

DARESBUURY LABORATORY

# INFORMATION QUARTERLY for COMPUTER SIMULATION OF CONDENSED PHASES

An informal Newsletter associated with Collaborative Computational Project No. 5 on Molecular Dynamics, Monte Carlo and Lattice Simulations of Condensed Phases.  
Number 19 DECEMBER 1985

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# THE NATIONAL BUREAU OF STANDARDS AND NATIONAL BUREAU OF METROLOGY REPORT

A REPORT OF THE NATIONAL BUREAU OF STANDARDS AND NATIONAL BUREAU OF METROLOGY  
 ON THE PROGRESS OF THE NATIONAL BUREAU OF STANDARDS AND NATIONAL BUREAU OF METROLOGY  
 DURING THE YEAR 1950

BY  
 THE NATIONAL BUREAU OF STANDARDS AND NATIONAL BUREAU OF METROLOGY

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GPO: 1951

The National Bureau of Standards and National Bureau of Metrology was established by the National Bureau of Standards and National Bureau of Metrology Act of 1901, which provided for the organization of the National Bureau of Standards and National Bureau of Metrology as a part of the Department of Commerce.

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CCP5 LITERATURE SURVEY: 1985 - AN APPEAL!

One of the more popular features of the CCP5 Newsletter over the past three years has been the CCP5 Literature Survey. Regretably the cost of this has risen dramatically to the point where we are unable to provide such a survey for the year 1985 through our usual source. We have spent some time in the last few months seeking out new sources for the survey and we are happy to report that we should be able to provide something for the year 1986. This however leaves 1985 unsurveyed.

A suggested solution of this temporary problem is to exploit the CCP5 mailing list and appeal for CCP5 members to provide us with list of their publications for that year. There are approximately 400 people on the mailing list, with about 55% of them from outside the United Kingdom, if every one of them wrote but one paper (or book) the survey would be potentially very useful.

There are several advantages to this suggestion: a) It is cheap and it is better than no survey! b) It will automatically cover those areas of computer simulation that CCP5 is interested in. (It has been a very difficult exercise in the past tailoring our search precisely to CCP5's requirements). c) Everyone participating will be sure that all their relevant work is cited. Past searches have been nowhere near complete in this respect.

There are also disadvantages: a) Not everyone active in computer simulation is on our mailing list and consequently we would produce a biased and possibly less useful survey. b) Perhaps too few CCP5 members will respond to produce a poor survey. c) The response will be overwhelming and we will not be able to cope with the amount of information! (Speaking realistically, if we get about 800 references, we will just be able to cope; our last survey reached this figure).

Notwithstanding the problems that may arise in attempting something like this, we believe that the venture is worth a try. With some trepidation therefore, we send out this appeal to our readers:

PLEASE PROVIDE A LIST OF YOUR PUBLICATIONS THAT HAVE APPEARED (OR WILL APPEAR) IN THE PERIOD OCTOBER 1984 TO DECEMBER 1985 GIVING:

- A) THE FULL LIST OF AUTHORS, (AND EDITORS IF NECESSARY),
- B) THE TITLE OF THE PUBLICATION, BOOK OR CONFERENCE PROCEEDINGS,
- C) THE JOURNAL, YEAR, VOLUME NUMBER AND PAGE NUMBERS, AND PUBLISHER.

AND SEND THEM TO:

DR. W. SMITH, TCS DIVISION, SERC DARESBUY LABORATORY, DARESBUY,  
WARRINGTON WA4 4AD, UNITED KINGDOM.

THANKS!

We conclude with the following warnings. In the happy (but  
unlikely) event of our receiving too many references, we will  
publish what we can in the chronological order in which we received  
them. We will not publish references that are not completely  
specified or fall outside the period specified. We will publish  
references to internal documents provided that they are suitably  
specified and publicly available.

Editorial.

The first few months of 1986 promise to be very active ones for CCP5. We have two workshops and one full meeting ahead; the details of which are described within. Another event, largely unseen by the members of CCP5, will be the movement of the CCP5 Renewal Proposal through the lengthy procedure before its re-endorsement for another three years. The people responsible for preparing the Renewal Proposal; Julian Clarke, Dominic Tildesley and Richard Catlow have an unenviable task in gathering together a concise case from the multifarious activities within CCP5. They deserve our most sincere thanks. We will not know the outcome until the second half of 1986, but there can be little doubt about the vitality and purposefulness of CCP5 and we can reasonably expect a happy outcome.

In addition to thanking our contributors this month, we take a special pleasure in wishing both them and our readers, a happy Christmas and good fortune in 1986.

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General News.

a) CCP5 is organising a conference on 'The Glass Transition', which will be held in Oxford from April 9th. to 11th. 1986, at Wadham College. A circular giving more information, and including a registration form, is included with this Newsletter.

b) Two workshops are being organised by CCP5 at present. These are on the subjects of 'Transport Processes' and 'High Temperature Properties of Defects in Ionic Materials'.

The Transport Processes Workshop is being organised by Dr. D.M. Heyes for 25th. and 26th. March 1986 at Royal Holloway and Bedford New College. The meeting will follow on from the British Society of Rheology meeting on 'Molecular Approaches to Rheology', which also takes place at Royal Holloway and Bedford New College on 24th. and 25th. March. Details and application forms of both these meetings are included with this newsletter.

The High Temperature Properties Workshop is being organised by Dr. M. Leslie for 6th. and 7th. January 1986 and will take place at Cosener's House in Abingdon. The number of participants is to be strictly limited. In view of this and the short time now available, interested parties should telephone Dr. Leslie at Daresbury Laboratory (Tel. 0925-65000 ext. 334).

c) The CCP5 Steering Committee has decided to carry out a study of the computational requirements of the CCP5 community, with a view possibly to proposing the construction of a special purpose 'simulation computer'. This study will be coordinated by Drs. C.R.A. Catlow, D. Fincham and P.A. Madden. Please would anyone with comments or proposals on this topic write to Dr. C.R.A. Catlow, Department of Chemistry, University of Keele, Keele, Staffs. ST5 5BG.

d) Everyone in the CCP5 U.K. community is reminded that CCP5 has an allocation of time on the ULCC Cray computer for the expressed purpose of program development. Anyone specifically requiring Cray time for this purpose may request some of this allocation. Please write to the CCP5 Chairman, Dr. J.H.R. Clarke, Department of Chemistry, UMIST, Sackville Street, Manchester M60 1QD.

e) It has been pointed out to the CCP5 Editor that our readers are adopting the habit of citing the CCP5 Newsletter in the established scientific journals. While we are pleased by the compliment implicit in this, we feel obliged to remind our readers that this newsletter is not itself a refereed journal and has the clearly specified function of being an informal circular. If our readers wish to cite the CCP5 Newsletter in more august journals, we humbly request that they indicate that the newsletter is informal in

nature and that it is freely available from the S.E.R.C. Daresbury Laboratory.

f) We have received a report from Dr. Y. Kataoka of Kyoto University that there is an error in the calculation of the cutoff or tail correction in the programs MDLIN and MDLINQ, leading to an incorrect configuration energy, virial and pressure. The calculated tail corrections are too big by a factor of four. (This constant error does not affect the dynamics of the system and can be easily subtracted from the results of previous runs of the program). To correct the program the user must locate the subroutine START, near the end of which the variable CLRTAIL is defined which is used in the calculation of the tail corrections. The correct expression for this variable is:

$$\text{CLRTAIL} = 0.25 * \text{PI} * \text{FLOAT}(\text{NM}) * \text{AVOGAD} * \text{EPSILON}(\text{NA})$$

The same correction applies to both MDLIN and MDLINQ. Our thanks go to Dr. Kataoka for pointing out this error.

g) At Daresbury Laboratory the recently installed MVS operating system has reached an acceptable level of stability. Loss of data is now a thankfully rare event. This is perhaps the time to remind CCP5 members of the availability of the FPS 164 attached processor, which is available for grant supported computing within the Science Board Community. In the first year of its operation U.K. research groups are invited to apply informally to the Director of Daresbury Laboratory (Professor L.L. Green) for time on the FPS for benchmarking purposes. If the FPS proves viable for a given project, a formal application (using the familiar forms RG2 and AL54) may be made. Advice on using the FPS at Daresbury may be obtained from the User Interface Group (in the person of Dr. D. Taylor) or from the CCP5 representative Dr. W. Smith. A document entitled 'Using the FPS Attached Processor at the Daresbury Laboratory' by Dr. M.F. Guest is available from the User Interface Group.

CCP5 members who are registered users of the Daresbury Computing facilities (including those using the FPS) should note that their representative on the Daresbury Computer Users Consultative Committee (DCUCC) is Dr. W. Smith of the Theory and Computational Science Division. Any matters (complaints, comments, recommendations etc.), which CCP5 users would like to be put before the Daresbury Computer Users Forum (DCUF) for discussion should be forwarded to Dr. W. Smith. (The DCUF replaces the User Representative Meetings, which were the previous means by which users conveyed their assessment of Daresbury compute services. The DCUCC replaces the erswhile Agenda Committee and the Advisory Committee. Its function is to advise Daresbury Laboratory on policy for computing facilities, inform the Laboratory of user opinion and consider proposed changes, and prepare the agenda for the DCUF.)

h) The Rutherford and Appleton Computer Centre report that their MVT operating system was finally removed in September 1985. The current operating system is the IBM MVT operating system. Now that MVS is stable, changes are in hand for the use of the MASSTOR M860 storage unit. In future it will be used to store infrequently used datasets, which will still be regarded as 'online'. This will allow the logical storage of the system to be extended and at the same time free actual disc space. Migration of datasets to and from the M860 will be invisible to users, though datasets that are very rarely used will eventually move offline and will need to be restored. The time of residence of datasets on the various storage media will be decided upon in the light of experience. Space on the M860 will not be available for users' data.

i) The University of London Computing Centre has announced its intention to upgrade the system software on the Cray-1s to level 1.14 at Easter 1986, when the COS 1.14 operating system will be installed. At present the FORTRAN compiler CFT 1.14 is available along with the associated libraries. Users should note that binary (load) modules compiled with the previous compiler 1.13 cannot be combined with newly compiled codes due to a change in the calling sequence.

Owing to the limited disc capacity on the AMDAHL at ULCC, users are being encouraged to make full use of the DARCHIVE AND DRESTORE procedures to archive and restore datasets to and from the MASSTOR system. The default disc allocation to users is 25 tracks, while the MASSTOR allocation is 500 tracks. It is therefore prudent to use these facilities. More information can be obtained from the ULCC Newsletter of November 1985.

ULCC has announced that a JTP service is operational. Transfer of datasets to and from remote sites is therefore possible.

j) The University of Manchester Regional Computing Centre has announced the withdrawal of the FTN4 compiler at the end of 1985. Users are being advised to convert to the FTN5 compiler immediately.

Some upgrades of software are imminent: ROSCOE is to be upgraded to level 5.4 on December 9th, 1985 and also MVS to SP1.3.3 at some unspecified date. VSOS on the CYBER 205 is to be upgraded to 2.1.6 in December. Meanwhile, on the CYBER 176 and the CDC 7600s, the FTN5 compiler is to be upgraded to level 628A.

CCP5 members interested in crystallography may be interested to know that the program XSTAL, a crystallographic program (refinement of X-ray structures) is available on the CYBER 205. Also, those interested in protein structures may find the Protein Sequence Database of the National Biomedical Research Foundation a useful resource. This is available on the AMDAHL 470 V/8.

k) Readers may be interested to know of a meeting being organised by our sister project CCP4. The meeting is on 'Protein Structure Prediction' and will take place on 24th. and 25th. January 1986. The objective of the meeting is to highlight the methods currently available for the prediction of the three dimensional structure of proteins from the known amino acid sequence and to consider likely developments in the area. Some of the invited speakers are: Dr. C. Chothia (Cambridge), Dr. F. Cohen (San Francisco), Prof. P. Kollman (San Francisco), Dr. A. Jones (Uppsala), Dr. C. Sander (Heidelberg), Dr. S. Wodak (Brussels) and Dr. M. Sternberg (Birkbeck). The meeting will take place at Daresbury Laboratory. There is a registration fee of £16, excluding accommodation. Accommodation for one night will be £14.50 for a single room and £13.50 for a shared room.

The official closing date for applications is 17th. December 1985, but if the meeting is under-subscribed late applications will be considered. Enquiries regarding the programme should be addressed to Dr. M. Sternberg, Department of Crystallography, Birkbeck College, London WC1E 7HX (Tel. 01-631-6278) or to P. Machin at Daresbury Laboratory (Tel. 0925-65000 ext. 350). Enquiries regarding applications should be addressed to Mrs. S. Lowndes at Daresbury Laboratory (ext. 305) to whom application forms and fees should also be sent. An information bulletin and application form is enclosed with this newsletter.

l) 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. It may also be possible to transfer a small number of programs over the JANET network to other computer centres in the U.K.. Users wishing to send magnetic tapes are instructed to write to Dr. Leslie for information before sending the tape. PLEASE DO NOT SEND TAPES WITHOUT CONTACTING DR. LESLIE FIRST. Delays are caused by applicants sending new tapes which have to be initialised at Daresbury (i.e. tape marks have to be written on them). Also tapes sent in padded bags have to be cleaned before use. Please do not use this form of packing. (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 alkali halide lamina. Molecular dynamics simulation for ionic laminae using the Tosi-Fumi / Born-Mayer-Huggins potential and the Evjen method for evaluating the lattice sums. The integration algorithm used is the Verlet method. The program calculates the system potential and kinetic energies, the pressure and the final averages and R.M.S. fluctuations. The program also calculates density profiles such as number density, temperature, energy and pressure.

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

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

MDATOM by D. Fincham.

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

MDDIAT by D. Fincham.

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

MDDIATQ by D. Fincham.

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

MDIONS by D. Fincham & N. Anastasiou.

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

MDMANY by D. Fincham & W. Smith.

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

**CARLOS** by B. Jonsson & S. Romano.

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

**MCN** by N. Corbin.

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

**SCN** by N. Corbin.

M.C. simulation of atomic fluids. Standard (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.

REVIEW OF THE CCP5 MEETING ON 'STOCHASTIC DYNAMICS AND MACROMOLECULES' HELD AT THE UNIVERSITY OF YORK 11 TO 13 SEPTEMBER 1985.

W. Smith

This was the first occasion that CCP5 had devoted an entire meeting to the subjects of stochastic dynamics and macromolecules. It was also the first time that CCP5 had ventured en masse into the very pleasant campus of the University of York. Together these factors made for a very interesting and enjoyable two days. The organisation of the meeting was excellently arranged by David Fincham of the Department of Chemistry of the University of York, assisted by Eric Dickinson of the Procter Department of Food Science at the University of Leeds. Somehow they had arranged for the sun to shine for the two days of the meeting and participants were seen walking about in shirt sleeves. British CCP5 members will fully appreciate the significance of these observations.

