DARESBURY LABORATORY

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# INFORMATION QUARTERLY for COMPUTER SIMULATION OF CONDENSED PHASES

An informal Newsletter associated with Collaborative Computational Project No. 5 on Molecular Dynamics, Monte Carlo and Lattice Simulations of Condensed Phases, Number 16 MARCH 1985

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Editor: Dr. William Smith Deputy Editor: Dr. Maurice Leslie Science 5 Engineering Research Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England.

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### Editorial.

The availability of the FPS 164 at Daresbury offers an interesting alternative to other vector processing machines; namely the CRAY1S, CYBER 205 and ICL DAP, which UK CCP5 participants have access to. Once the Daresbury AS7000 has been converted to MVS the FPS will become accessible to everyone who currently can access Daresbury TSO. The present machine is not a rival to the CRAY1S, but it does offer cost-effective computing and with the proposed enhancements could well be a serious competitor. For the time being, the machine is available to the academic community on a trial basis. Everyone would be well advised to give machine serious thought for future projects and apply to the Director, Professor L. Green, at Daresbury Laboratory for time on the FPS. (See below for further details).

On a less happy note, we have received reports (see within) that two of the programs in the CCPS Program Library have defective integration algorithms. The programs concerned are MDTETRA and MDPOLY. (In fact, if the program MDTETRA is regarded literally as a program for tetrahedral molecules i.e. molecules of the type CX , then the problem is confined to MDPOLY alone). Readers who have used these programs are strongly advised to read the article by Mike Allen and Dominic Tildesley. Meanwhile, we shall undertake the necessary corrections to the Program Library copies.

Finally, we thank the contributors to the current issue. It has been particularly pleasing to receive so many contributions, without prompting by the editor! We hope that our readers will enjoy reading the product.

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### General News.

a) The CCP5 collaboration with the Statistical Mechanics and Thermodynamics Group of the Royal Society of Chemistry in the form of a two day meeting on: 'Dense Fluids: Dynamic and Static Properties' is shortly to take place at Bristol in April from 10th. - 12th.

Late applications to attend are still possible up to 30th. March for an additional fee of £5 after the closing date of 20th. March.

The speakers for the meeting include: G.Stell, W.A. Steele, R. Desai, J.P. Hansen and P.A. Madden. Those interested should write to Dr. C. J. Wormald, School of Chemistry, The University of Bristol, Cantock's Close, Bristol BS8 1T5.

b) CCP5 is organising a conference on 'Stochastic Dynamics and Macromolecules' at the University of York from September 11th. to 13th. 1985. The conference is being organised by Dr. David Fincham (York) and Dr. Eric Dickenson (Leeds). An announcement of this meeting and a call for papers is included with this letter.

c) CCP5 is to hold its second workshop on Graphics in the early summer of 1985 (date to be decided upon). Also there is to be a workshop on Silicates, which is scheduled for July. Information regarding both of these events will be available in due course.

The CCP5 Executive Committee wish also to remind CCP5 participants that it is always open to suggestions for future conferences or workshops. Please write to the CCP5 Secretary (Dr. W. Smith, Daresbury Laboratory, Daresbury, Warrington WA4 4AD).

d) CCP5 participants are reminded that the project has an allocation of 19 hours program development time on the ULCC Cray Is, which is, at the discretion of the Executive Committee, available to the CCP5 community. Anyone who requires a small allocation of time to modify or develop programs, may apply to the CCP5 Chairman (Dr. J. H. R. Clarke, Department of Chemistry, U.M.I.S.T., Sackville Street, Manchester M60 10D) in the first instance.

e) Daresbury Laboratory recently took delivery of an FPS 164 Attached Processor, which was purchased by Science Board. The machine arrived at Daresbury in November, and is currently accessible via the AS5000. This configuration will remain until the MVS operating system is available on the AS7000, towards the end of March 1985. A major part of the machine will be available to the Science Board community for grant-supported computing. In the first year of operation, the community is invited to apply informally to Daresbury for time to try out and benchmark on the machine. If the FPS turns out to be appropriate for a particular research project, an application should subsequently be made to SERC for a block of time in the same way as applications are made for Cray time. Note that a conversion ratio to Cray CPU hours is very program dependent - experience to date suggests a factor of 1/10 for well vectorised codes. Time will be generally available once the machine has been connected to the AS7000.

Current upgrades to the FPS should realise an improved but still rather modest disc capacity of 400 Mbytes. This will be increased to 1 Gbyte by the summer of 1985, but clearly applications requiring large quantities of disc space will not viable in the short term. The total memory available is approximately 1/2 Mword, i.e. equivalent to that originally available on the Cray Serial 1. There are no plans to increase core storage in the short term.

f) At the Rutherford and Appleton Laboratory, the change to direct charging for the central computer usage, as recommended by the Central Review Working Party, is expected to start from 1 April 1985.

The scheme to be operated (which will by subjected to reassessment as time goes by) will levy a basic charge of £150 annually for registration plus £3 per annum for each magnetic tape users have in the tape library. There will be charges for disc space (integrated over time for MVS users) and eventually, for MASTORR allocation also. The charges for resources will be in terms of Allocation Units (AU) and will take into account job priority, CPU time, I/O volume, job size etc. The cost of each MVS AU will be £2.75 and each CMS unit £24. (Note 100 MVS AU's are roughly equivalent to one 360/195 CPU hour.) Charges for graphical output, manuals and magnetic tapes etc. are currently under review. More details are given in the January/February RAL newsletter FORUM.

Other items of interest include the final conversion to the MVS operating system and the availablity of a UNIX operating system (known as UTS) on the ATLAS10.

g) At the University of London Computing Centre users are being encouraged to use the data protection package ACF2 to protect their data on the Amdahl V/8 system. This is in line with the general move towards greater data protection on all computer systems. The ACF2 package may be used to define the level of security on each dataset as outined in the ULCC newsletters for January and February.

The new Cray operating system COS 1.12 BF1B is to be field tested in the Spring. This should not cause users any problems.

ULCC is also setting up an experimental microfilm plotting service, using a DICOMED microfilm recorder and which promises good graphical reproduction.

New software packages aviiable at ULCC include GAUSSIAN 82, the quantum chemistry package, and NAG FORTRAN 11.

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h) The University of Manchester Regional Computing Centre is undergoing a reorganisation of staff. By the end of March, two new service divisions; the National and Local Services respectively, will have been created, each with its own director. Three additional units will also be operating; the Network Unit, Operations Group and Administration. Of these, the Network Unit is new and it will be responsible for the hardware and software of the local and wide area networks.

The National Services division will be divided into the User Services and Systems groups. The former will look after national user liason, documentation and applications software for the mainframes and vectorisation problems on the CYBER 205. The Systems group will be responsible for the operating systems, compilers and resource allocation control software. The Local Services division will support the local machines and the local use of the national mainframes.

The CYBER 205 FORTRAN 77 compiler (FORTRAN 200) continues to have problems. A list of known problems is stored in a data file accessible online and users are recommended to look at it regularly to keep up to date on developments. (List file :WW.INFO.COMP.FORT200).

Recent software additions at UMRCC include NAG FORTRAN Mark 11 and the quantum chemistry code GAMESS.

i) Readers may be interested to know that the 'Sixth Summer School on Computing Techniques in Physics' will take place at Hotel SKI, Nove Mesto na Morave, Czechoslovakia 17 - 26 September 1985. The principal theme will be 'Software Engineering, Methods and Tools in Computational Physics'. Anyone interested should contact Dr. J. Nadrchal, Summer Schools on Computational Physics, Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, CS - 180 40 Praha 8, Czechoslovakia. (Closing date June 15th.)

j) CCP5 has arranged for a survey over the past year's literature in the areas of interest to CCP5 participants. The list produced will be similar to that produced in the CCP5 newsletter a year ago. Because of difficulties in reproducing the copy however, it has not been possible to publish the list with this issue. Instead, the list will be completed separately and sent out in a separate mailing towards the end of March.

We should also take this opportunity to point out that this may be the last such survey that CCP5 can udertake. The cost of has more than trebled since our last effort, due to increased search fees, exchange rates etc. and to the fact that the number of relevant references has approximately doubled since last year. Therefore, unless someone can suggest a cheaper alternative, we will probably have to abandon this useful exercise in the future.

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

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## List of Programs in the CCP5 Program Library.

MDATOM by S. M. Thompson.

en de la competencia de l 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. The stress sectors in sectors of the stress sectors and the 

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.

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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. new renew with the second s

MDLINQ by S. M. Thompson, the state of the second state of the sec and the second second

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.

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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.

and also pressure and temperature.

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

MDMPOL by W. Smith & D. Fincham.

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

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

CURDEN by W. Smith.

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

HLJ1 by D. M. Heyes.

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

HLJ2 by D. M. Heyes.

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

HLJ3 by D. M. Heyes.

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

HLJ4 by D. M. Heyes.

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

displacements and radial distribution function.

HLJ5 by D. M. Heyes.

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

HLJ6 by D. M. Heyes.

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

MCRPM by D. M. Heyes.

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

SURF by D. M. Heyes.

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

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

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

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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. The second second

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

### MDDIATQ by D. Fincham.

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

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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

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.

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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.

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### STOCHASTIC DYNAMICS AND MACROMOLECULES

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### University of York

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# September 11th - 13th 1985

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## CALL FOR CONTRIBUTIONS

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Contributions are invited for the sec	ond CCP5 meeting
broadly. There are likely to be ses	sions on polymers.
colloids and biological macromolecule	s, not necessarily
limited to stochastic methods. Theo	retical
appropriate. Invited speakers who h	ave already
accepted include:	anang Kabupatèn Kabup
د الاست. «المحمد المحمد ال المحمد المحمد	an a
H.J.C. Berendsen/W. van Gunster	en (Groningen)
- Stochastic dynamics of pr	oteins
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As always with our meetings the proce	edings will be fairly gress or discussion
of computational techniques will be w	elcome.
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send a title and if possible a short	abstract, to one of
the undersigned organisers. A regis	tration form will be
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Eric Dickinson	David Fincham
Procter Department of Food Science University of Leeds	Department of Chemistry University of York
Leeds LS2 9JT	York YOL 5DD

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### REPORT ON THE CCP5 SPONSORED VISIT OF PROFESSOR B. J. BERNE TO THE UNITED KINGDOM IN OCTOBER 1984.

M.P. Allen, R.M. Lynden-Bell, J.L. Finney

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### OXFORD (22 October)

Professor Berne gave a stimulating talk on quantum mechanical computer simulation methods, concentrating on approaches derived from the discretized path integral formalism. He mentioned the desirability of random resampling of moments in the molecular dynamics implementation of the "primitive" algorithm, so as to avoid stiff-chain ergodicity problems. He also recommended a numerical matrix multiplication method as an alternative to straightforward simulation, as being particularly useful for effectively one-dimensional problems. As an example, he described the calculation of the pair distribution function in the Argon dimer. Professor Berne went on to outline some of the difficulties in incorporating quantum mechanical effects in the simulation of water, and briefly mentioned time-dependent phenomena.

The talk was followed by a Workshop on quantum mechanical computer simulation. Dr. M.S. Child (Oxford) began by describing the various kinds of semiclassical approaches used in isolated atom-molecule collision problems. Typically, scattering functions are represented by sums of contributions from a few "classical" paths. However in some problems, classically forbidden behaviour dominates, and there are obvious difficulties associated with exchange symmetry. Gaussian wavepackets are quite low on the list of techniques used in scattering theory, although superpositions of "frozen" gaussians are successful in projecting out the quantum features of Franck-Condon transitions.

Professor K. Singer (Royal Holloway College) then described some of his work with gaussian wavepackets, which he thought to be the only dynamical method hitherto proposed for the simulation of quantum or semiclassical liquids such as neon. Only Heller's variational method is suitable for systems with stiff repulsive potentials and best results were obtained with spherically symmetric wave packets, whose widths, rather than being frozen, were allowed to vary equally under the influence of a "force" averaged over the whole system. Temperature could be measured by including a classical, heavy particle in the simulation: the temperature essentially corresponded to the kinetic energy of the wavepacket centres. The method gave an average kinetic energy that was too high, but reasonable pair distributions and velocity autocorrelation functions were obtained. There followed some discussion of gaussian wavepackets. It was generally agreed that, near the triple point of neon, exchange effects were probably not responsible for most of the quantum corrections. In the simulation of liquid neon, no spread of the wavepackets is observed; but to obtain satisfactory thermodynamic properties a more flexible trial function (than a spherical gaussian) is probably required. It was again pointed out that wave packets which cannot divide, cannot show quantum tunnelling. There was some doubt regarding the best way to test the results of such simulations; bearing in mind possible shortcomings of the potentials used in bulk simulation work.

The Workshop then turned to other techniques. Mr. B.H. Wells (Oxford) described some of his work on the calculation of small energy differences in isolated molecules and dimers, using the short-time Greens function Monte Carlo technique. He outlined the method used, which involves the solution of the time dependent. Schroedinger , equation as a diffusion equation (in imaginary time) with branching terms. The Monte Carlo sampling algorithm uses an importance function which is related to the trial wavefunction. Special techniques, involving nearly-duplicated runs with identical random number sequences, are used to evaluate the small energy differences of chemical interest. As an example, Mr. Wells described a calculation of the dipole moment of lithium hydride by a field on/field off method which, starting from a Hartree-Fock plus Jastrow correlation trial wavefunction, took just 6.5 hours of VAX time with small core requirements. This was followed by a talk by Dr. W. Coffey (Dublin) on escape from potential wells in the presence of electromagnetic radiation. Applications included the and the description of quantum noise in ring lasers, current-voltage characteristic of Josephson junctions. These problems could be reduced to the model of classical Brownian motion in a tilted cosine potential, and Dr. Coffey described the analytical solution of this model.

Finally, Dr. J. Jefferson (R.S.R.E. Malvern) gave a talk on electron transport in semiconductor devices. He emphasized the rapid growth of interest in quantum dynamics with the reduction in device size to the scale of the electron de Broglie wavelength. Historically, electron transport has been described in a quasi-hydrodynamic way, by approximate solution of the Boltzmann transport equation, and by Monte Carlo simulation of the Boltzmann equation. He forsaw great interest in some of the novel quantum simulation methods, and suggested that this might be one field in which gaussian wavepackets would be useful. During and after these talks there was some discussion of the various alternative simulation techniques.

Two posters were presented: Dr. M.P. Allen and Mr. T.T. Hughes-Davies (Oxford) presented results of path-integral Monte

Carlo simulations of rotors on a two dimensional lattice, and Dr. A. Sutton (Oxford) described the calculation of force constants and elastic constants using the tight binding formalism.

Overall the visit of Professor Berne to Oxford was regarded as a great success by those who talked with him in the department, those who attended his seminar and those who joined in discussions with him at the Workshop.

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## CAMBRIDGE (24 October)

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Bruce Berne gave a lively lecture on October 24th. at Cambridge on the simulation of rare events. His main theme was the use of simulations to calculate and understand rate constants for processes in liquids. If one tries to simulate the rate constant for crossing the barrier in a double well potential by running many trial trajectories, convergence is slow because the barrier crossing is a rare event. However, following ideas of Keck, Yamamoto and Chandler, one can start the system at the top of the barrier and investigate the time dependent quantity:

 $k_{\beta}(t) = \langle j(0) \Theta(t) \rangle$ 

where j(0) is the reactive flux and  $\Theta(t)$  is a step function, which is unity for the product side and zero for the reactant side. This quantity is useful because in the long time limit it gives the true rate constant, and in the short time limit it gives transition state theory or the RRKM result according to whether one samples a canonical or microcanonical enemble.

Using this approach he told us about various interesting and intriguing results. For example in a two dimensional model system it was not necessary to have random forces to obtain a rate constant. In a simulation of cis-gauche isomerisation in butane, the rate constant not only still existed when the solvent was frozen, but did not change much. Although it is usually believed that the statistical rate constant gives an upper limit to the true rate constant, and indeed this is nearly always true, he showed some calculations on a double stadium potential in which the true rate constant exceeds the statistical one. This is because some parts of phase space are inaccessible and do not contribute to the normalisation of the rate constant.

