \right) \right]}{\lambda a (2\pi\beta\lambda)^{1/2} (1 - \langle P_{\text{overlap}}^{n.n.} \rangle)} \quad (14)$$

This expression can be compared with the Monte Carlo results for the interacting Einstein crystal at high values of λ . Fig.1 shows such a comparison. Actually we found a very small difference between the Monte Carlo $\langle r^2 \rangle_\lambda$ and the corresponding virial result. This difference decreased rapidly with increasing λ ; we observed it fitted well to an expression of the form: $\Delta = \alpha \exp(-\lambda/\delta)$ with $\alpha \approx 10^{-3}$ and $\delta \approx 130$. We took this correction into account in evaluating the free energy but it had no significant effect on the final result. Finally, as mentioned above, we corrected for the fact that we were constraining the centre of mass of the system to be fixed. The partition function of an Einstein crystal with fixed centre of mass is given by:

$$Q'_E(T; \lambda) = N^{-3/2} \left(\frac{\pi}{\beta\lambda}\right)^{(3/2)(N-1)} \quad (15)$$

The partition function of the unconstrained hard sphere solid differs from the partition function of the constrained solid by a factor V . In table I we have collected all different contributions to the free energy of the hard-sphere solid, referred to the ideal gas at the same density. The table contains the results obtained for a 32,108 and 256 particle system. Fig.2 shows the N -dependence of the computed free energy (or actually, the entropy). To obtain the result at $N=\infty$, two different extrapolation methods were employed. In one it was assumed that the leading N -dependence of the free energy is of the form $\ln(N)/N$, in the second we assumed a simple $1/N$ dependence. In the present case the latter assumption is more realistic as the explicit $\ln(N)/N$ dependence both on the ideal gas side and on the Einstein crystal side were taken into account (see table I). In fact we find that the MC data fit a $1/N$ dependence far better than $\ln(N)/N$. The entropy difference between the hard-sphere solid at $\rho\sigma^3 = 1.041$ and an ideal gas at the same density was thus estimated to be:

$$\Delta S = -5.930 \pm 0.004 \quad (1/N - \text{extrapolation}),$$

$$\Delta S = -5.936 \pm 0.005 \quad (\ln(N)/N\text{-extrapolation}).$$

The error bars quoted correspond to 2 standard deviations. For the sake of comparison we give the Hoover-Ree results using the single occupancy cell method:

$$\Delta S = 5.924 \pm 0.015$$

Clearly, our results agree very well with the Hoover & Ree result.

In summary, we have developed a simple, efficient and accurate method to obtain absolute free energies of arbitrary solid phases. For hard spheres our results agree well with the results obtained by Hoover & Ree using a different approach. We are currently applying the present technique to a number of unsolved problems concerning the thermodynamic stability of solid phases in model systems.

ACKNOWLEDGEMENTS

This work was carried out during a CECAM workshop on transport in molecular fluids at Orsay, France. We thank Dr. Moser for creating the conditions which made this work possible; we thank the attendants of the workshop for many stimulating discussions.

REFERENCES

1. M. Parrinello & A. Rahman, Phys. Rev. Lett. 45, 1196 (1980); J. Appl. Phys. 52, 7182 (1981).
2. H.C. Andersen, J. Chem. Phys. 72, 2384 (1980).
3. See e.g.: M. Parrinello, A. Rahman & P. Vashishta, Phys. Rev. Lett. 50, 1073(1983); D. Levesque, J.-J. Weis & M.L. Klein, Phys. Rev. Lett. 51, 670 (1983).
4. W.G. Hoover & F.H. Ree, J. Chem. Phys. 47, 4873 (1967).
5. W.G. Hoover & F.H. Ree, J. Chem. Phys. 49, 3609 (1968).
6. H. Ogura, H. Matsuda, T. Ogawa, N. Ogita & A.Ueda, Prog. Theor. Phys. 58, 419 (1977).
7. W.G. Hoover, S.C. Gray, & K. Johnson, J. Chem. Phys. 55, 1128 (1971).
8. J.P. Valleau & G.M. Torrie in: Statistical Mechanics A, Modern Theoretical Chemistry Vol.5, B.J. Berne (editor), Plenum, New York, 1977, p.178.

Table I.

