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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 13 JUNE 1984

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Editorial.

Our thanks once again go to those participants in CCP5 who have kindly contributed to this, the thirteenth issue of the newsletter. J. H. R. Clarke and K. J. Doyle have provided a summary of the CCP5 workshop on the computer simulation of interfaces which took place in March this year and J M. Goodfellow has reported on the visit to Birkbeck College by Dr. M. Mezei of Hunter College, New York. Both of these events were sponsored by CCP5 (the latter only partially) and so it is appropriate that reports on them should be produced here.

Of more direct scientific interest we have an intriguing article on the recurrence time in molecular dynamics, provided by M. Schoen, R Vogelsang and C. Hoheisel. W. Smith and K. Singer have written a description of the dynamics of spherical gaussian wavepackets, which is a method which potentially offers a route to quantum corrected molecular dynamics. For our colleagues with interests in lattice simulations, S. C. Parker has written about vacancy ordering in calcium manganese oxides.

In keeping with our tradition of presenting examples of computationally efficient techniques, we are pleased to produce the article by R. F. Fowler on the identification of a droplet in equilibrium with its vapour. Lastly, our old friend D. M. Heyes has something to say on the subject of radiation damage by molecular dynamics.

Many thanks to all for their contributions.

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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. The theme of the Meeting will be recent developments in both theoretical and empirical potentials for use in simulation.

Full details of the structure of the meeting, the speakers and the required registration form are given in the circular included with this newsletter.

b) Readers may also be interested to know that CCP3 and CCP6 are jointly organising a strongly related meeting entitled 'Potentials for Gas Phase and Surface Scattering Calculations', which will be held at Cambridge after the CCP5 Meeting, from Monday 24 th. September to Tuesday 25 th. September 1984.

Full details of this meeting and the required registration form are given in the second circular supplied with this issue of the Newsletter.

c) CCP5 is sponsoring a visit to the U. K. by Professor B. J. Berne (Columbia University) in October 1984 (20 th. to the 27 th.). Professor Berne is an acknowledged authority in the field of computer simulation and his visit to the U. K. is designed to encourage developments in some of the newer areas of computer simulation. Professor Berne is expected to give seminars on the subjects of "Quantum Mechanical Computer Simulation", "Computer Simulation of Rare (Activated) Events" and "Water and Aqueous Solutions" as well as partake in more informal discussions over a wide range. His itinerary (subject to final confirmation) is as follows (local contacts are given in brackets):

Oxford - October 21 st. to 22 nd. (Professor J. S. Rowlinson).

Cambridge - October 23 d. to 24 th. (Professor A. D. Buckingham).

London - October 25 th. to 26 th. (Dr. J. M. Goodfellow).

The visit is being organised for CCP5 by Professor K. Singer, who will confirm details at a later date. Information is also likely to be available at the centres Professor Berne is to visit. Readers are welcome to visit one of these venues to have discussions with Professor Berne. Please make arrangements with the appropriate local contact.

d) In our attempt to rationalise the membership of the CCP5 Steering Committee, we publish again the 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 encouraged.

The membership of the Steering Committee is intended to be representative of the simulation groups participating in CCP5, particularly in the U.K.. We would therefore be pleased to hear from any group not adequately represented. Equally, whoever wishes to withdraw their membership 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)
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D. Fincham (Q.M.C.)
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M. Gillan (Harwell)
K. Gubbins (N.Y.)
D. Heyes (R.H.C.)
R. Hockney (Reading)
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R. Lynden-Bell (Cambridge)
W. Mackrodt (I.C.I.)
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D. Nicholson (Imperial)
N. Parsonage (Imperial)
S. Pawley (Edinburgh)
J. W. Perram (Odense)
J. Powles (Canterbury)
N. Quirk (N.Y.)
J. Rowlinson (Oxford)
J. Ryckaert (Brussels)
K. Singer (R.H.C.)
W. Smith (Daresbury)
D. Tildesley (Southampton)

e) Your editor has been contacted by Dr. A. K. Shukla of the Department of Chemistry, University of Delhi, Delhi 110007, India. Dr. Shukla is very interested in the CCP5 Project and is keen to enter into a collaboration involving computer simulation. His current interests include the thermodynamic and transport properties of molten salt mixtures, density and temperature dependence of transport properties in supercooled L-J liquids, thermodynamic properties of ionic clusters and the adsorption of rare gases on graphite. The computer he has available to him is an IBM 360 mainframe.

If any of our readers is also interested in the subject areas outlined by Dr. Shukla, perhaps he or she would consider contacting him?

f) Users of the Rutherford and Appleton Laboratory computing system are reminded once again that magnetic tapes stored without access for the past five years will be scrapped if not identified to the tape librarian before 31 st July 1984.

RAL has also announced that due to manpower shortages they are experiencing difficulties in organising courses for users and have had to cancel their schedule for the year.

g) The University of London Computing Centre has progressed beyond the initial phases of implementing the new Amdahl 470V/8 and Cray 1s configuration. Their efforts now seem to be more in the way of consolidation than initiation. Perhaps the most significant news from ULCC is that a new version of the Cray operating system COS 1.12 (and with it a new FORTRAN compiler CFT 1.11) was scheduled for field trials towards the end of May. This seems likely to have a significant (but not traumatic) effect on users of the Cray 1s and so they are recommended to examine the May issue of the ULCC newsletter to appraise themselves of the situation.

ULCC has also announced the appearance of the user archiving service promised some time ago. The system uses the MASSTOR M860 automatic filestore. Archive requests are processed every 12 hours; at noon and midnight, while retrieve requests are dealt with every ten minutes. Initially, two copies of the archived dataset will be saved on the MASSTOR system, but eventually one copy will migrate to conventional tape storage.

h) As reported in the last issue of this newsletter, the University of Manchester Regional Computer Centre launched the new Amdahl 470V/8 and CYBER 205 service on March 5 th.. The ROSCOE job submission and editing facility is working well and is a decided improvement over the GEORGE system on the ICL 1906A. Transfer of datasets between ROSCOE and the MVS operating system on the Amdahl and the MASSTOR backup is very smooth. There are however still a few problems to be ironed out. Loss of output is not unknown and transfer of datasets between the various mainframes has failed on occassion. However the system is gradually improving and it promises much for the future.

Users should note that the ICL 1906A is due to be withdrawn by July 31 st., which means that all file transfers to the Amdahl front - end processor should be completed by all users before then. Users are also requested to delete unwanted files to reduce the dump tape requirement of the 1906A.

In addition to the system upgrades reported in our last issue, the Amdahl 470V/7 is to be upgraded to a V/8 on May 2 nd., following an assessment of loading on the 470 by Amdahl and UMRCC.

The CYBER 205 FORTRAN 77 compiler (FORTRAN 200) has now been fully documented in the FORTRAN 200 manual, which is available from UMRCC.

i) Anyone wishing to make use of the CCP5 Program Library is invited 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.)

We should also like to remind our readers that we would welcome contributions to the Program Library. The Library exists to provide support for the research efforts of everyone active in computer simulation and to this end we are always pleased to extend the range of software available. If any of our readers have any programs they would like to make available, please would they contact Dr. Leslie.

* (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 alkalai 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 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 (Rossky,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.

Report of CCP5 Workshop

on

COMPUTER SIMULATION OF INTERFACES

Manchester March 29-30 1984

by

J.H.R.Clarke and K.J.Doyle.

This was our first attempt at a new venture - workshops involving 15-20 persons, at which they would be encouraged to talk in detail about what they do rather than about their pet results. By most accounts the 'round table' format of the meeting was a success. It is worth suggesting to organisers of future workshops, however, that they strictly limit the number of talks and give more time for guided discussion.

The object of this workshop was to survey the various aspects of interfacial phenomena currently under investigation by various simulation groups within the U.K., to identify problems and provide a basis for increased collaboration within the framework of CCP5. Four main areas were chosen for discussion: crystal surfaces, liquid - vapour interfaces, adsorbed layers on solids and various aspects of the solid-liquid interface. A catholic selection indeed ! Both static lattice (SL) and finite temperature (molecular dynamics ,MD, and Monte Carlo, MC) simulations were considered.

The first session was concerned with crystal surfaces and defect (internal interface) calculations. The essential features of SL simulations were introduced by Dr. Jackson, who emphasised the high precision and speed of the calculations whilst noting their limitations. For instance it is not possible to calculate free energies and explicit dynamical effects cannot be studied. The basic difference in the SL and MD approaches might be of significant consequence for the calculation of certain interfacial properties. As a case in point it was pointed out that dynamic simulations of alkali halide crystals [1] had revealed significant surface reconstruction and large mean squared vibrational amplitudes of surface ions compared to the bulk. It was concluded that a close comparison of the two techniques for some selected systems would be valuable. An appropriate case might be studies of surface segregation of impurity ions (Ba2+, Sr2+, Ca2+) at the surfaces of a cubic MgO crystal for which accurate SL calculations already exist (Mackrodt) using relatively simple potentials.

There was some discussion of the potentials used in ionic crystal simulations. The computationally faster SL calculations are of particular value since they can be used with highly realistic but often mathematically complex potentials. The general preference for using an exponential rather then power law repulsive component was emphasised. Although the Ewald summation is usually used to calculate long range coulombic interactions (with a reciprocal space term appropriate to two-dimensional translational symmetry) it was pointed out (Heyes) that other fast converging methods have recently been developed which might be useful in SL calculations.

The relative advantages of using rigid ion and shell model potentials wwere discussed. Although it was suggested that polarisation effects could be important at the surface, current evidence (Mackrodt, Tasker) suggested that the effective potential experienced by ions at a crystal surface was in fact very similar to that in the bulk. The importance of new atom scattering experiments (e.g. those at Gottingen) for obtaining information on real surface interaction potentials was emphasised.

Dr. Tasker outlined SL calculations of grain boundaries (internal surfaces) in NiO, with the object of predicting local structures which might be pathways for the enhanced diffusion that is known to occur in this material [2]. Comparison with MD studies of such systems would be very valuable.

The second session was concerned with liquid-vapour simulations. Prof. Powles introduced MD simulations of droplets as a means of studying the Lennard-Jones (LJ) liquid in equilibrium with its vapour [3]. Several methods of dealing with boundary conditions have been adopted. Powles used normal cyclic boundaries but others have used systems (vapour + liquid) confined by a rigid cage. Although there are some fundamental objections to the latter method, both appear to give quite similar results. The necessity for long periods of equlibration (c.50 000 time steps in MD) was emphasised. The problem of computing the surface tension was discussed at some length. Powles proposes a method utilising data from liquid droplet simulations and the Kelvin equation. The major uncertainty in this method, however, is determination of the droplet radius.

Recently simulations have also been attempted for droplets composed of particles interacting through a Stockmayer potential. The point dipoles were kept deliberately small in magnitude so that long range interactions in a periodic system could be ignored. The interest here is in the profile of the dielectric constant across the interface.

The MD and MC simulation of hard and soft sphere crystal-liquid interfaces was discussed by Dr. Bushnell-Wye [4] and , once again, the necessity to allow for the very sluggish equilibration in such systems was emphasised. One important problem encountered here was the choice of starting configuration which had a very strong influence on the time development of interfacial structure. The system size also influences equilibration which turned out to be more efficient for the (less constained) larger ($N > 4000$) systems.

Spatial uniformity of the chemical potential as a criterion for equilibrium was discussed by Dr. Van Swol during a talk in which he outlined a very comprehensive MD study [5] of the hard sphere fluid constrained by hard walls. The chemical potential across the sample was calculated using the test particle method based on the potential distribution theorem. For mechanical equilibrium both the chemical potential and the normal pressure should be spatially uniform. Examples were discussed.

Dr. Parsonage outlined the coupling parameter method of obtaining free energies, which are often more interesting for adsorption systems than for uniform systems. In this method values are computed relative to a reference state by progressively 'turning on ' the potential. The free energy difference is calculated by integration of the mean internal energy over the coupling parameter. If the reference is a hard sphere system care is necessary in the choice of cut-off in order to avoid poor initial statistics.

Three currently central problems in the simulation of adsorbed molecular monolayers of nitrogen on graphite were presented by Drs. Tildesley, Joshi and Talbot [6] :

(1) The extent to which the existence of periodic boundaries promotes the formation of domains,

(2) The nature of orientational disordering within domains and between domains,

(3) The best choice of order parameter to characterise such processes.

The rotational transition around 27 K has been studied using a lattice model of 1000 spins and (N,V,T) MC. One of the difficulties is that below the transition the system tends to lock in one of six degenerate ground states of the ordered herringbone structure as a result of the periodic boundaries. At higher temperatures the system breaks up into domains. The value of any single particle orientational order parameter is is affected both by molecules within a domain and by the relative orientation (which is continually changing) between domains. Care has to be taken to avoid misleading results. Above the transition where short range ordering is maintained the order parameter oscillates in value slowly about zero so that very long runs (in excess of 10^7 configurations) must be used. It was concluded that the transition is first order in the presence of 'weak' boundaries (e.g. an infinite strip with 20 layer periodicity)

Suitable pair order parameters are difficult to devise. At short range molecules in successive neighbour shells occupy different orientations and the effects will tend to cancel. At long range the existence of grain boundaries between domains can seriously affect the value of a pair order parameter.

Dr. Joshi concentrated attention on the relative spatial ordering of N2 molecules and their ordering with respect to the underlying graphite lattice at temperatures above the transition between 35 K and 45 K, as studied by MD. A gradual loss of solid-like structure with increasing temperature was characterised but the equilibration was found to be very slow and very long simulations will be necessary before conclusive results are obtained.

Dr. Talbot also discussed the determination of the 3-dimensional order of N2 adsorbed on graphite. MD simulations showed that even at high temperatures in the fluid phase (~75 K) the molecules tend to lie essentially parallel to the surface and over the centre of the hexagons of C atoms. Orientational structure was examined in this case using the spherical harmonic expansion of the pair correlation function.

Dr. Nicholson pointed out that simulations using the grand ensemble MC method can be used to distinguish stable from metastable phases and is particularly suitable for adsorption systems. Work on the monolayer phases of Ar and Kr on graphite using effective potentials has shown that well characterised adsorbate phases are not stable in the expected regions of the phase diagram. The introduction of a substrate-mediated 3-body potential does not rectify this situation for Kr. It was suggested that substantially higher barrier heights between sites might bring experiment and simulation into better agreement.

Some of the factors affecting the barrier heights were discussed, in particular the importance of the repulsive part of the potential. The possibilities of obtaining improved understanding here using ab initio methods were discussed. Several points were raised about the importance of 3-body contributions ; for example it might be necessary to take account of quadrupole and of 4th order terms.

In the final session Dr. Heyes compared a number of methods for producing shear flow in liquids by MD, in particular the homogeneous shear method and another simple modification which introduces wall effects by the inclusion of reflection boundaries at the top and bottom of the basic cell. At low shear rates both methods yielded essentially the same viscosities despite large differences in the fluid structures. At large shear rates differences in the viscosities calculated using the two methods became evident and the homogeneous shear simulations exhibited a strong N-dependence. Much more systematic work on methodology in this area was required.

Lastly (and unfortunately under undeserved pressure from the clock) Dr. Whittle briefly discussed some recent developments in the MD simulation of sputtering events at solid surfaces.

Thanks are extended to all the contributers who helped towards the compilation of this report.

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Persons attending the workshop were:

Mr. D.Brown, Dr. J.H.R.Clarke, Mr. K.Doyle and Dr. M.Whittle, Chemistry Dept., U.M.I.S.T., Manchester.

Dr. G.Bushnell-Wye, Crystallography Dept., Birkbeck College, University of London.