We were pleased to welcome CCP5 members from Kent, Harwell and Dublin to this talk, which was full of more results and ideas than can be done justice to in this short summary.

### BIRKBECK (26 October)

The emphasis in his lecture entitled "Water and Aqueous Solutions" was on recent new results on quantum effects in water simulations. In his introduction, Bruce emphasised the relevance of quantum effects in liquid water, which are particulary large in small clusters of water molecules. The work described used the Feynmann path integral formulation. This work in the 1950s demonstrated that a quantum electron moving in a field was isomorphic to a classical system of a larger number of particles which were connected in a closed polymer ("bead") arrangement (essentially a flexible ring) through harmonic forces. This "multiparticle electron" representation could then be treated by standard Monte Carlo methods.

The application of the path integral approach to a model of liquid water was described in detail. A modified central force model was used for water, the modifications being derived from considering the RWK2 model. Both hydrogen and oxygen atoms were represented by between 40 and 80 "beads" when considering the isolated molecule, and parameters were fixed to give  $H \ O H = 104.52^{\circ}$  and  $R_{OH} = .9572$ Å. Zero point motion is included, leading to larger oscillations than would be obtained using a classical model.

Calculations were performed initially on an 11/780 with an attached FPS164, though a transfer to a CRAY1S gave a speed-up of about a factor of 5. 216 water molecules with periodic boundaries were used, with no Ewald summation. At 300k, it was found sufficient to use 3-5 particle chains. Related work by Peter Rossky using ST2 was mentioned, although the problems of working with a rigid model were emphasised. MC and MD calculations gave the same results.

The results of the calculation were discussed largely in terms. of the effects on the partial pair correlation functions. Overall, the conclusions suggested a reduction in orientational ordering. The first peak in  $g_{\mu\mu}(r)$  was less sharp than in the classical calculation, and was shifted to longer distance. The second peak was shifted to a slightly shorter distance. The effects on  $g_{(r)}$ were, as expected, much less: there was a slight moving out and broadening of the first, and perhaps a marginal bringing in of the second peak to lower r. The difference between the classical and quantum calculations of  $g_{OO}(r)$  were less than the differences between different classical models, and also less than the difference between various classical models and experiment. Thus we do not seem justified in assuming the disagreement between experimental and computed g<sub>CO</sub>(r) for classical water models is due to ignoring quantum effects. There appear to be more basic problems to sort out. The nearest neighbour energy distribution was broader

than the classical distribution, and shifted to slightly higher mean energy. Berne stressed as a result of this work that water models should be optimised with respect to quantum effects rather than classical ones.

Quantum effects on small clusters of water molecules were much greater. The dimer energy distribution was very much broader for the quantum calculation, and tunnelling was observed between the cyclic and extended (single donor) trimers. Bifurcated hydrogen bonds were unstable.

The remainder of the talk discussed his published work on the potential of mean force between two apolar molecules in ST2-water, and also butane in water. This latter problem led to a discussion on convergence problems, which Berne stressed were severe even in this relatively "simple" case. This point was taken up in the Workshop discussion in the afternoon, when we were told that 4 months computation on an 11/780 is not enough to obtain adequate configurational space sampling. The problem is not the deep effective wells relating to different butane configurations, but rather the problem of solvent reorganisation. An extensive discussion ensued, in which recent work at Birkbeck was mentioned, which showed clear memory effects in water simulations of up to 2x10<sup>6</sup> MC configurations for 216 particles. Berne agreed there were severe problems still with water itself, and that more work was needed. The case for bringing these severe convergence problems into the open seemed overwhelming, before the bandwaggon of complex system simulation was allowed to run too far. A suitable topic for a CCP5 Workshop?

Other discussion points during the Workshop session concentrated on quantum effects. For example, the calculations indicated measurable D/H isotopic differences were to be expected, which were consistent with greater  $D_2O$  than  $H_2O$  coordination found around the nickel in NiCl<sub>2</sub> solutions (John Enderby). Problems of using cluster data for potential function development were discussed in the light of quantum effects.

The talk was informal and involved much discussion, as did the afternoon Workshop session. The concentration on new work (quantum simulations) and technical problems (convergence) led to very lively exchanges. I suspect there were some colleagues in the Workshop who would have preferred a more general discussion on aqueous <u>solutions</u>, and to them we should apologise. If we had known the major thrust of the talk beforehand, we could have advertised it differently.

The Workshop format adopted did not use short presentations to get discussion going. All that was needed was the stimulating points that came out of the lecture. We think the day was very stimulating, and overall very successful.

### Review of the CCP5 Transport Properties Workshop held at Royal Holloway and Bedford College, Egham on the 10/11th January, 1985.

Chief Reporter: D.M. Heyes Other Contributors: M. Allen, E. Dickinson, M. Gillan, C. Hoheisel, J.G. Powles and R. Szczeranski.

It is often frustrating at conferences to hear a chairman stifle an interesting discussion, which is often more informative than the talk itself (!), because "we must move on to the next talk". In an attempt to eliminate this problem, Julian Clarke, promoted the foundation of a new form of CCP5 meeting which is proving a very successful complement to more conventional conferences (which CCP5 also promotes). The present meeting is the fourth in a series of informal discussions (the previous ones being on Interfaces, Quantum Simulations and Graphics) in which open-ended presentations are given a lively atmosphere of informal questions and answers. This one and a half day meeting was based around Molecular and Stochastic Dynamics simulations of transport phenomena and coefficients.

The first session mainly developed into a discussion of methods for obtaining shear viscosity and thermal conductivity by MD. It was started, however, by a general discussion on achieving "isothermal" conditions in MD. I described the Gaussian Isokinetic scheme and possible formulations of it within the framework of different integration algorithms. I showed how it could be stably incorporated within a (Verlet) leapfrog algorithm. Also a modification allowing for a shift in temperature within the same framework (devised with Denis Evans) was presented and which is very useful in equilibrating to a new thermodynamic state. Martin Schoen and Richard Szczepanski talked about the Kubo integral method for

determining shear viscosity at liquid and dilute gas densities (LJ:  $\rho^* \sim 0.01$ ). Both suffer from uncertainties associated with the characterisation of the long time tails in the stress autocorrelation function (see the accompanying note). Professor Hess demonstrated how SLLOD <u>Non-Equilibrium MD</u> (NEMD) can be used to obtain shear viscosities with much the same computing effort over a wide range of the shear thinning rheological equation of state. He illustrated that shear thinning is present at gaseous densities (LJ  $\rho^* \leq 0.1$ ) to much the same degree as at high liquid densities. In both density regions the relaxation times,  $\tau$ , lengthen so that  $\dot{\gamma}\tau \geq 0.1$  for typical LJ  $\dot{\gamma}$  (shear rate) values (0.05-5, say).

Professor Powles talked about a new method for obtaining thermal conductivity by following inhomogeneous temperature relaxations in model MD systems. He writes, "J.G. Powles (Canterbury), in collaboration with N. Corbin and W.A.B. Evans, described a new method for calculating the thermal conductivity,  $\lambda$ , of a liquid. The kinetic energy of the particles were perturbed ( $\sqrt{10^{-3}}$ ) according to a superposition of sinusoids in one (or two) axes of a cuboid with cyclic b.c.'s so that there is zero total energy change. After local equilibration ( $10^{-13}$ s) the temperature disturbance relaxes according to the thermal diffusion (=2mm/L) by the method of 'perturbation and difference'. The decay is a superposition of exponentials which are 'orthogonal' and can be separated by integration with the appropriate function of space. The slope of a logarithmic plot gives  $D_{T}(k)$  and the intercept  $\lambda/D_{T}$ , so that  $\lambda(k)$  is determined. The use of a cuboid with one long dimension gives low values of k for modest numbers of particles. Moreover four or more

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values of k are given by one simulation. The extrapolation,  $k \neq 0$ presents no difficulty. For the LJ 12-6 sp2.5 potential (and for sp3) the values of  $\lambda$  are very close to those for liquid argon for conventional values of  $\varepsilon$  and  $\sigma$ . This is a simple-to-program and fast-to-compute algorithm for determining thermal conductivity, with potentially wide application for liquids and solids."

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There was some concern expressed about a similar approach adopted by me in a recent paper. It may be appropriate here to emphasise the approximations inherent in the derivation of this (admittedly simple) model. It involved increasing the kinetic energy of one of the molecules in the MD cell by  $\frac{3k_B}{2}\Delta T$  above its surroundings and then monitoring the reequilibration of the system. The "heated" or origin molecule effectively loses all its excess temperature to the other (N-1) molecules in the MD cell so that at long times  $(\sqrt{1-2\sigma(m/\epsilon)^2})$  for the LJ system typically) then AT is statistically indistinguishable from zero. Let the equivalent average temperature excess at a radius r from the origin molecule and at time t be T(r,t). It remains to express the form of T(r,t) in terms of the thermal conductivity,  $\lambda$ . The main assumption in my analytic formulation of T(r,t) is that at any time, t, the heat flux through any concentric sphere centred on r = 0 is a constant, K(t) say. This is the same as saying that thermal equilibration through space is more "rapid" that the time scale of the change of supply of this energy (i.e. at  $r = \sigma/2$ ).

$$K(t) = 4\pi r^2 \lambda \frac{dT}{dr}(r)$$

$$\therefore K(t)_{\infty} \int^{\sigma/2} \frac{dr}{r^2} = 4\pi \lambda_0 \int^T dT$$
  
as  $T(r \rightarrow \infty) = 0$ 

Hence 
$$K(t) = -2\pi\sigma\lambda T(r = \sigma/2; t)$$
  
but  $K(t) = C_{v} dT (r = \sigma/2)$   
dt

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where  $U_{y}$  is the specific heat per molecule.

 $C_v \frac{dT'}{dt} = -2\pi\sigma\lambda T'$   $\int dt = -2\pi\sigma\lambda T'$   $\int dt = -2\pi\sigma\lambda T'$ where  $T' = T(r = \sigma/2)$  are expressively the part of the property condition between the  $\text{let}^{\text{int}} = C_v / 2\pi\sigma\lambda$  $\frac{d\mathbf{T}^{\dagger}}{d\mathbf{t}} = -\mathbf{T}^{\dagger}/\tau_{\text{production}} + \mathbf{t}^{\dagger}$ la se está de la competencia en encontra en encontra como en encontra en encontra en encontra en encontra encon Hence we give as  $T_{\tau}^{t}(t) \neq T^{t}(o) exp(-t/\tau)$  and be average darked as well as allows

addina an an The temperature profiles obtained over a wide range of LJ state points do in fact follow the broad sweep of an exponential as predicted by the above approximation.

The second session was started by Myron Evans who gave results of NEMD computer simulations of electric field induced time correlation functions in polar molecules. In particular the first order rotation/ translation cross-correlation function  $\langle V(t)\omega^{T}(o) \rangle$  in the laboratory frame of reference. Here V is the molecular centre of mass velocity of a molecule and  $\omega$  is its angular velocity (both vectors being defined in the laboratory frame). Mike Allen presented some new NEMD results of frequency dependent shear flow on a model diatomic fluid. He writes, "My short contribution described the results of some oscillatory shear experiments carried out with G. Maréchal. The technique was described

in a CCP5 newsletter of ours last year. The results illustrated the significant differences in applying finite frequency oscillatory shears to the centres of mass of the molecules as compared with the atoms. The differences could be seen to disappear as the frequency decreased. Some consistency with square-root cusp limiting behaviour in both stress autocorrelation and stress/orientation cross correlation functions could be seen. However the conjecture of D.J. Evans, that such behaviour can be explained entirely through a cusp in the stress memory function, was shown to be incorrect."

Claus Hoheisel also made some very interesting remarks about the computation of S(k,w) for small k-values by MD. Three methods were compared:

(a) The Fourier transform of the van Hove function,  $S(\underline{k},w) \approx \underline{1} \qquad fe^{-i\underline{k}\cdot\underline{r}} d\underline{r} \qquad \overset{\infty}{\sim} e^{iwt}G(\underline{r},t)dt$ where  $G(\underline{r},t) = G_{d}(\underline{r},t) + G_{s}(\underline{r},t)$ (i.e. a Fourier transform with respect to time and space) (b) Fourier transform of the intermediate scattering function  $S(\underline{k},w) \approx \underline{1} \qquad \overset{\infty}{2\pi} e^{iwt}F(\underline{k},t)dt$ 

which involves a transform with respect to time only.

where  $F(\underline{k},t) = \frac{1}{N} \langle \rho_{\underline{k}}(t) \varrho_{\underline{k}}(0) \rangle$ and  $\rho_{\underline{k}}(t) = \sum_{i=1}^{N} e^{-i\underline{k}\cdot \underline{r}(t)}$  is a solution of the second difference of the second differenc

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(c) Fourier transformation of the current-current correlation functions
$S(\underline{k}, w) = \frac{1}{2\pi w^2} \int_{-\infty}^{\infty} e^{iwt} C_{11}(\underline{k}, t) dt$
en e
$C_{\rm H}({\bf k},t) \simeq \frac{k^2}{2} < j_{\rm L}^2 > 0  for a stars that of the stars that is that is the stars that is that is that is the star$
$\frac{1}{N_{\rm exp}} = \frac{1}{N_{\rm $
$(\mathbf{r}_{\mathbf{r}}}}}}}}}}$
$\mathbf{N}_{\mathrm{exp}}$ is the set of th
where $i_{1} = \sum_{k=1}^{N} u_{k} e^{-ik \cdot r(t)}$ space to be a stable end of the state of the s
i, being the longitudinal part of i.
2k k.
Basically it appears that none of the methods poses any major problems
for $k > 2\sigma^{-1}$ where $k = 2\pi/L$ ; L is the box sidelength and $k = (N, M, L)$
using 50,000 time steps and 256 particles (less than $\frac{1}{2}$ hr on a vector
machine such as the Cyber 205). However for small k values, viz.,
$k \leq 1\sigma^{-1}$ then large system sizes are needed (e.g. $\sqrt{0.5\sigma^{-1}}$ is the smallest
wave vector for a 2048 LJ particle liquid system in a cubic box). Also
as the equivalent time correlation functions are more slowly decaying
for these wave-vectors then attention to 'recurrence time', $\tau_{rec}$ ,
ar tefacts must be considered.

$$r_{rec} \approx L/V_s$$

where  $V_s$  is the velocity of sound and  $\tau_{rec}$  is  $\sim 5$  psec for 2048 molecules. Such calculations take about 10-20 hrs of Cyber 205 time for a single state point. Problems associated with fitting and extending the F(k,t) long time tails to a hydrodynamic (exponential) function were also discussed. The velocity of sound was derived in very good agreement with

the experimental values.

Mike Gillan described some of his recent work on thermotransport in solids. He writes, "Thermotransport is the phenomenon of diffusion driven by a temperature gradient; it was first properly recognised about a hundered years ago by Soret who found that a temperature gradient gives rise to a concentration gradient in aqueous solutions. Since then it has been extensively studied in gas mixtures and also in solids. In the solid, what one would like to be able to do is to perform simulations to predict the drift rate of vacancies, interstitials or impurities caused by a temperature gradient. A direct simulation of the problem for a realistic 3-dimensional system would be impossibly expensive, mainly because the hopping rate of defects in solids is very slow - much less than typical vibrational frequencies. But progress can be made by studying less realistic models. I sketched some of the work I have done on the Frenkel-Kontorova model - a one-dimensional system consisting of a chain of particles coupled by harmonic springs. and acted on by a static periodic potential. Simple though this is, it does show the effects of interest: it has vacancy and interstitial defects which are thermally created. It also has the big advantage of being very quick to simulate - for 100 particles they get nearly 10<sup>6</sup> steps a minute on the Cray and have been able to do runs of up to  $2 \times 10^7$  MD steps (is this a record?). They have done simulations to calculate the chemical diffusion coefficient and the thermal conductivity using both the Green-Kubo method and the external force method. When looking at thermotransport itself, the best method turns out to be to calculate the drift of particles caused by the special type of external force used when computing the thermal conductivity, rather than trying to simulate the system literally in a temperature gradient. They found

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Green-Kubo to be statistically very bad for the thermotransport calculation. Maybe there are lessons here for the MD study of thermotransport in liquid mixtures?"