Contributions to the free energy difference (= -(entropy difference)) between hard-sphere solid and ideal gas at same density, N: number of particles, $F_E(\lambda_{\max})$: estimated free energy of interacting Einstein crystal (eqn. 13), F_{CM} : free energy difference between "floating" and fixed center of mass Einstein crystals, ΔF : free energy difference along reversible path (eqn.6), $\Delta F_{\text{corr.}}$: estimated correction to $F_E(\lambda_{\max})$ (see below eqn.14). F_{IG} : free energy of N-particle ideal gas. ΔS_{tot} : estimated entropy difference between N-particle hard-sphere solid and ideal gas at the same density. The bottom rows show the estimated results for $N=\infty$. Our best estimate for the free energy difference is $F = 5.930$. All free energies quoted are per particle; $\lambda_{\max} = 632.026$.

N	$F_E(\lambda_{\max})$	F_{CM}	ΔF	$\Delta F_{\text{corr.}}$	F_{IG}	ΔS_{tot}
32	7.8885	-0.1071	-2.7933	-0.0008	-0.8771	-5.8644
108	7.9660	-0.0430	-2.9403	-0.0007	-0.9298	-5.9117
256	7.9761	-0.0215	-2.9776	-0.0017	-0.9455	-5.9208
∞	1/N extrapolation					-5.930(4)
∞	$\ln(N)/N$ extrapolation					-5.936(5)

FIGURE CAPTIONS

Fig.1 Mean square displacement of atoms in an interacting Einstein crystal as a function of the "spring" constant λ . \square : MC data, — : "virial" approximation (eqn.14), - - - - : Einstein crystal ($N \rightarrow \infty$), - - - - : Einstein crystal (fixed center of mass: $N = 108$). All results apply to the case: $\lambda_{\max} = 632.026$ and, unless stated otherwise, $N = 108$. To improve the legibility of this figure, all mean square displacements have been multiplied by $(\lambda + c)$, with $c = 33.115$.

Fig.2 N-dependence of the free energy difference between a hard sphere solid and $\rho\sigma^3 = 1.041$ and an ideal gas at the same density. As can be seen from the figure, the relation between ΔF and $1/N$ is very nearly linear. The intercept at $1/N = 0$ yields an estimate for ΔF at $N=\infty$: $\Delta F = 5.930$. For the same of comparison, the Hoover & Ree value $\Delta F = 5.924$ is also shown (\bullet).