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Computer Simulation of Aqueous Systems

A report on the visit of Dr. Mihail Mezei (Hunter College, New York) to Birkbeck College, London. *

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Introduction

Dr. Mihail Mezei visited the liquid group within the Department of Crystallography at Birkbeck College for one week at the beginning of March 1984. He has worked in Professor D. Beveridge's group for several years and has taken an active part in most projects on computer simulation of liquid water and aqueous solutions in which his laboratory specializes. As well as giving a seminar entitled 'Computer Simulation of Aqueous Solutions', we had several in-depth discussions on the following topics:

(i) Water models.
(ii) Free energy calculations.
(iii) Crystal hydrates.

Models for Water

The work of both laboratories depends critically on the potential energy functions we choose to model water molecule interactions. Dr. Mezei has used the MCY/CI model of Clementi and coworkers[1] whereas we have used the PE (polarisable electropole) model of Barnes et al[2] in one of its several forms. Dr. Mezei's seminar started with a summary of properties of water models MCY, ST2, SPC, TIPS2, TIPS4 and QPEN (see the review by Beveridge et al[3]). He also described a simulation of liquid water using the new CH1[4] potential of Clementi and Habitz. Unfortunately, the results of this simulation showed that while the pressure is far too high, the mean potential energy is much too low. This implies that it will be difficult to modify this potential (i.e. with addition of 3-body correction) to give both better pressure and potential energy. We also discussed the work over the

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* Partly sponsored by CCP5.

last two years to modify the PE model. To give better fits to (a) dimer surfaces, (b) second virial coefficients, (c) liquid phase r.d.f. and (d) properties of ices. The modifications we have used inlcude

(i) increasing the electropole terms to include dipole-octupole interactions and quadrupole-octupole;
(ii) modification of repulsive core from inverse 12th power to $^1/R^{7.3}$;
(iii) introduction of hydrogen---hydrogen repulsion;
(iv) Switching off polarisation energy.

As none of the models for water are completely satisfactory, both groups felt that it is important to compare results by use of more than one model.

Free energy Calculations

(SERC Grant Supported.)

(P. Barnes, J.L. Finney, J.M. Goodfellow and F. Sussman)

We have been attempting to calculate free energy differences for water in restricted environments. The ultimate aim is to calculate the free energy difference of water in an enzyme active site compared with that in bulk water. This restricted water has to be removed and replaced by a substrate molecule during enzyme catalysis. Our attempts to find a method of getting FE differences included use of the ratio overlap method[5] and umbrella sampling methods[6]. In order to check both these methods and the potential functions which were used, a control calculation was undertaken of the free energy difference for water at 55°C compared with 20°C and at 90°C compared with 55°. Both these differences could then be compared with experimental values[7]. The temperature ranges were chosen to give adequate overlap of the potential energy distributions. Several models for water were used including ST2, TIPS2 and PE.

Dr. Mezei is an ardent supporter of the method of thermodynamic integration (TI) for calculation of free energies[8]. The main reason for our not using this method is the number of state points which are required in order to get accurate integration. However, Dr. Mezei pointed out that with a small number of particles (~ $\lesssim$ 64) (there is no evidence for any strong dependence on a large number of particles) and the fact that the potential energy is one of the first properties to converge, runs of only 300K would be required for convergence within 2%. Thus one could afford to run the three simulations needed for the TI method.

Further discussions followed on our initial results to obtain the free energy differences in restricted environments. So far, we have only model environments such as spheres and ellipses without periodic boundary conditions. We have then introduced dipoles which model the electrostatic field of α-helices which are found in some proteins.

Crystal Hydrates

(SERC Grant Supported.)

Because of the problems of computer simulation in large heterogeneous systems of biological interest[10], we started to simulate systems for which we have experimental data i.e. crystal hydrates. It is essential to choose crystal hydrates in which all the solvent molecules are well-defined crystallographically for which high resolution X-ray data (and if possible neutron data as well) is required. This precludes most, if not all, protein crystals and leaves us with small amino acid[11] and nucleic acid[12] hydrates and a few medium sized systems much as vitamin B12 coenzyme[13] and dCpG-proflavin.

Both laboratories decided to study the dCpG proflavin hydrate initially. This structure was solved by H. Berman (Philadelphia) and S. Neidle (Kings College, London) with whom we have been collaborating. The solvent structure in this crystal has only slight static disorder and it is therefore relatively easy to compare the experimental with the simulated hydrogen bonded solvent networks. One simulation was undertaken using the MYC/CI potentials (at Hunter College) and another with PE potential (at Birkbeck College). Our initial results showed several regions of discrepancy between prediction and experiment[14].

Dr. Mezei has concentrated on the problem of optimizing the assignment of predicted solvent positions (which may change as the simulation progresses) to the experimentally determined solvent molecule positions. I have chosen to look at the problems of comparison of hydrogen bonded solvent networks whether they are between experiment and prediction or between predictions using different potentials. As we are interested in the total environment (including other solvent molecules and polar and apolar atoms from the macromolecules) of each solvent molecule, parameters (known as agreement factor[5,12,15]) have been devised in order to measure differences between such environments. We also discussed the most recent studies (at Birkbeck College) on the more disordered solvent networks[15].

Solution Studies

Dr. Mezei has or is about to publish a number of papers on aqueous solutions which are listed below. Further publications from Dr. Beveridge's laboratory are included in the 'references' section.

(1) "Monte Carlo Computer Simulation Study of the Hydrophobic Effect" by Ravishanker, Mezei and Beveridge, Faraday Symposium, Chem.Soc. 79-91, 1982.

(2) "Solvent-Separated Hydrophobic Interaction" by Beveridge et al in Structure and Dynamics: Nucleic Acids and Proteins, Ed. Clementi and Sarma, Adenine Press, 1983.

(3) "Aqueous Hydration of Benzene", Ravishanker et al, JACS in press 1984.

(4) "A pattern recogniton approach to the analysis of general features of solution" by Marchese et al, JACS in press 1984.

(5) "A Monte Carlo Study of aqueous hydration of formamide at 25°C" by Marchese et al, J.Phys.Chem. Submitted.

(6) "A Monte Carlo Computer Simulation Study of aqueous hydration of the glycine zwitterion at 25°C" by Mezei et al, J.Mol.Structure and Dynamics. Submitted.

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(15) F.Vovelle, J.M. Goodfellow, H.F.J. Savage, J.L. Finney and P.Barnes, Euro.Biophys.J. Submitted 1984

THE RECURRENCE TIME IN MOLECULAR DYNAMICS ENSEMBLES.

M. Schoen, R. Vogelsang, C. Hoheisel

Introduction

Most of the computer simulations on fluids use periodic boundary conditions to cope with the problems arising from the extreme smallness of the model systems (1). Nevertheless, all the quantities obtained by these simulations are limited through the actual number of particles and the size of the simulation box.

For the method of molecular dynamics (MD), this means in particular, that the time dependent phenomena can reliably be calculated only up to the recurrence time τ_{rec} of the model system given by the quotient of the box length L and the velocity of sound V_s.

$$\tau_{rec} = L / V_s$$

The various dynamic correlation functions f(t) which one is often interested in are therefore determinable directly only up to the value $f(\tau_{rec})$. For values larger than $f(\tau_{rec})$ one has inevitably to expect perturbations of f(t) owing to spurious correlations due to sound waves crossing the simulation box manifoldly (2). This is reasonable and can be read in text books and review articles (3,4). On the other hand, to our knowledge there is no published manifestation of these spurious effects, which possibly occur if one tries to pursue dynamic correlations much longer than the recurrence time of the system.

Perturbed mean square displacement of particles in a model mixture.

Clearly, in liquid - like systems, many of the dynamic correlation functions mentioned above decay very fast, and in MD runs with common accuracy there is no chance of observing such perturbations of the functions for times longer than τ_{rec}. However, the mean square displacement (MSD) of particles and related functions grow continuously in liquids and thus can provide distinct information about the long - time behaviour of the system.

During our studies on binary mixture systems we actually observed only one single case for which the MSD of both of the components was appreciably disturbed after the recurrence time. At first this interesting run was overlooked, as for this simulation we failed to supply the program with the regular input parameters and the program was interupted after the calculation of the MSD. We later noticed this remarkable behaviour of the two MSDs shown in Figure 1. The complete technical details of this run, the potentials used and the thermodynamic conditions are gathered together in Table 1. From the Figure 1 it is evident that the linear behaviour of both of the MSDs is disturbed beyond a time of 3.00×10^{-12} s. Considering this time as the actual recurrence time of the mixture system one easily finds a velocity of sound of 810 m/s, which is in good agreement with sound velocities in real liquids (5,6).

Subsequently we have attempted to reproduce this run with several very different start configurations (the original start configuration was lost) without any success: the MSD displayed a linear behaviour in every case, even if the function was computed for times larger than twice the recurrence time.

<u>Computation of the mean square displacements for systems of different box lengths.</u>

To study the effect of the recurrence time on the behaviour of the MSD in detail we performed the following two sorts of calculations (see Table 1):

(i) determination of the MSD for various times equal to and larger than the estimated τ_{rec} for a small 256 particle system

(ii) determination of the MSD for various times equal to and smaller than the estimated τ_{rec} for a large 2048 particle system.

The results obtained by these pilot simulations are presented in the Figures 2 and 3 for identical thermodynamic conditions: T= 111.5 k; ρ = 1.86 g/ml, and for both kinds of particles. The different lengths of the MSD are indicated in the Figures by vertical discontinuous lines. From these plots it seems to be evident that neither an appreciable shortening nor a strong lengthening of the MSD with respect to the recurrence time of the system leads to an altered behaviour of that function. Even for the case where these correlation functions have been pursued up to larger times than $2\tau_{rec}$, no perturbations can be observed: Figure 2. The indistinguishability of the curves guarantees nearly equal values for the self diffusion coefficients obtained from the slopes of the linear parts of the MSD. For comparison we list these values in Table 2. Although these values agree fairly well within the estimated error bars of 3 percent, a systematic trend in the coefficients is visible. Regarding the self diffusion coefficients (SDC) of the 2048 particle system determined by the longest MSD as the 'best' values, the SDC determined from functions out of the range of the permitted recurrence time interval lie below these values. In contrast, the SDC generated by the MSD functions ranging well in the interval of τ_{rec} agree exactly with the 'best' coefficients. This holds for the 256 particle system as well as for the 2048 particle system: see Table 2. However, attempting to obtain the SDC values from the linear branch of the perturbed MSD displayed in Figure 1, much larger values are discovered, which lie 16 percent above the 'best' values.

Discussion and conclusions

The present calculations indicate unambiguously that the time dependent correlation functions generated by MD simulations are influenced by periodic boundary conditions when computed for times appreciably larger than the recurrence time. However, normally the behaviour of these dynamic correlation functions is not drastically changed, so that quantities for the model liquid calculated from these correlation functions do not deviate largely from the 'true' ones. In those cases, for which remarkable structure changes of the computed correlation functions are observed for times larger than τ_{rec}, it is not possible to use the unperturbed part of these functions for the determination of any quantity of the model system, as we have shown for the example of the MSD.

We have at present no plausible explanation for the fact that in most cases ignoring the recurrence time limits does not lead to strange effects in the dynamic correlation functions comparable to those shown in Figure 1. Presumably such effects are predominantly to be expected when the averaging procedure is insufficient, say, the time origins exploited for the means are highly correlated. The perturbed MSDs displayed in Figure 1 are actually obtained by averaging over time origins which differed by only 1.0×10^{-13} s, whereas most of the test computations later performed involved time origins separated by more than 3.0×10^{-13} s. Nonetheless, extra simulations with an extremely small time origin distance revealed no other results than shown in Figure 2.

To ensure, however, that exploiting the observed disturbances of the MSD for a determination of the velocity of sound is a reasonable method, we additionally computed the dynamic structure factor of that system. The adiabatic velocity of sound is in principle accessible from the Brillouin peaks of the dynamic structure factor $S(k,\omega)$ in the hydrodynamic case (7).

As molecular dynamics calculations are again limited to not too small values of k and to times shorter than τ_{rec}, the hydrodynamic case can only approximately be reached. As we are here only interested in the frequency distance between the first side peak and the main peak of $S(k,\omega)$, it is sufficient to determine this function up to the side peak.

We show the results of our simulation for a 2048 particle system and two k - values in Figure 4. Plotted is the total dynamic structure factor $\bar{S}(k,\omega)$, which does not distinguish between the different kinds of particles in the mixture.

The velocity of sound estimated by the time position of the Brillouin peak amount to 801 m/s for $k = 0.4665\,\sigma^{-1}$ and to 751 m/s for $k = 0.9330\,\sigma^{-1}$. These numbers agree sufficiently well with the value given above.

Acknowledgement.

All the calculations have been performed on the Cyber 205 vector machine of the Rechenzentrum der Ruhr - Universität Bochum.

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Table 1

Technical details of the simulations of the mixture:

A. Lennard-Jones potential parameters

interaction type	$\epsilon k^{-1}/K$	$\sigma/Å$
1-1	94.297	3.591
1-2	141.445	"
2-2	212.167	"

B. Thermodynamic state

T/K	111.5
p/bar	100
$\rho/g\ cm^{-3}$	1.860 ($m_1=m_2=61.875$ a.u.)
x	0.500

C. Molecular dynamics

	run showing perturbed MSD	test runs
number of particles	256	256; 2048
box length	6.734 σ	6.734 σ ; 13.468 σ
time step	1×10^{-14}s	1×10^{-14}s
number of steps in equilibrium	2200	2000-8000 (12000 for S(k,ω
cut-off radius	2.5 σ	2.5 σ
start configuration	liquid	random, liquid, f_{cc}-lattice

D. Averaging process for the mean-square displacement (MSD)

	perturbed MSD	test MSD
number of time origins	60	60
minimal distance between time origins	1×10^{-13}s	1×10^{-13}s - 15×10^{-13}s
total time for the MSD	480×10^{-14}s	240×10^{-14}s - 1000×10^{-14}s

E. Recurrence times

particle number	assuming V_s=1000 ms^{-1}	using the V_s-value from this work; 810 ms^{-}
256	2.42×10^{-12}s	3.00×10^{-12}s
2048	4.84×10^{-12}s	6.00×10^{-12}s

Table 2

Self diffusion coefficients (SDC):

N=256	from perturbed MSD	from test MSD		
	$\Delta t^{*)}=480$	$\Delta t=300$	$\Delta t=640$	$\Delta t=1000$
$D_1/10^{-5}\mathrm{cm}^2\mathrm{s}^{-1}$	2.48	2.17	2.04	1.98
$D_2/10^{-5}\mathrm{cm}^2\mathrm{s}^{-1}$	2.08	1.75	1.61	1.55

N=2048	from test MSD		
	$\Delta t=180$	$\Delta t=280$	$\Delta t=480$
$D_1/10^{-5}\mathrm{cm}^2\mathrm{s}^{-1}$	2.24	2.17	$2.13^{**)}$
$D_2/10^{-5}\mathrm{cm}^2\mathrm{s}^{-1}$	1.88	1.82	$1.81^{**)}$

*) total time interval for the computation of the MSD: $\Delta t/10^{-14}\mathrm{s}$

**) 'best' value

Figure 1

Mean square displacement (MSD) of particles of a Lorentz-Berthelot model mixture. Upper curve: component 1, lower curve: component 2. The vertical line gives the time where the perturbation of the curves becomes visible.

