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Daresbury Laboratory

INFORMATION QUARTERLY FOR COMPUTER SIMULATION OF CONDENSED PHASES

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

Number 36 January 1993

Contents

Editor: Dr. M. Leslie

SERC Daresbury Laboratory
Daresbury, Warrington WA4 4AD UK

General News

CHAIRMAN AND EXECUTIVE COMMITTEE OF CCP5

A meeting of the steering committee of CCP5 was held on 12th. October 1992 at University College, London. Professor D. Tildesley's term of office as chairman had come to an end. At this meeting Professor M. Gillan (Dept. of Physics, Keele) was elected chairman. Dr. M. Allen (Dept. of Physics, Bristol), Dr. J. Goodfellow (Dept. of Crystallography, Birkbeck College London) and Dr. W. Mackrodt (ICI) were elected to the executive committee. They replaced Dr. N. Quirke, Dr. E. Colbourne and Dr. D. Fincham. The other members of the executive committee are N. Allan (Chemistry, Bristol), M. Rodger (Chemistry, Reading) and S. Price (Chemistry, University College London). The members present expressed their thanks to the retiring chairman and executive committee members.

FUTURE MEETINGS, WORKSHOPS AND VISITORS

A summary table is given below, further details may be found inside.

TOPIC	DATES	LOCATION
COMPUTER SIMULATION AND ATOMISTIC MODELLING OF MATERIALS.	FEBRUARY 4 1993	The Institute of Physics, London
COMPUTER MODELLING IN THE DESIGN AND STUDY OF NEW MATERIALS.	APRIL 6 1993	University of Southampton
SIMULATION OF SURFACES	APRIL 1 1993	UNIVERSITY OF BRISTOL
PROF. E. WESTHOF	1-5 MARCH 1993	LONDON, LEEDS, KEELE

CCP5 PROGRAM LIBRARY

Details are contained in this issue of accessing the CCP5 program library through E-mail automatically. Also details of accessing the Allen/Tildesley example programs at Cornell.

This issue contains a long article on a program written by Professor D. Evans which he has contributed to the program library. The program carries out non-equilibrium molecular dynamics and is designed to run on Apple Mackintosh computers. The program is being distributed as a binary converted to hexadecimal. Full details may be found in Professor Evans article.

CRAY NEWS

The Atlas Centre Cray Y-MP8I/8128 is now the production machine at RAL. CCP5 participants are reminded that CCP5 has an annual allocation of Cray time at Rutherford which has been transferred to the Y-MP. This is available for the development of simulation programs which are of general use to the CCP5 community. Readers who wish to use some of this allocation should write to the CCP5 Secretary, Dr. M. Leslie, TCS Division, SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD.

INTEL NEWS

The Parallel Supercomputing Committee (chaired by Professor C.R.A.Catlow) met in December 1992 to consider allocations for the coming year. CCP5 had submitted an application for time for use by the CCP5 community which was granted. If any CCP5 member wishes to make use of some of this time please contact M. Leslie at Daresbury.

CCP5 FUNDS FOR COLLABORATIONS

CCP5 can make available funds of up to £300 per annum for groups of two or more UK researchers wishing to undertake a collaborative project within the scientific area covered by CCP5. The funds are intended to cover travel and subsistence costs. Researchers who wish to apply for funds are requested to submit a brief proposal (about 1/2 a page) describing the intended work to Dr. M. Leslie, SERC Daresbury Laboratory, Daresbury, Warrington, Cheshire. Alternatively reply by Email to M.LESLIE@UK.AC.DARESBURY

CCP5 VISITORS PROGRAM

CCP5 organises a visitors program which funds the visit to the UK of overseas collaborators. We would normally expect a visitor to visit three sites in the UK and give a lecture at each site. These lectures would be open to all members of CCP5 as well as members of the host university. The visit would normally last between one or two weeks. CCP5 would pay for the cost of travel to the UK and within the UK between universities. CCP5 would expect some contribution towards accommodation expenses at the host university to be met by the university. We will also consider longer collaborations or visits just one place if this can be justified by the nature of the work to be done. If you have an overseas collaborator who you would like to invite under this program, please make a request to Dr. M. Leslie, SERC Daresbury Laboratory, Daresbury, Warrington, Cheshire. UK Alternatively reply by Email to M.LESLIE@UK.AC.DARESBURY

JANET: M.LESLIE@DARESBURY
INTERNET: M.LESLIE@daresbury.ac.uk
EARN/BITNET: M.LESLIE%daresbury.ac.uk@ukacrl

REQUEST FOR CONTRIBUTIONS

The deadline for contributions for the next newsletter will be 15 March 1993 Readers are reminded that contributions are always welcome.