The first speaker of the meeting was Dr. F. Vesely of the Institute of Experimental Physics, Vienna. Dr. Vesely spoke about the methods of stochastic dynamics and formally introduced the meeting to the fundamentals of stochastic methods. The motivation of stochastic dynamics is to apply the methods of computer simulation (molecular dynamics) to systems in which one is interested in only a subset of all the particles present and one needs to remove the remaining particles (which are in the greatest number) from explicit mechanical consideration. One way of doing this is via the Generalised Langevin Equation (GLE)

$$\dot{v}_i = \sum_j F_{ij} / m_i - \int_0^t M(t-t') v(t') dt' + a(t)$$

in which the first term on the right represents the systematic forces acting on the explicit particles (i.e. the pair forces modified by the presence of the non-explicit particles), the second is a so called memory integral (which accounts for the 'history' of the particles) and the third represents the stochastic or random force, which provides the dynamical 'heat bath' in which the explicit particles move. (The memory function  $M(t)$  is sometimes replaced by a delta function in cases where the explicit particles are massive in relation to the others. This allows the memory integral to be written as a simple drag term. This case corresponds to the simple Langevin equation (SLE).) The random force and the memory function are interrelated via the relation:  $\langle a(0)a(t) \rangle = \langle v^2 \rangle M(t)$ , which is obtained from the second fluctuation-dissipation theorem.

There are three methods available for solving the GLE: Mori chain dynamics, the Fourier synthesis method and the correlation matrix method. In the first of these, the Laplace transform of the

memory function is expanded as a continuous fraction (the Mori expansion), which is necessarily truncated at some stage and whose parameters may be fitted to MD data. This allows the system to be represented by a finite number of simple differential equations which may be solved by either predictor-corrector or Verlet algorithms. This method is particularly important as it can be shown to be the rational basis of several methods in the literature. In the Fourier synthesis method the random forces are represented as a (truncated) Fourier sum in which the Fourier coefficients are random variate and obtained from a normal probability distribution. The correlation matrix method, the random forces are considered to be a set of correlated random numbers with an associated correlation matrix. The diagonalisation of the correlation matrix is a necessary step in enabling correct sampling of the random forces. All these methods were described in detail by Dr. Vesely. In addition he gave thought to systems where hydrodynamic interactions are important (e.g. when several explicit particles are present and their masses are not great). In these circumstances a matrix of Mori functions is required.

Dr. S. Toxvaerd of the Panum Institute, University of Copenhagen discussed the application of stochastic dynamics in the problem of the fractal dimensionality of classical particle trajectories. Measurement of the length of a trajectory with a discrete divider of length  $\epsilon$  obeys the Mandelbrot relation:

$$L(\epsilon) \propto \epsilon^{1-D}$$

For a random walk (Markovian trajectory) the dimensionality  $D$  is 2. However Powles and Quirke (1984) have shown that MD simulated trajectories have a dimensionality  $D=1$  when  $\epsilon$  very small and a dimensionality  $D=1.65$  when  $\epsilon$  is sufficiently large. MC simulations have dimensionality  $D=2$ . The implication is that MC is always a Markovian process while MD is affected by memory.

Dr. Toxvaerd described in detail the stochastic dynamics method he used to investigate this phenomenon. The memory function of the GLE is assumed to involve only two terms of the Mori expansion. Methods of checking this assumption and the interrelations between the GLE, the memory function and the velocity autocorrelation function (VACF) were described. The fundamental check was the agreement between the input memory function (and its associated VACF) and the VACF produced by a simulation using the GLE. In addition both the diffusion coefficients and the temperature were checked for consistency.

In applying these methods to the fractal dimensionality problem Dr. Toxvaerd established that for larger distance scales the GLE gave a dimensionality  $D=2$ , like that of MC simulations, but on short scales gave a dimensionality  $D=1$ , which corresponded to the MD result. The conclusion was therefore, that it is memory effects which give rise to the observed MD dimensionality  $D=1.65$  at the larger scales.

The reliability of Langevin dynamics methods in reproducing the properties of a system was the subject of a talk by J.A. Padro of the University of Barcelona. He and his colleagues have performed Langevin dynamics and molecular dynamics on a series of model systems and compared the radial distribution functions (RDFs), VACFs and diffusion coefficients obtained in each. Three model systems were used, all representing liquid Krypton. The first system consisted of N<sub>2</sub> 'solvent' atoms with 2 'solute' atoms interacting via a Lennard-Jones 12-6 potential and simulated using the standard molecular dynamics method. (This system represented the 'infinitely dilute' reference system). The second system consisted of N<sub>1</sub> 'solute' atoms interacting through a mean force potential and simulated using Langevin dynamics. The third system consisted of N<sub>1</sub> 'solute' atoms in the 'solvent' of N<sub>2</sub> atoms interacting through the Lennard-Jones potential and simulated using MD. The Langevin dynamics were obtained using an algorithm due to Allen, while the MD was handled by the standard Beeman algorithm.

The MD RDFs were generally well produced by the Langevin dynamics method. The observed departures for different N<sub>1</sub>/N<sub>2</sub> ratios were explained in terms of the poor pair additivity of the mean force potential. The diffusion coefficients were somewhat poorer and showed a more marked dependence on the N<sub>1</sub>/N<sub>2</sub> ratio. In this case the absence of hydrodynamics effects from the Langevin dynamics treatment was invoked in explanation. The VACFs showed marked discrepancies. The 'rebound' region of the VACF was not well reproduced. The deviations were ascribed to the absence of hydrodynamic and memory effects. Further simulations using generalised Langevin dynamics (i.e. replacing the drag term by a memory function) gave a better account of the rebound region, but the diffusion coefficients were not improved.

Dr. David Heyes of Royal Holloway and Bedford New College (who as they say needs no introduction) lectured on the topic of 'Brownian Dynamics and Shear Flow'. He began by describing the general response of fluid systems under shear. At low shear rates the viscosity is constant (the Newtonian region) but at higher shear rates the viscosity falls rapidly to a second Newtonian region. The region of falling viscosity is known as the shear thinning region. At yet higher shear rates the viscosity rises again in the shear thickening region. Dr. Heyes described some the computational techniques available for simulating systems under shear (e.g. the SLLOD method) and also the experimental methods available.

In simulations of 'soft sphere' systems using standard molecular dynamics, Dr. Heyes has investigated the shear thinning phenomenon. The region is characterised by the onset of a structural transformation in the sheared fluid in which the particles align themselves in 'strings' along the direction of the shear. In this configuration the particles stream past each other with minimum hindrance. Various correlation functions (VACF and shear stress autocorrelation) are highly oscillatory in direction perpendicular to the flow and merely damped in the direction of

flow. This indicates that the particle motion is diffusive in the direction of flow (liquid like) and localised (solid like) in the perpendicular direction. These results show clearly the nature of shear thinning.

In scaling up the particle sizes to those of colloidal particles and immersing them in a solvent it was argued that the retarding effect of the solvent would bring about the onset of the shear thinning region at comparatively lower shear rates. Langevin dynamics simulations of such systems described and performed by Dr. Heyes have established this. This result is in line with experimental observations.

Dr. E. Dickinson of the Procter Department of Food Science, Leeds University, was concerned in his lecture with the techniques available for simulating colloidal systems with Brownian Dynamics. Brownian dynamics are essentially the same as stochastic dynamics except that the size of the particles explicitly considered (about  $1.0 \times 10^{-7}$  m) are large in relation to the solvent. This means that the fluctuation rates of the solvent ( $1.0 \times 10^{-13}$  s) are very much more rapid than the relaxation rates associated with the colloidal particles ( $1.0 \times 10^{-3}$  s for structural relaxation of the colloidal particles) and hence the simple Langevin equation (SLE), where the memory term is replaced by a frictional term, is applicable. Dr. Dickinson described the integration algorithm of Ermak and McCammon (J.C.P. V69 (1978) 1352) for the solution of the equations of motion. This algorithm has been adapted to deal with rotational motion and also to include external flow fields, especially shear flow fields. Factors which require consideration are the hydrodynamic coupling effects between particles (translation - translation, translation - rotation and rotation - rotation) and the boundary conditions ('stick' - suitable for colloidal particles and 'slip' - suitable for molecules and 'clean' droplets). In addition there are the many - body hydrodynamic effects to consider. However it is possible to exploit the different ranges over which the hydrodynamic effects operate to remove them from consideration in specific applications: for instance the common mutual repulsion between colloidal particles prevents close approach where some of the hydrodynamic effects would come into effect.

A suitable pair potential (potential of mean force) for simulating colloids is the Derjaguin - Landau - Verwey - Overbeek (DLVO) potential. This potential can show three kinds of behaviour; it can be strongly repulsive (giving stable colloids), strongly attractive (giving fast coagulation) and weakly attractive with a shallow minimum separated by small barrier from a strong attraction at short range (giving flocculation, a precursor to coagulation).

Dr. Dickinson gave three examples of simulations using the methods he described. Firstly, the application of a shear to a system of flocculated colloidal particles showed that the effect of the shear was to order the particles into a more regular structure. It was reasoned that the shear overcame the brownian motion within the flocculated mass and constrained the random motions. The second

simulation was of a large spherical particle with a number of 'active sites' to which model enzyme particles became attached. As the simulation proceeds more of these sites become reacted and the reaction rate can be determined. In the absence of interparticle hydrodynamic interactions, the reaction occurs faster but the evolving distribution of reacted sites is similar, which suggests that hydrodynamic interactions merely slow the reaction, and may be ignored in many instances. The third example was a simulation of a diffusion-limited aggregation of colloidal particles in 2-D. As the simulation proceeds the particles appear to form long chains, gradually using up the free particles. Eventually the chains form cross-links giving a final fractal-type aggregate structure. Further coagulation is diffusion controlled. In more dense systems the formation of chains is less likely to occur.

T. Akesson of the Chemical Centre Lund described the work which he and his colleagues have been doing in applying (and verifying) the Smoluchowski - Poisson - Boltzmann (SPB) approximation in a study of diffusion in nonuniform electrolytes, in this case, ion diffusion at charged interfaces. The SPB is produced from the many-particle Smoluchowski equation by reduction to a hierarchy of coupled  $n$ -particle equations and application of the Instantaneous Relaxation Approximation (IRA) to decouple the equation for the one-particle self-propagator. Further application of the Mean Field Approximation (MFA) results in the SPB equation.

The system on which this approximation was tested consisted of a solution of point ions immersed in a dielectric medium with uniformly charged parallel plates. The system was modelled using the generalised many-particle Smoluchowski equation in a stochastic dynamics simulation and also by solving the one-particle Smoluchowski equation numerically using the exact (simulated) equilibrium potential of mean force. Finally, the SPB equation was solved analytically. The properties studied were the diffusion propagators, mean first passage times and the survival probabilities of the ions. It was found that the IRA was a useful approximation, but the MFA could fail where there was strong Coulombic coupling. Using a realistic potential of mean force the one-particle Smoluchowski equation provided accurate results.

T.C.B. McLeish of Cambridge University provided an interesting review of the work in the Cavendish Laboratory on theoretical polymer physics. He began with the current model for the diffusion of hard rods. Depending on the parameters defining the system (the length of the rods  $L$ , their diameter  $d$  and their concentration  $c$ ) hard rods may show a number of different behaviours. At low concentrations solutions are isotropic but nematic ordering is apparent at higher concentrations. Diffusion is severely hindered in directions perpendicular to the rod axis and entanglement is possible. The motion of the rods is clearly easier along the direction of the axis and this leads naturally to the 'reptation' models for translational diffusion. The dynamical theory employed in these studies is due to Doi and Edwards. The theory has been tested by simulation and extended to thick rods that show a nematic phase. Additional work on 'cooperative correlations' by

Vilgis and Edwards have led to predictions of the behaviour of the diffusion constant near the glass transition. Near the glass transition a 'power law' dependence of the diffusion constant with concentration is expected and an exponential dependence (Vogel - Fulcher dependence) further away from the transition.

The second topic of interest was the modelling of entangled polymers as self avoiding random walks on a lattice. Such a model has application in the study of polymer chains in a gel or mixed polymers where the chains reptate through the bulk. The model also serves in describing electrophoresis, where the polymer chains are charged and are driven by an electric field. In these simulations it has been found that short chains travel relatively freely through the lattice but longer chains experience entanglement, which must be relaxed through conformational changes before a free response returns. The Doi-Edwards theory of polymer melts undergoing shear predicts a critical shear rate beyond which a region of instability exists. This has been invoked to explain the 'spurt' effect in capillary flow of monodisperse linear polymers.

The third topic covered was the simulation of diffusion limited aggregation on a 2-D lattice to model such phenomena as copper electrodeposition. It was found that the simulations produced 'fractal-like' behaviour in accord with observation, but that the simulation showed non-isotropic effects due to the lattice. Forced anisotropy produced needle shaped clusters, in line with a 'cone angle' theory of diffusion limited aggregation of R.C. Ball et. al.

Dr. J.H.R. Clarke of the Department of Chemistry, U.M.I.S.T. described an investigation of the elastic properties of textile fibres by simulation of model polymers under conditions of stress. Realistic modelling of polymers is hampered by lack of knowledge of the true structure, but enough is known to allow exploratory simulations. Two systems were studied, both of which consisted of model flexible polymer chains strung between fixed end zones which represented the fixed crystalline bulk. In one system chains of equal length were arranged in a regular (approximately parallel) configuration. In the other uneven chains were arranged in a disordered configuration, complete with entanglements and end defects to mimic the believed structure of an amorphous polymer. The interactions between chains were treated as Lennard-Jones site-site interactions and the intra-chain interactions included valence angle and dihedral angle forces as well as Lennard-Jones interactions between non-neighbouring sites. The systems were allowed to relax to a prescribed stress using a simulation variation of the Rahman-Parrinello technique. Statistical averaging was then conducted over a constant volume ensemble. The strain of the system was measured in terms of the extension of the distance between the end zones from the equilibrium (zero stress) value. A knowledge of both stress and strain allows the calculation of Young's Modulus, which for the ordered structure was 804 kbar and for the amorphous structure was 59 k bar. A theoretical calculation using Treloar's formula predicted 781 k bar for a single linear polymer chain.

The simulation technique allows the interesting possibility of determining the effect of the intermolecular forces on the elasticity. It was discovered in the ordered system that removal of these forces had a substantial effect. As the system is relaxed from a condition of high tension the chains become free to explore more configurations, this has the effect of pulling the system inwards. The effect continues to be apparent until the intramolecular 'excluded volume' forces begin to restrict the freedom of the chains and eventually dominate. In this condition, the system pushes outwards. This gives the polymer very different elastic properties from the case when intermolecular forces are included, except when the chains are strongly extended and the described effects are reduced. The results show that it is harder to extend a polymer chain when intermolecular forces are absent. Interestingly, in the amorphous system the opposite effect is observed, since here the extension helps to relax the chain tensions and thus gives them greater freedom to explore other configurations.

Another phenomenon investigated was the autocorrelation function of the normal stress at the interfacial region as a probe of the 'accordion' modes of vibration in the ordered chains. The Fourier transform of this correlation function resembles the known spectrum for the accordion modes and also possesses a remarkably similar dispersion curve. These results suggest that there is much that can be learned about the behaviour of real polymers, even in the absence of a sure knowledge of their structure.