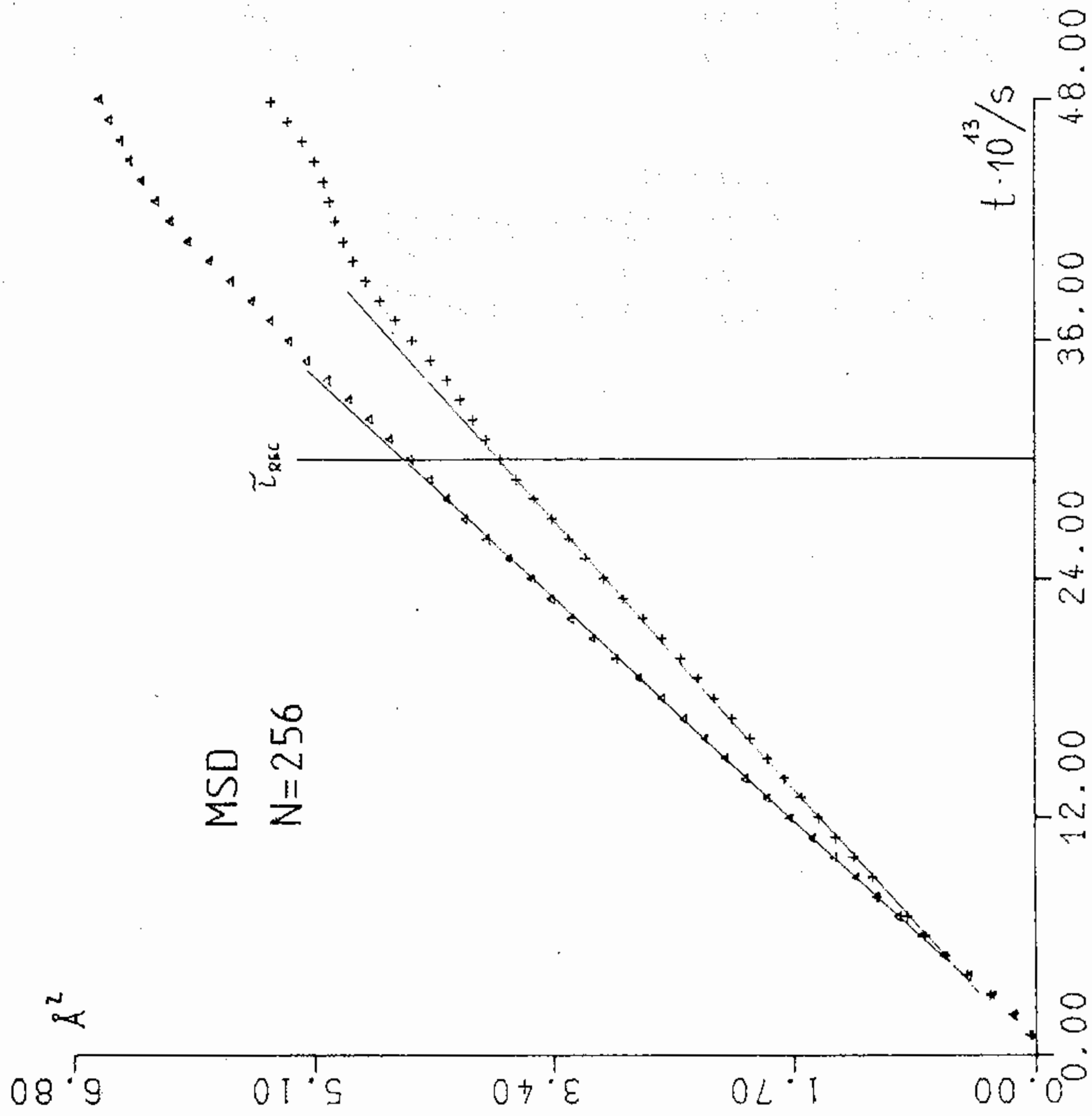

Figure 2

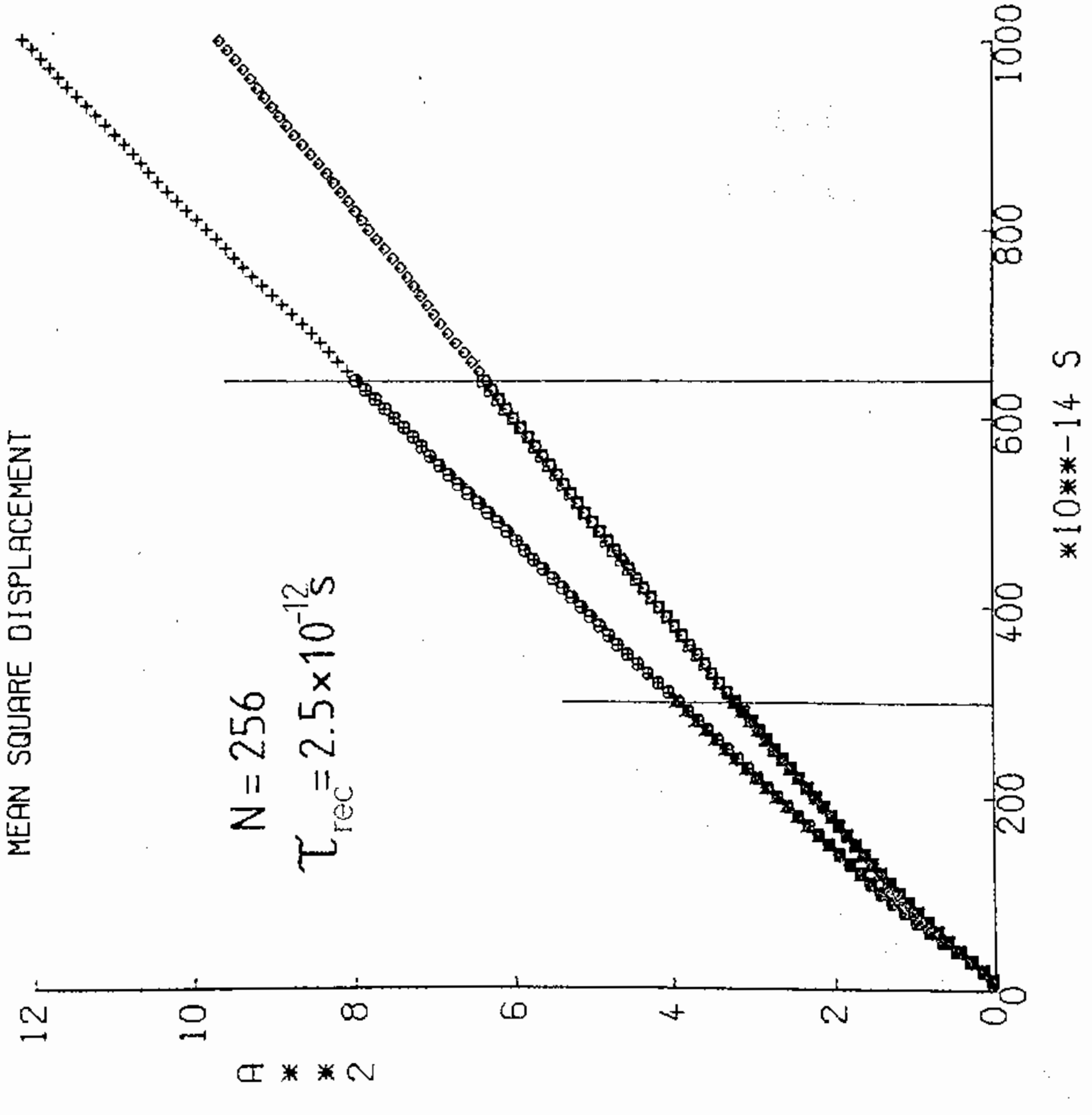

FIG. 2 As in FIG. 1, but for three lengths of the MSD. The lengths are marked by vertical lines.

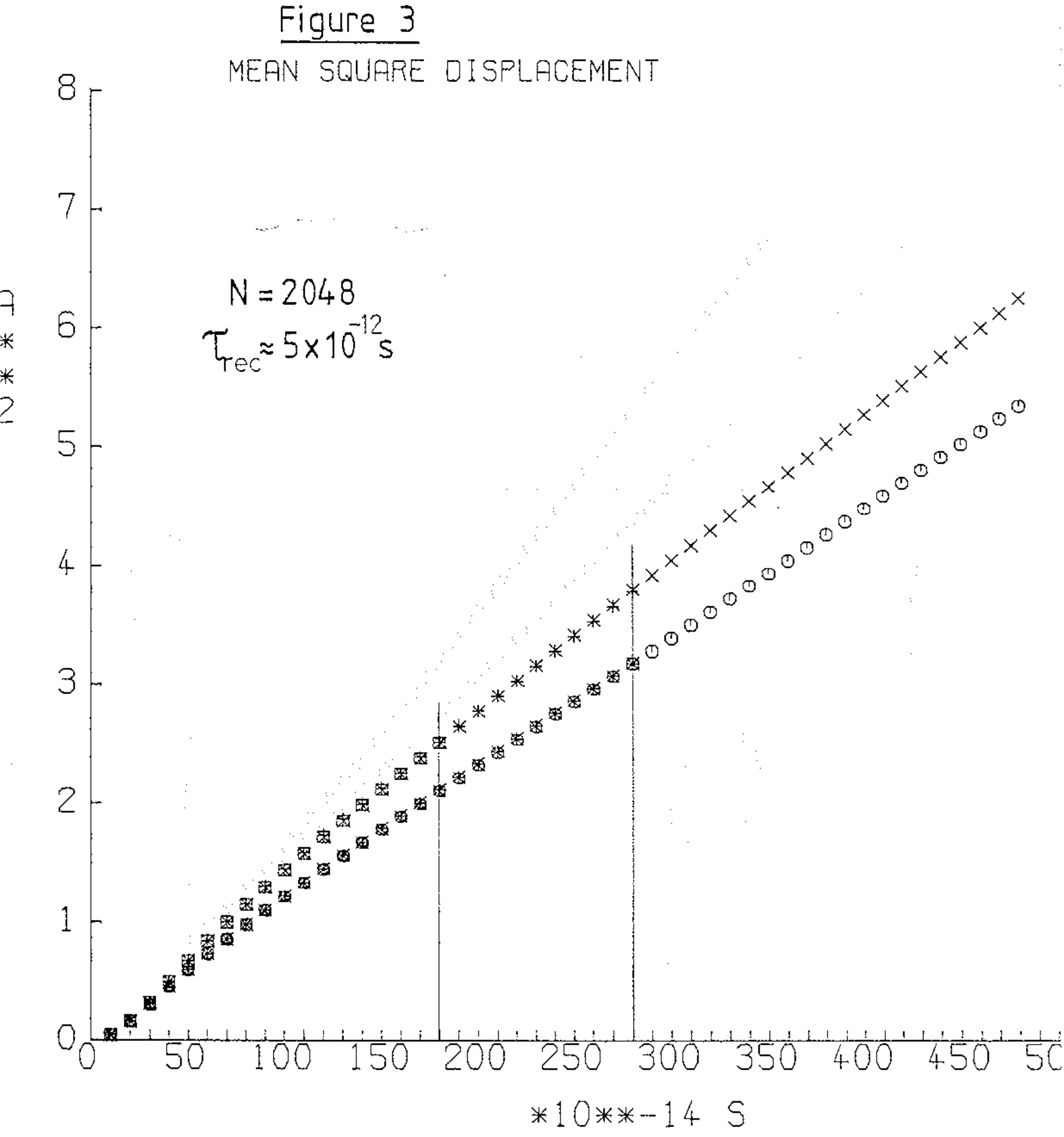

FIG. 3 As in FIG. 2, but for a 2048 particle system. The vertical lines indicate the lengths of the MSD.

Figure 4

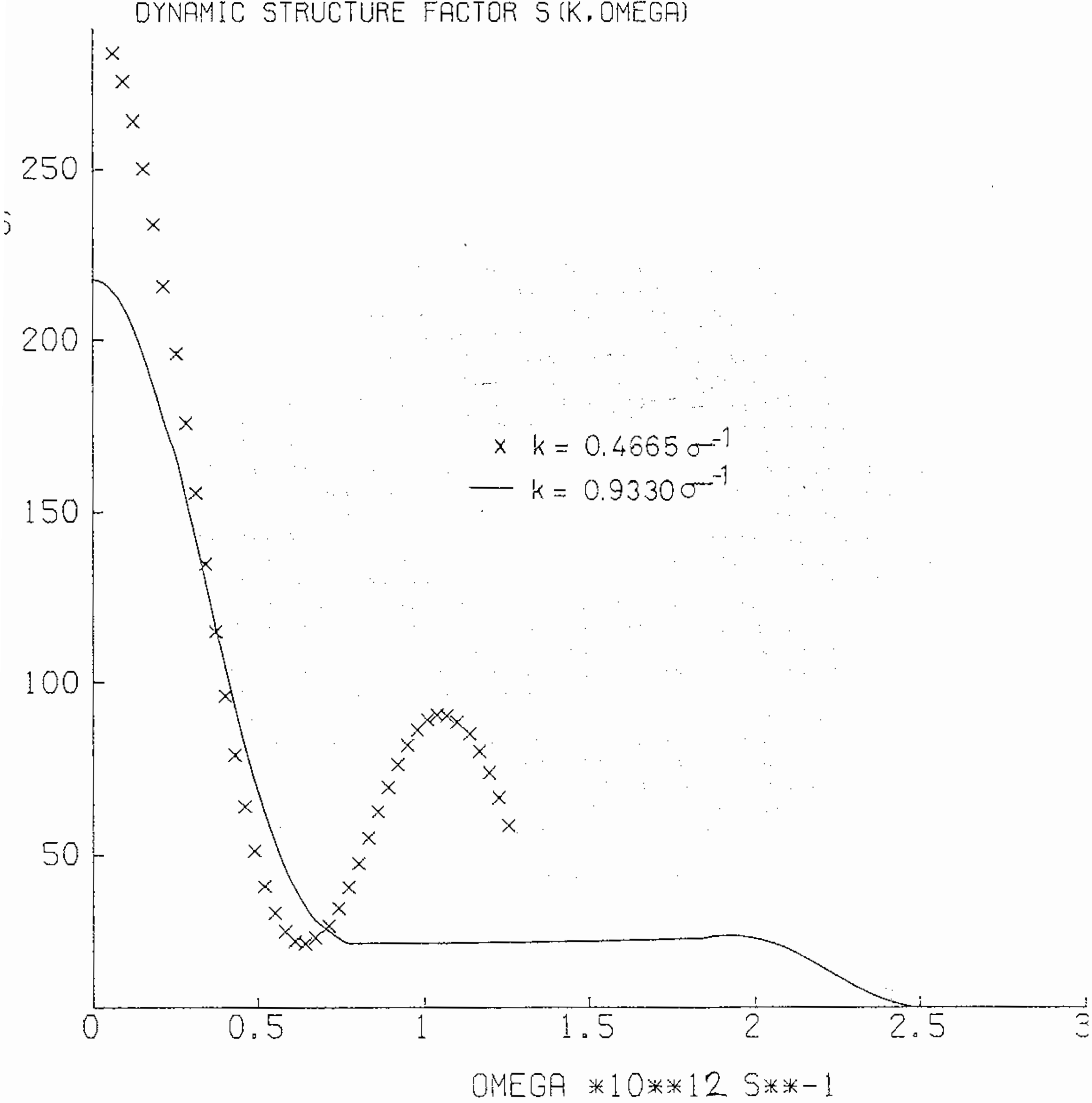

FIG. 4 Total dynamic structure factor for the mixture system at $k=0.4665\,\sigma^{-1}$, & $k=0.9330\,\sigma^{-1}$ determined for 2048 particles.

THE DYNAMICS OF SPHERICAL GAUSSIAN WAVEPACKETS.