Contributors to the current issue.
Our thanks go to:

M.J. Gillan	Department of Physics Keele University
V.S. Filinov	Russian Academy of Sciences Moscow
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N. L. Allan	School of Chemistry
M. D. Towler	University of Bristol
M. Braithwaite	ICI Explosives group
D. L. Cooper	Department of Chemistry University of Liverpool
W. C. Mackrodt	ICI Chemicals and Polymers Ltd.
D. J. Evans	Research School of Chemistry Australian National Laboratory

COMPUTER SIMULATION AND ATOMISTIC MODELLING OF MATERIALS

Thursday 4th. February 1993

The Institute of Physics, 47 Belgrave Square, London, SW1X 8QX

Organised by the Atomic Collisions in Solids Group of the Institute of Physics in collaboration with the Polar Solids Group of the Royal Society of Chemistry, The Institute of Materials and CCP5.

Speakers include

Professor M. Gillan	(Keele)	Fundamentals and Overview
Dr. R. Jones	(Exeter)	AB-Initio calculations of solid state properties.
Dr. A. Sutton	(Oxford)	Adhesion, Lubrication and Wear.
Professor D. Bacon	(Liverpool)	Defects in metals
Professor R. Catlow	(Royal Institution)	Ceramics and Catalysis
Professor B. Garrison	(Penn State)	Chemical reactions at surfaces

Further details may be obtained from

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Tel 0509 223192
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The Royal Society of Chemistry

Annual Chemical Congress

and CCP5

5th - 8th April 1993
University of Southampton

The main theme of the 1993 Annual Chemical Congress of the Royal Society of Chemistry is the design, synthesis and characterisation of new materials. As part of the Congress the Faraday Division will be holding a one day Symposium entitled "Computer Modelling in the Design and Study of New Materials". This meeting is being supported by CCP5 in its programme of one day workshops. The meeting will be held in the Chemistry Department at Southampton on Tuesday 6th April 1993 and the programme is as follows:

9.00 - 9.45	Computer Simulation of Liquid Crystals: from "Fascinating" to "Useful".	M.P. Allen, University of Bristol
9.45 - 10.30	Structural Modelling of Liquid Crystalline Polymers.	A.H. Windle, University of Cambridge
10.30 - 11.00	Coffee	
11.00 - 11.45	Bulk Polymer Properties from Realistic Atomistic Simulations.	U.W. Suter, ETH Zentrum, Switzerland
11.45 - 12.30	Computer Simulations of Surfactant Self Assembly.	B. Smit, Koninklijke/Shell Laboratorium, The Netherlands
12.30 - 2.00	Lunch	
2.00 - 2.45	The Simulation of Chain Molecules Close to Surfaces: Langmuir-Blodgett Bilayers and Fabric conditioners.	D.J. Tildesley, University of Southampton
2.45 - 3.30	Computer Simulations of Microporous Materials.	R. Catlow, The Royal Institution of Great Britain
3.30 - 4.00	Tea	
4.00 - 4.45	Buckyballs.	M.L. Klein, University of Pennsylvania, U.S.A.

It is possible to register for just one day of the Congress and so participate in this Symposium. The registration fees for one day are:

Member of the Royal Society of Chemistry	35.25 sterling
Non-Member	58.75 sterling

The registration fees for students cover the entire Congress and are:

Member	23.50 sterling
Non-Member	47.00 sterling

All prices include VAT. This fee also includes the cost of coffee and tea. Lunch can be purchased and the cost for this is expected to be approximately 5.00 sterling.

The second circular and registration forms for the Congress are about to be printed. If you wish to participate in what promises to be stimulating one day meeting then you should send a note to the Convener,

Professor G.R. Luckhurst
Department of Chemistry
University of Southampton
SOUTHAMPTON SO9 5NH

(or an email note to CHI002@UK.AC.SOTON.IBM). Please include your name and address so that the appropriate forms can be sent to you.

SIMULATION OF SURFACES

A one day workshop to be held at the University of Bristol on April 1st. 1993. Further details will be sent by Email when available. For further details please contact Dr. N. L. Allan (School of Chemistry, University of Bristol Tel 0272 304269) or Dr. S. C. Parker (Department of Chemistry, University of Bath Tel 0225 826505).