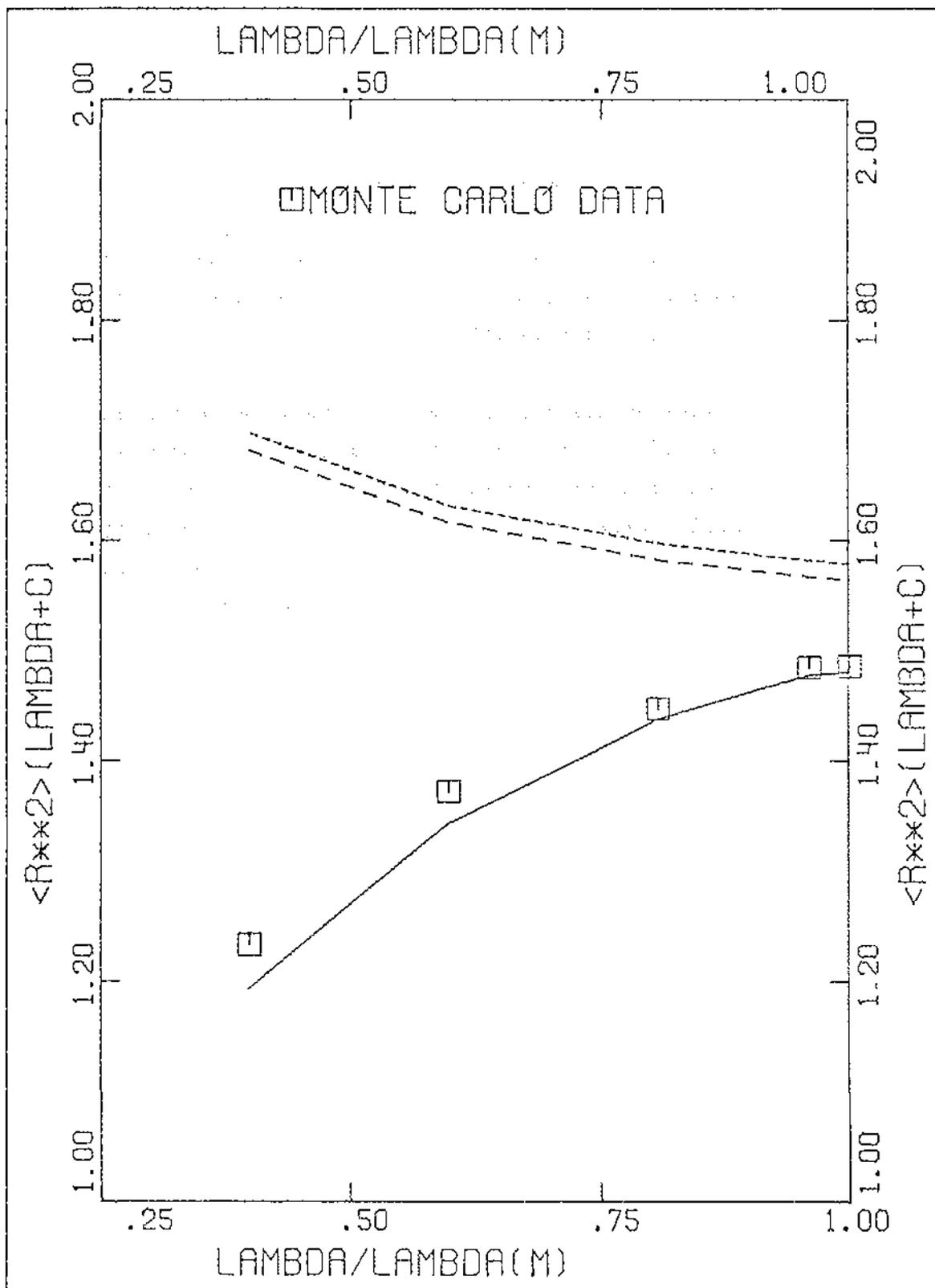
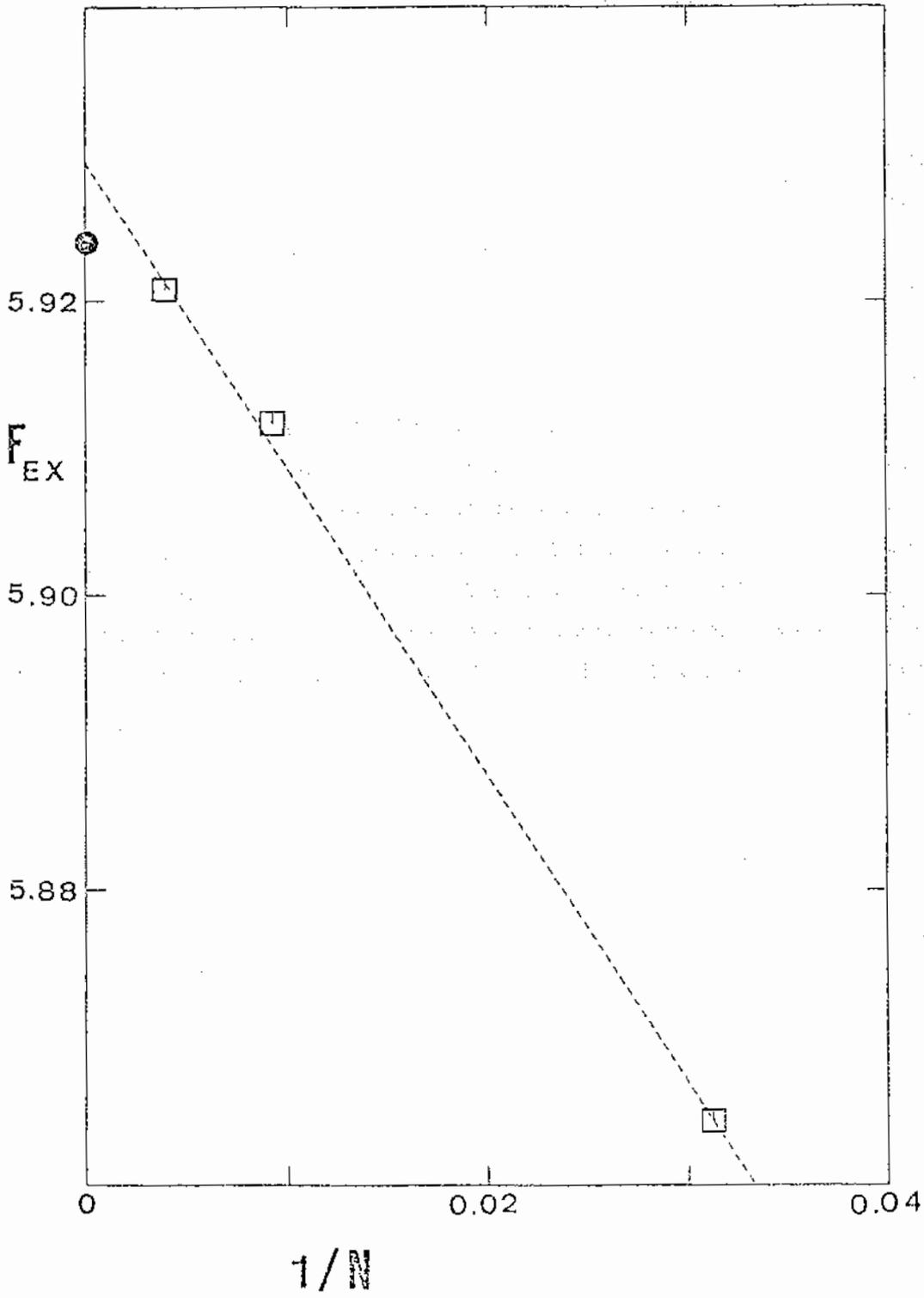