W. Smith & K. Singer.

The study of the dynamics of gaussian wavepackets represents an attempt to introduce some of the quantum effects absent from a conventional molecular dynamics simulation through a semiclassical model. The use of gaussian wavepackets is intuitively appealing; they provide a model which is very similar to classical particles in many respects but allow some insight into quantum effects (a feature exploited in many introductory texts on quantum mechanics). In addition, the gaussian waveform is stable; a given wavepacket will remain gaussian, without spreading, if the local potential experienced by the gaussian is of second or lower order in the spatial coordinates. Lastly, the gaussians have the computational advantage that they lead to integrals which in many cases are easily evaluated in a closed form. In common with other wave functions they cannot, of course, be integrated over singularities $\sim r^{-n}$ (n>2), but this difficulty can be overcome (see below).

The methods that we have employed are based on the work of E. J. Heller (1), who investigated the use of gaussian wavepackets as a means of solving the time dependent Schroedinger equation in scattering problems. The methods were adapted by N. Corbin and K. Singer (2) for use in semiclassical molecular dynamics of many - body systems. It is one of these methods that we will describe here, though restricted to the case of spherical gaussian wavepackets. This, we believe, offers advantages of simplicity and speed over the more complicated general gaussian (2), with no apparent disadvantage. In the spirit of the CCP5 Newsletter, we will not discuss results at length; these will appear elsewhere. Instead we will describe the foundation and methodology in some detail.

The functional form of a gaussian wavepacket is given by:

$$\phi_j(\underline{r}_j,t) = \exp\left\{i\hbar^{-1}\left(A_j(\underline{r}_j-\underline{R}_j)^2+\underline{P}_j\cdot\underline{r}_j+D_j\right)\right\} \qquad \langle 1\rangle$$

where: A_j, $\underline{R}_j$, $\underline{P}_j$ & D_j are time dependent parameters of particle j and:

A_j is a complex scalar parameter determining the width of the gaussian.

D_j is a complex scalar parameter determining the phase and normalisation of the wavepacket. The normalisation of the wavepacket requires that:

$$\pi^{3/2}\exp(i\hbar^{-1}(D_j-D_j^*))/(i\hbar^{-1}(A_j-A_j^*)) = 1 \qquad \langle 2 \rangle$$

$\underline{R}_j$ is a real vector locating the centre of the wavepacket.

$\underline{P}_j$ is a real vector giving the momentum of the centre of the wavepacket, which is to be regarded as the classical part of the momentum. (We will assume subsequently that the classical relationship:

$$\underline{P}_j = m\dot{\underline{R}}_j \qquad \langle 3 \rangle$$

holds for the motion of the centre of the wavepacket).

The general wavefunction for a system of N particles we assume to be a Hartree product of one - particle gaussians:

$$\Psi(\underline{r}_1,\ldots,\underline{r}_N,t) = \prod_{j=1}^{N}\phi_j(\underline{r}_j,t) \qquad \langle 4 \rangle$$

which implies the neglect of (anti -) symmetrisation required in a fully quantum mechanical treatment.

The product function <4> appears to neglect inter - particle correlations: there is no explicit dependence on coordinate differences $\underline{r}_j - \underline{r}_\ell$. Since however, the wave function is time dependent, both position and size of a wavepacket respond to the instantaneous potential field produced by the surrounding particles. Correlation effects are therefore at least partly taken into account.

Our aim is to solve, as accurately as possible, the time dependent Schroedinger equation:

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad \langle 5\rangle$$

where: $$\hat{H} = \sum_{j=1}^{N}\left\{-\frac{\hbar^2}{2m}\nabla_j^2 + \frac{1}{2}\sum_{\ell\neq j}^{N} u_{j\ell}\right\}$$

& $-\frac{\hbar^2}{2m}\nabla_j^2$ is the single particle kinetic energy operator.

& $u_{j\ell}$ is the inter - particle pair potential corresponding to pairwise additive central forces.

There are two methods available for solving the time dependent Schroedinger equation approximately. Both are due to Heller and consequently, are known to us as the HELLER I and HELLER II methods. We do not propose to discuss the HELLER I method here, except to say that it uses a locally quadratic approximation to the potential field acting on each gaussian. The Schroedinger equation can then be written as a set of linear equations in the time derivatives of the parameters of the one - particle wavefunctions. The method works well only when the potential is harmonic or nearly so, i.e. for crystals near T = 0 K. It appears to fail at higher temperatures (7).

The HELLER II method is based upon a variation principle due originally to Dirac, Frenkel and McLachlan (3) (the 'DFM principle'). This principle minimises the 'mean squared' difference between the left and right hand sides of the time dependent Schroedinger equation <5> and is expressed in the form:

$$I(\Psi,\theta) = \int(\hat{H}\Psi - i\hbar\theta)(\hat{H}\Psi - i\hbar\theta)^{*}\,dv \qquad \langle 6\rangle$$

$$= \text{minimum}$$

where : $\Theta = \partial\Psi/\partial t$

The integral is clearly zero when the Schroedinger equation <5> is exactly satisfied, but when this is only approximately so, the integral is quadratic in in the error in Θ, $\delta\Theta$. Thus if we minimise the integral <6> with respect to Θ we will optimise the solution of the Schroedinger equation for any given trial wavefunction.

If the trial wavefunction is a Hartree product of N gaussian wavepackets, each of which is defined by a set of time dependent parameters λ_{jm}, where λ_{jm} is one of $A_j, D_j, P_j^x, P_j^y, P_j^z, R_j^x, R_j^y, R_j^z$, the DFM principle may be expressed as:

$$\int \left(\frac{\partial\phi_j}{\partial\lambda_{jm}}\right)^{*} \left(\bar{H}_j\,\phi_j - i\hbar\,\frac{\partial}{\partial t}\phi_j\right) = 0 \qquad \text{<7>}$$

where: $\lambda_{jm}(t) \in \left\{A_j, D_j, P_j^x, P_j^y, P_j^z, R_j^x, R_j^y, R_j^z\right\}$

The operator $\bar{H}_j$ appearing in equations <7> is the one - particle Hamiltonian operator defined by <8a> in which, as a consequence of using the Hartree approximation, the potential term $\bar{V}_j$ is written as a sum of modified potentials <8b>.

$$\bar{H}_j = -\frac{\hbar^2}{2m}\nabla_j^2 + \bar{V}_j(\underline{r}_j) \qquad \text{<8a>}$$

$$\bar{V}_j(\underline{r}_j) = \sum_{\ell\neq j}^{N}\int \phi_\ell^{*}(\underline{r}_\ell)\,u_{j\ell}(|\underline{r}_j-\underline{r}_\ell|)\,\phi_\ell(\underline{r}_\ell)\,d^3\underline{r}_\ell \qquad \text{<8b>}$$

Since $(\partial\phi_j/\partial\lambda_{jm})^{*}$ turns out to be proportional to 1, $(\underline{r}_j-\underline{R}_j)$ or $(\underline{r}_j-\underline{R}_j)^2$, the set of equations <7> is in fact equivalent to the requirement that the zeroth, first and second moments of the difference between $\bar{H}_j\phi_j$ and $i\hbar\,\partial\phi_j/\partial t$ vanish (4). That is, the set of equations <7> may be replaced by the equivalent set <9>:

$$\int \phi_j^* \left(\bar{H}_j - i\hbar \frac{\partial}{\partial t}\right) \phi_j \, d^3\underline{\xi}_j = 0 \quad \text{<9a>}$$

$$\int \phi_j^* \underline{\xi}_j \left(\bar{H}_j - i\hbar \frac{\partial}{\partial t}\right) \phi_j \, d^3\underline{\xi}_j = 0 \quad \text{<9b>}$$

$$\int \phi_j^* \xi_j^2 \left(\bar{H}_j - i\hbar \frac{\partial}{\partial t}\right) \phi_j \, d^3\underline{\xi}_j = 0 \quad \text{<9c>}$$

where: $\underline{\xi}_j = (\underline{r}_j - \underline{R}_j)$ and $\xi_j^2 = |(\underline{r}_j - \underline{R}_j)|^2$.

After substitution of the explicit forms <1> and<5> into the integrals <9>, the DFM principle produces the following sets of single - particle equations, which we identify as the equations of motion of the N particle system:

$$\left(\dot{A}_j + \tfrac{2}{m} A_j^2\right)[\xi_j^2] + \left(\dot{D}_j + \dot{\underline{P}}_j \cdot \underline{R}_j + P_j^2/2m - i\hbar 3A_j/m\right) + [\bar{V}_j] = 0 \quad \text{<10a>}$$

$$\left(\dot{P}_j^\alpha - 2A_j \dot{R}_j^\alpha + 2A_j P_j^\alpha\right)[(\xi_j^\alpha)^2] + [\xi_j^\alpha \bar{V}_j] = 0 \quad \text{<10b>}$$
$$\alpha = x, y, z$$

$$\left(\dot{A}_j + \tfrac{2}{m} A_j^2\right)[\xi_j^4] + \left(\dot{D}_j + \dot{\underline{P}}_j \cdot \underline{R}_j + P_j^2/2m - i\hbar 3A_j/m\right)[\xi_j^2] + [\xi_j^2 \bar{V}_j] = 0 \quad \text{<10c>}$$

In the above equations the terms enclosed in square brackets represent expectation integrals over the gaussian wavepackets indicated by the suffices, e.g:

$$[\xi_j^2] = \int \xi_j^2 \, \phi_j^* \, \phi_j \, d^3\underline{\xi}_j \qquad \langle 11 \rangle$$

and account has been taken of the identity : $[\xi_j^\alpha] = 0$.

The integrals $[\bar{V}_j]$, $[\xi_j^\alpha \bar{V}_j]$, and $[\xi_j^2 \bar{V}_j]$ are obtained from <8b>; for example the basic potential energy integral is given by:

$$[\bar{V}_j] = \sum_{\ell \neq j}^{N} \int \phi_j^* \phi_\ell^* \, u_{j\ell}(|\underline{R}_{j\ell} + \underline{\xi}_j - \underline{\xi}_\ell|) \, \phi_j \, \phi_\ell \, d^3\underline{\xi}_j \, d^3\underline{\xi}_\ell \qquad \langle 12 \rangle$$

where: $u_{j\ell}$ is the pair potential function and $\underline{R}_{j\ell} = \underline{R}_j - \underline{R}_\ell$.

The potential function $u_{j\ell}$ is implicitly a Lennard - Jones function, but the usual 12 - 6 form of the potential is not suitable for integration. Instead we have used an approximation to the Lennard - Jones function proposed by Singer (5):

$$u_{j\ell}(r_{j\ell}) = \sum_{k=1}^{2} C_k \exp(-d_k \, r_{j\ell}^2) \qquad \langle 13 \rangle$$

where C_k and d_k are parameters adjusted so as to optimise the fit to the desired Lennard - Jones form over the effective range of interaction. With this modification we may evaluate the integral $[\bar{V}_j]$ as:

$$[\bar{V}_j] = \sum_{\ell \neq j}^{N} \sum_{k=1}^{2} C_k \, E_{j\ell k}^{3/2} \exp(-d_k \, E_{j\ell k} \, R_{j\ell}^2) \qquad \langle 14 \rangle$$

where: $E_{j\ell k} = (1 + d_k (B_j^{-1} + B_\ell^{-1}))^{-1}$

7

& $$B_j = -i\hbar^{-1}(A_j - A_j^*)$$

The integrals $[\xi_j^\alpha \bar{V}_j]$ and $[\xi_j^2 \bar{V}_j]$ may be obtained from <14> by simple differentiation:

$$[\xi_j^\alpha \bar{V}_j] = (2B_j)^{-1} \frac{\partial}{\partial R_j^\alpha}[\bar{V}_j] \qquad \text{<15>}$$

$$[\xi_j^2 \bar{V}_j] = (2B_j)^{-2} \frac{\partial}{\partial \underline{R}_j} \cdot \frac{\partial}{\partial \underline{R}_j}[\bar{V}_j] + 3(2B_j)^{-1}[V_j] \qquad \text{<16>}$$

To provide the solution to the Schroedinger equation we integrate the equations <10> forward in time. At this stage the problem becomes essentially one of molecular dynamics.

If we look first at equation <10b> and bear in mind the relation <3> we see at once that this is readily written in a simpler form:

$$P_j^\alpha = -[\xi_j^\alpha \bar{V}_j]/[(\xi_j^\alpha)^2] \qquad \text{<17>}$$

This equation may be easily integrated forward in time by any of the usual molecular dynamics algorithms. Integration of this equation gives us the position ($\underline{R}_j$) and momentum ($\underline{P}_j$) of the centre of the gaussian wavepacket at any given timestep. It should be noted however that while this equation appears simple, it is, through the integrals $[\xi_j^\alpha \bar{V}_j]$ and $[(\xi_j^\alpha)^2]$, dependent upon all the parameters defining the wavepacket. The motion of the wavepacket centres is therefore definitely not classical. In this respect the HELLER II method differs from the HELLER I method, where the centres of the wavepackets follow classical trajectories.

Equations <10a> and <10c> are best tackled together. By combining the two we may readily produce an equation of motion involving the A_j parameters alone:

$$(\dot{A}_j + \tfrac{2}{m}A_j^2)([\xi_j^4] - [\xi_j^2]^2) + ([\xi_j^2\bar{V}_j] - [\xi_j^2][\bar{V}_j]) = 0 \qquad \langle 18\rangle$$

This first order equation may be integrated directly, but we favour a reparameterised form, which we know as the Z- algorithm (6). This involves the substitution :

$$A_j = m\,\dot{Z}_j/(2Z_j) \qquad \langle 19\rangle$$

which results in the second order equations:

$$\ddot{Z}_j' = 2\,W_j\,Z_j'/m \qquad \langle 20a\rangle$$

$$\ddot{Z}_j'' = 2\,W_j\,Z_j''/m \qquad \langle 20b\rangle$$

where: $W_j = -([\xi_j^2\bar{V}_j] - [\xi_j^2][\bar{V}_j])/([\xi_j^4] - [\xi_j^2]^2)$

in which we have conveniently separated out the real (Z_j') and imaginary (Z_j'') parts of the parameter Z_j. This form of the equation of motion for the A_j parameter is also easily integrated forwards in time by conventional molecular dynamics methods. The values of the A_j parameters are readily obtained at all timesteps from the definition <19>.

Armed with a knowledge of all the other time dependent parameters at each timestep, we may integrate equation <10a> to obtain the value of each D_j parameter. If we are not interested in the phase, which is determined by the real part of D_j, we may opt instead to evaluate only the imaginary part of D_j using the normalisation condition <2>.

The above description outlines the basic molecular dynamics scheme for a system of N spherical gaussian wavepackets, how then may we initialise a molecular dynamics simulation? To begin with we may set the positions of the gaussian centres ($\underline{R}_j$) on a FCC lattice or we may use an 'aged liquid' configuration as may be done in conventional molecular dynamics.

The momenta of the gaussian centres ($\underline{P}_j$) we may set randomly, with removal of bulk motion and scaling to the desired temperature, as in classical molecular dynamics. However we note that there is a problem associated with this procedure, as it is apparent that not all the kinetic energy of the gaussian wavepackets is carried by their centres alone. Therefore this casual association of the temperature with the kinetic energy of the centres is open to question. This is not the only problem associated with temperature either, as the example simulation given below will indicate. However, in the absence of a clearer understanding, we adopt the convention of interpreting the momentum of the centres of the wavepackets as defining the classical kinetic energy, which in turn, defines the temperature of the system. The problem of the true temperature is shelved.