Visit of Professor E. Westhof

Professor Westhof is at the Institute for Molecular Biology, CNRS, Strasbourg. He has been involved in structure determination of DNA and RNA and wrote an essential part of the least squares refinement program, used for structure refinement of nucleic acids, which is used throughout the world. He has had a long standing interest in dynamics and has published several papers on the dynamics and modelling of DNA and RNA including the role of intrinsic curvature of certain sequences and the importance of hydration. He intends to visit the UK during the first week of March and will visit several locations. Further details will be sent by EMAIL when available. For further information please contact Dr. J. Goodfellow, Department of Crystallography, Birkbeck College, London. Tel. 071 580 6622.

The CCP5 Program Library

W. Smith

CCP5 Program Library Conditions of Distribution

The CCP5 Program Library provides programs and documentation free of charge to academic centres upon application to Dr. W. Smith, TCS Division, S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.. Please supply a magnetic tape to receive the copies. Industrial and commercial applicants should enclose a £100 handling charge. No magnetic tape need be sent in this case. Listings of programs are available if required. Please note that use of inappropriate packing for magnetic tapes (e.g. padded bags) may result in them being returned without the required software. Please ensure that these forms of packaging are not used. A list of programs available is presented in the following pages.

All applicants will be required to sign an agreement not to exploit the programs for commercial purposes e.g. for resale or distribution as part or whole of a commercial product.

Readers should also note that we are authorised to supply the example programs originally published in the book "Computer Simulation of Liquids", by M.P. Allen and D.J. Tildesley (Clarendon Press, Oxford 1987). These are supplied in the same manner as the resident CCP5 programs. We are grateful to Mike Allen and Dominic Tildesley for their permission.

We should also like to remind our readers that we would welcome further 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. Smith.

Please Note: For copyright reasons we are not able to supply the programs CASCADE, SYMLAT, THBFIT,THBPHON and THBREL free of charge to Universities outside the United Kingdom.

Programs from the Book: "Computer Simulation of Liquids" by M.P. Allen and D. Tildesley, Clarendon Press, Oxford 1987.

These programs originally appeared on microfiche in the book "Computer Simulation of Liquids" by M. P. Allen and D. J. Tildesley, published by Oxford University Press, 1987. They are made freely available to members of CCP5, in the hope that they will be useful. The intention is to clarify points made in the text, rather than to provide a piece of code suitable for direct use in a research application. We ascribe no commercial value to the programs themselves. Although a few complete programs are provided, our aim has been to offer building blocks rather than black boxes. As far as we are aware, the programs work correctly, but we can accept no responsibility for the consequences of any errors, and would be grateful to hear from you if you find any. You should always check out a routine for your particular application. The programs contain some explanatory comments, and are written, in the main, in FORTRAN-77. One or two routines are written in BASIC, for use on microcomputers. In the absence of any universally agreed standard for BASIC, we have chosen a very rudimentary dialect. These programs have been run on an Acorn model B computer. Hopefully the translation of these programs into more sophisticated languages such as PASCAL or C should not be difficult.

M.P.Allen

CCP5 Program Library E-Mail Service

From January 1 1991 it will be possible for CCP5 members to get copies of CCP5 programs through E-mail *automatically.* To do so they should send an E-mail message to **info-server@uk.ac.daresbury**. The contents of the e-mail message should be as follows (Note: the use of upper and lower case is significant - this is a unix system!):

```
request sources
topic index CCP/ccp5
topic CCP/ccp5/program-name
```

Where program-name is the name of the desired source code. A mail server will automatically process this message and return a copy of the source code to your e-mail address. Please note the following however:

The program source will be returned to you in **uue** format, which is a form of encoding most suitable for mail messages. It can easily be decoded on any unix system using the uudecode command. (Check your local unix *man* file for details). Also, to speed the transfer, the source will be split into files of 1200 records each, so expect two or three such files for the average CCP5 program. Once again, uudecode will help you to sort things out.

Readers who do not have unix facilities should include the following lines at the start of the above message:

```
line-limit: nnnnn
coding: off
```

Where nnnnn is the number of records in the source (in most cases 6000 should be enough). The program will be sent in plain FORTRAN as a single file. It may take a while to arrive, but be patient! Also beware in case your system mailer cannot handle messages of this size.

The programs from "Computer Simulation of Liquids" are also available. To access them use program-name F.01, for example.

Readers must realise that the terms of use and distrubution of the CCP5 programs that have applied hitherto will be maintained. Users should not redistribute or sell the programs, nor is any liability accepted for their use, either by SERC or the program authors. It is a requirement on the user that the programs be fully tested for their intended purpose. Any bugs found should be reported to the librarian, for the benefit of other users.

Lastly readers should realise that this means of transfer does not include any program documentation. So if you are unable to make sense of the programs, write for the documentation!

We are grateful to Mr. P. Griffiths of Daresbury's ITS Division for implementing this facility.