The final speaker on the first day was Professor W. Bruns of the Ivan Stranski Institute of Physical and Theoretical Chemistry, Berlin. He described his investigations of the 'theta' state point of polymer solutions by Monte Carlo simulation. The theta state point was first defined by Flory. It occurs when the repulsive energies between the segments of a dissolved polymer are balanced by the attractive energies. In this circumstance the second osmotic virial coefficient vanishes and the polymer behaves as an ideal random flight chain in which the configurations it adopts are governed by short range forces only. This condition is amenable to both analytical treatment and Monte Carlo simulation.

Professor Bruns described in detail the Monte Carlo simulations he has performed to investigate the validity of the theta state concept. The calculations were performed as a random walk on a simple cubic lattice with four choices of configuration (trans, cis, gauche(+) and gauche(-)). The state point of the simulation was chosen to ensure that the second osmotic virial coefficient vanished. Various chain lengths were studied and the results were extrapolated to infinite length. The results obtained were considerably different from those obtained from the random flight theories and this throws strong doubt on the validity of the theta state concept.

J.-P. Ryckaert of the University of Brussels described his work on the simulation of solid paraffins by molecular dynamics.

The solid paraffins have a complex phase diagram. The low temperature crystal is primitive orthorhombic but prior to melting the crystal may show one or several rotator phases, depending upon the length of the basic hydrocarbon chain. Dr. Ryckaert described in detail the structure of the basic crystal and the rotator phases. The structures clearly offered a severe test of the Parrinello-Rahman MD (PRMO) method and the constraint dynamics method, which Dr. Ryckaert pioneered.

In the MD simulations the crystal was modelled as a set of 30 hydrocarbon chains, each 16 carbon atoms in length. Periodic boundary conditions were used in all directions, with C-C bonds connecting the chains across the boundaries in the z-direction (the chains were aligned initially in the overall trans-configuration along the z-direction). A modification of the PRMD method was employed for these unique boundary conditions. To 'freeze out' the immense number of rapid degrees of freedom in the model, the constraint method was used. The C-C and C-H bonds were 'fixed' and the planes containing H-C-H and C-C-C bond angles were constrained to be perpendicular to each other and to bisect the included angle at the common carbon atom. The potential was modelled as a Buckingham site-site potential with Williams' parameters. Torsional strain was also included. Equilibration was achieved using Andersen's 'massive stochastic collisions' method.

The simulations showed the correct behaviour of the MD cell principal axes with temperature; the onset of the rotator phases is accompanied by a sudden change in the cell vectors. Also the simulation showed the diffusion of the chains as 'reptation' along the z-direction by individual chains. A study of orientational correlations showed that at higher temperatures rotational disorder occurred. At 325 K there were two distinct preferred orientations. This rose to four orientations at 375 K. At even higher temperatures complete rotational disorder was expected but the results were masked by noise. Also there were grounds for believing that in this instance (near the melt) the PRMD method was giving rise to spurious cell vectors. Nevertheless it was clear that the method developed so far had yielded much insight into the behaviour of solid paraffins.

A particularly pleasing aspect of the York Meeting was the contribution of several talks by postgraduate students. The first speaker in this category was Mr. C.M. Freeman of the Department of Chemistry of University College London. His subject was the 3-D structure of polypeptide known as apamin, which occurs naturally as bee venom. As well as being a powerful neurotoxin, apamin exhibits a stable structure under extremes of pH and solvents of different polarities. Despite this it seems not to have been crystallised. Proposed structures have therefore been inferred from NMR spectroscopy, circular dichroism, the polypeptide sequence structure and ab initio energy minimisation. No fewer than five plausible structures have been proposed.

Mr. Freeman and his colleagues have studied the question of the structure afresh using the energy minimisation technique. The

molecule was modelled with harmonic bonds and bond angles, a cosine torsional strain function and 'improper torsion' to conserve the bond hybridisation. The model also included Lennard-Jones site-site interactions, H-bonding (modelled as a 12-10 potential) and electrostatic interactions. The relative stability of the five possible structures was found to be strongly dependent on the dielectric constant used in the electrostatic calculations. However one particular structure, due to Hider and Ragnarsson was consistently of low energy and also explained the spectroscopic results.

A.C. Treharne described in some detail the the studies that have been undertaken with her colleagues at the Department of Crystallography, Birkbeck College in determining the structure and activity of the hormone Oxytocin. This was a study that brought together many of the techniques of structure modelling by computer, including molecular dynamics simulation and the use of computer graphics.

The actual hormone studied was the closely related Deamino - oxytocin. This has been solved crystallographically by Cooper et al. and has two distinct conformations in the crystal asymmetric unit. The main differences arising in the location of a disulphide bridge and Ile-3 side chain. Energy minimisation calculations by Haneef, using the program EMPNMA (an energy minimisation and normal mode analysis program) with potential functions due to Weiner et al., have determined the relative stability of the two structures, which differ by approximately 8 kJ/mol., and confirmed the crystallographic conformations. The Normal Mode Analysis, which used an algorithm due to Lanczos, provided mean - square amplitudes of vibration which compared well with refined thermal parameters.

To provide further insight into the hormonal activity of the molecule a one nanosecond molecular dynamics simulation was performed. Starting from the least stable of the two structures the molecule was thermalised to 300K over 50ps. After one nanosecond the structure more closely resembled the alternative structure. While the ring main chain atoms showed little flexibility during the simulation, some of the side chains showed considerable flexibility, particularly at the disulphide bridge and in the correlated motions of the Tyr-2 and Asn-5 side chains. Such observations are clearly important in understanding the functional activity of the molecule and indicate that molecular dynamics has an important and interesting role to play in elucidating the chemistry of macromolecules.

I. Haneef, also of the Department of Crystallography, Birkbeck College, described the various methods employed at Birkbeck to extract dynamical information from polypeptide and protein structures. High resolution X - Ray data have been obtained for a number of complex structures such as oxytocin (see above), aPP, RNase-A and others. The program RESTRAIN, a least - squares refinement program, has been used to extract dynamical data in the form of mean - squared amplitudes of vibration and frequencies of atomic motions and librations of rigid moieties. Complementary to

this approach theoretical methods are also employed, particularly conformational analysis, energy minimisation, normal mode analysis and molecular dynamics simulation. The principal programs used in these studies are EMPNMA and GROMOS. The comparability of the results obtained from these different methods was described by Mr. Haneef with reference to numerous examples.

The minima of calculated potential energy surfaces allow the torsion angles of rigid side chains to be determined along with the mean - squared amplitudes and frequencies of rotation. These show very good agreement with the results obtained from diffraction data. Also with regard to structure, energy minimisation and molecular dynamics methods show very similar RMS deviations from the refined structures and are comparably accurate methods for determining structure. Using normal mode analysis, the mean - squared amplitudes of main chain vibrations have been shown to agree closely with refined thermal parameters and the side chain atom amplitudes correlate reasonably well with those obtained from different models for the thermal parameters. Time averaged molecular dynamics structures have shown a strong correlation between the deviations from the refined thermal parameters and the genuine molecular flexibility. The anharmonicity of vibrations, reflected in the 'd-values' (parameters which show up the differences in vibrational amplitude of bonded atoms) obtained from either the diffraction data, molecular dynamics or normal mode analysis show interesting differences. In particular it appears that restrained least squares analysis overestimates the anharmonicity of the vibrations.

In a talk which took full advantage of computer graphics (in the form of motion films) Dr. P. Krueger of the Neues Klinikum, Aachen described the molecular dynamics simulation of two extremely large molecules; aPP and Hagfish insulin. The aPP molecule consists of three distinct regions; an alpha helix is connected to a polyproline helix via a 'beta turn' region. In the crystal the molecule exists as a dimer. Both the crystal and the solution have been simulated by MD and the structural differences investigated. In the crystal, the alpha helix is very stable and the tyrosine 36 residue is very flexible. In solution the positional differences are most apparent in the region of the beta turn and the phenyl alanine 20 residue shows a marked structural change. Space filling models show that the structure in solution is less compact than the crystal.

Hagfish insulin exists in two possible forms revealed in the analysis of the X - ray diffraction data. The resolution of this dimorphism was clearly within the compass of molecular dynamics simulation. The simulation showed that, as expected, the two structures were interconvertible. Other features of the molecular motions were revealed in a motion film of the simulation. Once again the alpha helices revealed themselves to be highly stable entities. The importance of intramolecular bridges, particularly the so called salt bridge and the disulphide links, in determining structure and stability was borne out. Also apparent was the high flexibility of the aromatic side groups and especially the Phe 25

unit. The convergence of the two forms in solution was seen.

Dr. C.L. Brooks of the Carnegie-Mellon University of Pittsburgh described an important method for modelling the behaviour of enzymes in solution, which provides a remarkable insight into the processes of enzyme action. Enzyme action proceeds in three distinct phases: (i) the encounter of the enzyme with the substrate in solution (an essentially electrostatic phenomenon, diffusion controlled); (ii) complexation of the enzyme and substrate (with conformational changes and solvent expulsion) and (iii) specific binding and catalysis (where detailed atomic and electronic interactions occur). The first two stages are accessible to MD simulation, and Dr. Brooks has devised a stochastic boundary method to deal with them.

The basic model requires surrounding the active site in the enzyme with a spherical 'reaction zone' about 1 nm in radius. Surrounding this is a 'buffer region' which interfaces with the outside 'reservoir region' and is perhaps .2 nm in thickness. The reaction zone is modelled explicitly using molecular dynamics and is the primary region of interest. The reservoir region is not explicitly modelled and the atoms are replaced by averaged and stochastic forces acting directly onto the buffer region, which is modelled by stochastic dynamics. The reservoir region provides the heat bath for the system and also maintains the integrity of the central region through the boundary forces. The stochastic forces are simple Langevin random forces scaled through the fluctuation - dissipation theorem. The averaged boundary forces are represented by a mean field force (based on the solvent RDF) in the solvent and by effective harmonic forces where the boundary cuts the enzyme macromolecule.

The model has been tested in two specific simulations: for ST2 water in a .9 nm sphere of 98 molecules, which gave RDFs, VACFs and spectral densities comparable with Stilliger and Rahman's results, and for the enzyme lysozyme, with the 1.1 nm reaction sphere centred on the Trp 62 residue, which reproduced the structural and dynamic properties of a complete lysozyme molecule simulation in vacuo.

Dr. Brooks discussed two examples of the application of the method to enzyme studies. The first was an investigation of the effects of the solvent on the dynamical properties of the atoms within the reaction zone of the lysozyme system mentioned above. Here there was evidence of solvent damping of the N atom displacements near the tryptophan residue, though this is not seen in the VACFs. The results were explained in terms of exposure to the solvent molecules (solvent accessibility) and the motional timescales of the solvent and the protein atoms. The second example was a study of the active site of the enzyme ribonuclease. Here it was revealed that in the native enzyme, the H-bonding of water to the enzyme closely mimics the H-bonding to the substrate. Also there are strong correlated motions between positively charged groups in the active site and the substrate, despite the spatial separations involved. These observations represent significant

progress in understanding the complexation process. The method clearly has great potential in investigating enzyme processes.

The final speaker of the meeting was Dr. R. Hubbard of the University of York, who described to all present the various graphics devices available today for the production of high quality graphics and how they may be used to produce motion pictures of MD simulations. The reasons for making such pictures were outlined. Firstly, they help to reveal correlated motions by exploiting the abilities of the human eye. Secondly, the use of colouring and selection aids description and understanding of the processes observed. Thirdly it is possible to follow the development of a phenomenon more easily than through interpretation of numerical data.

The simplest method of producing a motion picture is to photograph the output of any graphics device and produce a motion film piecemeal. This is cheap, if tedious, but its main disadvantage is that it is non interactive. Interactive methods allow some degree of interrogation of the output, such as freeze framing and zoom magnification etc.. This can be accomplished by streaming the MD data directly to the graphics device from the mainframe computer. Suitable devices are the Evans Sutherland PS2 and the Vector General MPS. This technique allows a greater degree of control over the pictures produced but has the disadvantage of tying up resources. A better method is to store the MD data on the actual graphics device itself (e.g. Evans and Sutherland PS300). This allows greatest flexibility in producing motion pictures. However, it is also the most expensive!

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REPORT ON THE CCP5 WORKSHOP ON THE COMPUTER SIMULATION OF SILICA AND SILICATES

Compiled by S. Parker

This meeting, although restricted to eleven participants, demonstrated the diversity of applications to silicates using computer simulation techniques. The areas discussed ranged from lattice dynamics of quartz and molecular dynamics of amorphous silica to static calculations of crystal structure and defect properties of complex silicates. The major problem with modelling silica and silicates is the difficulty in deriving reliable potentials for the silicate ( $\text{SiO}_4$  or  $\text{SiO}_6$ ) units. Thus one aim of the workshop was to identify the different types of potential models that have been developed, the limitations and possible improvements. The relative merits and the ways of evaluating the different potentials were also discussed, with the eventual aim of choosing a set of potential functions that should satisfy most demands. Another area was the relationship between the static and dynamic simulations and the relevance of ensuring that a particular potential model should be applicable to both types of simulation. We next include a summary of the talks in order of presentation and followed by a discussion of the problems raised and some of the general conclusions.

Dr. Parker spoke at length reviewing the potential models used in simulating the crystal properties, such as the crystal structure of orthosilicates. The major feature of orthosilicates is that the  $\text{SiO}_4$  tetrahedra are isolated. Three types of potential model were considered; (i) partially ionic two-body, (ii) fully ionic two-body and (iii) fully ionic three-body. The potential models (i) and (ii) are both two-body central force potentials that differ in the assumed charge on silicon and oxygen. In addition a Morse potential was added between silicon and oxygen to compensate in part for the loss of cohesion on reduction of ionic charge. The fully ionic three-body potential includes anion polarisability and a bond bending term for the O-Si-O bond angle. There are two philosophies for deriving the potential model parameters; first, fitting all parameters to the crystal structure of the silicate being examined and second, transferring the potential model from the component oxides e.g. for  $\text{Mg}_2\text{SiO}_4$  transfer the parameters derived by fitting the structural, elastic and dielectric properties to  $\text{MgO}$  and  $\text{SiO}_2$ .

These models were tested for  $\text{Mg}_2\text{SiO}_4$ , which has the olivine structure at ambient conditions and transforms to spinel at high pressures. The results show that the two structures can be reproduced if the parameters are derived by fitting to one of these structures, namely olivine. However, when the compressibilities were considered for those models which were constrained to the fully ionic charges, they failed to calculate the correct values. Thus fitting direct to the silicate structure alone, the partially ionic model is most appropriate. When transferring the potential parameters from the oxide (this has the advantage of being applicable to any silicate) both experimental crystal structure and

compressibility of the silicates are reproduced, particularly with the three-body potential model.

Finally Dr. Parker highlighted the difficulty in evaluating phase transition energies - due to the sensitivity of the transition energy, to small changes in the parameters. Thus the phase transition, if known, would be a good experimental measurement to be used in deriving the potential model parameters.