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The simulation of solvent retarded particulate dynamics was discussed by a number of participants. I introduced the method of Stochastic Dynamics and asked for suggestions on simulating systems with steep potentials using the SD technique while still maintaining the Brownian Dynamics form. Mike Allen emphasised that there is no minimum  $\Delta t$  within the solution of a set of stochastic differential equations - this being a separate matter from the time scale over which these equations are thought to be physically accurate. Therefore the time step could be made small enough (without restriction) until accurate dynamics are obtained, here, in the repulsive region of the pair potential. Eric Dickinson continued this theme. He writes, "I briefly mentioned our interest in Leeds in the simulation of colloid particle aggregation and dissociation by the method of Brownian dynamics using the algorithm of Ermak and McCammon. I then described two extensions of the original algorithm which we are presently working on. Firstly, the Brownian scheme has been generalized to include rotational Brownian motion in addition to conventional translational Brownian motion. The new extended algorithm allows for hydrodynamic rotation-translation coupling both in the systematic and the stochastic terms. Even for spherical particles with isotropic potentials of mean force, it is not clear that the effects of rotational Brownian motion can always be neglected even if one is considering only the translational displacements.

Secondly, I mentioned the inclusion of shear flow within the Brownian dynamics framework. Here an additional term must be added to the moving-on

routine to allow for the effect of the flow on the hydrodynamic interaction between the particles. Flocculated doublets of DLVO-type particles have been simulated in simple shear, and aggregate life-times have been determined as a function of shear-rate. Trajectory analysis shows that colloidal doublets may dissociate temporarily by Brownian motion only to be brought together by the action of the flow." Bill Van Megen discussed the use of Brownian Dynamics in simulating concentrated dispersions. He emphasized the problems inherent in a full treatment of the hydrodynamic interactions which involve many-body terms-reminiscent of the many body polarization problem for polarizable systems.

The meeting concluded with contributions from Dave Brown on using constant shear stress NEMD with a variable shear rate. The technical aspects of maintaining a constant shear stress and monitoring the fluctuating shear rate were described. This developed into a general discussion on possible methods for calculating viscosities in more viscous systems than is at present the case.

The meeting was concluded by Siegfried Hess who continued a discussion of NEMD studies on sheared monatomic molecules. He showed some very enlightening pictures of the structural changes that take place in the highly sheared liquids.

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CCP5 TRANSPORT PROPERTIES WORKSHOP - 10/11 JANUARY, 1985

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## Calculation of viscosity in dilute monatomic gas systems

R. Szczepanski, Department of Chemical Engineering, Imperial College, London, SW7 2BY.

This talk described equilibrium MD simulations of a monatomic system interacting via a shifted-force LJ 12-6 potential. Viscosity was evaluated by the Kubo-Green method.

The objectives of the work are:

A BAR CAR To investigate the density dependence of the dilute gas viscosity a) - specifically to evaluate the first density coefficient,  $n_{\rm h}$ , in the density expansion of the viscosity,

 $\eta = \eta_0 + \eta_1 n + \dots$ 

where  $n_0$  is the zero density value and n is the number density.

To check the validity of the simulation methods by comparing the b) calculated values of the viscosity with exact results. Exact results for any potential are only available in the zero density limit.

The following three simulation were carried out:

	No. Molecules	L/ơ	ρ*	T/K	Ţ*	P/bar	p*	No. time steps/10 <sup>6</sup>
A	77	20	.0096	302	2.52	10	.024	1.2
B	616	40	.0096	300	2.50	10	.024	1.18
С	392	20	.049	299	2.50	52	.123	.18

{ $\sigma = .3405 \text{ nm}, \epsilon/k_{\text{R}} \approx 119.8\text{K}, \text{time step} = .02\text{ps}$ }

Results	$(1,1,1) = \frac{1}{2} \left( \frac{1}{2} \left( \frac{1}{2} \right) + \frac{1}{2} \left( \frac{1}{2} \right) \right) \left( \frac{1}{2} \left( \frac{1}{2} \right) + \frac{1}{2} \left( \frac{1}{2} \right) \right) \left( \frac{1}{2} \right) \left( \frac$	$\gamma = 1.5$ , where $\gamma = 1.5$ , $\gamma = 1.5$ , $\gamma = 1.5$ , $\gamma = 3.5$ ,		
	second visial coefficient	viscosity n/10 <sup>-6</sup> Pas	ang balanta sub	
	B/10-6m3mo1-1	0 bar 10 bar	50 bar	
Exact (300K)	.67	23.39 23.6	24.3	
A	1.5 ± .9	$22.6 \pm 1$		
В	.5 ± .3	$22.8 \pm 1$		
C	.6 ± .2		26.7 ± .4	

Errors in viscosity are estimated as 3 times the standard error about the sample mean.

Typical results for the stress-stress correlation function and viscosity as a function of integration time are shown in Figs. 1 and 2. The values of viscosity quoted above correspond to the point on the viscosity/time graph where a plateau is reached. This is a highly subjective criterion.

### Discussion

Several problems arise in interpreting these results. Some criterion for deciding when the correlation function is effectively zero is necessary. The very long time tails shown in Fig. 1 are significant compared to the statistical uncertainty in the value of the correlation function, although physically such correlations would seem to be unlikely. The problem here probably arises from the use of too many time origins in evaluating the correlation function. This would mean that successive time origins would be correlated, resulting in an underestimate of the statistical uncertainty. In view of this the results reported above will be reanalyzed.

A second set of problems is related to the system size and length of simulation. The relaxation time for the correlation functions is

13.

compared below with the recurrence time (time for a sound wave to traverse the simulation cell):

	Relaxation	time/ps	Recurrence	time/ps
A	23		21	1.1.1
В	23		42	
С	. 4.	S	21	

It has been suggested that if the relaxation time is comparable to the recurrence time spurious correlations could be observed. No clear indication of this was noted in the simulations reported here. It is clear, however, that if time origins for the evaluation of the correlation function are to be uncorrelated they should be separated by at least one relaxation time. In order to obtain good statistics this would require simulations covering at least 50 ns, rather than the 24 ns in this study.

The only unambiguous conclusion which may be drawn at this stage is that the simulations give results of the right order of magnitude but the precision is difficult to estimate.

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The shear viscosity of a Lennard-Jones fluid calculated by equilibrium molecular dynamics

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### Abstract

Using the Green-Kubo relation we have calculated the shear viscosities for 10 different fluid states by molecular dynamics (MD) simulations. The common Lennard-Jones interaction potential was employed; and the statistical significance of the correlation function as well as the particle number dependence have been investigated.

Some of the main results are the following: (i) the obtained values are estimated to be accurate within 5 per cent; (ii) for particle numbers large or equal 256, no significant number dependence could be found (checked up to 2048); (iii) for the number of states studied up until now, good agreement is evident with the values obtained by D. Heyes /1/ using non-equilibrium MD; (iv) a noticeable tail of the time correlation function appears for states near the phase boundary to the solid state, however, the function decreases to practically zero within about 2.5ps in any case; (v) the computational effort necessary for the performance of equilibrium MD is well comparable to that needed for non-equilibrium MD.
#### COMPUTER MODELLING OF CERAMICS WORKSHOP

C. R. A. Catlow and M. Leslie

Ceramics are materials of growing technological importance; and both pure and applied research into their properties is advancing rapidly. Almost all of this work is experimental, commonly phenomenological in its approach. However, the development of computer simulation techniques, which can examine structural and defect properties of bulk phases and of interfaces offers a real opportunity for studying the fundamental processes in ceramics and hence guiding and interpreting experiment. Much of this progress on modelling these important materials has taken place in the UK. For this reason CCP5 sponsored a small workshop, held at New Science Group, ICI, the aim of which was to assess the present state of this field, paying special attention to areas where there are difficulties and to identifying those fields where there is the greatest opportunity for future progress.

In this report, we first summarise the presentations made by members of the workshop, following which we discuss the general points to have emerged.

Dr. Mackrodt (ICI) set the scene for the workshop by giving an overview of the materials and properties of interest. The materials can be classified as either ionic (eg. 2r02) or covalent (eg. SiC). Properties of interest are

(i) Structures (Lattice, surface and electronic)
 (ii) Thermodynamics (Energy and entropies)

(iii) Kinetics (Bulk and surface diffusion rates)

(iv) Reactivity (Oxidation reduction and catalytic properties)

(v) Mechanical properties.Dr. Mackrodt then elaborated on the importance of temperature effects in defect calculations. The temperature has two effects. (i) It causes the lattice expansion, which is usually treated by the array of the second second second second second second sectors and the defect. As an example Dr. Mackrodt presented some calculations on the Schottky defect in MgO. These showed that  $\Delta H^0$  was reasonably constant, over the temperature range 500-2500 K and also approximately equal to  $\Delta U$  at 0 K. However  $\Delta U$  and  $\Delta S$  vary widely with temperature. Dr. Mackrodt then posed the question of whether the approximation  $\Delta H \approx \Delta U$  should hold at a surface, and concluded that there was no good reason why it should be so. These facts should be borne in mind when comparing results of simulations with experiments.

Dr. Catlow (UCL) discussed the calculation of the electronic structure of ceramics. He showed that, providing simple localised models can be assumed for hole and electron states, it is possible by combining ionisation energies with lattice and relaxation energy terms obtained from simulations to calculate

- (1)band gaps - both thermal and optical
- (1) band gaps both thermal and optical
   (2) work functions and electron affinities
- (3) ionisation energies of donor and acceptor states
- mobilities of hole and electron states (4)
- values of the correlation or 'Hubbard-U' energy.... (5)

Examples of the use of such calculations were taken from work on transition metal oxides, and recent studies of BaTiO3. The main difficulties with the approach lie in

the necessity for assuming localised electronic states (1)

(2) the use of free ion ionisation energies.

The latter problem is most acute when calculating energies of hole states in O(2p) bands. These require knowledge of the 2nd electron affinity of oxygen, which is a poorly defined quantity owing to the unbound nature of the free 02- ion. Future work will need present approaches to be blended with band theory and increased use of quantum mechanical methods to calculate ionisation energies. Given these developments, it would seem feasible to make a number of accurate predictions concerning the electronic properties of ceramics. 

Dr. Leslie (Daresbury Laboratory) talked on angle bending forces. Manv ceramic materials are partially ionic and partially covalent. In these materials directional forces are important. These may be simulated by including angle bending forces in the static simulation programs. As an example Dr. Leslie discussed the simulation of quartz. Including angle bending forces in the standard Born model with a shell model to describe the polarisation of the oxygen allows a very good empirical fit to the properties of alpha quartz. The model was further tested by applying the empirically fitted potential to other polymorphs of SiO2. This example shows the scope for this type of potential in modelling partially ionic materials.

Dr. Tasker (Harwell) discussed interfaces in oxide materials. It is important to concentrate on real material problems, which means considering impure, polycrystalline substances. Our calculations should be addressing processes such as sintering, grain growth, electrical characteristics, corrosion and degradation and mechanical properties. With improvments in theoretical techniques, these real problems are now amenable to study. Examples of where calculations should go include

(i) Calculation of a complete phase diagram as a function of T and P for a ceramic (eg. Zr02).

(ii) Multi-component segregation to improve comparison with real impure systems,

Dr. Tasker then went on to discuss possible future fields of study. The lack of validation of the models was seen to be a major problem. Temperature effects need also to be considered; in this context the quasiharmonic approximation cannot be used at a surface. Finally, real grain boundaries are not necessarily the pure tilt or twist boundaries studied so far.

Dr. Egdell (Imperial College) then described three experimental techniques which can be used to study segregation in surfaces. These are ion scattering, Xray photoelectron spectroscopy and Auger spectroscopy. By ion scattering in 45° specular geometry, simple classical dynamics gives the energy loss of the beam in terms of the mass of the surface ions. This has been used to determine the enthalpy of segregation of Ca ions in MgO. SnO2 doped with 5b was also given as an example studied by XPS, where it is shown that Sb segregates to the surface and an enthalpy of segregation can be calculated.

Dr. H. V. Atkinson (Harwell) then discussed grain boundary migration, which is a process of great technological importance for both metals and ceramics. Remarkably little is known about the fundamental atomistic processes involved. Theoretical modelling of the structure of grain boundaries in ceramics and their response to driving forces and diffusional processes could provide a new tool for investigation of these materials. Although the present modelled structures (eg. those of Tasker and Duffy for NiO) are only for symmetric, non-facetted, coincidence site lattice boundaries, studies of their behaviour and the effects of inserting impurity atoms could provide clues to the limits of behaviour of the more complex boundaries thought to occur in real materials.

It might be possible with the modelled grain boundary structures to investigate the following questions:

What is the response of a boundary when displacements and curvature (1)are imposed to simulate the effect of a driving force for grain boundary migration?

Are ions detached from grains and reattached at certain preferred (2)

sites?
(3) Are detached ions free to move in the grain boundary before reattaching to an abutting grain?

(4) Is the rate determining step detachment, movement in the boundary or reattachment?

(5) Is migration governed by the movement of single independent ions or by the collective movement of groups of ions?

(6) Do facets of different grain boundary structure influence structure? (7) Can the glide and climb of grain boundary dislocations intrinsically associated with migration be modelled? (8) Is the structure of a migrating boundary different from that of a 

static one?

Dr. A. Atkinson (Harwell) discussed diffusion in oxides and oxide film The growth of thick oxide films is governed by diffusion growth. processes. As an example, in Fe304. Fe diffusion in the bulk is well understood but O diffusion is not. However, grain boundary diffusion is the rate-determining step for film growth, and a study of bulk diffusion may tell us little about actual film growth rates. Reactive elements (cg. CeO2 in NiO) are also known to influence film growth and this is thought to occur by blocking grain boundary diffusion. ... Nothing is known about the mechanism. In the consideration of thin oxide films, the important processes are the adsorption of oxygen onto the surface and the injection of defects into the bulk from the surface.

Dr. A. N. Cormack (UCL) spoke about modelling complex oxides. He described the possibilities and indicated how such studies could interact with, and enhance, comparable experimental studies, for example, bv discriminating between different possibile migration mechanisms for mass transport in structures with large unit cells such as pyrochlores and spinels.

He pointed out that the principal difficulty in this area was in obtaining suitable parameters for the potential model, particularly with

regard to those describing the dielectric response, via the widely used shell model of Dick and Overhauser. This was largely due to the unavailability of suitable experimental data on such crystal properties as the dielectric constants and was an area in which further experimental effort would be appreciated.

Taking the example of dopant cation-oxygen vacancy acsociation energies in CeO2, he showed how calculated defect energies could vary with changes in the shell model parameters for CeO2 (see figure) and hence that some care was needed in applying the results of such simulations to the interpretation of experimental data.

Notwithstanding these difficulties, he suggested that a systematic approach to possible potential model parameter variations and their consequences would not only provide additional physical insight into the simulations themselves, but would also prove beneficial to ceramicists and material scientists - which was, of course, the object of the exercise!

Dr. J. M. Parker (Sheffield) has studied silicate and fluoride glass forming melts, both experimentally and using MD modelling techniques. One difficulty had been the choice of model parameters to obtain sensible radial distribution functions, but the results for both types of glass are now consistent with available X-ray and spectroscopic data. In the silicate diffusion coefficients for Si, O, Na, and F ions showed a system, temperature dependence similar to that observed experimentally with DO values of the correct magnitude. In heavy metal fluorides, the models have been used to determine the effect of addition of various fluorides on structure and the results were correlated with such variables as glassforming ability. In the ensuing discussion the possibility of modelling diffusion processes at temperatures below Tg in vitreous silica was considered, and the existence of defect sites in glass structures was discussed.