Availability of the Allen/Tildesley example programs at Cornell

Appendix F of the Book "Computer Simulation of Liquids" by M. P. Allen and D. J. Tildesley describes a method whereby the example programs may be obtained from the statistical mechanics group FTP facility at Cornell. This facility is no longer operational as advertised, due to software and hardware changes. However, the programs are still available. To obtain them, please follow the procedure outlined here. The description below is taken from the HELP file that is distributed by the file server; to obtain the Allen/Tildesley example programs, simply use "ALLEN_TILDESLEY" as the package name (without the quotes, note underscore character _ not hyphen -).

STATMECH is a file distribution service for the Statistical Mechanics community that uses electronic mail facilities to deliver files. To communicate with STATMECH, send an EMAIL message to: statmech@cheme.tn.cornell.edu Commands are sent in the body of hte message you send to STATMECH (not in the subject line). Several commands may be sent at one time; just put one command per line.

STATMECH commands:

SENDME package	Sends all parts of the specified package.
SENDME package.n	Sends part n of the specified package.
LIST [pattern]	Gives a brief description of all packages matching "pattern". If pattern is omitted, a description of all packages is sent.
HELP	Sends this help file.

For each request you make, a transaction log is returned to you indicating the status of the request. The status report will indicate whether the request was successfully completed, and when the file was or will be sent. Large files are sent only during off-peak hours.

Problems, questions and comments about STATMECH service on this system should be directed to "statmech-mgr@cheme.tn.cornell.edu".
Steve Thompson, School of Chemical Engineering, Cornell University, Ithaca NY 14853 USA.

THE CCP5 PROGRAM LIBRARY.

ADMIXT	[MD,LJA/MIX,LF,TH+MSD+RDF]	W. Smith
CARLOS	[MC,VS+Aquo,TH]	B. Jonsson & S. Romano
CARLAN	[DA,CARLOS structure analysis]	B. Jonsson & S. Romano
CASCADE	[LS,DIL,EM,TH+STR]	M. Leslie & W. Smith
CURDEN	[DA,Current Density Correlations]	W. Smith
DENCOR	[DA,Density Correlations]	W. Smith
HLJ1	[MD,LJA,LF,TH+MSD+RDF]	D.M. Heyes
HLJ2	[MD,LJA,LF,TH+MSD+RDF+VACF]	D.M. Heyes
HLJ3	[MD,LJA,LF/LC,TH+MSD+RDF]	D.M. Heyes
HLJ4	[MD,LJA,LF/CP+CT,TH+MSD+RDF]	D.M. Heyes
HLJ5	[MD,LJA/SF,LF,TH+MSD+RDF]	D.M. Heyes
HLJ6	[MD,LJA,TA,TH+MSD+RDF]	D.M. Heyes
HMDIAT	[MD,LJD,G5+Q4,TH+MSD+QC]	S.M. Thompson
HSTOCH	[MD/SD,VS+BA,LF+CA,TH]	W.F. van Gunsteren & D.M. Heyes
MCN	[MC,LJA,TH]	N. Corbin
MCLSU	[MC,LJA,TH]	C.P. Williams & S. Gupta
MCMOLDYN	[MD/MC,LJS+FC+AQ,LF+QF/G5+QS,TH+RDF]	A. Laaksonen
MCRPM	[MC,RPE,TH+RDF]	D.M. Heyes
MDATOM	[MD,LJA,G5,TH+RDF+MSD+QC]	S.M. Thompson
MDATOM	[MD,LJA,LF,TH+MSD+RDF]	D. Fincham
MDCSPC2P	[PRMD,BHM,LF,TH+STF+RDF+VACF+MSD]	W.Smith
MDCSPC4B	[PRMD,BHM+FC,G5+G4,TH+STF+RDF]	W. Smith
MDDIAT	[MD,LJD,LF+CA,TH+MSD]	D. Fincham
MDDIATQ	[MD,LJD+PQ,LF+CA,TH+MSD]	D. Fincham
MDIONS	[MD,BHM,LF,TH+MSD+RDF+STF]	D. Fincham & N. Anastasiou
MDLIN	[MD,LJL,G5+Q4,TH+MSD+QC]	S.M. Thompson.
MDLINQ	[MD,LJL+PQ,G5+Q4,TH+MSD+QC]	S.M. Thompson
MD3DLJ_C	[MD,LJA/MIX,LF/LC,TH+MSD+RDF]	M. Bargiel, W. Dzwinel, J. Kitowski and J. Moscinski
MDMANY	[MD,LJS+FC,LF+QF,TH]	D. Fincham & W. Smith
MDMIXT	[MD,LJS/MIX,LF+QF,TH]	W. Smith
MDMPOL	[MD,LJS+FC/MIX,LF+QF,TH]	W. Smith & D. Fincham
MDNACL	[MD,BHM,LF,TH+MSD+RDF]	W. Smith
MDPOLY	[MD,LJS,G5+Q4,TH+MSD+QC]	S.M. Thompson
MDMULP	[MD,LJS+PD+PQ/MIX,LF+QF,TH]	W. Smith
MDSGWP	[MD,LJA/SGWP,LF,TH+VACF+RDF+QC]	W. Smith & K. Singer
MDTETRA	[MD,LJT,G5+Q4,TH+MSD+QC]	S.M. Thompson
MDZOID	[MD,GAU,LF+QF,TH+MSD+RDF+VACF]	W. Smith
NAMELIST	[UT, Namelist emulation]	K. Refson
NEMD	[MD,LJA,SLLOD,Macintosh]	D. J. Evans
NSCP3D	[UT, Hard sphere packing]	M. Bargiel & J. Moscinski
PIMCLJ	[PIMC,LJA,MC,TH+RDF+QC]	K. Singer & W. Smith