Dr. Catlow described recent progress in the simulation of zeolites. These important, framework-structure aluminosilicates have attracted considerable attention recently in view of their application as heterogeneous catalysts. Simulations have three main aims: (i) predictions of the positions of extra-framework cations, (ii) investigation of framework geometry, (iii) study of the location and energetics of adsorbed molecules. Successful work has been undertaken in the first area by Sanders (Ph.D. Thesis, University of London, 1984, see Sanders et al., J. Phys. Chem. v88, p2796, 1984). Problems arise with partial occupancy of cation sites which require complex and costly permuting procedures in order to identify the favoured configurations. In the area (ii) success has been enjoyed in the study of several zeolites (zeolite A, X and Y, and the ZSM class) employing potentials which include bond bending terms. Recent work has shown that useful predictions can be made regarding the energetics of sorption; but the results are critically dependent on the potentials, which are often uncertain.

In summary, reliable simulations of zeolites are now possible. Problems remain concerning the treatment of partial occupancy and sorbed molecule - framework interactions. Bond bending potentials seem to be very suitable for these systems.

A lattice dynamical study was described by Dr. Barron which modelled the thermal expansion of alpha-quartz. In alpha-quartz the atomic sites in the crystallographic unit cell are not fixed by symmetry but can be described by 'internal' strain coordinates. Thermal expansion involves the interplay of those strains which preserve the crystal symmetry. Experimental expansion coefficients, pressure - dependence of spectroscopic frequencies and third order elastic constants together comprise a large body of highly detailed information about the anharmonic behaviour of the crystal vibrations (Barron, Collins, Smith and White 1982 J. Phys. C. v15, 4311). A lattice dynamical model was fitted to this data, the model included six anharmonic force constants in addition to the short-range potential model of Barron, Hugg and Pasternak (1976 J. Phys. C. v9,3925), in which angle forces are replaced by 'struts' between neighbours of a given atom.

The fits of this simple model to the microscopic expansion was shown to be good except at the lowest temperature (<10K) and also reproduces the internal expansion observed by X-rays, which was not fitted. The strut model does fortuitously give a crude picture of a feature of the actual forces: as angles open up, so atom-atom bonds tend to contract. The model also confirms that tetrahedral tilt is the largest single effect in changing of the crystal structure with

temperature; and with anharmonic force constants small distortions of the  $\text{SiO}_4$  tetrahedra strongly affect the thermal expansion, especially at low temperatures. Dr. Barron also indicated that it was not possible to fit simultaneously all the anharmonic information available and therefore it should be possible to use this information to develop more sophisticated models.

Dr. Heggie discussed the use of computer simulation for modelling plasticity in minerals by examining dislocations in alpha-quartz. He described his progress in modelling the structure and mobility of dislocations. The potential models chosen were Keating potentials, one of which included the next-nearest neighbouring O-O interactions. The parameters for these models were obtained by fitting to the experimental elastic constants, phonon spectra and internal strain. Fifteen dislocations were considered and for a given Burgers vector and line direction the ground state structure was calculated using energy minimisation.

Dr. Heggie outlined the process of kink pair nucleation and migration, and the dependence of kink pair formation energy on kink separation, which should give the isolated kink formation energies and the kink-kink attraction. The major problem in these simulations is lack of sufficient computer time and store. However progress to date suggests that the kink pair formation energy is between 5 and 11 eV. Another important result from this work is that the dislocation and kink structures using the Keating potential model described above gave rise to defect states deep in the fundamental gap of alpha-quartz. This implies that these dislocations and kinks, when stationary, will not be affected by changes in the chemical potential for charge carriers.

Dr Doherty described recent progress made in the simulation of point defects and cation mobility in magnesium silicate ( $\text{Mg}_2\text{SiO}_4$ ) with the olivine structure. Interest is centred on olivine because it has a high natural abundance, particularly in the upper mantle, and studies of defect structure and migration will aid in understanding transport properties in the mantle.

A range of potential models were used to discover their relative merits and potential sensitive properties. The defect simulation technique (available to CCP5 from M. Leslie) used a two region approach; with a central region around the defect, which is treated explicitly, and an outer region that uses a continuum approximation. The potential models described were all two-body, central-force potentials, although both partially ionic and fully ionic models were used. All the models gave good agreement with the experimentally determined Schottky energy. However differences did occur when simulating the magnesium Frenkel defect, which is believed to be the dominant intrinsic defect, as the partially ionic model differed significantly from the experimental value. The fully ionic model reproduced not only the experimental magnesium Frenkel formation energy but also the activation energy for magnesium migration.

The conclusions were that this approach can be used to model point defects in silicates, the major difficulty arising when the partially ionic potential model is employed. Improvement is expected when three body terms are included, such as anion polarisability and bond bending terms. Finally, Dr. Doherty suggested that defect simulation may provide a sensitive test for the reliability of potential model parameters.

Dr. Jackson described recent simulation studies of zeolites and clays. The development of a bond bending potential for quartz has also enabled framework relaxation in zeolites to be accurately modelled. Recent calculations were reported in which the dehydrated form of Na<sup>+</sup> zeolite A was simulated; the structure after lattice energy minimisation was in good agreement with the experimental structure. It should be noted that rigid ion potentials were used; these appear to be adequate for structural simulations.

Clays, which are layer aluminosilicates, have proved difficult to simulate using the potentials that have been so successful for quartz, and for zeolites. The problem appears to be due to the difficulty in representing interlayer interactions; calculations using a shell model description of some ions seem to give improved results, but further work is needed, and is in progress.

Finally, Dr. Jackson described calculations using Hartree-Fock SCF methods to calculate potentials to describe ion - water interactions. These potentials will enable hydrated minerals to be simulated.

Dr. Price discussed recent work on magnesium silicates (MgSiO<sub>3</sub>) with the perovskite structure, which differs from all other silicates discussed in this workshop in that silicon is coordinated to six oxygen atoms in perovskite instead of the usual four. The high coordination arises from the high pressures under which it was formed, as may be observed in the earth's mantle. Indeed MgSiO<sub>3</sub> is believed to constitute 40% of the earth's volume. There are two problems currently under investigation: (i) the effect of pressure and temperature on the crystal properties and (ii) the physical properties affecting rheological behaviour, such as stacking fault and point defect energies, ionic conductivity and thermal expansion.

Fully ionic and partially ionic potential models were used; the parameters were obtained by fitting to the crystal structure found under ambient conditions. Both were successful in reproducing the high pressure crystal structure and also the relative stability of the two phases. However the partially ionic model gave best agreement when calculated compressibilities were compared with those determined from seismic studies. Finally, Dr. Price described a molecular dynamics simulation on MgSiO<sub>3</sub> under mantle temperatures and pressures. The simulation calculated successfully the thermal expansion and found that when Schottky defects are present the material becomes a superionic anion conductor, which could have major consequences for studies into the convective processes in the mantle. The major difficulty in this work is the lack of available

experimental data.

### CONCLUSION

The talks raised a number of problems that were of mutual interest. Perhaps the most important was which functional form was the most appropriate to modelling silica and silicates, answering such questions as (1) should an ionic model be used?, if so what charge states for silicon and oxygen?, (2) is an accurate representation of the electronic polarisability essential? and (3) does the inclusion of three-body effects such as bond-bending terms greatly increase the reliability of the simulation over the use of pairwise short range interactions?

The ionic model was successful in simulations ranging from melts and glasses to structural and defect calculations on minerals. However, the ionic model was not considered appropriate when there was a large number of particles due to the cost in computing time. This is particularly important when there is little symmetry e.g. for modelling ionic molten salts and dislocations in silica. The covalent model for silica described by Dr. Heggie was a Keating potential including three-body forces, and was capable of simulating the elasticity data of quartz. Other calculations used the ionic model with charges set to the formal oxidation states i.e.  $\text{Si}^{4+}$  and  $\text{O}^{2-}$ . The advantage of fixing the charges is that less parameters need be fitted and once obtained are simpler to transfer between silicates. The disadvantage is that the derivation of partial charges, because of the increase in parameters, does give better agreement with experimental observations. However, an additional problem with the partially ionic model is the difficulty in simulating point defects, which may result in having to arbitrarily reassign charge distributions.

There was general agreement that electronic polarisability should be included in the simulation studies. One of the simplest ways of incorporating the polarisability is by the use of the shell model. Dr. Jackson showed that the shell model was necessary when modelling the layered silicates such as clays. These calculations also demonstrated the need for three-body contributions, and although not strictly required for the less condensed silicates e.g. olivine, where  $\text{SiO}_4$  units were isolated, incorporation of bond-bending terms did give a marked improvement in agreement with experiment. Dr. Leslie also found that the potential models depend critically on the coordination of the cation, particularly for aluminium and sodium.

When empirically deriving potential models or testing their reliability it was agreed that the most appropriate properties that should be reproduced were (1) structure, (2) transport data, (3) lattice dynamics and (4) spectroscopic data, which has received little attention in computer simulation.

The final conclusion of this workshop was that a systematic catalogue of data would be a major aid to both experimental studies. This compilation should include silicates e.g. quartz and other silica polymers, olivines, pyroxines, garnets and perovskites. The data for each compound should include thermodynamic, structural, elastic and dielectric properties.

A VOLUME DEPENDENT POTENTIAL FOR THE MOLECULAR DYNAMICS OF SIMPLE METALS.

A.B. Walker, W. Smith and J.E. Inglesfield

In our recent work we have been attempting to study the phase behaviour of simple metals using the Molecular Dynamics (MD) technique of Parrinello and Rahman (1). This is not a trivial application of the technique because the cohesive energy differences between the various structures are very small in comparison with the total cohesive energy (of the order of 1 percent) and this requires very careful modelling of the potential. In addition, the potential energy of the whole system is necessarily volume dependent and this creates special difficulties in devising a realistic MD simulation. In our simulations we have allowed for the volume dependence of both the pairwise interactions and the structurally independent terms in a potential model developed by Pettifor and Ward (2). The volume dependence is needed since the phase structure of metals is generally dependent upon a balance between the pair and volume forces.

Our purpose in this article is to describe the formulation of the potential and its implementation within the MD technique of Parrinello and Rahman. The emphasis will be on the potential. Our initial work has been done on lithium and we will be reporting our main results elsewhere (7).

## The Potential

The expression for the total energy per ion, calculated to second order in pseudopotential theory was obtained by Finnis (3):

$$u = u_0(\Omega) + \frac{1}{2N} \sum_{\substack{i,j \\ i \neq j}} \Psi(r_{ij}, \Omega) \quad \langle 1 \rangle$$

where

$$u_0(\Omega) = Z u_{eg} - \frac{Z^2}{2n_0 K_{eg}} + \Psi(r=0, \Omega) \quad \langle 2 \rangle$$

This potential is explicitly dependent upon the system volume  $\Omega$ .

$Z$  is the ionic (core) charge,  $u_{eg}$  the energy per electron,  $K_{eg}$  the compressibility and  $n_0$  is the number density of the unperturbed electron gas.  $\Psi(r_{ij}, \Omega)$  is the volume dependent pair potential. The explicit form for the pair potential was obtained by Pettifor and Ward (2) who replaced the well-known Lindhard function in the expression for the dielectric function they used (4) by a ratio of polynomials, thus permitting a relatively simple expression for the pair potential:

$$\Psi(r, \Omega) = \frac{2Z^2}{r} \sum_{\nu=1}^3 A_{\nu} \cos(k_{\nu} r + \alpha_{\nu}) \exp(-K_{\nu} r) \quad \langle 3 \rangle$$

where

$$\left. \begin{aligned} A_\nu &= 2 d_\nu |V_{ps}(q_\nu)|^2 \\ \alpha_\nu &= \delta_\nu + 2 \arg(V_{ps}(q_\nu)) \\ q_\nu &= k_\nu + i K_\nu \end{aligned} \right\} \langle 4 \rangle$$

and  $k_\nu$ ,  $K_\nu$ ,  $\delta_\nu$  and  $d_\nu$  depend only on the dielectric function. We have further extended the approach of Pettifor and Ward to give an analytic expression for  $\Psi(r=0, \Omega)$  in terms of their parameters  $k_\nu$ ,  $K_\nu$ ,  $\delta_\nu$  and  $d_\nu$ . On choosing a Heine-Abarenkov pseudopotential (5) of the form:

$$\left. \begin{aligned} V_{ps}(r) &= -2Z/\omega & r \leq r_c \\ &= -2Z/r & r > r_c \end{aligned} \right\} \langle 5 \rangle$$

we obtain

$$\left. \begin{aligned} \Psi(r=0, \Omega) &= -\frac{2Z^2}{\omega^2} \sum_{\nu=1}^3 d_\nu \left\{ \left[ (2(\omega - r_c) \right. \right. \\ &- K_\nu \left( \frac{1}{k_\nu^2 + K_\nu^2} + (\omega - r_c)^2 \right)) \cos(2k_\nu r_c + \delta_\nu) \\ &+ k_\nu \left( \frac{1}{k_\nu^2 + K_\nu^2} - (\omega - r_c)^2 \right) \sin(2k_\nu r_c + \delta_\nu) \left. \right] \exp(-2K_\nu r_c) \\ &+ (-2\omega + K_\nu \left( \frac{1}{k_\nu^2 + K_\nu^2} - (\omega - r_c)^2 \right)) \cos \delta_\nu \\ &- k_\nu \left( \frac{1}{k_\nu^2 + K_\nu^2} + (\omega - r_c)^2 \right) \sin \delta_\nu \left. \right\} \end{aligned} \right\} \langle 6 \rangle$$

The remaining terms in <2> are reduced, with the Nozières Pines approximation for the correlation contribution to the electron gas energy (used in the dielectric function (4)), to

$$\sum U_{eg} - \frac{Z}{2n_0} K_{eg} = Z \left( \frac{4}{15} k_f^2 - \frac{7}{6\pi} k_f \right) - 0.089 - 0.0313 \ln k_f \quad \langle 7 \rangle$$

where  $k_f$  is the Fermi wavevector of the unperturbed electron gas.

Within this formalism, the potential requires only two empirical parameters to define it completely. These are the parameters  $\omega$  and  $r_c$  of the Heine-Abarenkov pseudopotential. The former determines the depth of the pseudopotential and the latter the effective core radius (Figure 1). We have 'fixed' the potential by minimising both the pressure ( $-du/d\Omega$ ) and the difference between the experimental and calculated bulk moduli at a 'standard volume' of the system of interest, in which the ions are placed at the sites appropriate to the known lattice structure. This procedure was found to give reasonable values for the energy per ion and a density-pressure relationship in good agreement with experiment. In Figure 2 we show the form of the potential obtained from our work on FCC lithium. The two plots show the potential for volumes of 0.59 and 1.0 times the standard volume of 3.177 cubic Angstroms per ion. ( $\omega$  and  $r_c$  were 1.43 Å and 0.8943 Å respectively for the standard volume at atmospheric pressure.)