The initialisation of the A_j parameters, which define the width of the gaussians, is a novel feature of this simulation method. Remembering that the parameters are complex, we first set the real part of each to zero (and rely on the subsequent dynamics to produce realistic values). The imaginary parts are obtained through a minimisation of the system energy (kinetic plus potential), with respect to A_j, at the start of the simulation. We use a simple 'steepest descent' method. In the case where a FCC lattice is used as the starting configuration, this means that all A_j parameters have the same value, but obviously, when an 'aged liquid' configuration is used, each gaussian has a unique A_j value. As for the D_j parameters; the real parts may again be set to zero, while the imaginary parts are fixed by the normalisation condition <2>.

Lastly we must set the initial values of the Z_j and $\dot{Z}_j$ parameters required for the integration of the equations of motion. The Z_j parmeters may be arbitrarily assigned and we chose to set both real and imaginary parts to unity. The $\dot{Z}_j$ are fixed by the initial choice of the A_j parameters and must be assigned as: $\dot{Z}_j' = -2A_j''/m$ and $\dot{Z}_j'' = 2A_j'/m$. The starting conditions are summarised in Table 1.

Thus far we have outlined the essentials of a semiclassical simulation method. The description would however be incomplete without some comments on the parameterisation of the pair potential <13>. At first the obvious choice of the parameters C_α and d_α

was that which gave the best fit to the Lennard - Jones (12 - 6) function appropriate to the system of interest (as had been done in (2) and (7)). However in the light of results and on reflection, we believe that the parameters should be adjusted so as to obtain close agreement between the Lennard - Jones function and the mean pair potential between two gaussian wavepackets <21>.

$$[\bar{\bar{V}}_{j\ell}] = \sum_{\lambda=1}^{2} c_\lambda \bar{E}_{j\ell\lambda}^{3/2} \exp(-d_\lambda \bar{E}_{j\ell\lambda} R_{j\ell}^2) \qquad <21>$$

where: $\bar{E}_{j\ell\lambda} = (1 + 2d_\lambda \bar{B}_j^{-1})^{-1}$

$\bar{B}_j$ is the mean of all B_j values. It is this function, the instantaneous value of the pair potential, which plays the role of the empirical effective pair potential. The problem arises because in the usual applications of Lennard - Jones and other effective pair potentials one assumes the system to consist of point particles, whereas here we are dealing with the extended interaction sites produced by the wavepacket. The two are not equivalent mathematically, whatever their functional form.

This prescription does in fact lead to better agreement between simulated and experimental values of the potential energy of the system, but it is at the price of a more complicted procedure. Through the term $\bar{E}_{j\ell\lambda}$ (cf. equation <14>) the interaction potential is dependent upon the mean width of the gaussian wavepackets. Thus before we can begin our simulation in earnest we must have a good idea of the value of the average width parameter. Therefore it is necessary to perform preliminary runs to obtain a potential consistent with the width parameters in the final simulation. This is an inconvenient feature of the method, but in most circumstances, fortunately, the sensitivity to the width parameter is not great.

One last comment on the semiclassical method is in order. Strange as it may seem, it does not appear to be possible to constrain our simulations to a prescribed temperature, as is done in a conventional classical simulation. If we attempt to do so, by scaling the classical momenta ($\underline{P}_j$) in the usual way, we find that no equilibrium condition results. Instead the kinetic energy of the gaussian wavepackets grows without limit, which in turn produces an upward drift in energy. This is the problem we hinted at earlier and it appears to be intrinsically bound up in the problem of defining the temperature of the semiclassical system, but it is not at present understood.

This is not to say however, that there is no solution to this problem. In the meantime we have adopted the suggestion of N. Corbin (7) and abandoned temperature scaling altogether. When this is done the system does eventually achieve its own equilibrium after a reasonable period of time, though not at the temperature one may have desired. If the original crystal melts the temperature invariably falls to some equilibrium value below the initial value. Thus by the simple expedient of starting at a higher temperature than that required it is possible, with a little experience, to arrive at a temperature close to that desired. It is also possible to re - scale the initial classical kinetic energy at the start of subsequent runs.

We conclude this article with a short examination of a typical run of our semiclassical MD program. The run presented in Table 2 is a short simulation of 108 Neon atoms with a molar volume of 1.65E-5 m^3 and at a 'temperature' of 33 K. The potential parameters used were C_1=9.04E-18 J, C_2=-2.71E-21 J, d_1=1.37E20 m^{-2} and d_2=1.59E19 m^{-2}, corresponding to the Lennard - Jones parameters ε / k_B = 36.8 K, σ = 2.789E-10 m and a mean square width of 3.0E-22 m^2. The timestep used was very short by normal MD standards at 8.0E-16 s. Such a short timestep is necessary because of the rapid rate of change of the gaussian width parameters A_j.

We note first of all, the fall in temperature expected as the simulation proceeds. Starting from a FCC lattice with the initial temperature of 80 K, the system equilibrates itself quite quickly to about 33 K. Nevertheless the quantum kinetic energy remains high throughout the simulation; showing what is perhaps the least satisfactory aspect of these simulations. The expected quantum correction for the kinetic energy is approximately 30 percent of the classical kinetic energy for Neon, but here it is of the order 100 percent. The high quantum component of the kinetic energy appears to be inherent in the chosen trial function and probably can only be overcome by a more flexible form, perhaps involving a linear combination of two or more gaussian wavepackets.

A more pleasing aspect of the simulation is the very good energy conservation that is maintained after the first 500 timesteps. The total quantum energy <QTE> remains fixed at -592.0 J/mole to within 8.0E-2 J/mole for the last 3000 timesteps (approximately 3 ps).

The 'classical potential energy' <CPE> is in fact merely the potential energy of point particles sited at the centres of wave packets, interacting with the potential <13> with the parameters given above. It serves to show that it is significantly different from the 'quantum potential energy' <QPE> calculated with the same potential function by <12>.

One effect we might expect to be present, is the tendency for the gaussian wavepackets to spread in the course of the simulation. This is expected since the local potential experienced by the gaussians is likely to be far from quadratic. After an initial period during which the average width of the gaussians, which is measured by the parameter <WXX>, decreases, there does appear to be some tendency for the gaussians to spread thereafter. However, the data presented here are inconclusive. Other runs indicate that the spreading during 8 ps is minimal.

In Figure 1, we present the 'classical' radial distribution function obtained from this simulation. It is calculated from the relative positions of the centres of the wavepackets. (A full calculation involving integration over all distances between points in two wavepackets is possible, but it is likely to be very expensive!). The significant thing to note here is that there is apparently a degree of penetration of the hard sphere radius of the Neon atoms, (the closest approach is approximately 0.85σ). Qualitatively this behaviour is correct.

Lastly, by way of a demonstration that the method can provide data on time dependent effects, we present a plot of the velocity autocorrelation function in Figure 2. The function is calculated from the motion of the wavepacket centres and has a normal appearance.

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TABLE 1. Initialisation of G.W.P. M.D. Method.

$\underline{R}_j$ - set on FCC lattice or 'aged liquid' Configuration.

$\underline{P}_j$ - set randomly, remove bulk motion, scale to temperature.

A_j - set real parts to zero, set imaginary parts to give the minimum total energy for the system at the start.

D_j - set using A_j and normalisation condition <2>.

Z_j - set both real and imaginary parts to unity.

$\dot{Z}_j$ - set real part to $-2A_j''/m$, imaginary part to $2A_j''/m$. (A_j'' is the imaginary part of A_j).

TABLE 2. Example Run of G.W.P. M.D. Program.

Time	<CPE>	<CKE>	<CTE>	TEMP	MELT
Step	<QPE>	<QKE>	<QTE>	<WXX>	FACT
1	-1799.0	997.8	-801.2	80.0	108.0
	-1750.5	1159.0	-591.5	4.648	
500	-1761.5	438.2	-1323.2	35.1	23.7
	-1456.0	863.9	-592.0	3.034	
1000	-1746.5	387.9	-1358.6	31.1	7.1
	-1437.1	845.1	-592.0	2.983	
1500	-1753.4	421.6	-1331.9	33.8	1.8
	-1505.7	913.6	-592.0	2.698	
2000	-1769.6	430.0	-1339.5	34.4	1.1
	-1521.3	929.4	-592.0	2.884	
2500	-1765.1	415.9	-1349.1	33.3	0.9
	-1516.5	924.6	-591.9	2.955	
3000	-1760.6	402.3	-1358.4	32.3	0.6
	-1491.0	899.0	-592.0	2.953	
3500	-1753.0	398.6	-1354.4	32.0	0.5
	-1467.3	875.4	-591.9	3.349	
4000	-1765.7	411.0	-1354.7	33.0	0.3
	-1470.2	878.0	-592.2	3.539	
4500	-1760.3	414.0	-1346.3	33.2	0.6
	-1471.5	879.6	-591.9	3.305	
5000	-1751.3	399.6	-1351.7	32.0	2.4
	-1449.5	857.5	-592.0	3.163	

Note: All energies given in J/mole.,
(potential energies do not include a long range
correction of approximately -119 J/mole).
<WXX> in units of 1.0E-22 m^2 .
Temperature is in K.
Timestep is 8.0E-16 s.

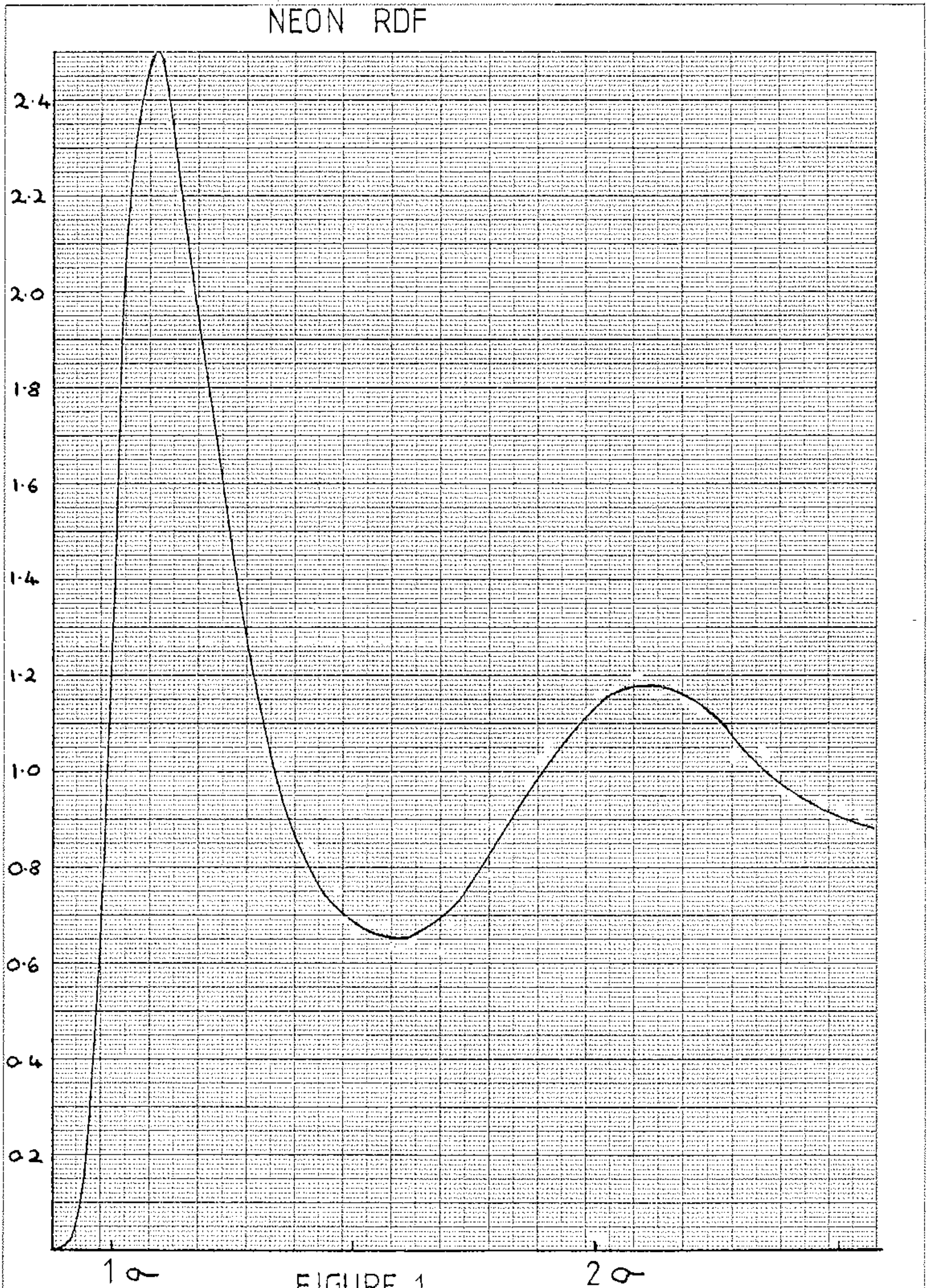


FIGURE 1

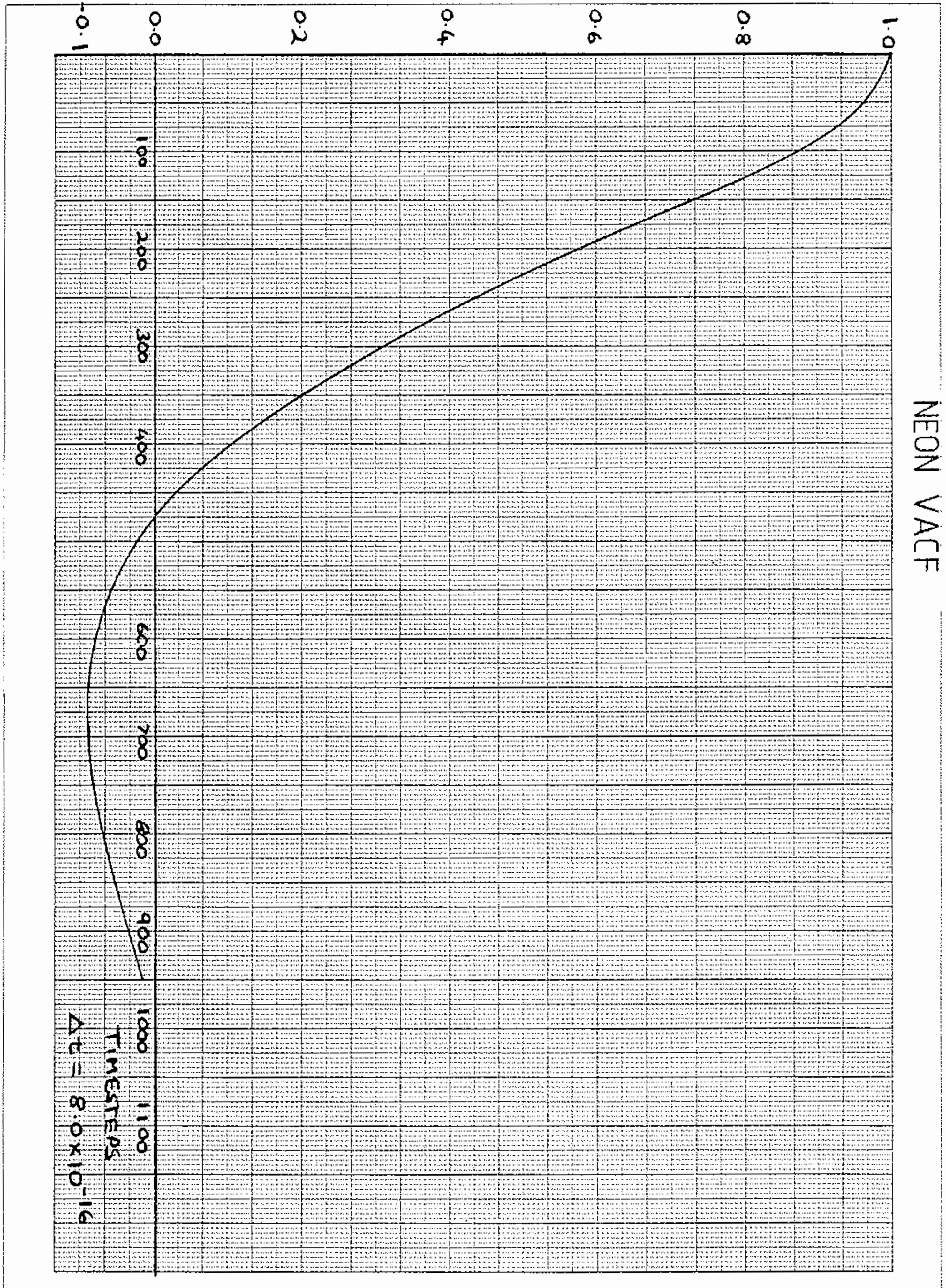

NEON VACF
1.0
0.8
0.6
0.4
0.2
0.0
-0.1
100
200
300
400
600
700
800
900
1000
1100
TIMESTEPS
Δt = 8.0×10-16

FIGURE 2

VACANCY ORDERING IN $CaMnO_{3-x}$.