SCN	[MC,LJA,RFD,TH] N. Corbin
SMFK	[MC-SCF, Cylindrical Polyelec.] A.P. Lyubartsev
SLS_PRO	[MD,Proteins,LF,TH+RDF] A. Raine
SOTON_PAR	[MD,LJA,LC,TH] M.R.S. Pinches
SURF	[MD,BHM/TF/2D,LF,TH+RDF] D.M. Heyes
SYMLAT	[LS,PIL,EM+SYM,TH+STR] Harwell
TEQUILA	[GP] A. Wilton and F. Mueller-Plathe
THBFIT	[LS,PIL,EM,Potential fitting] Harwell
THBPHON	[LS,PIL/3B,EM,Phonon dispersion] Harwell
THBREL	[LS,PIL,EM,TH+STR] Harwell

Key:

Program types:	MD	Molecular dynamics
	MC	Monte Carlo
	PRMD	Parrinello-Rahman MD
	LS	Lattice simulations
	SD	Stochastic dynamics
	DA	Data analysis
	UT	Utility package
	PIMC	Path Integral Monte Carlo
	GP	Graphics program

System models:	LJA	Lennard-Jones atoms
	LJD	Lennard-Jones diatomic molecules
	LJL	Lennard-Jones linear molecules
	LJT	Lennard-Jones tetrahedral molecules
	LJS	Lennard-Jones site molecules
	RPE	Restricted primitive electrolyte
	BHM	Born-Huggins-Meyer ionics
	SGWP	Spherical gaussian wavepackets
	TF	Tosi-Fumi ionics
	VS	Variable site-site model
	BA	Bond angle model
	PD	Point dipole model
	PQ	Point quadrupole model
	MIX	Mixtures of molecules
	GAU	Gaussian molecule model
	FC	Fractional charge model
	PIL	Perfect ionic lattice model
	DIL	Defective ionic lattice model
	3B	3-body force model
	2D	Two dimensional simulation
	SF	Shifted force potential
	FC	Fractional charge model
	AQ	Aqueous solutions

Algorithm:	G5	Gear 5th order predictor-corrector
	Q4	Quaternion plus 4th. order Gear P-C.
	LF	Leapfrog (Verlet)
	QF	Fincham Quaternion algorithm
	QS	Sonnenschein Quaternion algorithm
	LC	Link-cells MD algorithm
	CP	Constant pressure
	CT	Constant temperature
	TA	Toxvaerd MD algorithm
	CA	Constraint algorithm
	EM	Energy minimisation
	SYM	Symmetry adapted algorithm
	RFD	Rossky-Friedman-Doll algorithm
	SLLOD	Thermostatted SLLOD equations

Properties:	TH	Thermodynamic properties.
	MSD	Mean-square-displacement
	RDF	Radial distribution function
	STF	Structure factor
	VACF	Velocity autocorrelation function
	QC	Quantum corrections
	STR	Lattice stresses

Programs from the Book “Computer Simulation of Liquids”