### Implementation

In the Parrinello - Rahman technique, the MD cell is allowed to change its shape in response to the imbalance between the instantaneous internal pressure and the fixed external pressure. The cell shape is specified by a matrix  $\underline{h} = (\underline{a}, \underline{b}, \underline{c})$  where  $\underline{a}$ ,  $\underline{b}$ , and  $\underline{c}$  are vectors specifying the edges of the cell. Particles within the cell are located by cell coordinates  $\underline{s}_i$ , which are related to their absolute positions  $\underline{r}_i$  by the simple equation  $\underline{r}_i = \underline{h} \underline{s}_i$ . Proceeding from a postulated Lagrangian, Parrinello and Rahman were able to derive equations of motion for the particles and for the MD cell.

The volume dependence of the potential requires us to look a little more closely at the Parrinello - Rahman algorithm, since the latter was originally formulated for pair potentials which are fixed throughout the simulation. Re-deriving their equations with our volume dependent potential gives the following equations of motion:

$$m \ddot{\underline{s}}_i = \left. \begin{aligned} & \sum_{j \neq i}^N -\frac{1}{r} \frac{\partial \Psi(r, \Omega)}{\partial r} \Big|_{r=r_{ij}} (\underline{s}_i - \underline{s}_j) \\ & - m \underline{G}^{-1} \underline{\dot{G}} \underline{\dot{s}}_i \end{aligned} \right\} \langle 8 \rangle$$

(with  $\underline{G} = \underline{\tilde{h}} \underline{h}$ , the tilde denotes a transpose) and

$$W \ddot{\underline{h}} = (\underline{\Pi} - p_{\text{ext}} \underline{\mathbb{I}}) \underline{\Omega} \tilde{\underline{h}}^{-1} \quad \langle 9 \rangle$$

where the internal pressure tensor  $\underline{\Pi}$  is given by:

$$\underline{\Pi} = \frac{m}{\underline{\Omega}} \sum_i^N \dot{\underline{r}}_i \dot{\underline{r}}_i + \frac{1}{2\underline{\Omega}} \sum_{\substack{i,j \\ i \neq j}}^N -\frac{1}{r} \frac{\partial \Psi}{\partial r} \bigg|_{r=r_{ij}} \underline{r}_{ij} \underline{r}_{ij} - \left\{ N \frac{du_0}{d\underline{\Omega}} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^N \frac{\partial \Psi}{\partial \underline{\Omega}} \bigg|_{r=r_{ij}} \right\} \underline{\mathbb{I}} \quad \langle 10 \rangle$$

where  $\underline{r}_{ij} = \underline{r}_i - \underline{r}_j$  and  $\underline{\Omega} = \text{Det} \underline{h}$  is the volume of the cell,  $m$  is the mass of each atom and  $\underline{\mathbb{I}}$  is the identity matrix. The parameter  $W$  is an effective mass for the MD cell itself, permitting us to write an equation of motion for the cell. This has no influence on the thermodynamics of the system of particles, but does affect the rate of the fluctuations in the cell dimensions. (Equations similar to  $\langle 8 \rangle$ ,  $\langle 9 \rangle$  and  $\langle 10 \rangle$  were also obtained by Barnett et al. (6).)

The potential expressions presented so far are, despite their pleasing analytical simplicity, computationally expensive to evaluate. Furthermore, in the course of the MD simulation we need to evaluate first derivatives with respect to inter-particle separation (to obtain the forces) and volume (to obtain the pressure tensor) - and we have yet to account for the volume dependence! Because of these difficulties we have opted for the

following scheme.

The volume dependence of our pair potential is contained in the parameters  $A_v$ ,  $k_v$ ,  $K_v$  and  $\alpha_v$ . We have therefore tabulated these parameters over volumes ranging from 1/3 to 3 times the 'standard volume' mentioned above. For a given volume we calculate the values of the parameters by interpolation using a Chebychev polynomial of high accuracy. The derivatives of the parameters are treated similarly. Using the parameters we then construct tabulation arrays containing the values of the potential function, its derivative with respect to volume and the radial force, as functions of the inter-particle separation. From these arrays, the potential, force and terms contributing to the pressure tensor may be interpolated. (This kind of interpolation is commonly used in MD when the potential energy function is expensive to evaluate). It is important to realise that we must go through this whole procedure for every time step of the MD simulation because at each new time step the system volume will be different. In all other respects the method is identical to the familiar method of Parrinello and Rahman.

### Lithium

Using the methods described above we have begun a study of the phase properties of simple metals. Our preliminary results for lithium (7) are encouraging in that we see the expected phase

properties (i.e. the metal transforms to FCC at low temperatures and pressures and to BCC at high temperatures and pressures). However we have found that, at atmospheric pressure and in the FCC structure, our system melts between 250K and 275K, whereas it is believed to undergo a FCC-BCC transition at a temperature around 120K (8) and melt at 454K (9). This failure clearly arises from the potential we have used, and we believe we can correct this deficiency by using a nonlocal pseudopotential. This avenue is currently being explored by us.

We have also found that there exists a large region of the phase diagram in which the structures FCC and BCC appear to be equally stable and if placed in either of these phases, the system shows no tendency to change. Our belief is that the volume dependence of the potential creates special difficulties when the energy difference between two phases is small and the fluctuations in volume give rise to energy fluctuations of comparable magnitude. This may be the reason that Munro and Mountain (10), who used a fixed pair potential, did not report similar difficulties. It must be remarked however that difficulties in observing expected phase transitions in MD simulations are not unknown! The solution to this problem may be to increase the size of the system and thus reduce the fluctuations or to run the simulation for very long times in the hope that thermodynamic equilibrium will prevail. Both of these options however are likely to be expensive.

While we undoubtedly have much to learn in the application of this technique, we are confident that we have the basis of a useful

method for the study of phase transitions in simple metals. As our understanding of the method develops we hope to uncover some very interesting phenomena.

### Acknowledgements

We would like to thank M. Silbert and D. Pettifor for helpful discussions.

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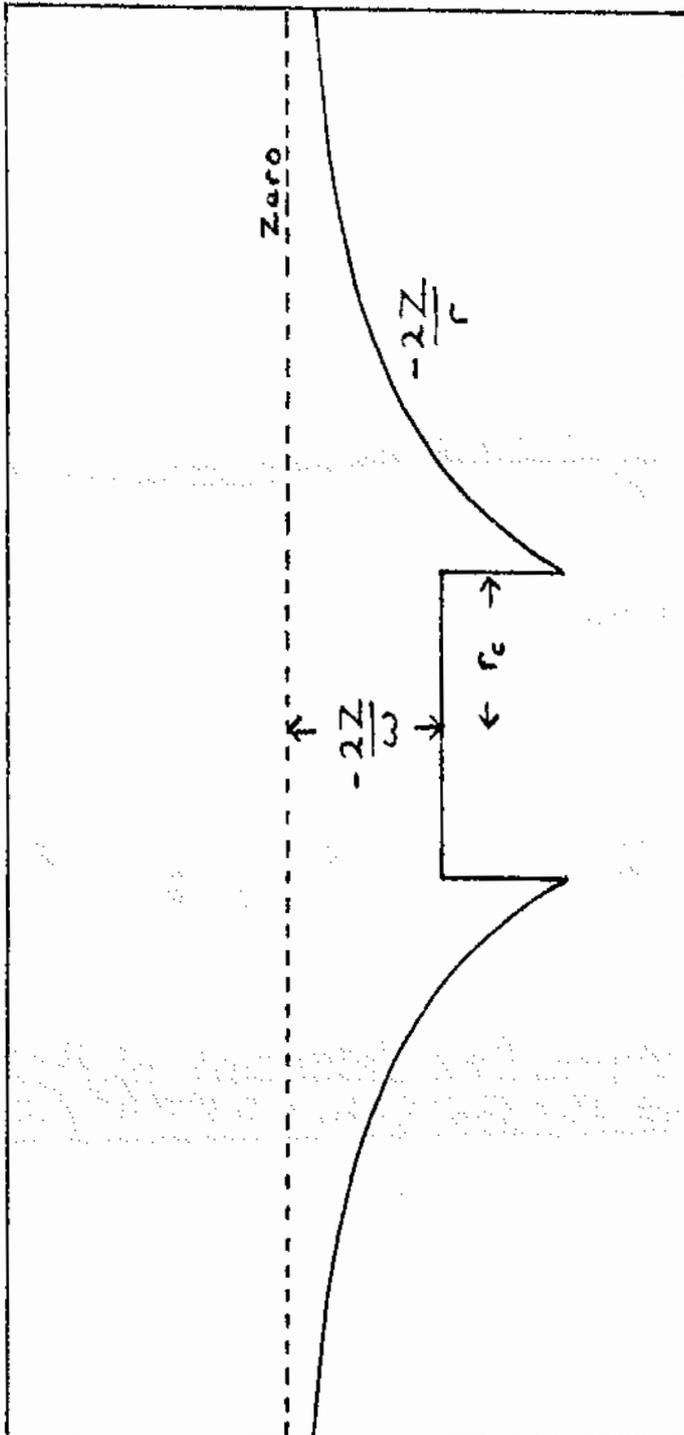


Figure 1: Heine - Abarenkov Pseudopotential

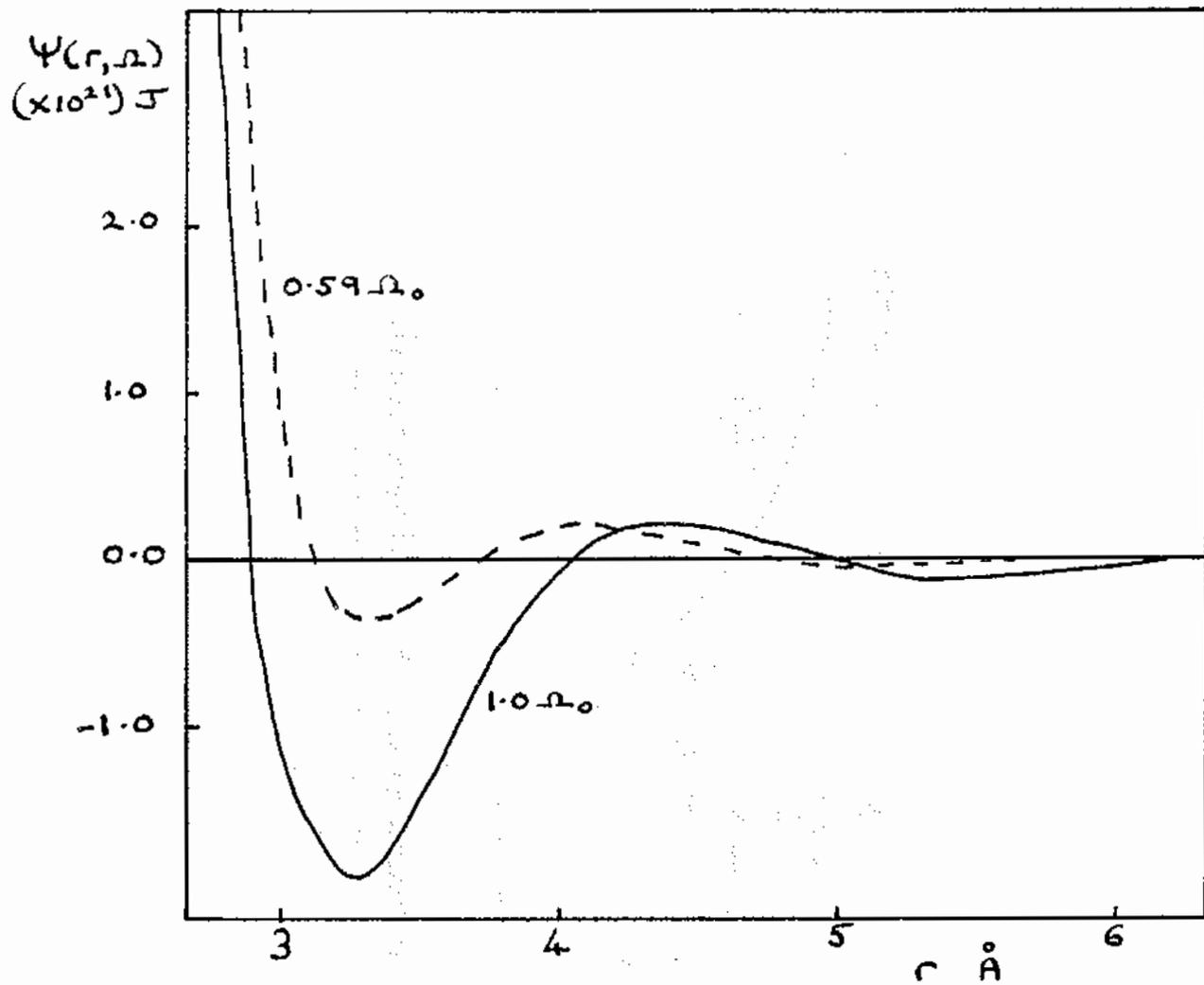


Figure 2: Lithium Pair Potential at  $\Omega = 0.59 \Omega_0$  and  $\Omega = \Omega_0$  ( $\Omega_0 = 3.177 \text{ \AA}^3/\text{ion}$ )

MORE ON THE CHOICE OF TIMESTEP MAGNITUDE IN MOLECULAR DYNAMICS

by

David M. Heyes

The most sensible choice of the timestep in Molecular Dynamics, MD, is rarely the subject of discussion in the literature. This is perhaps surprising as it can affect the cost effectiveness of a simulation project considerably. Also the results could be changed by varying the magnitude of the timestep, which is much more important. It is therefore heartening to read contributions in the CCP5 quarterly on this subject. This note is another in this series!

Nigel Corbin [1] devised an ingenious scheme for assessing the effect of timestep on single particle motion. He calculated the velocity and force autocorrelation functions (vacf and facf, respectively) of nominally identical trajectories, starting from the same point in phase space, but evolved with different time steps. Using the LJ fluid and LJ reduced units [2] (e.g.  $\sigma(m/\epsilon)^{1/2}$  for time) he correlated the trajectories using time steps, of 0.001 and 0.002 reduced units. The normalised vacf and facf were essentially unity until a time of approximately 2.5 after which there was a precipitous drop to zero by a reduced time of 4. This sudden 'decorrelation' is very interesting and indicates the limit to

realistic assessment of dynamical correlations. Provided the ratio of the two time steps is the same the decorrelation time remains more or less unchanged over a range of fluid densities [3]. Unfortunately it is not possible to determine the accuracy of trajectories derived using a single time step from these calculations (i.e., "what's the best time step to use") because [1] always compares the dynamics of two similar runs. Consequently they only monitor relative errors. (Although these simulations do provide a time-scale within which a particular timestep is likely to give sensible dynamics.) This point is particularly telling in another related technique, that of "differences-in-trajectories" MD [4,5]. Here the two trajectories through phase space are different because in one case the equilibrium trajectory is perturbed by a small force field. (The timestep magnitudes are the same in both cases.) The difference in system properties from the two simulations are followed. The total energy difference, for example, can be constant to within  $10^{-5}$  [4]. Therefore although the individual paths through phase space can have energy fluctuations of order 0.01, their difference can be many orders of magnitude smaller. Absolute algorithm errors are essentially the same in both cases and largely cancel on subtraction. In other words, the perturbation does not significantly induce further algorithm errors. Perturbation trajectories are therefore surprisingly 'free' of algorithm errors; noise at long times being due to insufficient sampling of phase space.