Dr. D. E. Lloyd (BCRA) gave the commercial point of view with a talk on advanced ceramics for engineering applications. Active commercial research is currently concerned with the covalent ceramics Si3N4, SiC, B4C and BN and the ionic ceramics A1203, MgO, BeO and ZrO2. Dr. Lloyd then listed the basic properties of ceramics of interest to engineers.

(1) High mechanical strength

- (2) Toughness. Good impact strength can be the weak link and careful control of particle size and impurities is necessary.
- (3) Retention of strength at temperature. The oxide ceramics loose strength with temperature.
- (4) Resistance to thermal shock and thermal stress. Alumina is particularly prone to this.
- (5) Good surface finish and hence good tribological properties.
- (6) The thermal expansion is important and needs to be matched to metal components.

# DISCUSSION

	In the discussions during the workshop the following themes emerged
••• ••• •••	(i) <u>Surface Interface and grain boundary structure</u>
·	n. Na sing sa manananan katala manananan katala sa mananan mananan katala mananan katala mananan katala sa katala
	At present, only two systems have been thoroughly studied by simulation techniques: the surface of MgO and a variety of grain boundaries in NiO. There is no scientific reason why calculations could not be extended to a wide range of ceramic materials. However, before this is accomplished, there is a need for quantitative validation of present models and results. This can probably best be achieved in the study of segregation phenomena; and further studies in this field are clearly necessary. There is a need to extend present calculation methods to simulate dynamic properties of interfaces in order to meet the needs of the experimentalist in areas such as oxidation, corrosion and final stage densification. The development of dynamical simulation codes for surfaces and grain boundaries would therefore be of great value.
to de la Secto La Secto	(ii) <u>Modelling complex oxides</u>
	Recent calculations of perovskite structure oxides (eg. 8a103), spinels and pyrochlores have demonstrated the useful role which simulations can play in the study of these complex materials. However, there are problems many of which were highlighted in Cormack's talk, concerning interatomic potentials. There is now good evidence that pair potentials are transferable provided that they are modified sustainatically for the
	effects of coordination number. More serious difficulties are encountered in treating shell-model parameters. The reliable calculation of these
9 3	terms is evidently a priority.
	。
•	(iii) <u>Many-Body_effects</u>
	The bond-bending terms successfully incorporated into static simulation
	codes by Leslie are proving to be of considerable use in simulations of
	silicates. It is still not clear how generally applicable they are to this
	class of material, or whether the approach can usefully be extended to
	other materials. Another question concerns the implementation of these
	terms in dynamical simulations. The general belief in the simulation
	community has been that inclusion of many-body terms increases the computer
	time required for the calculation by a very large amount. It is probable,
	nowever, that the three body terms of the bond-bending type would be relatively inexpensive. Their inclusion could greatly enhance the efficacy of simulation studies of glasses.

# (iv) Temperature effects

Recent work - particularly that of Jacobs, Harding and Gillan who have developed techniques for calculation of vibrational entropies - has led to realistic calculations of high temperature defect parameters. As stressed by Mackrodt's talk this is of considerable importance in the study of ceramics where we are generally concerned with high temperature behaviour. Further work is needed - particularly on the question of the variation of effective potentials with temperature. A coordinated effort on this topic would be of value:

would be of value:  $\langle v \rangle = \frac{\langle v \rangle}{\langle v \rangle} =$ 

Several talks drew attention to this important point. If simulations are to achieve their aim of predicting and guiding experiment, predictions must be verified by comparison with experiment for a number of systems. This has been achieved in, for example, simulation studies of ionic halides. But for ceramics there have to date been surprisingly few opportunities to compare theory with experiment. Even for such a simple case as NiO, there is still controversy about the status of the comparison of calculated and experimental parameters. For this case, and for a number of 'model' systems, detailed comparisons are needed.

In addition to the specific aspects discussed above a number of general points emerged from the workshop.

(i) The small size of the ceramics modelling community means that it is essential that individuals remain in regular contact. CCP5 could attempt to provide a focus for such contacts.

- (ii) Joint programmes of research on particular topics or materials could prove to be fruitful. The group discussed the possibility of a concerted program on ZrO2 - a material discussed by most of the participants - including bulk and surface defect structure, properties of dopants, grain boundary structure and segregation phenomena. Such a project could interact well with experimental work - for example that discussed by Egdell in the workshop.
- (iii) The interface simulation codes developed by AERE by Tasker and coworkers would be of value to the CCP5 community. The programs should be acquired from AERE.

In summary, the workshop identified a lively area of activity in the simulation field in which there is considerable strength in the UK, and where CCP5 can play a valuable coordinating role.

The organisers would like to thank ICI New Science Group for acting as host for the meeting. We are also grateful to Dr. A. E. McHale for her assistance in preparing this report.

BINDING ENERGY OF ANION VACANCY 0.9 TODOPANT CATION IN CeO, E. (calc) 0.5 13.7 🛥 Butler etal 18.9 experiment Gerhardt & Nowick 25.9 新闻的过去式 法保证部分法保证 医生肉的 0.0 E exp : 21-24 Y Gd Sc а.... ionic radius (A) In the spirit former than the second as the second se E. C. Scherer, M. M. Martin, A. Martin, and A. Martin, and M. Martin, Phys. Rev. B 199 (1998) 1100 (1998). 0.0 set a second as a construction of the second Gd and when the second e per all e care a l'herrarigen a ser a anna a ser and the second second Sc 0.5 -1.0  $\mathcal{E}_{o}^{calc}$ 15 12 20 25 41

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# REPORT ON GRAPHICS WORKSHOP HELD AT BIRKBECK COLLEGE, DEC. 18TH. 1984.

#### M. Leslie

A. Morffew of IBM UK The workshop opened with a presentation by Dr. He described the three main uses of graphics as being Scientific centre. representational graphics, database interface and 3D modelling. MП simulations are concerned exclusively with representational graphics. The merits of raster and vector graphics were then discussed. The ideal graphics device would be fast, capable of producing effective colour and shading. However a compromise between these always has to be reached. In cases where speed is important, vector graphics may need to be used. I٤ was not yet possible to use any graphics device in real time. Dr. Morffew then discussed some examples of graphics, with the emphasis on the need to move away from the stereotype ball and stick representation. For example, he showed a dot surface representation of a molecule and an example of an electrostatic field around a protein represented by arrows. In the MD simulation field he showed an example of a trajectory plot and also of a distance matrix plot.

Maurice Leslie (Daresbury Laboratory) then described the central facilities available. Of greatest interest to CCP5 members are the SIGMA graphics display terminals at Rutherford Lab and Daresbury Lab. These are high resolution raster graphics devices which can produce colour and shading. Dr. Leslie described a molecular modelling program, MORIA, which is available at Daresbury, and would be of interest to MD simulators.

Julian Talbot (Southampton) then showed a movie of the simulation of N2 on a graphite surface. A film frame was shown for every 10 MD time steps, each frame being repeated twice. The film took 1 CRAY CPU sec. per frame.

Mike Gillan (Harwell) showed some slides of trajectory plots of the fluoride ions in the fast ion conductor CaF2. These clearly showed that the ions move by correlated jumps over several sites. The major limitation of the trajectory plots is that they can only represent motion in two dimensions.

Roger Webb (Surrey) showed a surface damage generation movie which had taken 2 days on a PDP11 to produce. Martin Dove (Cambridge) showed a film of a plastic crystal which had been produced on a PERQ, taking 2 minutes per picture to produce. There were also contributions from Jan Abas (Bangor), Elizabeth Colbourne (ICI) and Rod Hubbard (York).

There was a lengthy discussion following the workshop. There was a feeling that graphics, in particular movies, were more useful as an aid to presentation and that it was difficult to extract useful science from them in the MD simulation field. This was particularly true when complicated correlated motions are being sought. This may be because people stick to producing ball and stick pictures of the positions of molecules, and that a movie of some other function of the system may allow science to be obtained. There were suggestions that studies of perturbed systems and second order phase transitions may benefit from good graphics. Finally it was agreed that it would be useful to compile a library of hardware and software used by the CCP5 community.

A demonstration by John Quinn (QMC) of vector and raster graphics was held during the workshop.

#### QUESTIONNAIRE ON GRAPHICS HARDWARE AND SOFTWARE

At the recent workshop on graphics it was decided to compile a library of graphics hardware and software used within the CCP5 community. To assist me in carrying this out, could you please answer the following questions and return to me at Daresbury.

M. LESLIE FEB. 1985

(la) Give a brief description of any graphics software that you use.

(1b) Is it raster or vector graphics?
(1c) On which computer does the software run?
(1d) Give an estimate of the time taken to produce a picture
(1e) Does the program use any graphics libraries?
(1f) Is the program easy to use and is there any documentation?

(2) Describe hardware facilities that you use. Describe screen, hardcopy and slide/film facilities. Indicate if you have any special difficulties, such as delay in processing films.
 (3a) Would the facilities described be available for use by other

members of CCP5?

(3b) Would you be able and willing to transfer the software to other sites? Please return to M Leslie SERC Daresbury Laboratory Warrington WA4 4AD

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# RAHMAN FESTSCHRIFT

#### November 12-13 1984 Argonne National Laboratory, Illinois 60439, U.S.A.

J.H.R. Clarke

To celebrate the twentieth year since the appearance of Aneesur Rahman's first paper describing molecular dynamics simulations of liquid argon, a group of his colleagues organised this two day meeting at Argonne Laboratory. There were eleven review talks covering most of the areas of computer simulation endeavour which have been directly or indirectly stimulated by Aneesur's contributions to the field. The meeting was attended by over a hundred scientists from all over the world. It was indeed an auspicious occasion which one felt priveliged to attend. Thanks are due to the organising committee and Argonne National Laboratory for their excellent organisation and hospitality.

As if to emphasise the rapid expansion of computer simulation in studies of condensed matter, only two of the talks mentioned the word 'liquid' in their titles! Jack Powles discussed the calculation of the dielectric properties of Stockmayer droplets from spontaneous fluctuations of the dipole moment, whilst David Ceperley outlined recent progress in finite temperature quantum simulations of bosons (alias liquid helium) which bridge the gap between the classical work of Rahman and 0 K Monte Carlo simulations of Kalos and others. Michael Parrinello reviewed his pioneering work with Aneesur on electron localisation in molten salts. Two papers discussed the formation and characterisation of dense

Two papers discussed the formation and characterisation of dense amorphous structures in molecular dynamics simulations, and area again pioneered by Aneesur. Hans Anderson discussed his own work on the formation of one and two component Lennard-Jones glasses in computer experiments, showing that despite the vast difference between simulation and laboratory time scales the model liquids exhibit a very similar phenomenology to real glass forming materials. Frank Stillinger discussed his fascinating work in which the structure of dense liquids was analysed in terms of the distribution of potential energy minima underlying the instantaneous liquid structure. This representation was likened to image enhancement when compared with the usual finite temperature radial distribution function.

Simulations of proteins and other macromolecular systems featured in two of the later talks. Martin Karplus reviewed his extensive work on protein simulations whilst Herman Berendsen gave a broader survey of work in the field of large molecules and micellar structures, including calculation of solvation free energies and binding constants. This talk started with an excellent and somewhat nostalgic discussion of liquid water simulations, emphasising the outstanding contributions made by Aneesur (and not forgetting Frank Stillinger!). Three talks concentrated on various aspects of the solid state. Ian McDonald described recent efforts to develop interaction potentials for crystalline potassium cyanide. Although polarisation effects were not considered the inclusion of a charge distribution to represent the CN<sup>--</sup> quadrupole yielded a pair potential which was effective in reproducing a wide range of the crystal properties, including the elastic constants. Jacucci discussed diffusion in the bulk and on the surfaces of crystals emphasising a general need to accompany simulations with developments in analytical theory. Farid Abraham showed an excellent film displaying the dynamical behaviour of physisorbed atomic films. Everyone was duly impressed by the enormous computing power available to one in the employ of IBM Inc.!

Last but not least one must make mention of a fascinating and more philosophical talk by Charles Bennett on simple causes with complicated effects. One rather aetherial theme of this presentation was the probable ingredients of systems with a total capacity for self organisation. Even the example of the behaviour of mortal worms hardly served to bring a listener down to earth!

J.H.R.Clarke

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(a) A set of the second secon second sec ERROR IN CCPS PROGRAMS MOTETRA & MDPOLY D.J. Tildesley and M.P. Allen 6 ·

The rigid body equations of rotational motion about the centre of mass are [1]  $L + w \times L = N$  (1)

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where the time derivative is taken in a body-fixed frame of reference,  $\underline{w}$  is the angular velocity,  $\underline{L}$  the angular momentum and  $\underline{N}$  the torque. In the principal body-fixed frame we may write  $L_1 = I_1 w_1$   $(\underline{i} = 1, 2, 3)$  where  $\underline{w} = (w_1, w_2, w_3)$ ,  $\underline{L} = (L_1, L_2, L_3)$  and the inertia tensor is diagonal with components  $(I_1, I_2, I_3)$ . Then equation (1) may be

written

$$I_{1} \tilde{w}_{1} = w_{2} w_{3} (I_{2} - I_{3}) \neq N_{1}$$

$$I_{2} \tilde{w}_{2} = w_{3} w_{1} (I_{3} - I_{1}) \neq N_{2}$$

$$I_{3} \tilde{w}_{3} = w_{1} w_{2} (I_{1} - I_{2}) \neq N_{3}$$
(2)

The equations are written out in full here to emphasize that they are wnambiguous: there is only <u>one</u> way to define the time derivative of a Scalar quantity such as  $w_i$ , in contrast to that of a vector, where the motion of the reference frame must be considered.

In a well-known paper [2], Evans suggested combining these equations with a quaternion representation of molecular orientation, to obtain singularity-free equations of rotational motion. However,

in the accompanying paper demonstrating the technique in a molecular dynamics simulation of methane [3], Evans and Murad wrote down equations applying in the case of a spherical top, with  $l_1 = l_2 = l_3$ :

$$\hat{w}_{1} = N_{1} / I_{1}$$

$$\hat{w}_{2} = N_{2} / I_{2}$$

$$\hat{w}_{3} = N_{3} / I_{3}$$

Essentially the same equations apply to linear molecules, where  $w_3$  and  $N_3$  are taken as zero, and  $I_1 \neq I_2$ . Equations (3) do <u>not</u> apply to symmetric and asymmetric top molecules.

However, equations (3) have been quoted in the general context of the simulation of molecular liquids [4] and have found their way into the CCPS programs MOTETRA and MDPOLY which are intended to simulate general tetrahedral and polyatomic molecules. Specifically, intermolecular torques are evaluated in the space-fixed frame, converted to principal body-fixed axes, divided by the inertia components, and used in a predictor-corrector algorithm for the angular velocity based on equations (3). This is coupled to a predictor-corrector method for the quaternion parameters. Thus, for symmetric and asymmetric top molecules, <u>these programs generate</u> <u>incorrect trajectories</u>. The extra terms on the left of equation (2) should be included in the algorithm to make the trajectories correct.