FIGURE 1

FIGURE 2.



PARALLEL COMPUTERS AND NON-CUBIC BOUNDARY CONDITIONS

David Fincham

Several previous articles [1,2] have discussed the use of non-cubic periodic boundary conditions in simulation. The advantages claimed are that a more nearly spherical shape of computational box enables longer range correlations to be studied for a given number of particles, and that the anisotropy between interactions of a non-spherical molecule and its different images is reduced. The purpose of this note is to point out that the converse of the first argument is also true - a given range of correlations can be studied using a smaller number of particles - and that the resultant saving in computer time is particularly significant in the case of the parallel computer.

Let us illustrate this with a simple example. Suppose we perform a conventional MD simulation with 256 molecules in a cubic box of side $2L$, so that the maximum cut-off radius, and the range to which correlations can be measured, is L . The number density is $256/8L^3$. Now consider a similar simulation performed in truncated octahedron (TO) boundary conditions. The TO is obtained, in the manner described by Adams [1], by cutting off the corners of a cube of side $2A$ until half its volume (half of $8A^3 = 4A^3$) remains. The maximum cut-off distance is then the radius of the inscribed sphere, which is $A\sqrt{3}/2$. If we wish this to be the same as in the first simulation we require:

$$A = 2L/\sqrt{3}$$

The volume of the TO is:

$$\text{Vol} = 4A^3 = 32L^3/3\sqrt{3}$$

and the number of particles inside the TO is:

$$\begin{aligned} \text{number} &= (\text{vol})(\text{number density}) \\ &= (32L^3/3\sqrt{3})(256/8L^3) \\ &= 197 \end{aligned}$$

A similar argument for rhombic dodecahedron boundaries shows that the number of particles required in this case is only 181.

On a serial computer the saving in computer time may not be very great. Only part of the code is executed for all pairs in the system, namely the nearest image

transformation and calculation of the pair separation squared distance. Pair forces are not evaluated for pairs whose separation is greater than the cut-off radius. The situation with the parallel computer is different in that it is not possible to jump over some interactions; the pair force is evaluated for all pairs in the system (unless neighbour lists are used. However, these are hardly advantageous for systems of up to 256 molecules because of the extra overheads involved [3]). Thus the execution time is roughly proportional to the square of the number of particles, and so non-cubic boundaries can lead to a considerable reduction in the expense of computation, providing that the extra complication of applying the nearest image transformation does not slow things down too much. To confirm this I will give code and timings for the DAP. I would expect similar results to be applicable to the Cray. Adams [1] states that TO boundaries are 'very slow' on the Cray; I do not understand this, and perhaps the problem could be overcome. It is worth while discussing first how cubic boundaries are programmed. A favourite trick, I think originally due to Konrad Singer, is to have the internal co-ordinates lie between -1 and +1, when the nearest image transformation for the x-co-ordinate (with similar expressions for y and z) is:

$$RX = RX - 2*INT(RX)$$

Two comments may be made in passing. First, an alternative approach is to have internal co-ordinates between -0.5 and +0.5 when the expression becomes:

$$RX = RX - INT(2.0*RX)$$

Computationally the difference is that the second expression involves a floating point rather than integer multiplication. The particular computer being used will determine which is better. It may be possible to exploit the fact that integer multiplication by two is simply a left shift along the binary word [4]. Second, identical code may be used in putting particles back into the computational box after the dynamic update. A word of warning however: if any particle is ever more than half a box length outside the box it will never be put back in!. This situation can arise all too easily if a slight mistake is made in specifying the density of the simulation, because of the strong hard core repulsion of the molecules. It is wise to check your configurations for this error to avoid all your simulations having lower density than you think because some particles are permanently outside the computational box.

The 2*INT method works well on the DAP which is very good at short word fixed point arithmetic. The code is:

```

REAL    RX(,)
INTEGER*1  IX(,)
:
IX = IFIX(RX)
RX = RX - FLOAT(LENGTH(2*IX,4))

```

(The LENGTH function is used to convert its argument from 1 byte to 4 byte length which is necessary before floating it). For 256 Lennard-Jones particles this gave an execution time per complete timestep of 0.112 s. However, there is a better method. We note that we have to either add or subtract two. Changing the sign of a quantity on the DAP is performed simply by flipping the sign bit, and this is a very rapid operation. The code is:

```

REAL    RX(,),TWO(,)
LOGICAL  RXSIGN(,),TWOSIGN(,)
EQUIVALENCE  (RX,RXSIGN),(TWO,TWOSIGN)
TWO = 2.0
:
TWOSIGN = .NOT.RXSIGN
RX(ABS(RX).GE.1.0) = RX + TWO

```

This gave an execution time of 0.106 s per step, which is about one-third Cray speed [3].

Adopting similar ideas for TO boundaries the code is:

```

:
:
Transform RX,RY,RZ as in cubic case
:
CORNERS = ABS(RX) + ABS(RY) + ABS (RZ).GE.1.5
ONESIGN = .NOT.RXSIGN
RX(CORNERS) = RX + ONE
Similarly for RY and RZ

```

Again for 256 LJ molecules, the execution time was 0.119 s per step. For the very slightly more complicated rhombic dodecahedron it was 0.121 s. These results show that the extra overheads of the non-cubic boundaries are only around 10% even in the case of LJ atoms where the force calculation itself is very simple.

To test whether it really is possible to save computer time by adopting non-cubic boundaries with a smaller number of particles I compared two simulations on a system of two-centre LJ diatomics. The first had 256 molecules in cubic boundaries, the second had 192 molecules in TO boundaries. I took 192 rather than 197 because the DAP 'likes' multiples of 64; this meant that the cut-off radius was very slightly smaller in the second simulation. The execution time for cubic boundaries was 0.49 s, whereas for TO boundaries it was 0.32 s, a saving of 35%. Results from the two simulations were indistinguishable. My conclusion is that TO (or rhombic dodecahedron) boundaries should be the standard choice for MD simulations on a parallel computer.

References

- [1] D. Adams, CCP5 Newsletter no. 10, p. 30 (1983)
- [2] W. Smith, CCP5 Newsletter no. 10, p. 37 (1983)
- [3] D. Fincham and B.J. Ralston, Comput. Phys. Comm. 23 127-134 (1981)
- [4] N. Corbin and D. Fincham, CCP5 Newsletter no. 2, p. 3 (1981)

More on rotational motion of linear molecules

David Fincham

In a previous article [1] I described the constraint algorithm for the rotational motion of rigid linear molecules. The orientation of the molecule is specified by \underline{e} , a unit vector along its axis. If the force centres are at positions $d_\alpha \underline{e}$ relative to the COM, the torque on the molecule is

$$\begin{aligned}\underline{T} &= \underline{e} \times \sum_\alpha d_\alpha \underline{f}_\alpha \\ &= \underline{e} \times \underline{G}\end{aligned}$$

By considering the motion of an 'equivalent diatomic' it is easily shown that the equation of motion (splitting into two first order equations) is

$$\dot{\underline{e}} = \underline{u} \tag{1a}$$

$$\dot{\underline{u}} = \underline{G}/I + \lambda \underline{e} \tag{1b}$$

where λ is an undetermined multiplier for the constraint force along the bond axis. My previous article solved this equation by using a simple leapfrog and then obtaining a quadratic equation for λ by using the constraint that the length of \underline{e} should remain unity. The purpose of this note is to give an alternative and simpler algorithm for integrating equation (1).