F.1	Periodic boundary conditions in various geometries
F.2	5-value Gear predictor-corrector algorithm
F.3	Low-storage MD programs using leapfrog Verlet algorithm
F.4	Velocity version of Verlet algorithm
F.5	Quaternion parameter predictor-corrector algorithm
F.6	Leapfrog algorithms for rotational motion
F.7	Constraint dynamics for a nonlinear triatomic molecule
F.8	Shake algorithm for constraint dynamics of a chain molecule
F.9	Rattle algorithm for constraint dynamics of a chain molecule
F.10	Hard sphere molecular dynamics program
F.11	Constant-NVT Monte Carlo for Lennard-Jones atoms
F.12	Constant-NPT Monte Carlo algorithm
F.13	The heart of a constant `$\mu$VT` Monte Carlo program
F.14	Algorithm to handle indices in constant `$\mu$VT` Monte Carlo
F.15	Routines to randomly rotate molecules
F.16	Hard dumb-bell Monte Carlo program
F.17	A simple Lennard-Jones force routine
F.18	Algorithm for avoiding the square root operation
F.19	The Verlet neighbour list
F.20	Routines to construct and use cell linked-list method
F.21	Multiple timestep molecular dynamics
F.22	Routines to perform the Ewald sum
F.23	Routine to set up alpha fcc lattice of linear molecules
F.24	Initial velocity distribution
F.25	Routine to calculate translational order parameter
F.26	Routines to fold/unfold trajectories in periodic boundaries
F.27	Program to compute time correlation functions
F.28	Constant-NVT molecular dynamics - extended system method
F.29	Constant-NVT molecular dynamics - constraint method
F.30	Constant-NPH molecular dynamics - extended system method
F.31	Constant-NPT molecular dynamics - constraint method
F.32	Cell linked-lists in sheared boundaries
F.33	Brownian dynamics for a Lennard-Jones fluid
F.34	An efficient clustering routine
F.35	The Voronoi construction in 2d and 3d
F.36	Monte Carlo simulation of hard lines in 2d
F.37	Routines to calculate Fourier transforms

CAN WE TRUST THE SHELL MODEL?

M.J. Gillan
Physics Department, Keele University
Keele, Staffordshire ST5 5BG, U.K.

I am not a great believer in staring at your navel. Trying something out in practice is usually better than hours of self-questioning. Nevertheless, from time to time a moment of introspection can be good for the soul. Sometimes you need to ask: Is this method that I have used for so long really what it seems?

The shell model for the energetics of ionic materials [1] has been used enthusiastically for many years. But there has always been the odd awkward customer who has seen fit to question its basis. We know that ions in crystals are electronically polarised by the electric fields due to neighbouring ions. We know that they are also polarised simply because neighbouring ions press against them. These two physical facts form the basis of the shell model. Each ion is represented by a massive core and a massless shell, both charged, coupled by a harmonic spring. The short-range interactions between ions are usually assumed to act between the shells. Both the field polarisation and the polarisation due to short range interactions are incorporated in this simple model.

It is easy to pick holes. Polarisation of an ion really occurs by distortion of the orbitals occupied by the valence electrons. Can the distortion of a p-orbital in an oxygen ion really be adequately represented by the simple relative displacement of core and shell charges? What about the redistribution of electrons in the unfilled d-shell of a cobalt ion? Such doubts have not prevented the shell model from being routinely applied to oxide materials (including, incidentally, cobalt oxide) [2] . Matters are not helped when you look at the shell model parameters. Very often the shell model is parameterised by fitting to selected experimental data for bulk crystals - things like the lattice parameter or the dielectric and elastic constants. The shells are supposed to represent valence electrons - in spite of which, the cation shell charges that emerge from fitting very often have positive values (examples can be seen in ref. [3]). What is this supposed to mean? Strange shell charges might not matter if the shell model was only applied in situations close to those it has been fitted to. In practice, though, it has been widely used for things like the properties of surfaces - which are about as different from bulk crystals as you could imagine. This raises all kinds of questions. You could imagine that a material might be fully ionic in the bulk, but only partially ionic at the surface, for example. There is plenty to keep you awake at night!

It looks as though worries like these will very soon be a thing of the past, thanks to first principles-methods. The idea of first-principles simulations is to solve Schroedinger's equation to determine the electronic ground state of the system. These methods have become so accurate and reliable in the last few years that they can now be used as an independent way of testing and constructing interaction models. The problem in the past in parameterising an interaction model using experimental data was that usually only data on the perfect crystal would be available. First-principles methods give you the means to calculate the energy for any configuration of the ions that may be relevant. First-principles calculations on the structure and energy of defects and surfaces can now be used to provide a direct test of shell model predictions.

Two main first-principles approaches are being used. The work we are doing at Keele [4,5] is based on density functional theory (DFT) and pseudopotentials. Other groups, particularly at Daresbury Laboratory, at ICI, and at the Royal Institution in London, are making use of Hartree-Fock methods [6,7]. I will say something first about our own work, and then mention the Hartree-Fock methods later.