The error is not immediately apparent on running the programs, because the incorract equations of motion still conserve energy. This is because energy conservation follows from taking the scalar product with  $\underline{w}$  of the equations above. From equations (2) and (3) we obtain

 $\mathbf{I}_{1} \boldsymbol{\omega}_{1} \tilde{\boldsymbol{\omega}}_{1} + \mathbf{I}_{2} \boldsymbol{\omega}_{2} \tilde{\boldsymbol{\omega}}_{2} + \mathbf{I}_{3} \boldsymbol{\omega}_{3} \tilde{\boldsymbol{\omega}}_{3} = \boldsymbol{\omega}_{1} \boldsymbol{N}_{1} + \boldsymbol{\omega}_{2} \boldsymbol{N}_{2} + \boldsymbol{\omega}_{3} \boldsymbol{N}_{3} = \underline{\boldsymbol{\omega}}_{1} \boldsymbol{N}_{1} \qquad (4)$ 

The left hand side is the time derivative of the rotational kinetic energy. On the right, it is not difficult to show that  $\underline{w},\underline{N}$  is the negative of the rate of change of potential energy due to rotational motion. The extra terms of equation (2) do not appear in this equation. The incorrect equations fail in not conserving total angular momentum in the space-fixed frame. This is not noticed in simulations employing periodic boundary conditions, which themselves destroy total angular momentum conservation. Nonetheless the trajectories generated are incorrect, as may be demonstrated in the simple example of torque-free motion of a single rigid rotor.

The other programs in the CCP5 Library which deal with polyatomic molecules (MDMULP, MDMPOL, MDMANY, MDMIXT) are based on a quaternion leapfrog algorithm. These programs generate correct equations of motion, since they solve the equations  $\frac{1}{L} = \frac{N}{2}$  in the space-fixed frame. Conversion to body-fixed coordinates only takes place when  $\underline{w}$  is required in the quaternion part of the algorithm.

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SIMULATION OF A HOPPING PROCESS IN A LATTICE

R. Vogelsang and C. Hoheisel

### 1. The modelling of a jump of a defect atom in a lattice

Consider a fcc-lattice with an impurity, denoted in the following as defect atom D, which contains a vacancy site (VS) in the neighbourhood of D (see fig. 1). During a jump, D has to pass from its equilibrium position (EP) through the gate of four atoms, GA (numbered 1,2,3,4), to the VS leaving a vacancy site at its former position. In other words, on its migration path D has to cross an energy barrier formed by the four GA. The configuration where D has arrived the top of the barrier is called saddle point configuration (SPC).

Near the melting line, D possesses sufficient kinetic energy to cross the SPC often  $en^{ough}$  to allow for an investigation of those jumps with reliable statistics by standard computer simulations /4/. Computer simulations are also directly usable for the investigation of fast ionic conductors like CaF<sub>2</sub>, where the F-Ions show a liquid like diffusion.

Apart from these specific cases, the jumping frequencies, f, (SPCcrossings per time unit) of defect atoms are very rare within simple solids compared with the time scale of molecular dynamics simulations (MD):

 $f = 10^{6} - 10^{8} s^{-1}, \frac{1}{\tilde{c}_{Ar}} = 3.19 \times 10^{12} s^{-1}.$ 

Therefore, no jump event would be observable within a MD run of reasonable length.

Due to this, one has to enhance the jump frequency artificially to model the jump behaviour of a crystal by MD. This method of inducing successful trajectories was first suggested by Bennett/2/ to investigate diffusion in solids.

# 2. The method of induced trajectories

This method is based on a restricted potential:

 $u^{*}(r_{1}...r_{N}) = u_{LJ}(r_{1}...r_{N}) + u_{D}(\xi) +$ 

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waa ahaa ahaa ahaa waxaa w with  $u_{D} = \begin{cases} 0 & |\xi| < R_{x} \\ 0 & |\xi| > R_{y} \end{cases}$ an de la construction de  $u_{WS}$ : single occupancy term, which keeps atom other than D  $\sim$ within its Wigner-Seitz cell. is the reaction coordinate of the jumping atom given in terms of the four gate atoms, 1, ..., 4: ... and pression pression of the  $\int_{\mathbb{R}^{n}} \left\{ \sum_{i=1}^{n} \left\{ \sum_{i=1}^{n} \frac{1}{4} \left( \sum_{i=1}^{n}$ the and all the contract of the start was the the set of the start where j is a unit vector in jump direction, chosen to be a (110) direction.  $R_x$  is an arbitrary boundary value for  $\xi$ . By the statement of the second s na se contra againe contra agained contra contra contra e contra terra e la facto e a seto contra e a u\* restricts the system to a region of phase space which the intersects all successful jump trajectories between the two lattice sites in question, except for a few unsuccessful states trajectories. That means, in terms of  $u_{\rm D}$  the jump atom is reflected by an  $x_{i_{ab}}$  infinite potential wall whenever  $x \in \mathbb{R}_{\mathbf{x}}^{+}$  , a subset of the set xA reflection is roughly an inversion of the velocity  $\underline{v}_n$ . This momentum inversion has to be dissiputed to the lattice, otherwise the total momentum (P=0) and the energy are not conserved. Due to our choice of { the four gate atoms have to be involved in the momentum dissipution. We achieved this in a similar way known from the collision of ... hard spheres: At time t=t, assume

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 $\Delta \mathbf{R}_{\text{Di}} = \Delta \mathbf{R}_{\text{D}} - \Delta \mathbf{R}_{\text{i}}.$ 

Project  $\Delta R_{Di}$  onto the jump direction:

 $\underbrace{\mathbf{j} \, \mathbf{j} \, \mathbf{j} \, \mathbf{j} \, \mathbf{k} \, \mathbf{F}}_{\mathbf{k} \mathbf{k} \mathbf{k}} = \mathbf{k} \, \mathbf{k} \,$ 

$$\Delta \underline{R}_{Di} = -(\Delta \underline{R}_{Di} \cdot \underline{j}') \underline{j}'$$

and recalculate  $\Delta \underline{R}_{D}$  and  $\Delta \underline{R}_{i}$  is a contract of the second seco

On the other hand, for  $\oint (t=t_0) < R_x$  one has to check whether  $\oint$  has changed its sign with respect to  $\oint (t=t_1)$  or not. A change of the sign indicates a saddle point configuration. This configuration is then stored. The decision whether the jump is successful or not is made in a MD run described in section 3.

For computational purposes, we used a cube of edge  $d_{\rm WS}$  of half the lattice constant rather than a Wigner-Seitz dodecahedron.

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Whenever the separation between an atom j and its ideal lattice position is larger than  $d_{WS}^2$ , the atom is displaced back by  $\Delta r_j(t)$ . The potential term  $u_{WS}$  is only necessary for calculations near the melting line.

### 3. Details of the simulation

The simulation of the hopping process consists of four MD-runs:

#### run 1

Thermalize a fcc-lattice with D in a normal lattice place and without a split vacancy. Store the coordinates of the ideal lattice sites and the deviations of the last configuration with respect to the ideal lattice.

#### run 2

Start from the thermalized ideal lattice configuration, search for the centre particle and exchange its coordinates with those of D. Remove one particle from the nearest neighbourhood of D to obtain a certain jump direction (here (110)). After setting D into a SPC ( $\int = 0$ ), all the neighbours of D in a certain range are marked.

Choose a reasonable limit value for  $R_x$ . Due to some geometrical considerations one finds that  $|\xi|$  could reach a maximum value of about 0.55. Therefore a value of  $R_x = 1.05$  ensures that  $u_D$  has no direct influence on D.

Add the coordinate deviations to retain the configuration of run 1 and thermalize this configuration again. The last configuration is stored with D set into the saddle point.

run 3 Start from the last configuration of run 2 and set  $R_x$  to 0.16-0.26. Store a certain number of SPC during this run.

#### run 4

Use the SPC collected in run 3 to compute exact trajectories for a distinct time interval by common MD.

During this run you can obtain the correlation functions according to the list of particles made in run2. In fig. 2-4 we show for example the reaction coordinate, the mean square displacement of the gate particles and the Fourier inversion of the velocity autocorrelation function of the gate particles as a function of time /3/.

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In pursu ing each trajectory of the SPC one is able to decide whether D settles in a new vacancy or falls back into its old position. A jump is regarded as a successful one only when the sign of  $\xi$  remains unchanged and a final value of  $\xi = 0.5$  is reached. The fraction of successful jumps is denoted by  $c(R_{\rm s})$ .

In order to increase the number of averaging events for the evaluation of the CF one can repeat either run 1 - run 4 starting each run from the last configuration of run 1 or run 3-run 4 starting from the last SPC. Some details for the runs are summarized in table 1.

#### 4. Jump frequency and diffusion coefficient

In run 3 we can obtain the jump frequency in jump direction f\* under the restricted potential u\*. To determine f we have to extrapolate to the case where only  $u_{LJ}$  acts. To achieve this we need knowledge of the transition probability  $P(R_{x1}, R_{x2})$  indicating how often D is in a region of phase space of  $\int \leq R_{x1}$  when u\* with  $R_{x2}$  is acting. For this purpose we have to perform MD runs with various  $R_{x2}$ parameters:

 $P(0.15, 0.85) = P(0.15, 0.25) P(0.25, 0.35) \dots P(0.75, 0.85)$ 

Finally f is given by

 $f = f^* \cdot P(0.15, 0.85) \cdot c(R_y)$ .

The diffusion coefficient  $/\frac{4}{7}$  is related to f by  $D_{D} = \frac{1}{6} z r^{2} f \oplus x_{VS}$ where r is the displacement per jump,  $\oplus$  is a correlation factor 15/2z denotes the coordination number and  $x_{vS}$  denotes the concentration of vacancy sites in the lattice. In a fcc lattice,  $\oplus$  can be estimated by .78 and z equals 12. Using an experimental value of  $D_{D}$ , specifically the self-diffusion coefficient in argon films /6/2, we are enabled to determine the vacancy site concentration.

These value have been summarized in table  $\mathcal{Q}$ .

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Table 1

# A. Potentials, thermodynamic states, MD

L.J. 12-6 potentials, unshifted truncated at  $r_c=2.5 \ \sigma_{11}$ host lattice:  $\xi_2/k_B^+$  = 119.8 K;  $\xi_{22}^-$  = 3.405 Å  $m_2^-$  = 39.95 a.u. impurity:  $\xi_1/k_B^-$  = 119.8 K,  $\xi_{11}^-$  = 3.405 Å  $m_1^-$  = 39.95 a.u. mixing rules:  $\xi_{12}^- = \sqrt{\xi_{11} \cdot \xi_{22}}; \ \sigma_{12}^- = \frac{1}{2} (\sigma_{11}^- + \sigma_{22}^-)$ reduced temperature:  $T^* = T \cdot k_B/\epsilon_{12}^- = 0.501$ reduced density:  $n\sigma_{11}^3 = 1.00279$ nearest neighbour lattice parameter:  $a/\sigma_{11}^- = 1.1214$ time step:  $\Delta t = 10^{-14}$ s number of particles: 256 +)  $k_p$ : Boltzmann constant

### B. MD runs

run	number of time	CPU-time/	specification
	steps	100 time-steps	
1	3,000	2.0 s	
2	4,000	2.18s	
3	16,000	2.195	for 100 SPC
4	200	2.215	per 1 SPC

Table 2 Diffusion in solid argon films

D <sub>D</sub> (exp):	$2.9 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$
f*:	5.18.10 <sup>11</sup> +3% s <sup>-1</sup>
P(0.15,0.85):	1.2x10 <sup>-9</sup> <u>+</u> 9%
$C(R_{x}=0.15):$	0.93 <u>+</u> 2%
$f \cdot \mathcal{Z}_{Ar}$ :	$1.81 \times 10^{-5} \pm 14\%$ ( $2_{Ar} = 3.13 \cdot 10^{-13} s$ )
× <sub>VS</sub> :	2.2.10 <sup>-6</sup>



FIGURE 1. Lower: Illustration of the energy barrier which has to be crossed by D.



(a) A set of the s FIGURE 3. Mean square displacement of the four gate atoms. As a second state of the

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FIGURE 4. Spectral density of the velocity auto-correlation function of the four gate atoms.

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# A FAIRLY GENERAL ALGORITHM FOR STOCHASTIC DYNAMICS.

F.J.Vesely

After the publication of Turq's 1977 paper /1/ an ever increasing number of authors have tried their hands on what has since been called Brownian, or stochastic, or Langevin dynamics (see, e.g., /2/, /3/, /4/). A number of algorithms have been devised which at first glance look quite dissimilar although they were all constructed to treat the same kind of problem. It may be demonstrated, however, that all these formulae are really just different disguises of one general stochastic dynamics algorithm. For a detailed derivation of this unified algorithm and for some test calculations the reader is referred to reference /5/. Here T will give only the necessary definitions and relations, giving more room to the explicit recipes for applying the algorithm in its general form.

In stochastic dynamics we set out to solve - or rather, construct a specific solution to - a stochastic equation of motion of the type /6/

$$\dot{\mathbf{x}}(t) \equiv \mathbf{v}(t) \tag{1a}$$

$$\dot{v}(t) = -\int M(t-t') v(t') dt' + a(t) + b(t)$$
, (1b)

where M(t-t') is a given memory function (postulated or distilled from MD data), a(t) is the stochastic acceleration, and  $b(t) \equiv b[x(t)]$  denotes the systematic acceleration due to external or interparticle potential forces. M(t) and a(t)are interrelated by

 $\langle a(o) a(t) \rangle = \langle v^2 \rangle M(t)$  (2) (but see /5/, equ.3).

In many cases the memory function M(t) may be represented, via its Laplace transform, by a suitable truncated continued fraction,

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$$\mathcal{L}_{s}\left\{M(t)\right\} \approx \frac{M_{1}}{s + \frac{M_{2}}{s + M_{3}}}$$
(3)

 $\frac{M_{m-1}}{S+\beta}$ 

where for our purposes it suffices to regard the quantities  $M_1, M_2, \ldots, M_{m+1}, \beta$  just as fit parameters to the given function M(t). Of courses the index of truncation, m, will be decisive for the quality of the fit. In practical applications it may be chosen to have a value between m=10 (equivalent to the simple Langevin equation without memory) and m=250 (practical limit) see /4b/). Using the fit parameters  $M_1, \ldots, \beta$  we can then transform the integrodifferential equations (1) into a finite number of simple linear differential equations, namely /7/.../4/...

$$\dot{\chi}(t) \equiv \chi(t)$$
 (4a)

 $\dot{\Sigma}(t) = \underbrace{M} \cdot \Sigma(t) + \alpha(t) + b(t), \quad (4b)$ where we have defined the m-dimensional vectors a(t) =  $(0,0,\ldots 0, a_m(t)), b(t) = (b(t),0,\ldots 0)$  and the matrix

a<sub>m</sub> is a random variate with  $\langle a_m(0)a_m(t) \rangle = \frac{2kT}{\mu}\beta M_1 \cdot M_{m-1}\delta(t)$  ( $\mu$ . particle mass). The first components of the vectors y(t) and x(t) are just the ordinary particle velocity v(t) and position x(t), respectively, while the other components represent ever higher time derivates of v(t) and x(t). Having to keep track of these latter quantities is the price we have to pay for getting rid of the memory integral in equ.(1). It should be noted here that the vectorial equations (4a,b) describe the evolution of one cartesian coordinate only, the extension to threedimensional motion being trivial.