David Fincham looked at the effect of timestep magnitude on thermodynamic, structural and dynamical properties of a LJ state at a reduced density,  $\rho^* = 0.6$  and reduced temperature  $T^* = 1.52$  [6]. The simulations were performed using a simple leapfrog algorithm for integrating the equations of motion in single precision. For the thermodynamic properties (configurational and total energy, and pressure) he found that there was a small but steady positive drift in these quantities through reduced timesteps of 0.005 to 0.015 using kinetic energy constraints; 0.1% in the configurational energy and 4% in the pressure. These figures rise to 5% and 79% at a  $\Delta t$  of 0.030. At constant energy these sorts of latter figures are reached at a  $\Delta t$  of 0.020. Therefore a constant kinetic energy scheme stabilises the system against a self-developing dynamical catastrophe. The pair distribution functions and vacf of an 'exact' simulation and ones at  $\Delta t = 0.002$  (unconstrained temperature) and  $\Delta t = 0.003$  (fixed temperature) show that there are only minor differences between them, despite the major deviations in thermodynamic properties. The  $g(r)$  of the large  $\Delta t$  runs start to rise from zero marginally before the exact one. As the first order thermodynamic properties are related to the integrals of  $g(r)$  then these small differences in  $g(r)$  at close separations are very influential in affecting these quantities. If one is mainly interested in gross structure then one could get away with a time step of 0.03.

In keeping with the previous work I have performed some

similar calculations at the LJ state point  $\rho^* = 0.8442$  and  $T^* = 0.7$ , which is the near-triple point state made popular by Verlet and co-workers [7]. This was to see what effect density has on these conclusions. Also the vacf, facf and some collective correlation functions were evaluated. The latter were derived from the diagonal and off-diagonal components of the stress tensor. Simulations were performed at constant energy and constant kinetic energy using the Verlet leapfrog algorithm. Gaussian isokinetic multipliers were used to effect constant kinetic energy as described in a previous CCP5 quarterly article [8]. Results for thermodynamic quantities at time steps ranging from 0.005 to 0.0025 are presented in Table 1. Realistic standard errors were evaluated in [6] taking  $t = 10$  [6]. Within statistics and taking account of the slightly different  $T^*$  the numbers are indistinguishable. The time correlation functions and  $g(r)$  did not show any statistically significant differences. The statistics were very good for the  $g(r)$ . No anomaly at small  $r$  values was found. So that the situation is even better at this high density than at  $\rho^* = 0.6$ , used in [6]. I can see no reason why a timestep of 0.025 could not be used in future rather than the (extravagant) value of 0.005 frequently used.

#### Acknowledgement

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Table 1

The effect of timestep magnitude on system properties for a LJ liquid at  $\rho^* = 0.8442$  and  $T^* = 0.7$ . The number of molecules in the MD cell,  $N$ , was 256. The cut-off for interactions was  $3.36\sigma$  (half the MD cell's side length). Ensemble: NVE, constant total energy; NVT, constant kinetic energy. Each simulation was for 3000 timesteps. Simulations at the same  $t$  and with NVT were consecutively run (descending the table).  $X$  and  $X'$  denote, respectively, the average values of property  $X$  and the realistic standard error (SE) according to [6]. ( $t = 10$ , chosen)  $\bar{\Phi}_R$  is the average potential energy of the MD cell (divided by  $N$ ) from the repulsive part of the LJ potential.  $\bar{\Phi}_A$  is the corresponding value for the attractive part of the LJ potential.  $\bar{\Phi} = \bar{\Phi}_R + \bar{\Phi}_A$ .  $P$  is the pressure taken from the virial as usual. The usual long range corrections assuming  $g(r) = 1$  for  $r \gg$  the cut-off were taken.

Table 1 (continued)

Ensemble	$\Delta t^*$	$T^*$	$\bar{\Phi}_R$	$\bar{\Phi}'_R$	$\bar{\Phi}_a$	$\bar{\Phi}'_a$	$\bar{\Phi}$	$\bar{\Phi}'$	$P$	$P'$
NVE	0.005	0.722	5.820	0.006	-11.897	0.003	-6.077	0.003	0.176	0.014
NVT	0.005	0.722	5.797	0.005	-11.888	0.003	-6.090	0.003	0.116	0.013
NVT	0.010	0.718	5.804	0.006	-11.889	0.004	-6.085	0.003	0.131	0.015
NVT	0.010	0.718	5.817	0.006	-11.902	0.004	-6.085	0.003	0.154	0.015
NVT	0.015	0.712	5.810	0.006	-11.892	0.004	-6.082	0.003	0.142	0.015
NVT	0.020	0.703	5.812	0.006	-11.894	0.003	-6.082	0.003	0.139	0.015
NVT	0.020	0.703	5.810	0.006	-11.894	0.004	-6.084	0.003	0.131	0.014
NVT	0.020	0.703	5.801	0.006	-11.887	0.003	-6.086	0.003	0.113	0.014
NVT	0.025	0.692	5.811	0.006	-11.896	0.003	-6.084	0.003	0.124	0.014
NVT	0.025	0.692	5.803	0.006	-11.885	0.0629	-6.083	0.003	0.112	0.014

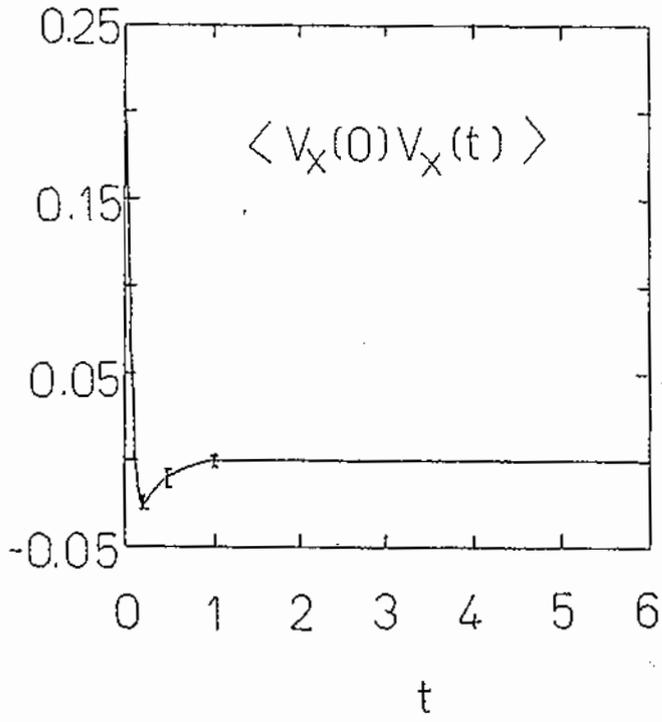
Captions to the figures.

Fig. 1 Time correlation functions from 3000 timestep subaverages. One of the LJ molecules served as an object for the velocity and force autocorrelation functions in (a) and (b)  $F_x = (x\text{-Force})^*/L^*$  where  $L$  is the MD sidelength in units of  $\sigma$ . The  $P_{xx}$  component of the pressure tensor was used for (c) where  $P_{xx} = P_{xx} - \langle P_{xx} \rangle$  and  $\langle \dots \rangle$  denotes a  $t$  average. The shear stress autocorrelation function is given in (d). All the correlation functions for  $\Delta t$  from 0.005 to 0.025 fall within the range denoted by the uncertainty bars,  $I$ , with no systematic trend.

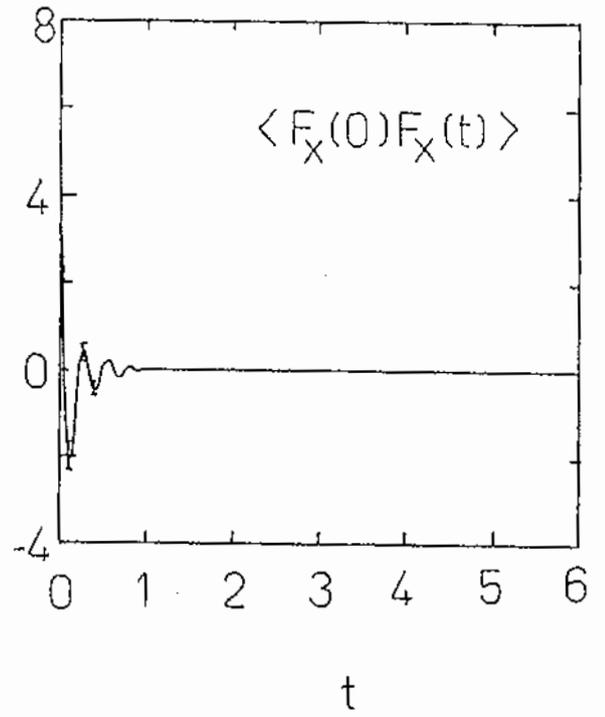
Fig. 2 The pair radial distribution function,  $g(r)$ , for the above states. The uncertainty bars are almost the thickness of the line.

Fig. 1

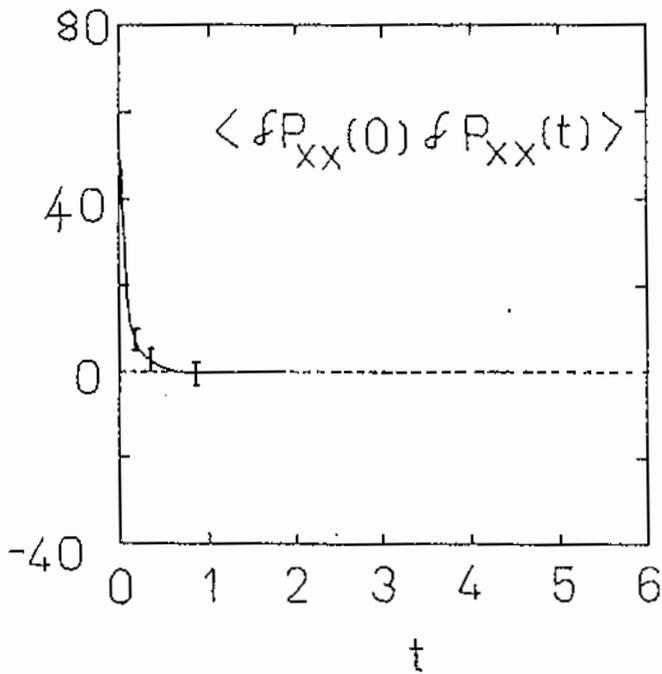
(a)



(b)



(c)



(d)

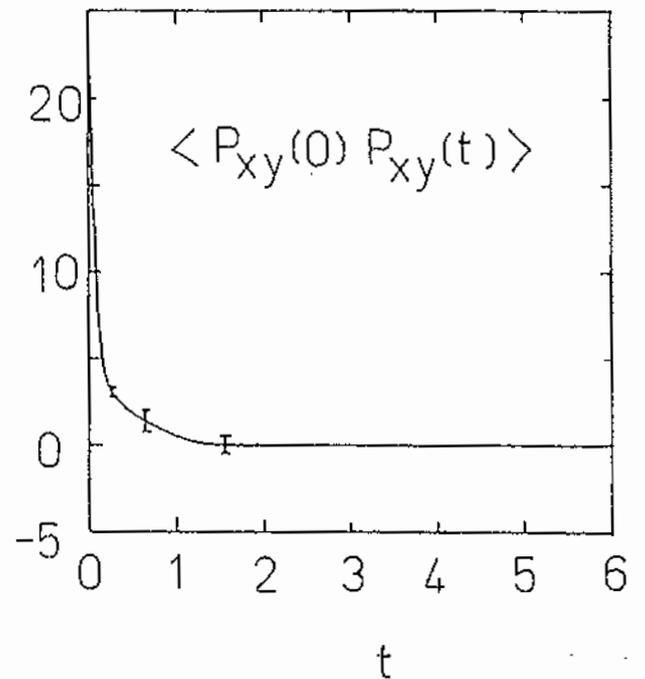
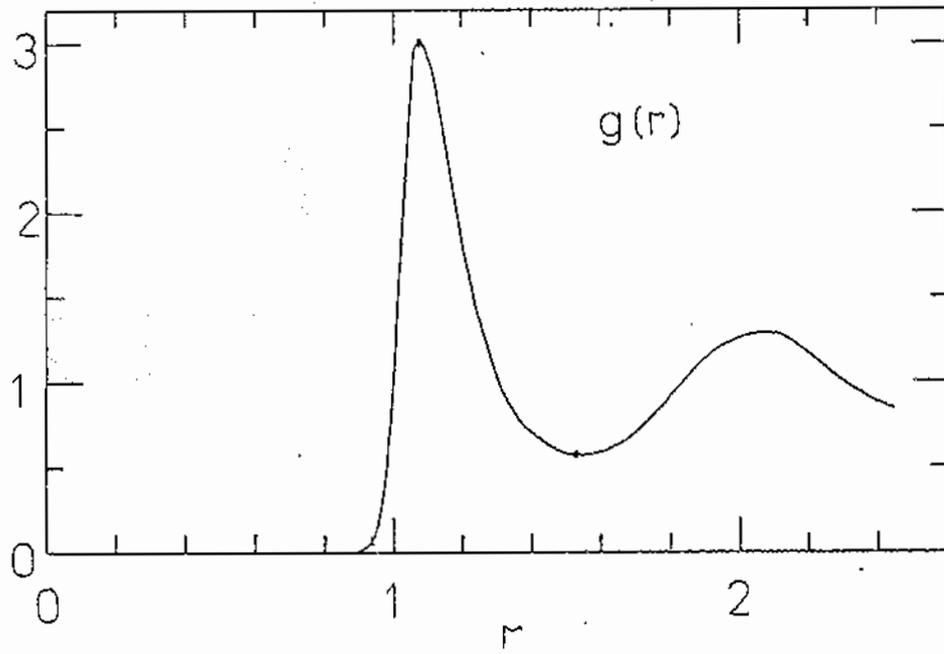


Fig. 2



## Setting up Random Configurations

D.P. Fraser

Consider the problem of setting up a dense system of randomly positioned hard-core molecules. For a low density system it is a simple matter to use a random number generator to pick the co-ordinates of each molecule in turn. If a molecule overlaps with those already in position then the co-ordinates are re-picked until a random low density configuration is established. With a high density, typical of that found in a liquid, there is little chance of placing all the molecules using this random sequential packing procedure. For single sized disks in 2-dimensions it is limited to packing fractions below 0.5473 (1), corresponding to a density of 0.4298. In (1) values for the random packing fraction of finite systems were obtained using a random sequential packing procedure. These values were extrapolated to give the random packing fraction of an infinite system, as given above but referred to as the random packing density.