S. C. Parker.

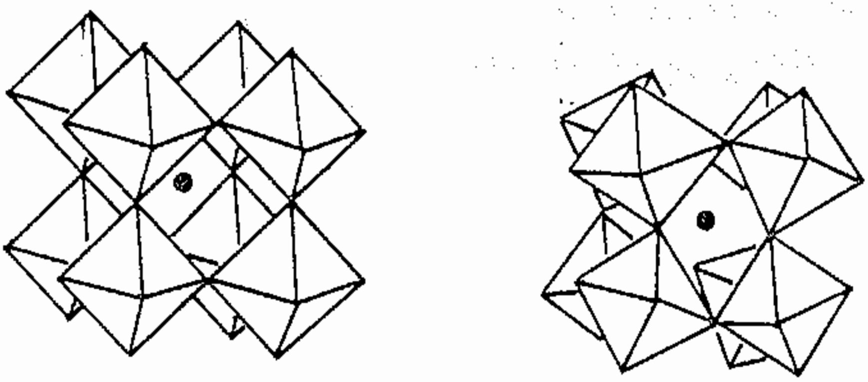
The calcium manganese oxides, $CaMnO_{3-x}$ (where x varies from 0 to 0.5), have generated much interest recently (1-2) as oxidation catalysts. Their structures are based on perovskite ($CaTiO_3$), Figure 1 (i), which is comprised of TiO_6 octahedra sitting at the corners of a cube with calcium at the cube centre.

We were interested in a number of problems; firstly, we wished to model the observed distortions of $CaMnO_3$ from the ideal perovskite structure. Secondly, to show that on loss of oxygen, manganese, which is reduced to an oxidation state of III from IV, remains close to its original position, but in a square pyramidal site. Finally, to explain why, for some stoichiometries (i.e. $CaMnO_{2.75}$) many different ordering schemes for oxygen vacancies coexist.

The potential model used to study this system was comprised of coulombic and parameterised two body short range interaction energy terms. In addition we allowed for electronic polarisability using the shell model. The parameters were derived empirically by fitting to the structural, elastic and dielectric data of the component simple oxides (i.e. CaO, Mn_2O_3 and MnO_2). Once we had obtained the desired parameters we checked that they were indeed transferable by considering the two end - members; $CaMnO_3$ and $CaMnO_{2.5}$. In each case we started the simulation with atoms at or near sites corresponding to the ideal perovskite structure and proceeded to minimise the forces affecting both atomic coordinates and cell dimensions.

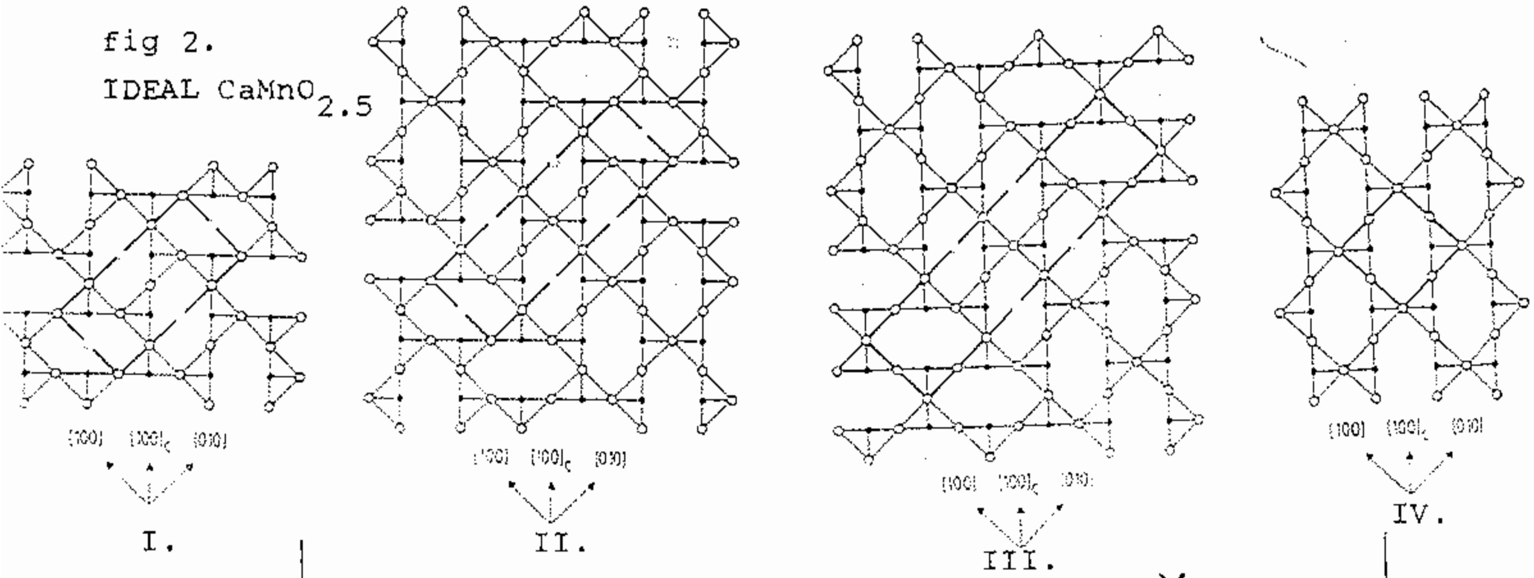
We found that we reproduced the observed structure of $CaMnO_3$ to within 1 - 2 % (3), Figure 1 (ii), showing that the potential model for Ca^{2+} and Mn^{4+} was reliable. The other end - member presented a problem because one could envisage a variety of ordering schemes for the oxygen vacancies, (see Figure 2), thus we calculated the lattice energy of each. The relative lattice energies after equilibration are plotted in Figure 2, which shows that the relative lattice energy is approximately proportional to the coulombic repulsion between neighbouring vacancies. The graph also includes the energy in terms of kT with the dotted line corresponding to the temperature at which the sample was quenched. This agrees with experiment in that, assuming a boltzman distribution, one would expect mostly phase I, which is observed. Moreover, the calculated structure for phase I is in good agreement with a recent neutron diffraction study (3).

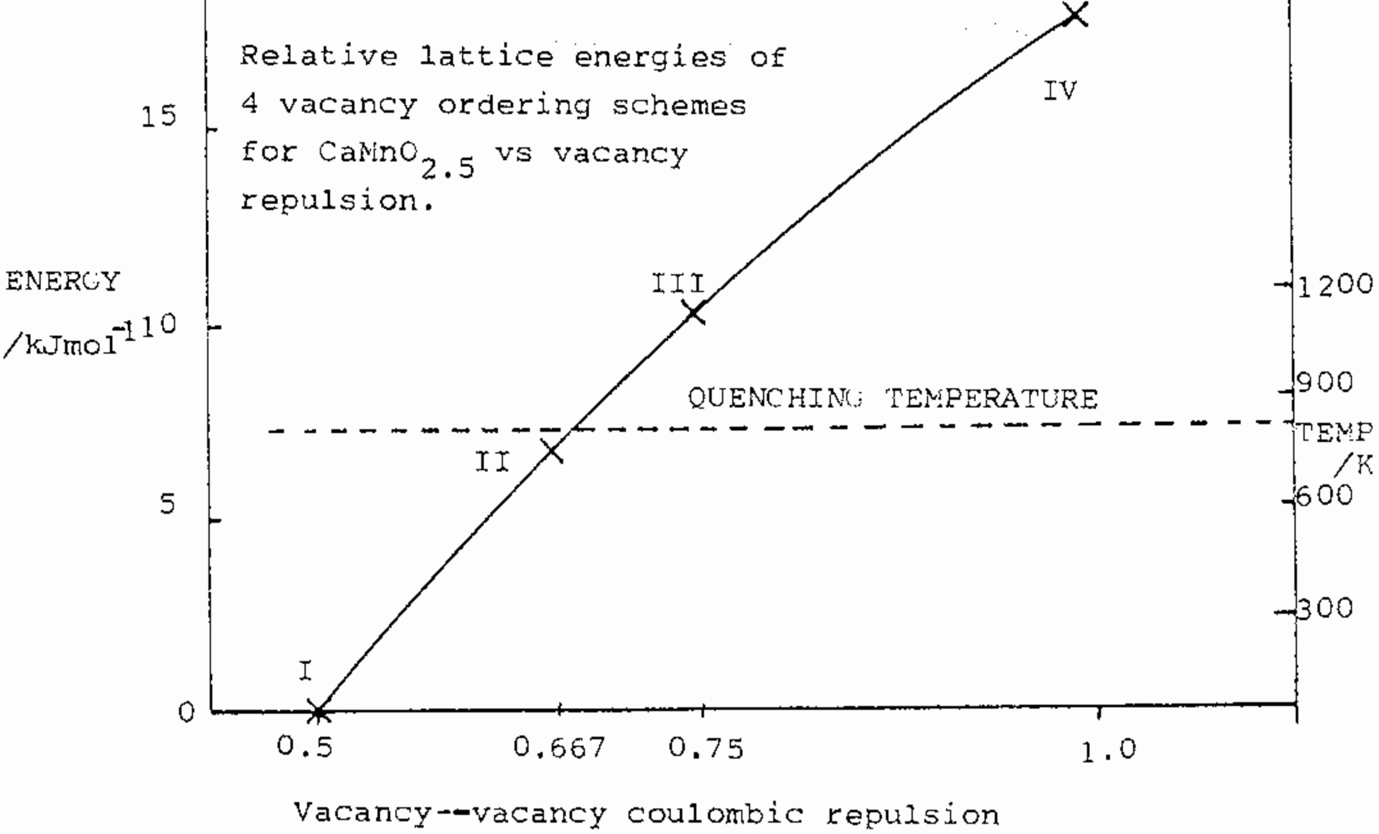
The same procedure was applied to the intermediate phase $CaMnO_{2.75}$, where half the manganese ions have the oxidation state III. The relative energies of a number of phases were calculated as before and are given in Figure 3. However, we note that all the fig 1. PEROVSKITE STRUCTURE ($CaMnO_3$)



(i) IDEAL (ii) EQUILIBRATED

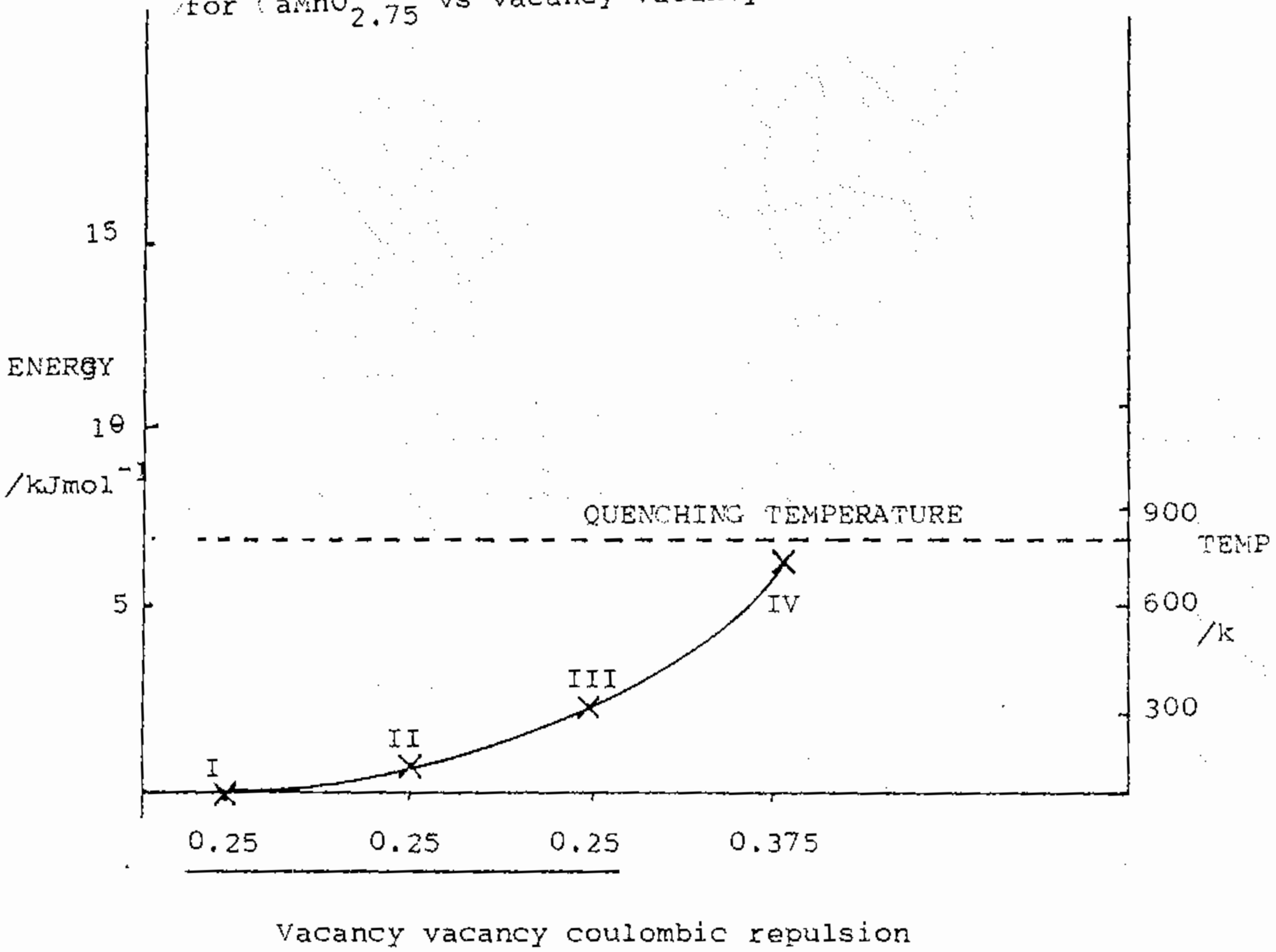
fig 2.
IDEAL $CaMnO_{2.5}$





Relative lattice energies of 4 vacancy ordering schemes for $CaMnO_{2.5}$ vs vacancy repulsion.

fig 3. Relative lattice energies of 4 vacancy ordering schemes for CaMnO$_{2.75}$ vs vacancy-vacancy coulombic repulsion



relative energies of the given phases are below the quenching temperature which suggests that all the phases may be present, as is observed experimentally.