By writing down the formal solution to (4a,b) and expanding it to third order in  $\Delta t$  we arrive at /5/

$$\Sigma_{n+1} = \underbrace{\mathbb{E}} \cdot \Sigma_n + \underbrace{\mathbb{V}}_n + \underbrace{\mathbb{E}} \cdot \underbrace{\mathbb{E}}_n + \underbrace{\mathbb{G}} \cdot \underbrace{\mathbb{E}}_n + O(at^3)$$
(6a)

$$X_{n+1} = X_n + \underbrace{F} \cdot \underbrace{X_n} + \underbrace{X_n} + \underbrace{G} \cdot \underbrace{b_n} + \underbrace{H} \cdot \underbrace{b_n} + O(\Delta t^4) , \qquad (6b)$$

where we have written  $v_{n+1}$  for  $v_n(t_n + \Delta t)$  etc., and where the auxiliary matrices E, F, G and H are given by (I..unit matrix)

$$E_{a} = I_{a} + M_{a} \Delta t + M_{a}^{2} \frac{\Delta t^{2}}{2} + M_{a}^{3} \frac{\Delta t^{3}}{6} + O(\Delta t^{4})$$
(7a)

$$F = I \text{ at } + M \frac{\Delta t^2}{2} + M^2 \frac{\Delta t^3}{6} + O(\Delta t^4) \text{ transmission (7b)}$$

$$G = \underbrace{I}_{2} \underbrace{\Delta t}_{2}^{2} + \underbrace{M}_{6} \underbrace{\Delta t}_{4}^{2} + O(\Delta t^{2})$$
(7c)

Note that the matrix  $\underline{M}$  as defined in equ.(5) contains only a relatively small number of non-zero elements. Lowpower polynomials in  $\underline{M}$ , like  $\underline{E}$ ,  $\underline{F}$ ,  $\underline{G}$  are therefore sparse, too. In particular, the elements of  $\underline{E}$  and  $\underline{F}$  are non-zero only along five and three diagonals, respectively. These properties might be used to speed up the matrix multiplications in (6a,b). The matrix  $\underline{G}$  has to be multiplied with vectors ( $\underline{b}_n$  and  $\underline{b}_n$ ) that by definition have only a top component each. We therefore need only the leftmost column vector of  $\underline{G}$ ,  $[\underline{G}]_{11}$  - which, indeed, has only two non-zero elements. The handling of  $\underline{H}$  is even more trivial: we need only  $[\underline{H}]_{11} = \Delta t^3/6$ . Furthermore, inspection of equs.(6a,b) shows that only the first line of (6b), namely

$$x_{n+1} = x_n + \left[ \underbrace{F}_{\approx} \cdot \underbrace{x_n}_{1} + \left[ \underbrace{X_n}_{1} + \left[ \underbrace{G}_{\approx} \cdot \underbrace{b_n}_{1} \right]_{1} + \left[ \underbrace{H}_{\approx} \cdot \underbrace{b_n}_{1} \right]_{1} + O(4t^4) \right]$$
(8)

must be evaluated, since the other components are never needed. Thus only the first line of  $\underline{F}$ , as well as its first column (see (6a)) will be needed.

The stochastic vectors  $\underline{V}_n$  and  $\underline{X}_n$  in (6a,b) have only a few non-zero components whose statistical characteristics are well known and may be utilized to sample  $\underline{V}_n$  and  $\underline{X}_n$  correctly. In particular we have, with  $\gamma \equiv 1-\beta \Delta t$  and  $\delta \equiv \beta^2 - M_{m-1}$ ,

$$[V_n]_{m-2} = T_0 \frac{\Delta t^2}{2} - T_1 \Delta t + T_2$$
(9a)

$$[V_n]_{m-1} = T_0 \Delta t \left(y + \frac{\beta \Delta t}{2}\right) - T_1 y - T_2 \beta$$
(9b)

$$V_{n}]_{m} = T_{o}\left(y + S\frac{\Delta t^{2}}{2}\right) + T_{1}\left(\beta - S\Delta t\right) + T_{2}S$$
(9c)

(all other  $[V_n]_i$  being zero), and  $[X_n]_{m-1} = [V_n]_{m-2}$  (10a)  $[X_n]_m = [V_n]_{m-1}$ , where we have defined

$$T_{k} \equiv \int_{0}^{t} \alpha_{m}(t_{n}+t') \frac{t'^{k}}{k!} dt', \quad k = 0, 1, 2. \quad (11)$$

The covariance matrix of the random variates  $T_k$  is

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In order to sample  $T_0$ ,  $T_1$ ,  $T_2$  at successive time steps in accordance with this covariance matrix, we will proceed as follows /5/ :

i) Sample 3 statistically independent normal random variates z<sub>i</sub> (i = 0,1,2) with variances σ<sub>1</sub><sup>2</sup>, where σ<sub>1</sub><sup>2</sup> are the eigenvalues of ∑<sub>T</sub>.
ii) Apply the linear transformation (with T=(T<sub>0</sub>,T<sub>1</sub>,T<sub>2</sub>) etc.)

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$$\mathfrak{Z} = \mathfrak{D} \cdot \mathfrak{Z} , \qquad (13)$$

where D is an orthogonal matrix which diagonalizes  $\sum_{T}$  (see below).

 $\tilde{\varkappa}^{\perp}$ . The derivative  $b_n(t)$  in (4a,b) is approximated by the backward difference quotient

$$\dot{b}_{n} \approx \left[ \dot{b}_{n} - \dot{b}_{n-1} \right] / \Delta t = 0.000 \text{ (14a)}$$

Equations (6a,b) give a predictor for  $y_{n+1}$ ,  $x_{n+1}$  which may be improved upon by a corrector, using the predicted systemic

matic acceleration  $b_{n+1}^{p} = b[x_{n+1}]$  in a better estimate on b, namely

$$\dot{b}_{n} \approx \left[ \dot{b}_{n+1}^{P} - \dot{b}_{n} \right] / \Delta t \qquad (14b)$$

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The detailed procedure of applying the general predictor-corrector algorithm (6a, b) may now be described as follows :

- 1) Given a specific m x m matrix  $M_{\text{compute and store}}$ the matrix  $\mathbf{E}$  (equ.7a), the vectors  $[\mathbf{F}]_{1j}$  and  $[\mathbf{F}]_{1i}$ (equ.7b) and  $[G]_{11}$  (equ.7c) and the scalar  $[H]_{11}$ (equ.7d).
- 2) Find the eigenvalues  $\sigma_i^2$  and the normalized eigenvectors  $s_{i}$  (i=0,1,2) of  $\sum_{T}$  (equ.12). Standard library subroutines like NAG-FØ2AMF, or explicit low-order matrix algebra, may be used for this. Combine the column vectors  $s_i$  to a 3x3 matrix  $\underline{\mathbb{D}}$  which diagonalizes  $\sum_{T}$ . Store D for use in sampling the stochastic vectors  $\widetilde{\mathcal{V}}_n$  and  $\underset{\sim}{x}_n$  (see step 5 below).
- 3) Initialize the vectors  $\underline{x}_n$  and  $\underline{y}_n$  by a suitable assumption, e.g.  $x_0 = (x, v, 0, ..., 0), v_0 = (v, 0, ..., 0);$  or start from an "aged" pair of vectors  $x_0$ ,  $y_0$  stored from an earlier run. The same applies to the past systematic  $\mathbb{R}^{2}$  acceleration  $\mathbb{B}_{-1}$ .
  - 4) Assuming that at time t the quantities  $x_n$ ,  $b_{n-1}$ are known, compute the systematic acceleration  $b_n \equiv b[x_n]$  from the given potential (x<sub>n</sub> being the top positional-element of  $x_n$ ). Also, evaluate  $b_n$  according to (14a).
  - 5) To produce the few non-zero elements of the stochastic vectors  $V_n$  and  $X_n$ , sample a triplet of correlated random variates  $T_0, T_1, T_2$  according to the recipe given above (see equ.(13)). Insert the  $T_k$  in (9a-c) and (10a,b) to get the three elements of  $y_n$  and the two elements of  $X_n$ , respectively.

Using all the known quantities, evaluate formula (6a)

to find  $y_{n+1}$ , and the first line of (6b) (see equ.(8)) to find  $x_{n+1}$ .

7) It is possible at this stage to insert a corrector step in the usual manner, namely by i) calculating the predicted systematic acceleration  $b_{n+1}^{P} = b[x_{n+1}]$ from the predictor  $x_{n+1}$ , ii) replacing the former estimate on  $\dot{b}_{n}$ , equ.(14a), by the improved estimate (14b), and iii) redoing step 6. Note that such a corrector step influences only the last two terms on the r.h.s. of equs.(6a,b).

8) Return to step 4.

In place of the predictor-corrector algorithm (6a,b) we may alternatively derive a Verlet-type algorithm for solving the stochastic equation of motion (4a,b). It is of the same (third) order of accuracy in  $\Delta t$  and reads /5/

$$\begin{aligned} \chi_{n+1} &= \left[ \underbrace{I}_{\pm} + \underbrace{E}_{\pm} \right] \cdot \chi_{n} - \underbrace{E}_{\pm} \cdot \chi_{n-1} + \underbrace{\chi}_{n} + \underbrace{E}_{\pm} \cdot \underbrace{\chi}_{n}^{-} + \underbrace{E}_{\pm} \cdot \underbrace{b}_{n} \Delta t + (15a) \\ &+ \left[ \underbrace{G}_{\pm} - \underbrace{E}_{\pm} \underbrace{A}_{\pm} \right] \cdot \underbrace{b}_{n} \Delta t + O(\Delta t^{4}) \end{aligned}$$

$$\begin{aligned} \chi_{n+1} &= (\Delta \underline{\mathbb{E}})^{-1} \cdot \left[ \chi_n - \chi_{n-1} - \chi_n + \chi_n^2 - \Delta \underline{\mathbb{G}} \cdot \underline{\mathbb{b}}_n - \Delta \underline{\mathbb{H}} \cdot \underline{\hat{\mathbb{b}}}_n \right] + (15b) \\ &+ O(\Delta t^3) , \end{aligned}$$

where we have defined (see (7a-d))

$$\Delta \underline{F} \equiv \underline{F}(\Delta t) - \underline{F}(-\Delta t) = 2 \underline{I} \Delta t + \underline{M}^2 \frac{\Delta t^3}{3} + O(\Delta t^5)$$
(16a)

$$\Delta G = G(\Delta t) - G(-\Delta t) = \qquad \qquad M = \frac{\Delta t^3}{3} + O(\Delta t^5) \qquad (16b)$$

$$\Delta \underbrace{H}_{\underline{a}} = \underbrace{H}_{\underline{a}}(at) - \underbrace{H}_{\underline{a}}(-at) = \underbrace{I}_{\underline{a}} \frac{\Delta t^{3}}{3} + O(at^{5}) . \tag{16c}$$

In (15a,b) the matrices  $\underline{F}$ ,  $\underline{G}$ ,  $\Delta \underline{G}$  and  $\Delta \underline{H}$  are to be multiplied with vectors  $(\underline{b}_n \text{ and } \underline{b}_n)$  that have only a top component each. Thus only the leftmost column vectors of these matrices are really needed. Moreover, we can see that only the first line of equ.(15b), namely

$$v_{n+1} = \left[ \left( \Delta \underline{F} \right)^{-1} \right]_{ij} \left[ \underline{x}_n - \underline{x}_{n-1} - \underline{X}_n + \underline{X}_n - \Delta \underline{G} \cdot \underline{b}_n - (17) - \Delta \underline{H} \cdot \underline{b}_n \right]_j + O\left( \Delta t^3 \right)$$

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must be evaluated, since the other components of  $y_{n+1}$  are never needed. Thus only the first line of  $(\Delta \overline{z})^{-1}$  will be needed.

The stochastic vector  $X_n$  has (like  $X_n$ ) only two non-zero components.  $X_n$  and  $X_n$  are uncorrelated, but  $X_{n+1}$  is correlated with  $X_n$  via the random variates  $T_1, T_2$  defined above. In detail, we have

$$\begin{bmatrix} X_{n+1} \end{bmatrix}_{m-1} = -T_2 \text{ as the rest of the descent of the rest of the descent of the rest of the$$

$$[X_{n+1}]_{m} = \overline{T}_{1} + \overline{T}_{2}\beta = 2 \text{ for a set of a set o$$

while the components of  $X_n$  are given by (10a,b).

We can thus describe the procedure of applying the Verletalgorithm (15a,b) as follows :

- 1) Given a specific m x m memory matrix  $\underline{M}$  compute and store the matrix  $\underline{E}$  (equ.7a), the column vectors  $[F]_{i1}$  (equ.7b),  $[G]_{i1}$  (equ.7c),  $[\Delta G]_{i1}$  (equ.16b), the line vector  $[(\Delta F)^{-1}]_{1j}$  (equ.16a), and the scalar  $[\Delta H]_{11} = \Delta t^{3}/3$  (equ.16c).
  - 2) Find the eigenvalues  $\sigma_i^2$  and the normalized eigenvectors  $\underline{s_i}$  (i = 0,1,2) of  $\sum_{\mathbf{T}}$  (equ.12). Standard library subroutines like NAG-FØ2AMF, or explicit low-order matrix algebra, may be used for that. Combine the column vectors  $\underline{s_i}$  to a 3x3 matrix D which diagonalizes  $\sum_{\mathbf{T}}$ . Store D for use in sampling the stochastic vactors  $\underline{x_n}$  and  $\underline{x_n}$  (see step 5 below).
  - 3) Initialize the vectors  $\underline{x}_n$  and  $\underline{x}_{n-1}$  by a suitable assumption, e.g.  $\underline{x}_0 = (x, v, 0, ...0)$ ,  $\underline{x}_{-1} = (x - v \Delta t, v, 0, ...$ ..0); or start from an "aged" pair of vectors  $\underline{x}_0, \underline{x}_{-1}$ stored from an earlier run. The same applies for the past systematic acceleration  $\underline{b}_{-1}$ , and to  $\underline{x}_0$ .

4) Assuming that at time t the quantities  $x_n$ ,  $b_{n-1}$ 

are known, compute the systematic acceleration  $b_n \equiv b[x_n]$  from the given potential (x<sub>n</sub> being the top-positional-element of x\_). Also, evaluate b\_ according to (14a).

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5) To produce the few non-zero elements of the stochastic vectors  $X_n$  and  $X_{n+1}$ , sample a triplet of correlated random variates  $T_0, T_1, T_2$  following the recipe given above (see equ.13). Insert the  $T_{\mu}$  in (10a,b) and (18a,b) to get the two elements of  $\underline{x}_n$ and of  $\tilde{x_{n+1}}$ , respectively.  $\tilde{x_{n+1}}$  is stored and will be used under the name  $X_n$  at the next time step.

6) Using all the known quantities, evaluate formula (15a) to find  $x_{n+1}$ , and the first line of equ.(15b) (see equ.17) to find  $v_{n+1}$ . 7) Returnito step 4. di la concentra della d

The two versions given here of the general SD algorithm may easily be tuned to any specific application by choosing a particular set of parameters  $M_1, \ldots, M_{m-1}$ , B defining the memory matrix M. If a predictor-corrector scheme of higher order than  $\Delta t^3$  were desired, it could be derived following the lines given in /5/.

It is worth remembering that Van Gunsteren et al. have shown how to incorporate SHAKE into Brownian dynamics (i.e. m = 1) algorithms /2a/, /2b/. In fact, the first lines of our formulae (6a,b) and (15a,b) contain, at each time step, all the information necessary for the call to SHAKE. It should be an easy task, then, by adapting the recipes given  $\ln / 2b /$  to construct a simulation scheme for the stochastic motion of a simple chain in a viscoelastic medium with memory.

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HOMOGENEOUS SHEAR NEMD AT 'CONSTANT' APPLIED STRESS.

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Introduction server server and server and server as a server of the observation

In the measurement of the shear viscosity of fluids by non-equilibrium molecular dynamics the policy in the past has been to impose a shear rate of predetermined temporal and spatial dependence and then to measure the response of the significant component of the stress tensor (1). Recent developments (2) have led to the possibility of inverting this process and so to measure the viscosity by applying a known stress to the system and observing the fluctuations in the shear rate. Apart from the possibility of obtaining more precise viscosities, a method of this type also produces conditions more akin to those found in the laboratory, and thus, allows the more realistic study of such phenomena as creep and Bingham plasticity.

The purpose of this article is to outline a practical method of applying stress to a fluid and to compare its merits with those of the more conventional applied strain rate approach. The method to be described is the off-diagonal analogue of Evans and Morriss's (2) technique for performing isothermal-isobaric molecular dynamics. It differs sufficiently to warrant a separate description and some of the comments I shall make concerning the consistency of the equations when used with periodic boundaries apply equally to both.