Higher density configurations can be obtained by setting the molecules on a regular lattice and then moving them around using the normal Metropolis algorithm until a random configuration is obtained. This Monte Carlo procedure introduces two problems. An overlap can result when setting up the lattice if the molecules are of very different sizes and the order imposed by the lattice tends to remain in the configuration at high densities.

A particle scaling algorithm can also be used to generate high density configurations. A low density configuration is set up using the random sequential packing procedure. The molecule diameters are increased until two molecules touch. These are then moved apart along the line joining their centres to allow further scaling to take place. A consequence of this method is that once two molecules come into contact with each other they remain in contact. The final configuration thus shows order indicative of an infinitely strong very short range attractive potential.

Cornell et al (2) have compared configurations of disks at a packing fraction of 0.5 generated by particle scaling, random sequential packing and Monte Carlo procedures. The Monte Carlo procedure is the most suitable for generating configurations which show only mutual volume exclusion effects. None of the procedures are suitable for much higher densities, especially if the molecules vary in size.

The new procedure described here is similar to that of particle scaling. Induced order is removed by introducing Monte Carlo moves into the algorithm. A low density system is first set up using the random sequential packing procedure. This low density system is scaled down until two of the molecules touch and each molecule is then moved using the normal Metropolis procedure for a number of cycles. This is

repeated until the required density is obtained. The cell size and molecule co-ordinates are scaled in preference to the diameters to reduce cumulative rounding errors. (The method given is valid for any n-dimensional system where the symmetry of the hard core extends into all n dimensions. That is, the hard core is described by the locus

$\underline{c} = (c_1, c_2, \dots, c_n) : \underline{c} \cdot \underline{c} = r^2$  for some r. For ease of representation a 2-dimensional system is illustrated).

A point  $\underline{p}$  is chosen arbitrarily and the centre of mass co-ordinates  $\underline{q}$  of the molecules are scaled towards P by a factor S. The new co-ordinates  $f(\underline{q})$  are given by

$$f(\underline{q}) = \underline{p} + S (\underline{q} - \underline{p})$$

Appendix A shows that all choices of  $\underline{p}$  are equivalent and it is convenient to choose the origin.

Consider a pair of molecules i,j as shown in figure 1. They will touch when

$$|f(\underline{q}_i) - f(\underline{q}_j)| = \sigma_{ij}$$

In this case the scale factor for a particular pair,  $S_{ij}$ , is given by

$$S_{ij} = \sigma_{ij} / |\underline{q}_i - \underline{q}_j|$$

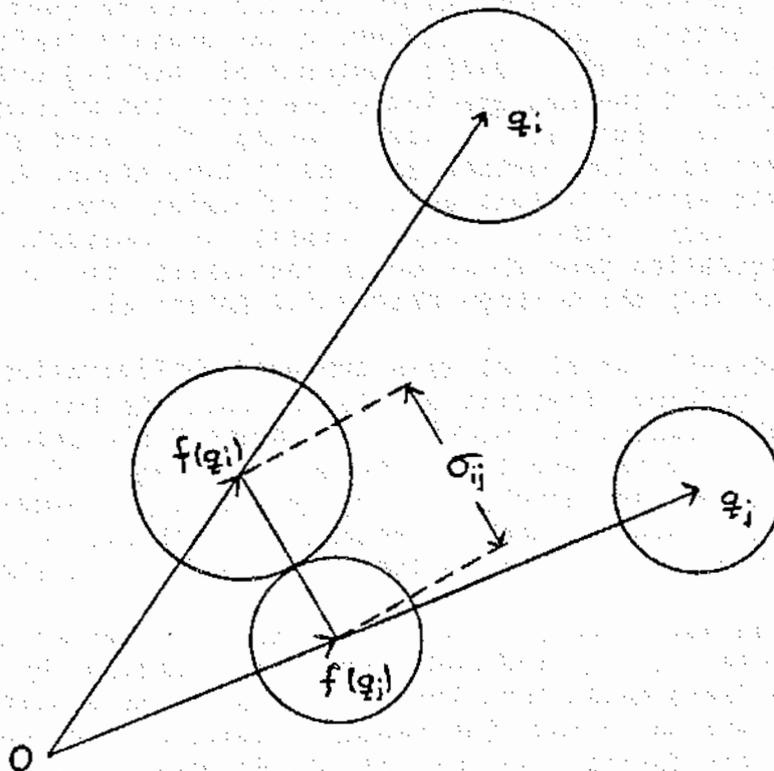


figure 1.

For a system containing more than two molecules we compute all the  $S_{ij}$ 's and select the largest,  $S_{max}$ . (Where a neighbour list is implemented we examine only the molecules on the list).

$$f(\underline{q}) = S_{max} \underline{q}$$

The method can be extended to a composite hard-core molecule made up from a set of hard discs or spheres. Each molecule is described by its centre of mass co-ordinates  $\underline{q}$  and the vector from the centre of mass of the molecule to a site  $\alpha$  in the molecule  $\underline{l}_\alpha$ .

Consider the  $\alpha$ th site of molecule  $i$  and the  $\beta$ th site of molecule  $j$ . In this case the scaling factor  $S_{i\alpha j\beta}$  is calculated for each site-site separation.

$$S_{i\alpha j\beta} = [-\underline{Q}_{ij} \cdot \underline{L}_{\alpha\beta} + ([\underline{Q}_{ij} \cdot \underline{L}_{\alpha\beta}]^2 - \underline{Q}_{ij}^2 \underline{L}_{\alpha\beta}^2 + \underline{Q}_{ij}^2 \sigma_{ij}^2)^{1/2}] / \underline{Q}_{ij}^2$$

Where

$$\begin{aligned} \underline{Q}_{ij} &= \underline{q}_i - \underline{q}_j \\ \underline{L}_{\alpha\beta} &= \underline{l}_{i\alpha} - \underline{l}_{j\beta} \end{aligned}$$

As before the largest  $S_{i\alpha j\beta}$  in the system is selected and

$$f(\underline{q}) = S_{max} \underline{q}$$

If either  $|\underline{l}_{i\alpha}| > \sigma_{ij}/2$  or  $|\underline{l}_{j\beta}| > \sigma_{ij}/2$  then the term  $([\underline{Q}_{ij} \cdot \underline{L}_{\alpha\beta}]^2 - \underline{Q}_{ij}^2 \underline{L}_{\alpha\beta}^2 + \underline{Q}_{ij}^2 \sigma_{ij}^2)$  can be negative. If this is true then as the system is scaled, the two molecules move to a minimum separation and then move apart without ever touching. Consequently that particular  $S_{i\alpha j\beta}$  can be set to zero without affecting the scaling.

This technique applies equally to soft potentials where we define  $\sigma_{ij}$  by

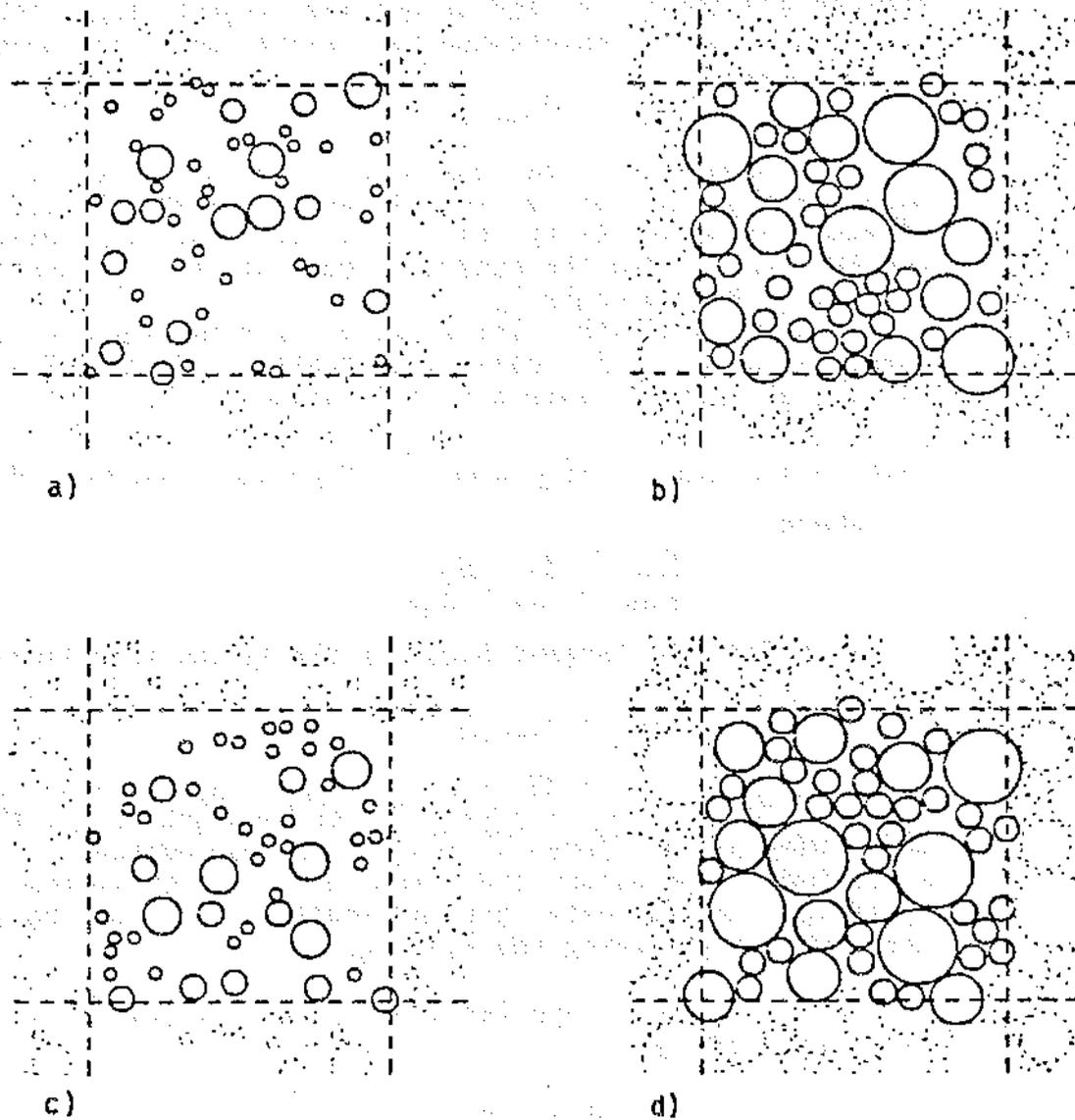
$$u_{ij}(\sigma_{ij}) = 0.$$

### An example

A three component mixture of 50 disks of size  $\sigma, 2\sigma, 3\sigma$  in the ratio 7:2:1. A square cell is used and periodic boundary conditions are applied. 10 Monte Carlo moves per disk are made between scalings. The scale factors, densities and CPU times for two different final densities are given in tables I and II and the initial and final configurations for each run are shown in figure 2. The program used is written in Fortran and is run on a PRIME 750.

The CPU time per iteration can be reduced by reducing the number of moves between scalings. Fewer iterations are required if the number of moves is increased.

Overall the total CPU time used is found to increase with



**Figure 2.** The initial and final configurations for the data given in Tables I and II.  
 a) Initial config. for  $\eta = 0.6$  :  $\eta = 0.15$ ,  $\rho\sigma^2 = 0.191$     b) Final config. :  $\eta = 0.6$ ,  $\rho\sigma^2 = 0.734$   
 c) Initial config. for  $\eta = 0.7$  :  $\eta = 0.175$ ,  $\rho\sigma^2 = 0.223$     d) Final config. :  $\eta = 0.7$ ,  $\rho\sigma^2 = 0.891$   
 The cell used is indicated in bold dash.

the number of moves. The aim of keeping the CPU time to a minimum has to be compromised with the necessity of having sufficient moves between scalings so that induced order is removed. 10 moves per disk was found to be a suitable choice.

#### Appendix A

Consider the mapping  $f: \mathcal{R}^n \rightarrow \mathcal{R}^n$  such that point  $\underline{p}$  is mapped onto itself and all other points  $\underline{a}$  are mapped such that the vectors  $(\underline{a} - \underline{p})$  are scaled by a factor  $S$ .

$$f(\underline{a}) = \underline{p} + S(\underline{a} - \underline{p})$$

This is the same as the mapping

$$g(\underline{a}) = S\underline{a} + (1 - S)\underline{p} \quad g: \mathcal{R}^n \rightarrow \mathcal{R}^n$$

which represents a scaling of  $\underline{a}$  by the factor  $S$  followed by a translation of  $(1 - S)\underline{p}$ . Consequently distances between points are scaled by  $S$  independent of  $\underline{p}$ . This can also be seen by looking at

$$f(\underline{a}) - f(\underline{b}) = S(\underline{a} - \underline{b}).$$

#### References

1. Tanemura, M., Ann. Inst. Stat. Math. 31, 351-365 (1979)
2. Cornell, B.A., Middlehurst, J., and Parker, N.S., J. Colloid Interface Sci. 81, 280-282 (1981)

Table I

Packing fraction  $\eta = .6 \rightarrow$  density  $\rho\sigma^2 = .7639$

Iteration no.	Scale factor.	Density. $\rho\sigma^2$	CPU time.
		.1910	0m 2.45s
1	.9954	.193	0m 6.09s
2	.9519	.213	0m 8.60s
3	.9903	.217	0m 11.40s
4	.9493	.241	0m 14.24s
5	.9770	.252	0m 16.80s
		.	
51	.9999	.505	2m 21.66s
52	.9994	.505	2m 24.50s
53	.9944	.511	2m 27.32s
54	.9980	.513	2m 30.12s
55	.9937	.520	2m 32.95s
		.	
101	.9998	.705	4m 43.65s
102	.9978	.708	4m 46.35s
103	.9998	.709	4m 49.36s
104	.9978	.712	4m 52.06s
105	.9994	.713	4m 54.77s
		.	
126	.9985	.759	5m 52.63s
127	.9993	.760	5m 55.39s
128	.9977	.763	5m 57.88s
129	.9998	.764	6m 0.39s
130	.9998	.764	6m 3.15s
	1.0001	.7639	
			Total 6m 5s CPU

Table II

Packing fraction  $\eta = .7 \rightarrow$  density  $\rho\sigma^2 = .8913$

Iteration no.	Scale factor.	Density. $\rho\sigma^2$	CPU time.
		.2228	0m 2.55s
1	.9863	.229	0m 6.27s
2	.9436	.257	0m 9.15s
3	.9136	.308	0m 12.32s
4	.9948	.311	0m 15.53s
5	.9880	.319	0m 18.45s
		.	
51	.9937	.550	2m 39.47s
52	.9982	.552	2m 42.64s
53	.9876	.566	2m 45.80s
54	.9975	.569	2m 48.97s
55	.9974	.572	2m 52.44s
		.	
101	.9982	.801	5m 14.19s
102	.9998	.801	5m 17.31s
103	.9966	.807	5m 20.08s
104	.9995	.807	5m 22.84s
105	.9995	.808	5m 25.88s
		.	
146	.9983	.886	7m 23.40s
147	.9985	.889	7m 25.91s
148	.9969	.894	7m 28.67s
	1.0018	.8913	
<b>Total</b>			<b>7m 31s CPU</b>

THE CALCULATION OF HUGONIOTS IN IONIC SOLIDS.