We first subtract out the component of \underline{G} parallel to \underline{e} i.e. replace \underline{G} by

$$\underline{G}_\perp = \underline{G} - (\underline{G} \cdot \underline{e})\underline{e}$$

Writing a leapfrog for (1) then gives

$$\underline{u}^{n+\frac{1}{2}} = \underline{u}^{n-\frac{1}{2}} + \Delta t \underline{G}_\perp^n / I + \lambda \underline{e}^n \tag{2a}$$

$$\underline{e}^{n+1} = \underline{e}^n + \Delta t \underline{u}^{n+\frac{1}{2}} \tag{2b}$$

The reader may have noticed that since G_{\perp}^n has no component along \underline{e} the constraint force is required only to produce the centripetal acceleration, and in fact it can be shown that $\lambda = \underline{u}^2$. However we can obtain an algorithm without going through this step. The constraint on the bond length requires $\underline{u} \cdot \underline{e} = 0$; since we know \underline{e}^n we can use this if we have an estimate for \underline{u}^n . As explained in [2] where I discussed a similar equation for non-linear molecules the correct procedure is to use a first order expansion over $\frac{1}{2}\Delta t$ to obtain this estimate. Thus

$$\underline{u}^n = \underline{u}^{n-\frac{1}{2}} + \frac{1}{2}\Delta t \left[\underline{G}_{\perp}^n / I + \lambda \underline{e}^n \right]$$

Then, using $\underline{G}_{\perp}^n \cdot \underline{e}^n = 0$, $\underline{e}^n \cdot \underline{e}^n = 1$ and applying the constraint $\underline{u}^n \cdot \underline{e}^n = 0$ we find

$$0 = \underline{u}^{n-\frac{1}{2}} \cdot \underline{e}^n + \frac{1}{2}\Delta t \lambda$$

Substituting back for λ in (2a) gives

$$\underline{u}^{n+\frac{1}{2}} = \underline{u}^{n-\frac{1}{2}} - 2\underline{u}^{n-\frac{1}{2}} \cdot \underline{e}^n + \Delta t \underline{G}_{\perp}^n / I \quad (3a)$$

Equations (3a) and (2b) then constitute a leapfrog type algorithm for the rotational motion, since we have expressed the centripetal acceleration in terms of the known quantities $\underline{u}^{n-\frac{1}{2}}$ and \underline{e}^n . In tests of this algorithm I have found that it gives identical results to the more complicated constraint algorithm of [1].

References

- 1 . D.Fincham, CCP5 Newsletter No.10, September 1983.
- 2 . D.Fincham, CCP5 Newsletter No.2, September 1981.

A THREE BODY POTENTIAL MODEL FOR SILICON DIOXIDE

M. Leslie Daresbury Laboratory
 Dept. of Chemistry
C.R.A. Catlow University College London
M. Sanders 20, Gordon Street,
 London WC1H 0AJ.

Previous studies ((1) and references therein) have attempted to model silicates using classical Born model pair potentials, but these have proved inadequate to describe silicates with framework structures. We have recently extended these models by including a three body additive term in the potential. The three body additive term is assumed to act about the O - Si - O bonds, and to vary quadratically with the bond angle.

$$E_B = \frac{1}{2} k_B (\theta - \theta_0)^2$$

where $\theta_0 = 109.47^\circ$

The variable parameters of our model were determined by a least squares fit to the observed structure of α -Quartz(2), the lattice constants, elastic constants(3) and dielectric constants. Table 1. gives the complete potential used for α -Quartz; those quantities held fixed in the least squares fit are given in parentheses. Table 2. gives the observed and calculated crystal properties using this model.

As a test of this model we have

- a) Calculated the phonon dispersion curves and compared these with the experimental results for the lowest six branches.(4).

The results in the (\mathcal{E} , \mathcal{E} , 0) direction are shown in Figure 1.