#### Method

The starting point for this method is the SLLOD equations of motion (2) for the isothermal planar Couette flow in the xz plane:

$$\dot{q} = \rho/m + q_{\pi} \dot{\delta} \dot{\tilde{x}}$$
 (1)

$$\dot{\mathbf{p}} = \mathbf{E} - \mathbf{a} \cdot \mathbf{p} - \dot{\mathbf{\delta}} \cdot \mathbf{p}_{\mathbf{x}} \hat{\mathbf{x}} \qquad \langle 2 \rangle$$

where  $\tilde{\mathbf{x}}$  is the unit vector in the x direction.  $\mathbf{x}$  and  $\check{\mathbf{z}}$  are treated as undetermined parameters and are evaluated from the
constraints applied to the system. Firstly, we require that the total kinetic energy of the system:

$$K_{e} = \pm \sum_{i=1}^{n} \underline{P}^{2} / m$$

remains fixed. This implies that  $K_a = \emptyset$  i.e.

 $\sum_{i=1}^{n} \mathbf{p} \cdot \mathbf{\dot{p}} = \emptyset$ (unless specified  $\sum_{i=1}^{n}$  indicates a sum over all N particles.) Substituting for  $\mathbf{\dot{p}}$  gives the value of  $\mathbf{\Delta}$  required to satisfy the constraint

the constraint 
$$\frac{1}{2} \approx \left[ \sum_{p \in F} - \dot{s} \sum_{p_{x}} p_{x} \right] / \sum_{p_{x}} p^{4}$$
 (3)

The second constraint applied is that the rate of change of the xz component of the stress;  $\dot{\sigma}_{xz}$ , is known.  $\sigma_{xz}$  is defined by

$$-V\sigma_{xz} = \sum (p_x p_z / m + q_x F_z) \qquad (4)$$

where V is the volume of the system, so differentiating w.r.t. time gives

$$-V\dot{\sigma}_{x_{2}} = \sum \frac{1}{m} (\rho_{x}\dot{\rho}_{z} + \dot{\rho}_{x}\rho_{z})$$
$$+ \sum (\dot{q}_{x}F_{z} + q_{x}\dot{F}_{z}) \qquad (5>$$

Substituting for  $\dot{\mathbf{p}}_{1}$  and  $\dot{\mathbf{q}}_{2}$ , equations <1> and <2>, and <2>.

rearranging implies that leaves are then well of an Alfert of the sectors of the sectors of the sectors of the sectors are the sectors are the sectors of th

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$$\dot{\vartheta} = \sum \left[ \frac{1}{m} (2\rho_{x}F_{z} + F_{x}\rho_{z} - 2\alpha\rho_{x}\rho_{z}) + q_{x}F_{z} \right] + \dot{\sigma}_{xz} V$$

$$\sum (P_{z}^{2}/m - q_{z}F_{z}) - 2(\sum \rho_{x}\rho_{z})^{2}/(m\sum p^{2}) \qquad (6>$$

and substituting for QL, equation <3> gives  

$$\dot{\delta} = \left\{ \sum_{m}^{+} (2\rho_{x}F_{z} + F_{x}\rho_{z}) - 2\sum_{p} P \cdot E\sum_{p} \rho_{x}\rho_{z} / (m\sum_{p} p^{2}) + \sum_{q} q_{x}F_{z} + \dot{\sigma}_{x2} \sqrt{3} \right\} / \left\{ \sum_{p} (p_{z}^{2}/m - q_{z}F_{z}) - 2(\sum_{p} \rho_{x}\rho_{z})^{2} / (m\sum_{p} p^{2}) \right\}$$

$$-2(\sum_{p} \rho_{x}\rho_{z})^{2} / (m\sum_{p} p^{2}) \right\}$$
(7)

The term involving  $F_z$  is not immediately calculable, so a further substitution has to be made. Firstly, it is assumed that the particles interact through a pairwise additive potential,  $\Delta c_r$ , which is a function of their separation only i.e. f=1 give, where  $g_i = q_i - q_i$ . The force on the particle i due to j is then given by

where  $\overline{\Phi} = d \overline{\Phi}/d\epsilon$ . Converting the term involving  $\overline{F}_z$  to a double sum (  $\sum \sum_{i=1}^{i} implies \sum_{i=1}^{i} \sum_{j>i}$  ) gives  $\sum q_x \overline{F}_z = \sum \sum q_{xij} \overline{F}_{zij}$ 

$$= \sum \sum q_{xij} \frac{d(-\overline{\Phi}'\hat{q}_{zij})}{dt}$$
(8)

Evaluation of the differential in equation <8> introduces yet another term in  $\dot{S}$  and after some tedious but straightforward algebra, one arrives at the final equation and the second

$$\begin{split} \dot{\vartheta} &= \left\{ \sum_{n=1}^{\infty} (2\rho_{x}F_{z} + F_{x}\rho_{z}) - 2\sum_{p} \sum_{p} \sum_{n=1}^{\infty} \rho_{x}\rho_{z} / (m\sum_{p}\rho_{z}) - \sum_{n=1}^{\infty} \left[ q_{xij} \rho_{zij} \Phi'/(m | q_{ij}|) + (q_{ij} \cdot p_{ij}/m) q_{xij} q_{zij} (\Phi'' - \Phi'/| q_{ij}|) / q_{ij}^{2} \right] + \dot{\sigma}_{xz} \sqrt{3} / \left\{ \sum_{p} \rho_{z}^{2} / m - 2 (\sum_{p} \rho_{z})^{2} / (m\sum_{p}\rho_{z}) + \sum_{n=1}^{\infty} q_{xij}^{2} q_{zij}^{2} \left[ \Phi'' - \Phi'(1 - q_{ij}^{2} / q_{xij}^{2}) / (q_{ij}) \right] / q_{ij}^{2} \right\}_{(q)} \end{split}$$

4

In this form lpha can be readily calculated from quantities either stored or evaluated in the normal MD procedure, with the exception of  $ec{\Phi}''$ .

#### Implementation

As with other methods in which planar shear flow is simulated, the equations of motion are integrated in conjunction with the moving boundary scheme of Lees and Edwards (see (2)). the integration of the coupled first order differential equations presents no problems if predictor-corrector methods are used, but there are some extra considerations concerning the moving boundaries due to the fluctuating shear rate.

If at time t=0 the periodic images are orthogonal, then at a later time t the distance moved by the image cell, h(t), is given by



If  $\delta$  is constant then n(t)=0LC. In this case though, the shear rate is a function of time so the evaluation of n(t) is more complicated. A convenient way of doing this is to reformulate equation <10> as a differential equation

$$\dot{h}(t) = \dot{\mathcal{Y}}(t)$$
 La cance on a second with  $\mathcal{X}$ 

and then use a fourth order predictor-corrector scheme to solve for h(t). This is useful when we consider the displaced periodic image of a particle, q', in the positive z direction, say.



Now as qx=qx+h, differentiating w.r.t. time gives

$$\frac{1}{2}x = \frac{1}{2}x + h$$

which from equation <11> is the second of the second second back of the back of the back of the back of the second second

Differentiating repeatedly gives per addentices and the second tracks

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etc. As  $\delta$  is a function of time  $\delta$  and the higher derivatives are non-zero so if a particle moves out of the primary cell through a z face then not only does its position and velocity change to that of its periodic image, q', but also all the higher derivatives in the integration scheme.

To test the method initially, an argon system of N=256 particles at a reduced number density 2 = 0.83481 and temperature of 86.5K was used. As usual the Lennard-Jones 12-6 potential,

 $\bar{\Phi}(r) = 4 \in ((\sigma/r)^{12} - (\sigma/r)^{6})$ 

where E/k=119.8 K and  $\sigma=3.405$ Å, determined the interactions between particles and was truncated at half the box length. The coupled first order equations of motion were then integrated using a fourth order Gear predictor-corrector scheme (a good description which is given in reference (2)). After a period of equilibration, i.e. with and of set equal to zero, the constraints of constant kinetic energy and 🕶= 0 were imposed on the system, having first ensured that the kinetic energy corresponded to a temperature of 86.5K. It was found that although the temperature could be maintained constant to order  $10^{-4}$  K using a time step of  $0.5 \times 10^{11}$  s, the stress still fluctuated and drifted slowly, but surely, downwards. This occurred even with a time step of 0.15 \*10"3. Having eliminated the possibility of programming errors, attention was turned back to equation  $\langle 9 \rangle$ , that which determines  $\dot{\delta}$ . It was first thought that a long range correction should be added to the denominator because of the term in  $\mathbf{q}_{\mathbf{z}} \mathbf{F}_{\mathbf{z}}$ , (see equation (6)), but but this is not so because the sum is defined as being over those particles which define Gaz, which does not contain a long range correction. However, inconsistencies are introduced computationally by the periodic boundaries. This affects any of the properties evaluated as a double sum. Take for example the potential part of the stress tensor

$$-VO_{xz}^{P} = \sum_{i=1}^{N} Q_{x_{i}} F_{z_{i}} = \sum_{i=1}^{N-1} \sum_{i>i}^{N} Q_{x_{i}j} F_{z_{ij}}$$
(12)

be	shown to be so by simply writing: the descent state of the second
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	and a standard standard and the second standard standard standard standard standards and standard standards and
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In	molecular dynamics the double sum in equation <12> is calculated
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In as	molecular dynamics the double sum in equation <12> is calculated $\sum_{i=1}^{N-i} \sum_{i' \leq i}^{N} q_{x_i j'} F_{z_i j'}$

will not be at any given instant. Only on average are these two quantitles equal. This means that although the equations of motion are formulated for the fixed set of N particles, defined by their initial positions, we are effectively sampling a much larger set made up of all the periodic images in evaluating the double sums. This does not affect the temperature constraint as it involves momenta, which are invariant to the choice of reference frame, but it does affect the stress constraint. This was substantiated by temporarily removing the periodic boundaries; it was then found that a similar degree of stability could be achieved for the stress the temperature. Thus, the problem stems from the as for inconsistencies introduced by the periodic boundaries rather than from the integration algorithm itself. This argument applies equally well to Evans and Morriss's (2) isothermal-isobaric MD and is the likely cause of the majority of the drift in the pressure reported by Berendsen et al. (3) when using it.

Despite this drawback, further simulations were performed on <A> the same system as already described and <B> on a similar system which differed only in the interaction potential,  $\Phi_{s}(r)$ , instead of  $\Phi(r)$ , where  $\Phi_{s}(r)$  is defined as

 $\Phi_{s}(r) = 0$ 

 $\bar{\Phi}_s(r) = \bar{\Phi}(r) + \epsilon$ 

r < 2 %

arphi (r) is simply the LJ 12+6 potential raised by the well-depth and truncated at the minimum so that the potential and its first derivative go to zero at the cut-off. As the probability of taking a periodic image increases with the cut-off, this ploy was used as method of reducing this probability and hence increasing the stability of the solution of the equations of motion.

For both  $\langle A \rangle$  and  $\langle B \rangle$  two simulations were undertaken; one at constant stress and one at constant shear rate. To "drive" the system to a certain stress, in this case 510bar,  $\hat{\mathbf{O}}_{\mathbf{x}\mathbf{z}}$  was given a value of 1bar/ $\Delta$  t, where  $\Delta$ t was the timestep used throughout of **015**×10<sup>-1</sup>/<sub>5</sub>, until the desired level of stress had been achieved, at which point  $\hat{\mathbf{O}}_{\mathbf{x}\mathbf{z}}$  was set to zero. If the stress then drifted below that required then  $\hat{\mathbf{O}}_{\mathbf{x}\mathbf{z}}$  was set back to 1bar/ $\Delta$  t for the number of timesteps required to re-attain the desired level. This was found to occur quite often in case  $\langle A \rangle$ ; approximately every 100 steps, but virtually not at all in case  $\langle B \rangle$ . After allowing a period for the setting up of a steady state, the shear rate was then averaged over a period of 9,500 $\Delta$ t. The mean shear rate  $\langle \bullet \rangle$  and the initial configuration were then used as the input for the second

calculation and the stress was then averaged over the same period of time. The variation of the stress and strain rate are shown in Figs. 1 and 2 for case <B> at constant stress and constant shear rate respectively. In all the calculations the total momentum,  $\sum_{i=1}^{n} \frac{P_{i}}{P_{i}}$ , was found to be conserved to better than 10<sup>-10</sup> of a typical particle momentum, (  $m \, \mathrm{kT}$  )<sup>10</sup>.

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# Results.

The results obtained for the stress, shear rate and  $\propto$  are given in the table along with their root mean square deviations expressed as a percentage,  $\Delta Q$ , where

 $\Delta Q = (\langle (Q - \langle Q \rangle)^2 \rangle)^{V_2} \times 100 / \langle Q \rangle$ Also given is the resultant viscosity obtained from the usual expression

 $\eta = \langle \sigma_{xx} \rangle / \langle \dot{v} \rangle$ 

<13>

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and also from the relationship. There address an example address and first and all the second provide and the second  $\mathcal{U}_{a} = 2 \langle a \rangle \langle \kappa_{e} \rangle / (\langle \delta \rangle^{2} \vee)$ a da an shekara ta ƙwallon 🖌 Bera persana a sana araw where Ke is the kinetic energy of the system. Equation <14> is the simply derived by substituting the SLLOD equations of motion and equation <13> into the equation for the rate of change of the total energy, (see Acknowledgement). 

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<u>Table</u> , a specific second se

The mean values of  $\Im_{X2}$ ,  $\Im$  and  $\Im$  together with their percentage RMSD's and the resultant viscosities, determined from equations <13> and <14>, obtained from the runs at (1) constant stress, and (ii) constant strain rate, on the two systems: <A> LJ 12-6 potential, and <B> shifted LJ 12-6 potential.

Sec. Sec.	<b>40 x27</b> /bar	<b>∆σ<sub>×z</sub></b> /bar	くざう /10 <sup>10</sup> s	۵× /10°°5	/10"3	2104 / 10 <sup>10</sup> 5	η /mpa s	/mpa s
(i)	510.5	0.1	24.55	40.2	16.57	170.1	0.208	0.207
(11)	512.9	19.6	24.55	0.0	16.61	163.3	0.209	0.208
(i)	511.7	0.1	30.35	35.5	20.73	137.3	0.169	0,170
(ii)	513.2	21.0	30.35	0.0	20.57	134.1	0.169	0.169

#### Discussion

From the results it can be seen that, in both cases, the viscosity evaluated at constant stress, constant strain rate and from  $\langle \boldsymbol{\alpha} \rangle$  are all in excellent agreement. The likely errors in these values are related to the  $\Delta \mathbf{Q}$  and these are significantly different. Even ignoring the small fluctuation in  $\mathbf{G}_{\mathbf{x}\mathbf{z}}$  at constant applied stress  $\Delta \dot{\mathbf{x}}$  is a factor of  $\sim 2$  higher than the value of  $\Delta \mathbf{G}_{\mathbf{x}\mathbf{z}}$  obtained at constant strain rate in both cases. Under these conditions both methods are several times more precise than estimating the viscosity from  $\langle \boldsymbol{\alpha} \rangle$ .

Thus it can be concluded that of the methods described, that of applying a constant shear rate to the system is the most precise for the calculation of the viscosity for the conditions used here. At lower strain rates/stresses the situation may be reversed and it may even be better to calculate  $\mathcal{A}$  from  $\langle \mathcal{A} \rangle$ . This remains to be seen, but calculating the viscosity from  $\langle \mathcal{A} \rangle$  is certainly a very useful consistency check. One other consideration is the efficiency of the methods. The calculation of the extra terms in the main dynamics double loop for the constant stress method inevitably

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increases the amount of computing time required. Without any large scale attempt to improve the coding the increase in the amount of CPU time was about 60 percent for <A> and about 10 percent for <B>.

Despite its drawbacks the constant stress method does work and could be quite useful for certain special circumstances. One possibility already proposed is the re-examination of shear induced melting of soft spheres previously studied by Evans (4) and Woodcock (5) and thought to show Bingham plastic type behaviour. This method could be used to determine its yield stress directly and to probe the mechanism of the melting phenomenon.