We have shown that for a given stoichiometry an important factor for determining relative stability is the coulombic repulsion between oxygen vacancies, and where structural information is available we are in good agreement. The next stage of this work is to study the dynamic properties (i.e. oxygen vacancy mobility) and thereby predict which stoichiometry would be best suited as a catalyst.

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THE IDENTIFICATION OF A DROPLET IN EQUILIBRIUM WITH ITS VAPOUR.

R. F. Fowler

1. Introduction

In the simulation of small droplets in equilibrium with their vapour [1,2] it is often necessary to locate accurately the centre of the droplet, which can drift away from its original position. If the number of particles in the vapour phase is significant, the centre of mass of the whole system is not an accurate guide to the centre of the droplet.

We assume spherically symmetric particles and say that any two are "neighbours" if their centre-to-centre separation is less than some value Rn. Then particle B is in the same group as A if they are neighbours, or a neighbour of A is in the same group as B [2]. With a suitable choice of Rn, the largest of these groups defines the droplet. The centre of mass of the droplet is then readily found. For the Lennard - Jones 12-6 interaction it was found that the largest cluster size was virtually independent of Rn for Rn in the region of 1.9 σ (see figure) and so that was taken as the criterion for separating the drop from its vapour and in defining the centre of the drop. The difference between the centre of mass of the whole system, and that of the cluster is of the order 0.3 σ for a 260 particle system (σ is the particle diameter).

2. Simple-minded sorting

At first we used a simple-minded routine for finding the largest cluster, which is listed in section 4. This assumes that one particle (number IC) is already known to be within the cluster. We then search for the nearest neighbours of IC, according to the distance criterion Rn, and any that are found are recorded in the array NCL. The search then proceeds to find the neighbours of these that are not already recorded in NCL, and repeats this until the size of the cluster in NCL does not increase. The first NC elements of the array NCL then contain the index numbers of atoms within the cluster. This method has been found to be extremely slow and takes many times longer to compute than one simulation step. Since we need to relocate the cluster fairly frequently (say every ten steps) to follow changes, it slows the simulation to an intolerable degree. The coding given in section 5 is more complex, but is about fifty times faster. No doubt experts on sorting could improve this further, but as the routine takes rather less than the time for a simulation step, such improvements would have little effect on the total time taken.

3. More sophisticated sorting

This FORTRAN 77 subroutine is composed of three parts:

(1) For each atom, find all the unique neighbours (i.e. if 2 is a neighbour of 1, do not count 1 as a neighbour of 2). All the neighbours are stored in the large array LIST.

(2) Go through the list obtained above assigning "group numbers" to each atom such that two atoms have the same group number if they are linked via neighbours.

(3) Find the largest group and return the members of it in the array ICLUST.

In more detail the sections work as follows:

(1) The loops DO 10 and DO 20 run over all possible pairs. RCUTSQ is the square of Rn. Any neighbours that are found for a given atom I are stored in the array LIST, with the "pointer" array elements IPTH(I) and IPTT(I) giving the start (Head) and end (Tail) of its neighbours.

(2) The integer array IGROUP contains a "group number" for each atom that is initialized to zero, indicating no neighbours. The loop DO 40 then processes each atom and its neighbours. The code up to label 50 stores any non-zero group numbers that these atoms have in the array IGNUM, with IPTGN giving the top element. If more than one group number has been found, then these groups are all linked together by the present atom. Hence the loop DO 70 makes all the other group numbers equal to the first one. If no group numbers are found, a value of I is used. The loop DO 90 ensures that all the neighbours have the correct group number.

(3) The final loop DO 100 finds the first group to contain more than one third of the total number of atoms (NP), and returns them as the first LEN elements of the array ICLUST. The choice of one third is arbitrary, but works at most reasonable temperatures.

Note that the size of NLIST required depends on NP and the value of Rn used.

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4. Simple subroutine

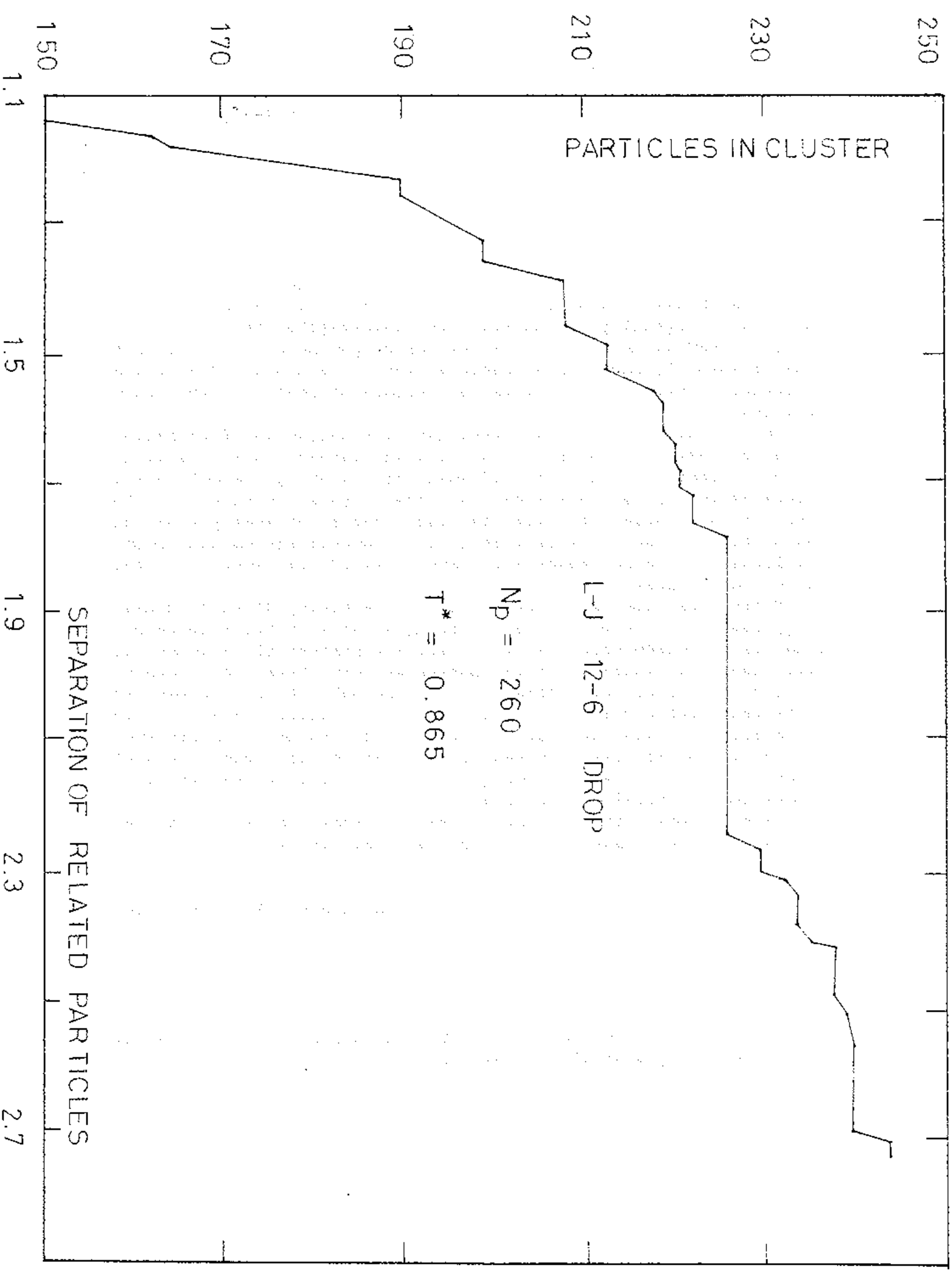
```
c       POSITIONS OF PARTICLES ARE IN ARRAYS X,Y,Z
        ..........
        NC=1
        NCL(1)=IC
2       NCP=NC
        DO 10 II=1,NCP
           I=NCL(II)
           DO 20 J=1,NP
              DO 21 JJ=1,NC
21               IF(J.EQ.NCL(JJ))GO TO 20
              R2=(X(I)-X(J))**2+(Y(I)-Y(J))**2+(Z(I)-Z(J))**2
              IF(R2.GT.RCUTSQ)GO TO 20
```

```
            NC=NC+1
            NCL(NC)=J
20        CONTINUE
10      CONTINUE
        IF(NC.GT.NCP)GO TO 2
        ..........
```

5. More sophisticated subroutine

```
      SUBROUTINE GETDRP(ICLUST,LEN,RCUTSQ)
      PARAMETER(NP=900,NLIST=12000)
      COMMON /POS/ X(NP),Y(NP),Z(NP)
      INTEGER ICLUST(NP)
      INTEGER LIST(NLIST),IPTH(NP),IPTT(NP),IGNUM(50),IGROUP(NP)
      LCOUNT=1
      DO 10 I=1,NP-1
         IPTH(I)=LCOUNT
         DO 20 J=I+1,NP
            R2=(X(J)-X(I))**2+(Y(J)-Y(I))**2+(Z(J)-Z(I))**2
            IF(R2.LT.RCUTSQ)THEN
               LIST(LCOUNT)=J
               LCOUNT=LCOUNT+1
            ENDIF
20       CONTINUE
         IPTT(I)=LCOUNT-1
10    CONTINUE
      DO 30 I=1,NP
30      IGROUP(I)=0
      DO 40 I=1,NP-1
         IPTGN=0
         IF(IGROUP(I).NE.0)THEN
            IPTGN=IPTGN+1
            IGNUM(IPTGN)=IGROUP(I)
         ENDIF
         DO 50 J=IPTH(I),IPTT(I)
            NJ=LIST(J)
            IF(IGROUP(NJ).NE.0)THEN
               DO 60 K=1,IPTGN
60                IF(IGNUM(K).EQ.IGROUP(NJ))GO TO 50
               IPTGN=IPTGN+1
               IGNUM(IPTGN)=IGROUP(NJ)
            ENDIF
50       CONTINUE
         IF(IPTGN.GT.0)THEN
            DO 70 K=2,IPTGN
               KG=IGNUM(K)
               DO 80 KK=1,NP
80                IF(IGROUP(KK).EQ.KG)IGROUP(KK)=IGNUM(1)
70             CONTINUE
            ELSE
               IGNUM(1)=I
            ENDIF
            IGROUP(I)=IGNUM(1)
            DO 90 J=IPTH(I),IPTT(I)
               NJ=LIST(J)
```

```
                  IGROUP(NJ)=IGNUM(1)
90             CONTINUE
40          CONTINUE
            LEN=0
            DO 100 I=1,NP
               IF(IGROUP(I).GT.0)THEN
                  ICOUNT=1
                  IG=IGROUP(I)
                  IGROUP(I)=-IG
                  DO 110 J=I+1,NP
                     IF(IGROUP(J).EQ.IG)THEN
                        ICOUNT=ICOUNT+1
                        IGROUP(J)=-IGROUP(J)
                     ENDIF
110               CONTINUE
                  IF(ICOUNT.GT.NP/3)THEN
                     LEN=ICOUNT
                     IG=-IG
                     DO 120 J=1,NP
                        IF(IGROUP(J).EQ.IG)THEN
                           ICLUST(ICOUNT)=J
                           ICOUNT=ICOUNT-1
                        ENDIF
120                  CONTINUE
                  ENDIF
               ENDIF
100         CONTINUE
            IF(LEN.EQ.0)THEN
               WRITE(*,'('' ********* NO CLUSTER > NP/3'')')
               STOP
            ENDIF
            RETURN
            END
```


PARTICLES IN CLUSTER
SEPARATION OF RELATED PARTICLES
L-J 12-6 DROP
N_p = 260
T^* = 0.865
150
170
190
210
230
250
1.1
1.5
1.9
2.3
2.7

RADIATION DAMAGE BY MOLECULAR DYNAMICS.

D. M. Heyes.

The purpose of this note is to point out a subject of study for MD which has been somewhat neglected, despite the fact that MD was partly originally formulated to investigate this area of research. Radiation damage is the rearrangement of solids by hot atoms or ions. It comes in a number of sub - branches. One being Sputtering, which is the removal of surface molecules by impinging particles.

MD is well suited to investigate the mechanism of radiation damage. For example, the figure shows time elapsed track histories of the effects of a 2000 eV model Ar^+ hitting a model 2D KCl surface at 20 degrees incidence (1). The regular nature of the atoms in a crystal facilitates the removal of energy from the impact point by the physical transport of nonequilibrium ions along correlated collision sequences (so - called "focusons"), as the figure demonstrates.

There are special difficulties in applying MD to such high energy events. Firstly, one is exploring a range of the interatomic potential for which there is often little experimental information. Small changes in these potential parameters can have an enormous effect on the course of a damage event. Secondly, it is not easy to follow the lattice relaxation (following the radiation's entry into the material) within the framework of periodic boundary conditions. (The correlated collision sequences can extend for many crystal layers). The alternative configuration of a microcrystallite soon becomes computationally expensive.

Nevertheless this topic seems a timely area of study, especially in the light of new graphics capabilities.

(1) D. M. Heyes, M. Barber and J. H. R. Clarke, Surf. Sci. 105 (1981) 225 - 239

Acknowledgements

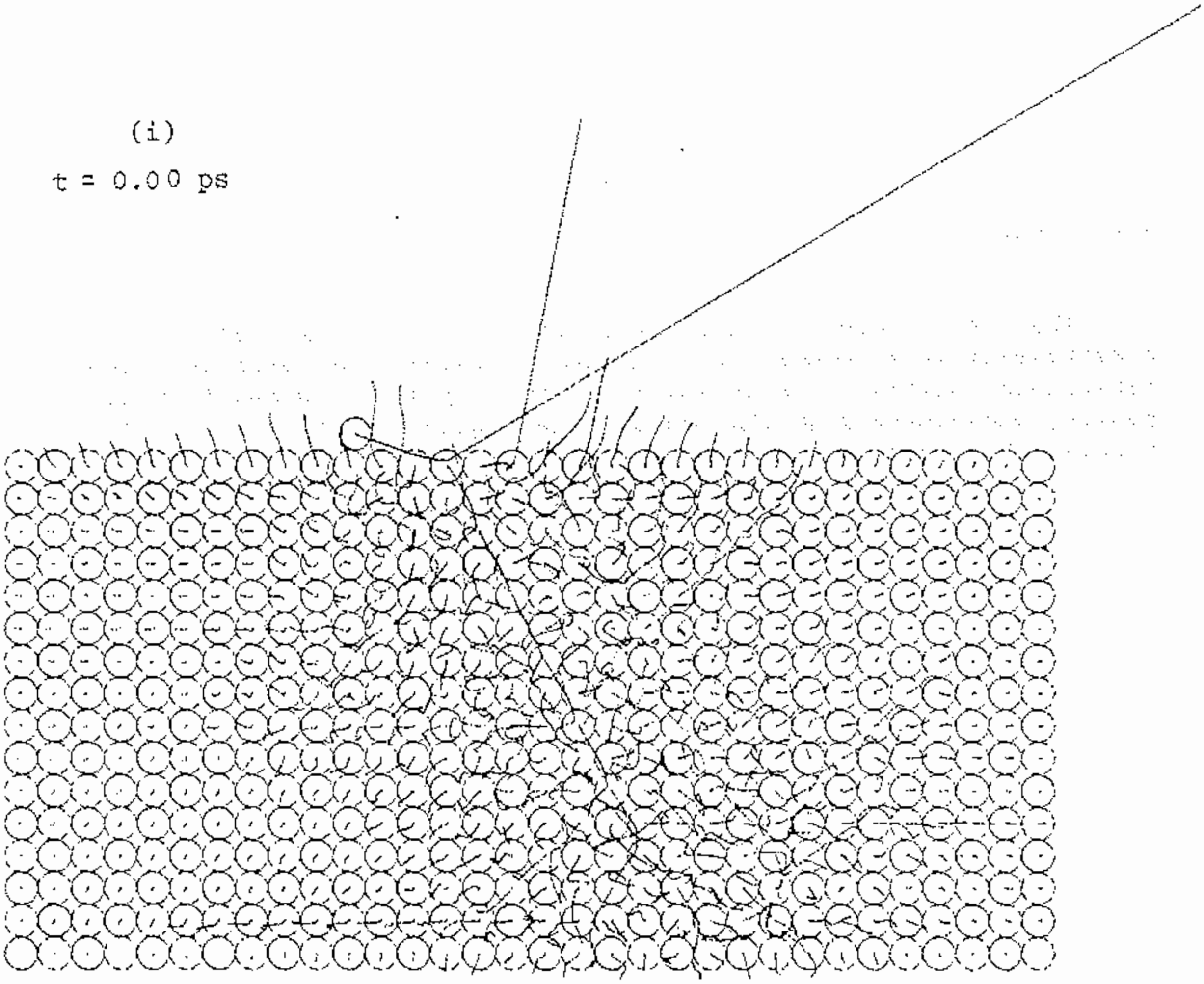
Invaluable discussions with Dr. M. Barber and Dr. J. H. R. Clarke are most gratefully acknowledged.