The basis of the density functional method is the idea that you can write the total energy as a unique functional of the density distribution of the electrons. This leads naturally to a simple approximation for the electronic exchange and correlation energy. The approximation assumes that at each point in the system there is a density of exchange and correlation energy and that this density depends only on the density of electrons at that point - this is called the local density approximation (LDA). There is now a wide range of results which shows that the LDA gives very accurate results for many systems and situations. The idea of the pseudopotential method is to set up the calculations in such a way that only the valence electrons have to be explicitly treated. This makes sense because the atomic cores are usually almost completely inert and have no effect on the energetics of the system. The pseudopotential for any atom represents the effective interaction of the valence electrons with the atomic cores. Nowadays, pseudopotentials are constructed from first principles, and there is no loss of rigour in following the pseudopotential approach.

A number of research groups have written DFT-pseudopotential codes for calculating the total ground state energy of materials. In the U.K., the most important is the code CASTEP written by Mike Payne and his group at Cambridge with the support of a CCP9 project. This is now becoming widely used, both in the U.K. and in the rest of Europe. In the last two years, as part of the U.K. Car-Parrinello project, this code has been rewritten in parallel form to run on machines like the Intel iPSC/860 at Daresbury Laboratory and the Meiko Computing Surface 'Maxwell' at the Edinburgh Parallel Computing Centre [8]. This code already has a number of important scientific achievements to its credit, including a study of the famous 7x7 reconstruction on the silicon (111) surface, which involved simulations on 400 silicon atoms [9,10].

At Keele, we have been using the code CETEP on the parallel machines at both Edinburgh and Daresbury to study the energetics and structure of defects and surfaces in oxide materials. As a by-product of these calculations, we have obtained some extremely instructive insights into the validity of shell-model potentials for these materials. But before saying anything about these results, it is worth taking a look at how the DFT pseudopotential method does for the properties of the perfect crystals. As an example, Table 1 shows some of the results we obtained for the equilibrium lattice parameter, the bulk modulus, and some of the vibrational frequencies of perfect crystal MgO. When you look at the results, you should bear in mind that these calculations are done completely from first principles and contain no adjustable parameters at all. You can see that results like these are certainly reliable enough for constructing interaction models.

We have used these methods to look at the energetics of point defects in both MgO and Li_2O. The dominant thermally produced defects in MgO are Schottky defects, in other words vacancies on the magnesium and oxygen sublattices. In lithium oxide, the dominant defects are cation Frenkel defects, in other words lithium vacancies and interstitials. What we have aimed to do is to calculate from first principles the energy of formation of these defects and their migration energies - the energy barriers that the defects have to get over as they jump from one site to another in the lattice. Of course, when you do calculations on defects, you have to use systems containing many ions. The calculations are all done in periodic boundary conditions so that, in effect, what we are doing is calculations on periodically repeating arrays of defects. Since the defects carry net charges, we have to be very careful about correcting for the effective Coulomb interaction between defects and their periodic images. Even with such corrections, you need to do calculations on systems of about 50 ions in the repeating cell to obtain reliable results. In addition, because of the large polarisation effects for charged defects, it is important to get the system mechanically relaxed so that the forces on all the ions are extremely small.

Table 2 shows some of the results we have obtained for the energies of Schottky defects in MgO and Frenkel defects in Li_2O. These results are compared with the predictions of shell model potentials, and also, in some cases, with experimental results. The point about these comparisons is that the agreement between the first principles results and the predictions of the shell model are actually very close, even in cases where experimental results do not exist. This already provides useful support for the validity of the shell model, at least for these problems. Further support comes when you look at the relaxed structure of the defects. What we find is that the relaxed positions of the ions surrounding the defects - both the equilibrium defects and the migration saddle points - is extremely similar in the shell model and first principles calculations. Put another way, this means that if you take the relaxed structure predicted by shell-model calculations, and put it into the first-principles calculations, then you find that the first-principles forces on the ions are all extremely small.

The shell model thus comes through with flying colours for the point defects we have looked at. But you might argue that point defects are not so very far from the perfect crystal structure. A much more severe test is provided by crystal surfaces. Here, the ions at the surface find themselves in an environment which is completely different from what they see in the bulk. One of the cases we have been looking at is the structure of the basal-plane surface of alpha-alumina. This is a particularly dramatic case, because the shell model potentials predict a huge relaxation of the surface structure [11,12]. For example, the spacing between the plane of the surface aluminiums and the plane of oxygens beneath it is predicted to be at least 50 % less than in the bulk crystal. These predictions are based on the assumption that the material is completely ionic even at the surface - in other words, that the ions are Al^{3+} and O^{2-}. But the Madelung potential must be completely different at the surface from what it is in the bulk. The charge transfer between ions might well be strongly influenced by the Madelung potential, and it is easy to imagine that the degree of ionicity at the surface might be considerably less than what is found in the bulk. The first-principles calculations give us a way of answering this question.