J.H. Harding and A.M. Stoneham.

Equations of state at very high temperatures and pressures have many uses. These include geophysical studies of planetary cores, the behaviour of nuclear fuels in studies of hypothetical reactor faults, and transient high-temperature behaviour needed in materials processing. In all these cases we must use theory to extrapolate from readily-accessible conditions to the extreme conditions required. The validation of theories and of models is thus of importance. Central to many theories is the use of interatomic potentials together with various prescriptions for estimating thermodynamic quantities. We have shown that shock-wave experiments can be used as a stringent test of potentials in extreme conditions.

Reviews of the approximations used in analysing shock-wave data are given in Rice (1) and Marsh (2). If we consider the shock to be an adiabatic process we can obtain the Rankine-Hugoniot relation

$$(E_1 - E_0) = (1/2)(P_1 - P_0)(V_0 - V_1),$$

where  $E$ ,  $P$  and  $V$  are energy, pressure and volume respectively and the subscripts refer to properties behind the shock front (1) and to the undisturbed solid (0). We require a general equation of state to calculate the Hugoniot trajectory and assume the Mie-Grüneisen equation

$$P = -(d\phi/dV) + \gamma(V) kT/V,$$

where  $\phi$  is the static part of the crystal internal energy and  $\gamma(V)$  the mean Grüneisen constant.

We calculate the internal energy  $\phi$  as a function of volume by means of the Harwell PLUTO program. The Grüneisen constants for individual lattice modes are calculated by using the approximation

$$\gamma_i = -(d \ln \omega_i / d \ln V) \approx (V/\omega_i) (\Delta \omega_i / \Delta V)$$

and these  $\gamma_i$  are averaged over the Brillouin zone to obtain

Table 1

## Comparison of potentials with experiment

Interatomic Potential	Catlow, Diller and Norgett	Sangster and Atwood	Mackrodt and Stewart	Experiment
Derivation of potential	Lattice parameter, cohesive energy, $C_{11}$ - $C_{12}$ , $C_{44}$ fitted exactly. $\epsilon_0, \epsilon_\infty, \omega_{T0}$ fitted approximately	Lattice parameter, $\epsilon_0, \epsilon_\infty, \omega_{T0}$ fitted exactly over a wide range of alkali metal halides	Electron-gas calculation using Clementi's wave-functions	
Static pressure-volume experiments Pressure at phase change (GPa)	30	30	No phase change	30
Transition volume at phase change ( $\text{cm}^3/\text{mole}$ )	-1.2	-1.1		$-1.9 \pm 0.5$
Lattice parameter at phase change (Å) rock-salt CsCl	4.91 3.02	5.00 3.08		4.872 2.997
Hugoniot Results Rock-salt structure Pressure at phase change (GPa) CsCl structure	volume too low 18 volume increasingly low	Good 20 Good	Volume too high No phase change Never stable in conditions tested.	22-28

$\gamma(V)$ .

As an example we consider the Hugoniot trajectory for sodium chloride and compare three interatomic potentials: those for Catlow, Diller and Norgett (3), Sangster and Atwood (4) and Mackrodt and Stewart (5). The results of this comparison are shown in Table 1., together with some results from static pressure-volume measurements. It is clear that the Hugoniots provide a very stringent test for the potentials, and it is gratifying how well some perform even though they were obtained only from data near the equilibrium geometry under normal ambient conditions.

From our equation of state it is possible to obtain the temperature of the shock front. This may exceed 2500 K at high pressures. This suggests the possibility of electronic structure changes or of significant defect production. These effects may be especially important in systems that can exist over a wide range of non-stoichiometry, for example  $UO_{2+x}$  or  $Fe_{1-x}O$ .

#### REFERENCES

- (1) M.H. Rice, R.G. McQueen, J.M. Walsh, Solid State Physics Vol. 6, eds. F. Seitz and D. Turnbull, Academic Press, New York, (1958) p.1.
- (2) S.P. Marsh (Editor), LASL Shock Hugoniot Data (Univ. of California Press, Berkeley, 1980).
- (3) C.R.A. Catlow, K.M. Diller and M.J. Norgett, J.Phys. C12, 451 (1979).
- (4) M.J.L. Sangster and R. M. Atwood, J.Phys. C11, 1541 (1978).
- (5) W.C. Mackrodt and R.F. Stewart J. Phys. C12, 431 (1979).

CCP5 CIRCULAR: THE GLASS TRANSITION - A MEETING AT WADHAM COLLEGE  
OXFORD, APRIL 9TH. - 11TH. 1986.

The objective of this meeting is to assess the current status of computer simulations of the glass transition, with particular regard to the recent advances made in the theory of the transition. Besides lectures on simulation studies per se, invited speakers will describe the recent progress in theory and others will survey the phenomenology of the transition on real systems which are sufficiently simple to be amenable to simulation studies. Invited speakers include: Anderson (Stanford), Angell (Purdue), Yip (MIT), Sjolander (Gothenberg), Woodcock (Bradford). Contributions are also expected from Hansen (Paris), Pusey (Malvern), Clarke (UMIST) and others. Contributed talks on simulation studies closely related to the glass transition are invited. There will also be a poster session; posters on any aspect of the study of glasses, supercooled or quenched liquids, or distorted solids will be welcomed.

The Meeting will commence with dinner on Wednesday 9th. of April and finish mid-afternoon on Friday the 11th. of April. There will be a conference dinner on Thursday evening. Sessions will be held in the Chemistry Department, which is close to the College. Accompanying members are welcome (at the full fee): your spouse would enjoy a couple of days exploring the beautiful and historic city of Oxford. Oxford is served by fast trains from Paddington station (approx. 70 mins.) and by extremely fast and regular buses from Victoria Coach Station (90 mins.), Heathrow (1 hr.) and Gatwick (2 hrs.) airports.

The Meeting Fee is £60; CCP5 may refund part of the fee to students who submit a contribution.

Please complete and send the Registration Form to: Paul Madden, Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ. A provisional programme and travel information will be sent to registered participants shortly before the Meeting.

OXFORD CCP5 MEETING - REGISTRATION FORM

Name: .....

Address: .....  
.....  
.....

Tel. No.: .....

Please tick boxes if applicable

Accompanying members:

I will be accompanied by (name):

We prefer a double room

two singles

Student requesting reduced fee:

I am a registered student and am  
submitting a contribution

Contribution:

I hope to present a talk

poster

Title:

For a talk - I enclose a short abstract

Conference Fee:

I enclose a cheque for £  
"The Glass Transition"

payable to

I will pay later

on arrival.

Announcement:

Two closely related workshops will be held in the spring. They will be at the same place and partially overlapping so that you can attend both!

1. THE BRITISH SOCIETY OF RHEOLOGY PRESENTS:

"MOLECULAR APPROACHES TO RHEOLOGY\*"

at

Royal Holloway and Bedford New College

University of London.

on

24th and 25th March 1986.

\* Rheology is the study of deformation and flow of materials.

Startling new advances have been made in the theoretical and computer modelling of rheology starting from behaviour at the molecular level. For example, it is now possible to follow the motions of model molecules within liquids under shear flow using the new technique of Non-Equilibrium Molecular Dynamics (NEMD), enabling us to discover the microscopic origins of non-Newtonian flow[1]. In recognition of these exciting new developments the BSR is sponsoring a workshop aimed at bringing together scientists interested in rheology from a variety of backgrounds to discuss their rheological work in the context of its microscopic origins. Expertise in these new modelling techniques, and on polymer theories and continuum macrorheological approaches will be present. Participants will take part in a loosely structured 'round-table' discussion designed to promote the informal interchange of ideas and establish the most profitable directions for new research. Collaborations might even be initiated! To assist this task it is suggested that attendees come along with short presentations (say, of 10-15 minutes duration) outlining their interest and problems in this area, and which can be called upon at opportune moments (!)

[1] see for example, D.J. Evans, H.J.M. Hanley and S. Hess, Phys. Today 37(1) (1984) 26.

. The BSR workshop will start with lunch on Monday 24th March and concludes late in the afternoon on Tuesday 25th March.

. The cost of the Meeting is £30.00 and includes all meals and refreshments, and accommodation on the night of the 24th.

. If you would like to attend please send a cheque made out to "BSR Meeting" for £30.00 and send it to:

Dr. D.M. Heyes,  
Department of Chemistry,  
Royal Holloway and Bedford New College,  
Egham,  
Surrey, TW20 0EX.  
U.K.

by Monday 24th February, 1986 if possible.

. It would be appreciated if you would give me your name (full first name please), whether you are female or male, and your complete address so I can construct a list of names and addresses for us all.

. Do you think you could also outline your interests in this area and what you hope to get out of the meeting?

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2.

CCP5 proudly presents a workshop on:

"TRANSPORT PROCESSES"

at

Royal Holloway and Bedford New College,

University of London,

on

25th and 26th March 1986.

In January 1985 CCP5 held, what many commented, was a successful workshop on modelling of dynamical effects and transport coefficients by Molecular Dynamics. Topics that were discussed were:

- . Green-Kubo integrands versus Non-Equilibrium Molecular Dynamics, NEMD, as a route to shear viscosity of monatomic and polyatomic molecules.
- . Novel NEMD routes to thermal conductivity.
- . Parity breaking in rotational-translational coupling due to effects of external fields, with special emphasis on consequences for interpretation of spectra.
- . Simulation of colloids using Stochastic Dynamics.

There were many free-flowing discussions interspersed with informal presentations.

Developments in this area are taking place rapidly and consequently CCP5 is sponsoring "round 2" of this format.

Again as above, if you would like to attend this workshop please write to me:

Dr. D.M. Heyes,  
Department of Chemistry,  
Royal Holloway and Bedford New College,  
University of London,  
Egham,  
Surrey, TW20 OEX.  
U.K.

Please would you give me your name (full first name), whether you are female or male and your full address.

Also it would help me if you could indicate your interests in this area.

THEREFORE TO CONCLUDE: IF YOU WANT TO GO TO BOTH WORKSHOPS SEND ME THE CHEQUE FOR WORKSHOP 1 AND ALSO LET ME KNOW ABOUT YOUR INTEREST IN WORKSHOP 2.

: IF YOU WANT TO GO TO ONLY ONE OF THE WORKSHOPS THEN JUST FOLLOW THE PROCEDURE FOR THE APPROPRIATE ONE.

(Got it?!)

Science and Engineering Research Council  
Daresbury Laboratory

PROTEIN STRUCTURE PREDICTION

24-25 JANUARY, 1986

INFORMATION BULLETIN

The Meeting will commence at 11.00 on Friday, 24th January, and close at approximately 16.00 on Saturday, 25th January. Details of the programme will be announced later.

1. Attendance and Financial Arrangements

If you wish to attend the Meeting please complete and return the attached form as soon as possible and no later than 17th December, 1985.

FEE: The Conference fee is £16 excluding accommodation, and lunch on Friday. All other meals will be provided, including a dinner which will be held on Friday, 24th January, at the Lymm Hotel. Please indicate under section 5 on the attached form if you wish to attend the dinner.

2. Accommodation

Single room : £14.50 per night, per person (Bed and Breakfast)

Shared room : £13.50 per night, per person (Bed and Breakfast)

Accommodation has been reserved for delegates on the night of 24th February at the Lymm Hotel which is situated 9 miles from the Laboratory. Requirements should be listed under section 2 of the enclosed form. Further accommodation, which we regret is not at the privilege conference price, can be arranged providing sufficient notice is given (e.g. accommodation for Thursday night would be £34.00 single or £22.00 shared, bed and breakfast.

Those arriving on Thursday evening may obtain dinner at the Hotel up to approximately 22.00 hours and after this time may request sandwiches and coffee. These arrangements will, however, be at their own expense.

3. Travel

Participants must find their own funds for travel with the exception that the Laboratory will provide transport on arrival and departure to and from neighbouring airports and railway stations, and coach transport between the Hotel and the Laboratory.

Daresbury is conveniently situated for travel by air, train or car. There are major airports at Manchester (Ringway) and Liverpool (Speke), and railway stations at Runcorn and Warrington. The Laboratory is one mile from Junction 11 on the M56 motorway. A map can be provided, on request, for those arriving by car.

4. Office Facilities

There will be an information desk at the Laboratory where participants will be able to make transport arrangements. There will be no banking or currency exchange facilities. Postal arrangements will be limited to a mail delivery and pick-up service. Telephone, Library and photocopying facilities will be available.

Postal address: c/o SERC Daresbury Laboratory  
Daresbury  
Warrington WA4 4AD

Telephone: Warrington (0925) 65000

Telex: 629609 DARLAB G

Science and Engineering Research Council  
Daresbury Laboratory

PROTEIN STRUCTURE PREDICTION  
24-25 JANUARY, 1986  
COMMENCING AT 11.00 a.m.

APPLICATION FORM

SURNAME: (Prof., Dr., Mr., Mrs., Ms.\*) \_\_\_\_\_  
(BLOCK letters please)

FIRST NAME: \_\_\_\_\_

INSTITUTION ADDRESS: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

Tel. No: \_\_\_\_\_ Telex No: \_\_\_\_\_

1. I intend to be a Resident/Non Resident participant\*

The Conference Fee is £16.00 excluding accommodation. N.B. Cheques should be made payable in sterling to: SERC Daresbury Laboratory. (The Daresbury Laboratory VAT Registration No. is 232-5338-83.)

2. ACCOMMODATION

The hotel accommodation charge is £14.50 per night single or £13.50 for a shared room (bed and breakfast). Delegates should pay their own accommodation bills.

I will require accommodation for the night of:

Friday, 24th January, 1986 YES/NO\*

If all single rooms have been allocated  
would you be willing to share: YES/NO\*

If any further accommodation is required please specify: \_\_\_\_\_

3. SPECIAL REQUIREMENTS: Please state any special requirements such as diet, disability, etc.

4. TRAVEL ARRANGEMENTS

Car: I will arrive by car: YES/NO\* My registration No. is \_\_\_\_\_

Please send a map: YES/NO\*

Train/Plane: Arrival

I will arrive at \_\_\_\_\_ (Station/Airport)

ON \_\_\_\_\_ (Date)

AT \_\_\_\_\_ (Time of Arrival/Flight No.)

FROM \_\_\_\_\_ (Place)

I will require transport to the Laboratory/Hotel: YES/NO\*

Train/Plane: Departure

I will depart from \_\_\_\_\_ (Station/Airport)

ON \_\_\_\_\_ (Date)

AT \_\_\_\_\_ (Time of Departure/Flight No.)

TO \_\_\_\_\_ (Place)

I will require transport to the Station/Airport: YES/NO\*

5. DINNER

I will/will not\* attend the dinner on Friday, 24th January.

Please complete and return this form by 17th December, 1985, to:  
Mrs. S.A. Lowndes, SERC Daresbury Laboratory, Warrington WA4 4AD,  
Cheshire.

\*Please delete where inapplicable.