- b) We have calculated the change in Si - O - Si bond angle with applied pressure and obtain excellent agreement with experiment (5) (Table 3.)
- c) We have attempted to model other polymorphs of SiO_2 using this potential. This involves minimising the energy of the unit cell, using the observed structure as a starting point, and comparing the minimised structure with the observed. We have carried this out for the polymorphs Tridymite, Coesite, and Cristobalite. In all cases agreement between the observed and minimum energy structures is excellent, the calculated cell constants all being within 1.5% of the observed, and the maximum atom displacement being 0.1 Å.

TABLE 1.

POTENTIAL PARAMETERS FOR α - QUARTZ.

Si (rigid ion) ionic charge / e		(+4)
O (shell model) ionic charge / e		(-2)
O (shell model) shell charge / e		-2.8482
O shell model spring constant / (eV/Å ²)		74.92
Buckingham two body short range potentials		
	$V_{ij} = A \exp (- r_{ij}/B) - C / r_{ij}^6$	
	Si - O _{shell}	O _{shell} - O _{shell}
A /eV	1283.9	(22764.0)
B /Å	0.3205	(0.149)
C / (eV/Å ⁶)	10.66	(27.88)

TABLE 1. (continued)

Bond bending constant $O_{\text{shell}} - \text{Si} - O_{\text{shell}}$ / (eV/radian ²)		2.097
Oxygen core - shell displacement /A	x	+0.0997
	y	-0.0302
	z	-0.0666

TABLE 2.

THE OBSERVED AND CALCULATED CRYSTAL PROPERTIES
OF α -QUARTZ.

	EXPERIMENTAL	CALCULATED
ELASTIC CONSTANTS (10^{11} Dyn cm ⁻²)		
C_{11}	8.683	8.815
C_{33}	10.598	10.605
C_{44}	5.826	5.296
C_{66}	3.987	4.269
C_{14}	-1.8054	-1.012
C_{13}	1.193	1.151
STATIC DIELECTRIC CONSTANTS		
E_{11}	4.520	4.452
E_{33}	4.640	4.812
HIGH FREQUENCY DIELECTRIC CONSTANTS		
	1.549	2.04

TABLE 3.