#### Acknowledgements

I would like to acknowledge helpful discussions at the initiation of this work with fellow attendees of the August 1984 CECAM workshop, in particular Bill Hoover and Tony Ladd. I should also like to thank David Heyes for allowing me to crib his derivation of equation <14>.

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# Fig.1 Constant applied shear stress

(a) Stress vs. time (b) Shear rate vs. time



Fig.2 Constant applied shear rate (b) Shear rate vs. time (a) Stress vs. time (a)800 700 600 - Oxz 500 400 STRESS/bar 300 200 100 0 -100 t/ps 2 -200 7 Z. (Ъ) es esta en entre 30 20 ×/10<sub>10</sub>-1 化化合理 计分子分词 法法公司法公司 计可能分析 化氯化合物 化合金 10 0 <sup>5</sup> t/ps 24 3 0 1 4

## 영화에 있는 것을 전 것을 한 것 만큼 한 것 같아.

# STATISTICAL ERRORS WHEN CALCULATING TRANSPORT COEFFICIENTS USING AN EXTERNAL FORCE

M. J. Gillan, Theoretical Physics Division, AERE Harwell, U. K.

There are several different ways of using MD simulation to calculate transport coefficients, as was amply demonstrated at the recent workshop on the subject at Royal Holloway College. For example, suppose you want to calculate the thermal conductivity K of liquid Lennard-Jonesium. Firstly, and most obviously, you can just simulate the system between parallel walls held at different temperatures and work out the ratio of the heat flux to the temperature gradient<sup>(1)</sup>. Secondly, you can use the Green-Kubo formula<sup>(2)</sup>, which allows you to calculate  $\kappa$ from the time integral of the autocorrelation function of the fluctuating heat flux in full thermal equilibrium<sup>(3)</sup>. Thirdly, there is the non-equilibrium method developed by Denis Evans (4) and myself  $^{(5)}$ , in which you study the response of the heat flux to a special kind of steady, uniform external force; this technique can be applied either straightforwardly with a force big enough to produce a response detectable above the noise, or, more subtly, by using the differential trajectory method. At the RHC meeting, two new methods were discussed: there was David Heyes! proposal<sup>(6)</sup> to calculate  $\kappa$  by monitoring the temperature of a single particle which has been supplied with a small increment of energy; and there was Professor Powles' idea of observing the decay of a small-amplitude temperature wave, which his calculations with Nigel Corbin showed gives very satisfactory results. That makes five different approaches some of which exist in different variants. The situation is of course similar for other transport coefficients: bulk and shear viscosity, diffusion coefficients, electrical conductivity of ionic systems, etc.

Faced with this embarras du choix, how can you tell which method to use? Of course the answer to this may depend on what you are trying to achieve, but external force methods do have great advantages. Firstly, they allow you to calculate the transport coefficient at zero wavevector, which is usually what you want, and secondly they generally seem to be statistically better than other methods — certainly better than Green-Kubo, anyway. But there is also a less well-known advantage that they have, which became particularly apparent in some recent calculations we did at Harwell on diffusion in a temperature gradient. This advantage is that you can calculate in advance the size of the statistical errors. This means that you can estimate what length of MD run will be needed to calculate your transport coefficient to any given accuracy; the only requirement is that you should have a rough idea of the value of

the transport coefficient you are trying to calculate. The way this comes about is very simple, and may already be discussed in the literature somewhere (perhaps someone can tell me where?), but it seems to me interesting enough to bear repetition, even if it is.

Suppose we are interested in some transport coefficient  $\alpha$ 

which can be calculated as the ratio of the average value of some flux J to the value of some external force F which induces it:

where 
$$p_i^{(M)}$$
 is a latent of  $\langle J 
angle_{\pi} \Rightarrow lpha F$  is the other line of the states in the set of the state  $(1)$  . The states is a set of the states in the stat

(Examples: for thermal conductivity, J would be the heat flux and F would be the strength of the force discussed in refs. 4 and 5; for viscosity, J would be an element of the stress tensor and Fwould specify the shearing rate; etc.) We assume the calculation is being done by direct computation of the mean Jcaused by F, this mean being estimated from the time average of Jin an MD run of duration t:

$$\langle J \rangle \approx \frac{1}{t} \int_0^t dt' J(t') = \int_0^t dt' J(t') = \int_0^t dt' J(t') = 0$$

But the estimate will be subject to statistical errors, whose rms value  $\delta J$  is given by:

$$\delta J^2 = \left\langle \left[\frac{1}{t} \int_0^t dt' J(t') - \left\langle J \right\rangle\right]^2 \right\rangle , \qquad (3)$$

the averages  $\langle \cdot \cdot \rangle$  being taken of course in the steady-state perturbed ensemble. The rms error in the calculation of  $\alpha$  will be  $\delta J/\langle J \rangle$ . If we are in the linear region  $(\langle J \rangle \propto F)$ , the value of  $\delta J$ will be calculated well enough by evaluating equation (3) in the equilibrium ensemble:

$$\delta J_1^2 \simeq \frac{1}{t^2} \int_0^t dt_1 \int_0^t dt_2 \left\langle J(t_1)J(t_2) \right\rangle$$

$$\rightarrow \frac{2}{t^2} \left[ t \int_0^\infty dt_1 \left\langle J(t_1) J(0) \right\rangle - \int_0^\infty dt_1 \int_{t_1}^\infty dt_2 \left\langle J(t_2) J(0) \right\rangle \right] \tag{4}$$

for large t, as is readily shown. For a long simulation run, the first term in square brackets will dominate. But this is just the time integral of the autocorrelation function of the flux in thermal equilibrium, which is related to the required transport coefficient  $\alpha$  by the Green-Kubo formula:

$$\alpha = A \int_0^\infty dt \, \langle J(t)J(0) \rangle \quad , \qquad (5)$$

where A is a known constant. Hence the rms statistical error in  $\alpha$  is:

$$\delta \alpha / \alpha = \delta J / J = \left(\frac{2}{A\alpha t}\right)^{\frac{1}{2}} / F \quad \text{a set of the set of th$$

This shows that the statistical error in the transport coefficient, besides being governed in an obvious way by the size of the force F and the duration t of the simulation, depends only on  $\alpha$  itself and on nothing else.

I think this is likely to be most useful when you are contemplating using the external force method, you have an idea of the value of the transport coefficient  $\alpha$ , and you want to know whether you are going to get something useful out of a manageable length of run (since  $\alpha$  comes under the square root, you don't have to know it very well). We were in exactly this situation with some calculations we did recently<sup>(7)</sup> on diffusion in a temperature gradient, in a simple one-dimensional model (actually the Frenkel-Kontorova model). We were applying the special force of refs. 4 and 5 and looking at the induced heat flux and particle flux to get the thermal conductivity and the heat of transport. The Figure shows the fluctuations of these two fluxes averaged over subsections, compared with the rms values of these fluctuations estimated from the average fluxes using formula (6). The length of run used in these calculations was in fact chosen in advance using the formula, on the basis of expectations about the values of the two transport coefficients, and the formula provided a very useful guide in planning the whole set of calculations.

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# FIGURE CAPTION

Energy and particle fluxes (top and bottom curves) induced by an external force in a MD simulation of the Frenkel-Kontorova model. Fluxes are averaged over subsections of 50000 steps. Dashed lines show the rms fluctuations calculated from the overall means using equation (6).





ENERGY FLUX PARTICLE FLUX

# How accurate are molecular dynamics trajectories?

# Nigel Corbin

# University of Kent

The recent workshop at Royal Holloway College, on transport properties, highlighted the effort now being invested in long MD simulations, as many as 10<sup>6</sup> timesteps. Often this work requires the computation of time correlation functions, which are found to have long-time tails. It is not easy to estimate the standard error of the computed values. Another approach involves applying a small perturbation, and computing the response to it by looking at the difference between perturbed and unperturbed trajectories. This response, as is well known, is ultimately swamped by "noise". This is attributed to the divergence of the trajectories, but it is not clear whether this is due to the perturbation or to global truncation errors dependent on the method used to compute the trajectories.

Writing  $\underline{x}_i$ ,  $\underline{p}_i$  for the position and momentum of the i'th atom, and  $\underline{x}$  for the set  $\underline{x}_1, \dots, \underline{x}_n$ , the equations of motion are:-

$$\frac{\mathbf{x}(t)}{\mathbf{p}(t)} = \mathbf{p}(t) / \mathbf{m}$$
$$\frac{\mathbf{p}(t)}{\mathbf{p}(t)} = \mathbf{F}(\mathbf{x}(t))$$

subject to the initial condition  $\underline{x}(0) = \underline{x}_0$ ,  $\underline{p}(0) = \underline{p}_0$ . The exact solution of these equations defines a trajectory in phase space. We obtain the solution by numerical, and approximate, methods, and it is not clear that the resulting trajectory in fact approx-imates the true result for all t.

To investigate this, we define the correlation C(t) between two trajectories at time t by:-

 $C(t) = \langle q(t)^{n}, \dot{q}'(t) / (|q(t)| |q'(t)|) \rangle$ 

where q(t), q'(t) are the momentum of, (or force on, etc), one atom, at time t, in the two trajectories. The angular brackets denote an average over all atoms in the system. Since we do not know the true trajectory, we will use two simulated trajectories, obtained with different timesteps. The simulated system was the usual Lennard-Jones system, for either N=32 or N=108 atoms, and at a number of different statepoints. For each case, two simulations were carried out, one with a timestep of 5 fs, the other 2.5 fs, starting from the same configuration, and C(t) computed from the two. Typical results are shown in Fig.l for the velocities, and in Fig.2 for the forces. The leapfrog algorithm used was implemented in single precision on a VAX 11/750. Changing to double precision made no difference, beyond slowing the computation down! The results are not particularly sensitive to either N or to the state point used.

Clearly the two trajectories, differing only in the timestep used to obtain them, have diverged within 3 ps. We must conclude that at least one of the trajectories differs from the true result. We might conclude that:-

a) these timesteps are too large,

b) the algorithm used was inadequate,

c) both the above hold.

Alternatively, we might conclude that MD is incapable of giving time-dependent properties with more than 2 ps timescales. A consequence of this is that long-time tails that are observed by MD are artefacts of the MD, to some extent.

Some further thought would appear necessary!

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Fig 1. Correlation between velocities obtained in two MD simulations from the same starting point, with timesteps 2.5 and 5 fs, as a function of the time t from the start.



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# THE BEHAVIOUR OF PROTONS IN OXIDES.

A.N. Cormack, P. Saul and C.R.A. Catlow.

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## INTRODUCTION

It is increasingly apparent that there is a need to understand the behaviour of protons in oxides. It has been suggested, for example, that all oxides, even of nominal high purity, will contain some residual hydrogen that is, for practical purposes, impossible to remove: this has been termed 'unextractable water' (1). There are, in fact, conflicting reports in the literature: some features of the ESR spectra of rutile, for example, have been ascribed to OH groups (2), whereas IR spectra have been interpreted in terms of both OH groups (1) and H- ions trapped at oxygen vacancies (3).

Additionally, many interesting processes in oxides involve the participation of protons; dehydroxylation reactions in the calcination of refractory oxides, and, of topical technological interest, 'wetside' corrosion.

Another area of current interest is that of fast ion proton conductors. Materials such as SrCeO3 and KTaO3, which have been doped with a divalent cation and reoxidised or compensated with H2O are used industrially as water vapour sensors.

The common themes underlying these different areas are questions relating to the presence of hydrogen in oxides: what is the nature of the protonic species - e.g. H, H-, H2, OH-, H3O+ etc.; how is it incorporated into the structure; and what reactions between these various species and between the protonic species and the host lattice are possible.

We are currently using computer simulation techniques to address these questions. The contribution to our understanding of defect solid state chemistry that these simulation techniques can provide is now well established through previous studies (4).

It will be recognised that a central problem in the simulation of proton behaviour is that a classical approach alone, as adopted in studies of other materials, will not be adequate and thus the major feature of this work is the treatment of the O.....H potential interaction.

In the next section, we discuss our approach to the derivation of these interactions, using quantum mechanical methods, and then we will describe some preliminary results on the structure of OH incorporation into MgO.

# TREATMENT OF PROTON INTERACTIONS

Our approach has been twofold, both of which are based on a quantum mechanical treatment. Firstly, we derive an 'effective' pair potential for the O.....H interaction, for use directly in the classical simulation codes such as HADES (5) and CASCADE (6). This interaction is extracted from the potential surface calculated from an ab initio quantum mechanical simulation. Secondly, we model the proton behaviour using an explicit quantum mechanical calculation on a cluster which is embedded in an array of point charges. The embedding is absolutely essential if the long range Madelung potentials found in crystalline materials are to be reproduced properly. We have found that a large array of point charges is needed if both the Madelung potential and its derivatives are to be correctly represented everywhere in the cluster: if this is not the case, then the electrons may spill out into unphysical orbits, ... giving worthless results. Our calculations were performed at the ab initio Hartree-Fock SCF level using the GAMESS and ATMOL (7) programs, with gaussian basis sets. The effect of the choice of basis sets was carefully investigated for their influence on the O....H pair potential in order to justify our choice. The reliability of the 'effective' interaction derived in this manner was examined in a simulation of the structure of NaOH. This has an orthorhombic unit cell and its relatively low symmetry provided a good test of the potential. It was found that the calculated bond lengths matched the observed ones to within experimental error. Finally, we note that the transferability of the 0..... H potential to other systems was confirmed by the fact that it was found not to be strongly dependent on its environment.

# INCORPORATION OF H IN OXIDES

Various mechanisms may be invoked to describe the incorporation of the different hydrogenic species in oxides. For example the reaction:

 $H_2^{0} ----> O_0^{*} + 20H_0^{*} + V''M_g$ 

in which a cation vacancy has been created to compensate for the formation of the OH species, has been suggested as a likely means of water uptake. Whilst this reaction may account for OH formation and a number of other related species, it cannot explain the existence of H- species which have been found substituted on oxygen lattice sites. Here, we present some initial results on the

incorporation of OH groups in MgO, using the effective pair potential in the HADES code. First we consider the structure of the interstitial proton or  $OH_O$  group, in the absence of any cation vacancies. Figure <1> shows the minimum energy configuration for this species. We find that the proton clearly prefers to be associated with a lattice oxygen, as a distinct OH group, which will be oriented along [111] towards a next nearest neighbour cation.

Secondly, we find that the energy of substitution is considerably lowered in the presence of a cation vacancy, to form a  $V_{OH}^{-}$  centre, or partially compensated vacancy. In addition, the alignment of the OH group changes from [111] so that it is now oriented towards the vacancy along [100].

Thirdly, we predict that the fully compensated vacancy is bound with respect to  $V_{OH}$  and  $OH_O$ . These binding energies are listed in Table 1. Their calculated stability is borne out by experiment since no isolated OH groups have been seen spectroscopically in MgO. We find that the difference between the energies of the linear and non-linear fully compensated vacancy is quite small. This is, in fact, required by Freund's model for H2 formation from a V<sub>OM</sub> centre, in which a change from the linear to non-linear structure occurs.

These results were obtained, as already indicated, from classical (static) simulations. To evaluate the energetics of the dissociation reaction postulated by Freund (1), one needs to perform an explicit quantum mechanical embedded cluster calculation, such as was described earlier. These calculations are currently in progress and will be reported in the near future.

#### SUMMARY AND CONCLUSIONS

In this presentation, we have described how important questions concerning the behaviour of protons in oxides may be addressed using computer simulation techniques that have been interfaced with a proper quantum mechanical treatment of the structure in the vicinity of the hydrogen ion. We have elucidated details of the structural incorporation of OH groups, both in the presence and absence of cation vacancies and shown how far these are consistent with the reaction mechanisms proposed by Freund.

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TABLE 1. Binding Energies of OH to Cation Vacancy

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Defect Association		Energy /eV	1. 1. 1. 1. 1.
V(Mg) + OH <sub>O</sub> >	[V(Mg).HO] [OH,V(Mg).HO]	3.22	