Figure Caption.

The KCl crystal structure at times t (ps) after the commencement of a model Ar moving towards the surface. The subsequent motion of each ion is denoted by a line drawn from its centre, superimposed on the starting configuration. K is a solid circle, Cl is a dashed circle.

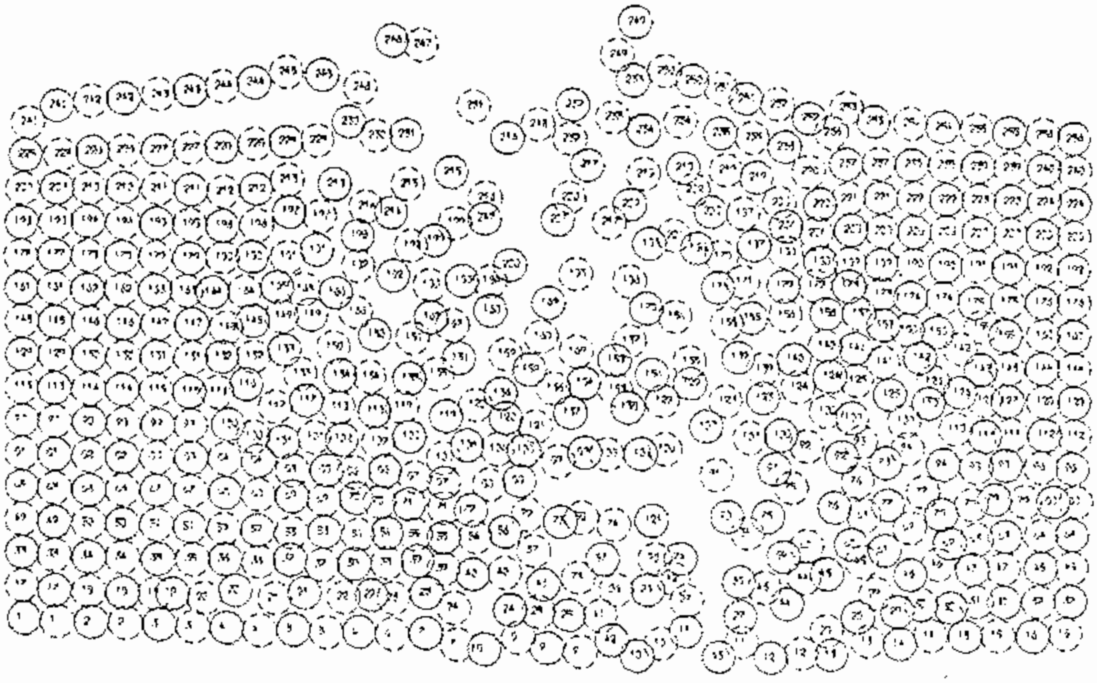
(i)

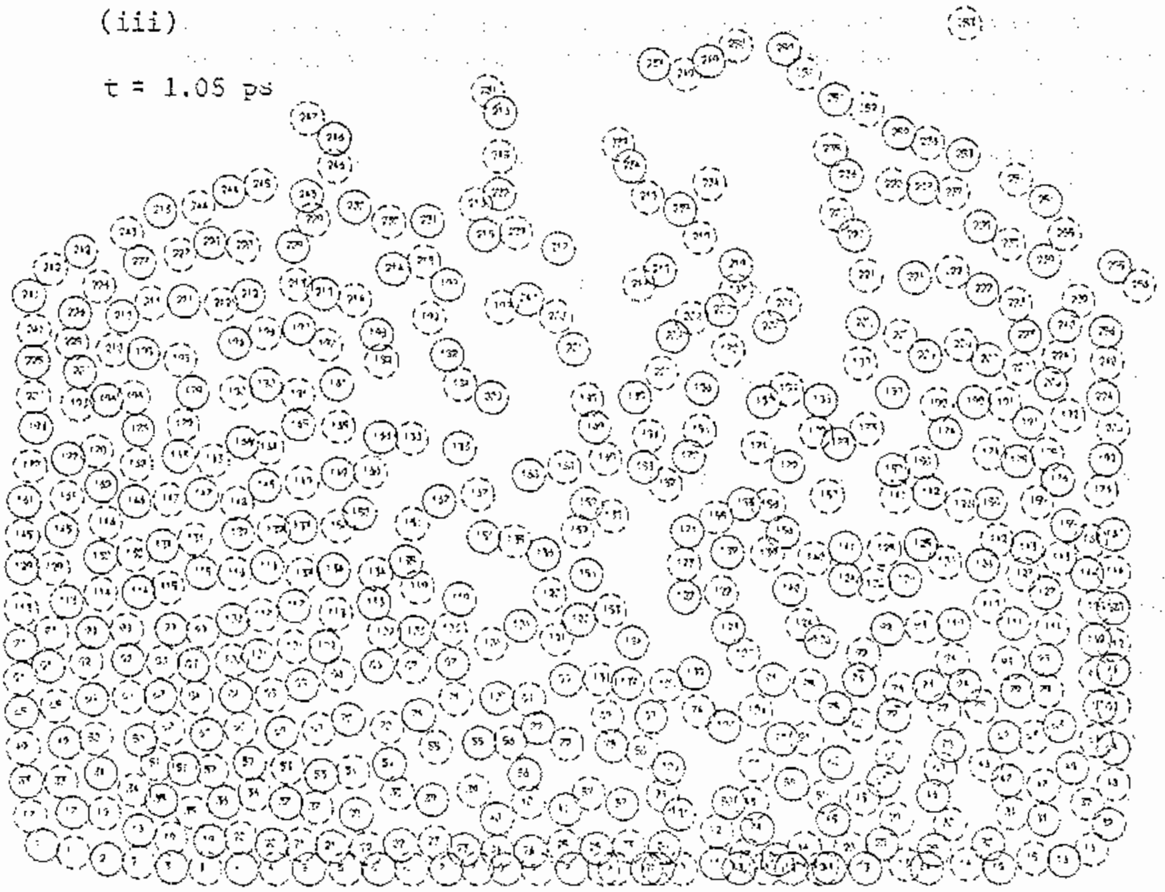
t = 0.00 ps



(ii)

t = 0.37 ps





(iii)

t = 1.05 ps

POTENTIAL MODELS FOR COMPUTER SIMULATION

This circular gives a preliminary programme for the CCP5 sponsored Meeting on 'Potential Models for Computer Simulation', which 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 £30 per person attending. The reduced fee of £10 will be charged to postgraduate students. Postgraduate students who contribute lectures or posters will not be charged.

The theme of the Meeting will be recent developments in both theoretical and empirical potentials for use in simulation and will 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 and the subjects proposed for their lectures are as follows:

W. Busing (Oak Ridge Laboratory, U.S.A.)
Effective potentials for the simulation of molecular crystals.

P. van Duijnen (University of Groningen)
Potentials for polymeric systems.

J. Kendrick (I.C.I. Runcorn)
Non empirical potentials for non - metallic solids.

G. Lewis (University College London)
Effective potentials for oxide materials.

S. Price (University of Cambridge)
Intermolecular forces - new clues from molecular crystal structure.

M. Rigby (Queen Elizabeth College)
Effective potentials and non - additive terms.

G. Scoles (University of Waterloo, Canada)
Surface scattering and three - body forces.

A. J. Stone (University of Cambridge)
Intermolecular potentials: insights from quantum mechanical calculations.

Readers who wish to contribute a lecture or poster to the Meeting should send a completed registration form not later than 31 st. July 1984, to:

Dr. C. R. A. Catlow,
Department of Chemistry,
University College,
20 Gordon Street,
London WC1 0AJ

Please provide an abstract with your application. Preference will be given to contributions from postgraduate students. A poster session will be arranged for disappointed contributors and others who wish only to present a poster display.

The Chemistry Department of University College London is within easy walking distance of the Euston Railway Station.

A registration form for attendance at the Meeting is attached.

CCP5 MEETING: 'POTENTIAL MODELS FOR COMPUTER SIMULATION'

LONDON 20 - 21 SEPTEMBER 1984.

REGISTRATION FORM

I wish to attend the CCP5 Meeting on 'Potential Models for Computer Simulation' to be held at University College London from 20 th. to the 21 st. September 1984:

NAME ....(Prof.,Dr.,Mr.,Mrs.,Miss.)
ADDRESS ....
....
....
....
....
....

Please indicate your accommodation and meals requirement.

Delete as appropriate:

1) Bed and breakfast for two nights (19 th & 20 th. Sept.), cost: £ 30.

2) Bed and breakfast for two nights (19 th & 20 th. Sept.), (postgraduate not contributing poster or lecture), cost: £ 10.

3) Bed and breakfast for two nights (19 th & 20 th. Sept.), (postgraduate contributing a poster or lecture), cost: Nil.

Please specify any special requirements or diet:

....
....

Delete as appropriate:

I wish to present a lecture / poster display entitled:

....
....

Please forward an abstract with this registration form.

I enclose a cheque for .... payable to 'CCP5 POTENTIALS MEETING'.

Signed: ....

Please return before 31 st. July to

Dr. C. R. A. Catlow,
Department of Chemistry,
University College,
20 Gordon Street,
London WC1 0AJ

POTENTIALS FOR GAS PHASE AND SURFACE SCATTERING CALCULATIONS

Preliminary programme for conference to be held 24-25 September 1984,
Cambridge, England

The meeting will begin at 2.00 pm on Monday 24 September, and will continue until 6.00 pm on Tuesday 25 September. It is sponsored jointly by the Collaborative Computational Projects on Heavy Particle Dynamics (CCP6) and Surface Science (CCP3) of the UK Science and Engineering Research Council.

The purpose of the meeting will be to review recent theoretical progress in the determination of potentials for use in gas phase and surface scattering calculations. These two areas of research are often reported in different strands of the scientific literature; it is the aim of this meeting to illustrate the similarities in both the underlying physics and the theoretical techniques used, and to promote contact between researchers in the two fields.

The invited lectures will be as follows:

W. Allison (University of Cambridge)
Empirical Helium-metal Potentials and Their Relation to Surface Structure

R.B. Gerber (Hebrew University of Jerusalem)
The Inversion Problem in Heavy Particle Dynamics:
Interaction Potentials from Scattering Intensities and Spectroscopy

J. Harris (Institut für Festkörperforschung, Jülich)
Interaction of H_2 molecules with Simple and Noble Metal Surfaces

S. Holloway (University of Liverpool)
Gas-Surface Interaction Potentials Using the Effective Medium Theory

J.N. Murrell (University of Sussex)
Title to be announced

R. Schinke (Max-Planck-Institut, Göttingen)
Rainbows and Resonances in Molecule-Surface Scattering and Their Relation to the Interaction Potential

G. Scoles (University of Waterloo, Canada)
The Joys and Sorrows of Multiparameter Interactions

Contributed papers on the following topics are invited:

Fitting of potential energy surfaces to experimental data
Ab initio calculation of potential energy surfaces
Potentials for inelastic and reactive processes
Methods for gas phase and surface scattering calculations

There will only be room for a few additional oral presentations, and most contributed papers will have to be in the form of posters.

Those interested in attending the meeting are requested to complete the attached registration form and return it to

Dr. J.M. Hutson,
Potentials Conference,
University Chemical Laboratory,
Lensfield Road,
Cambridge CB2 1EW
England

by 20 August 1984 at the latest. Those wishing to present papers should reply as soon as possible.

There will be no registration fee. Accommodation will be in single study bedrooms at Pembroke College, Cambridge. Lectures will be held at the University Chemical Laboratory (5 minutes walk). Accommodation, including conference dinner on 24 September and breakfast and lunch on 25 September, is available at a (subsidised) cost of £30. Bed and breakfast for the nights of 23 and 25 September is available at an additional cost of £18 per night if desired. Fees for accommodation are payable at the start of the conference.

Full details, including the final programme and a map, will be sent out about 2 weeks before the meeting.

Travel to Cambridge

From London: There are frequent trains (about hourly) from London's Liverpool Street and King's Cross Stations. The latest trains arriving in Cambridge in time for the start of the meeting are as follows:

Liverpool Street	12.05	(arrives Cambridge 13.10)
King's Cross	12.04	(change at Royston for Cambridge at 13.20)

From Heathrow: There is a direct bus to Cambridge (no. 079) leaving Heathrow at 10.30 and arriving at Cambridge at 12.45; otherwise, take the train (Piccadilly line) into King's Cross (very frequent, journey time 60 minutes) and thence to Cambridge.

From Gatwick: Take the train to Victoria (trains every 15 minutes, journey time 45 minutes). Then
either Victoria Line to King's Cross and train to Cambridge
or Coach to Cambridge from Victoria Coach Station

Luton and Stansted Airports are more convenient for Cambridge than either Heathrow or Gatwick. From Luton, catch Percival's bus around 11.40 (from Bay 1 or 2, arriving Cambridge 13.00); from Stansted, there are frequent trains to Cambridge (journey time less than 1 hour).

By Car: There is no car parking available in Pembroke College, although there is an (expensive!) multi-storey car park about 5 minutes walk away, approached down Pembroke Street from Trumpington Street.

Organising committee:
R.J. Blake
D.C. Clary
J.M. Hutson
J.E. Inglesfield

Registration form

I wish to attend the conference on "Potentials for Gas Phase and Surface Scattering Calculations", to be held in Cambridge from 24-25 September 1984.

Name Prof./Dr./Mr./Mrs./Miss* . . . .

Address . . . .

. . . .

. . . .

Please indicate accommodation and meals required:

1) Bed and breakfast for night of 23 September (£18) (yes/no)*
2) Room and meals during conference (£30) (yes/no)*
3) Bed and breakfast for night of 25 September (£18) (yes/no)*

Special requirements or diet: . . . .

I wish / do not wish* to present an oral contribution / poster* entitled

. . . .

. . . .

Please return this form to

Dr. J.M. Hutson,
Potentials Conference
University Chemical Laboratory,
Lensfield Road,
Cambridge
CB2 1EW
England

by 20 August 1984. Please do not send payment for accommodation before the meeting; money will be collected at the start of the conference.

* Delete as necessary