OBSERVED AND CALCULATED CHANGE OF Si - O - Si ANGLE
WITH PRESSURE

PRESSURE (Kbar)	EXPERIMENTAL	CALCULATED
0.0	144.1	143.9
10.6	141.5	141.2
21.1	139.4	139.1

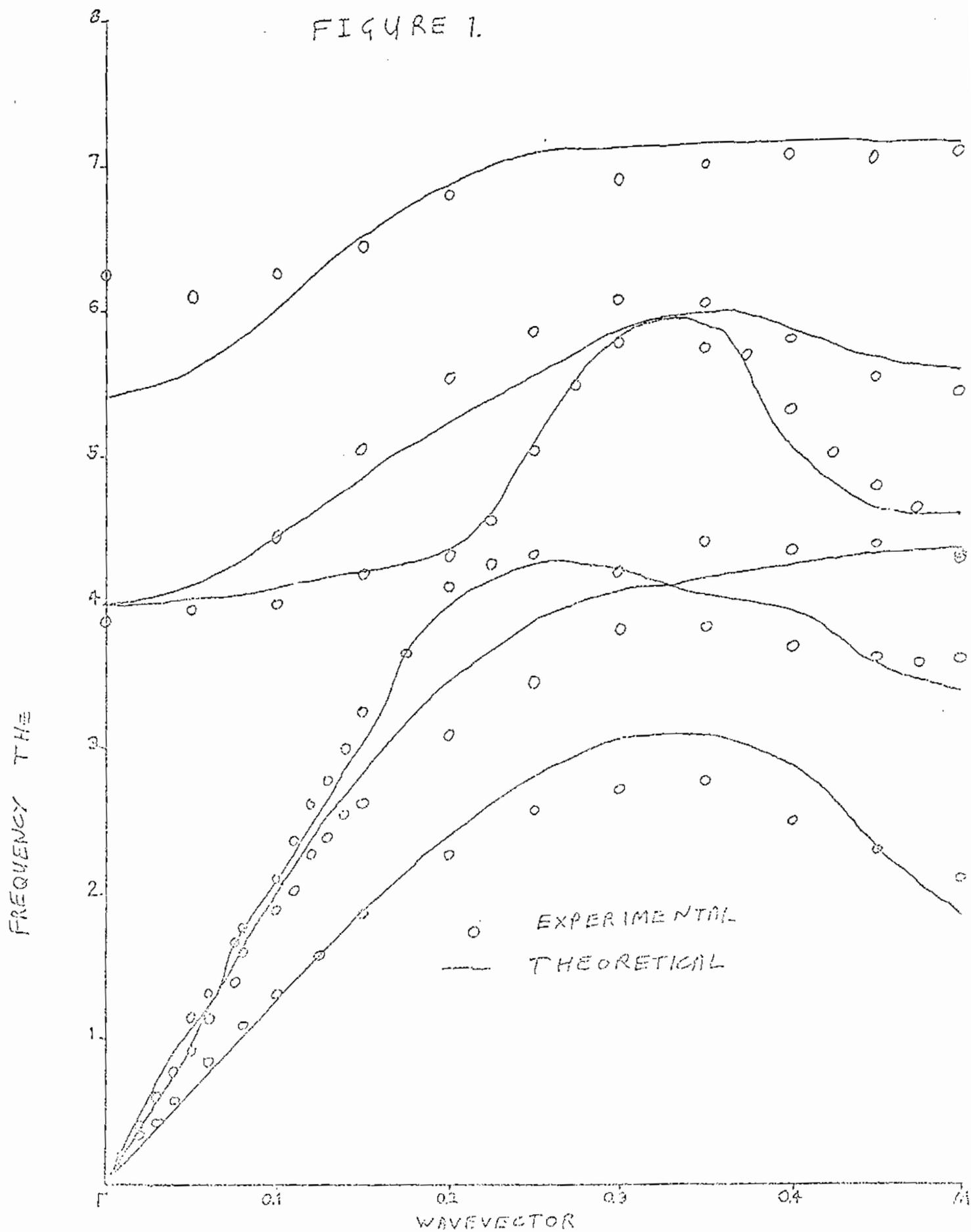
TABLE 3. (continued)

PRESSURE	EXPERIMENTAL	CALCULATED
28.2	138.7	137.9

REFERENCES

- 1) S.C. Parker., C.R.A. Catlow., A.N. Cormack. Chem. Comm. 936 (1983)
- 2) G.S. Smith., L.E. Alexander. Acta Cryst 16, 462-471 (1963)
- 3) I. Koga., M. Aruga., Y. Yoshinaka. Phys. Rev. 109, 1467 (1958)
- 4) B. Dorner., H. Grimm., H. Rzany. J. Phys. C. 13 6607 - 6612 (1980)
- 5) J.D. Jorgensen., J. Appl. Phys 49, 5473, (1978)

FIGURE 1.



CCP5 Literature Survey Addendum.

W. Smith

The following references have been indicated to me as having been omitted from the last CCP5 Literature Survey. To make amends for this they are listed below.

Molecular dynamics simulation study of negative hydration effect in aqueous electrolyte solutions.

A. Geiger.

Ber. Bunsenges. Phys. Chem. 85, 52 (1981)

Low density patches in the hydrogen-bond network of liquid water: evidence from molecular dynamics computer simulation.

A. Geiger, H. E. Stanley.

Phys. Rev. Letters. 49, 1749 (1982)

Test of universality of percolation exponents for a three dimensional continuum system of interacting waterlike particles.

A. Geiger, H. E. Stanley.

Phys. Rev. Letters. 49, 1895 (1982)

Gelation models of hydrogen bond networks in liquid water.

H. E. Stanley, R. L. Blumberg, A. Geiger.

Phys. Rev. B. 28, 1626 (1983).

A new algorithm for molecular dynamics calculations.

S. Toxvaerd.

J. Comput. Phys.. 47, 444 (1982).

Energy conservation in molecular dynamics.

S. Toxvaerd.

J. Comput. Phys.. 52, 214 (1983).

A grand ensemble Monte Carlo study of Krypton adsorbed on graphite.

J. S. Whitehouse, D. Nicholson, N. G. Parsonage.

Molec. Phys.. 49, 829 (1982)

Computer simulation and the statistical mechanics of adsorption.

D. Nicholson, N. G. Parsonage.

Academic Press (1982).