We have done a series of calculations on the relaxed surface structure of the basal-plane surface of Al_2O_3. The calculations have been done in slab geometry, so that each slab of material is separated from the next slab by a vacuum layer. It turns out that quite thin slabs of typically 6 Å thickness and similar thicknesses of vacuum are quite enough to get fully converged results. Remarkably, when we relax the surface structure we find very similar results to what is predicted by the empirical shell-model potentials. To show this, table 3 gives the surface inter-planar spacings predicted by the two methods. The agreement is, indeed, not exact, but the systematics of the spacing changes is identical in the two calculations. The predictions for the relaxed surface energy are also in rather good agreement. For this particular surface, the first-principles calculations predict a surface energy of 1.76 J m^{-2}, while the shell model prediction [11] is 2.03 J m^{-2}.

I have not said anything yet about Hartree-Fock methods. A big effort to develop

Hartree-Fock codes for treating periodically repeating systems has been put in by the group of Pisani and co-workers at the University of Turin in collaboration with Vic Saunders at Daresbury Laboratory. This has led to the widely used code CRYSTAL [6,13], which has been used in a range of calculations on both ionic crystals and other materials. It is already clear that the Hartree-Fock method too gives very good predictions for the properties of bulk crystals of materials like MgO and Al_2O_3. Calculations on defects and surfaces in ionic materials are not yet as far advanced as those using DFT-pseudopotential methods. Part of the reason for this seems to be that it is less easy with the Hartree-Fock methods to get the calculations fully converged with respect to the size of the basis set. However, there will be great advantages in being able to compare the predictions of two completely independent methods, and there is every sign that the Hartree-Fock approach will also give very reliable results. The CRYSTAL code has already seen very important use in the construction of interaction models [7,14].

So can we trust the shell model? It is probably too early to be sure, but so far it has emerged unscathed from the rigorous testing provided by first principles calculations. I certainly do not expect to see first-principles methods put the shell model out of business. The ability to do rapid static and dynamical shell-model simulations on ionic materials will be important for many years to come. What will happen, though, is that the first-principles methods will allow us to distinguish much better between good and bad shell-model potentials, and will improve the quality of good shell models still further.

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	calculated	experimental
a_0 (Å)	4.17	4.22
B (Mbar)	1.54	1.55 - 1.62
TO(Γ) (THz)	12.39	12.23
TA(X) (THz)	8.65	8.96
LA(X) (THz)	12.57	12.65
TO(X) (THz)	13.24	13.15
LO(X) (THz)	16.36	16.61

Table 1: Calculated and experimental values of lattice parameter a_0, bulk modulus B and five phonon frequencies of MgO. Phonon modes are the transverse optic mode at the Γ point and the transverse and longitudinal acoustic and optic modes at the X point of the Brillouin zone.

		first-principles	shell-model	experimental
MgO	E_S	6.88	7.72	...
	ΔE_m (cation vacancy)	2.39	2.07	2.2, 2.28
	ΔE_m (anion vacancy)	2.48	2.11	2.42, 2.61
Li_2O	E_F	2.20	2.12	1.58, 2.53
	ΔE_m (cation vacancy)	0.34	0.21	0.40, 0.49
	ΔE_m (cation interstitial)	0.58	...	...

Table 2: First-principles, shell-model and experimental results for the Schottky energy E_S and the cation and anion vacancy migration energies ΔE_m of MgO, and the Frenkel energy E_F and the cation vacancy and interstitial migration energies ΔE_m of Li_2O (all energies in eV). All calculated results are for a 32-ion system of MgO and a 48-ion system of Li_2O.

	First principles	Empirical
	Slab	Semi-infinite
aluminium		
	-86 %	-59 %
oxygen		
	+3 %	+2 %
aluminium		
	-54 %	-49 %
aluminium		
	+25 %	+26 %
oxygen		

Table 3: Percentage changes of interplanar spacing due to relaxation of the α-alumina basal-plane surface. Planes of atoms are specified in the left-hand column, the topmost plane being the layer of aluminiums on the surface; changes of spacing are given between successive planes. Results are given for the present first-principles calculations and for shell-model calculations on the surface of the semi-infinite crystal reported by Mackrodt [11].

A VISIT TO THE UK.

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In February 1992 I got an invitation from Professor K.Singer and Dr. W.Smith to visit UK within the frame of the CCP5 project. This invitation was quite unexpected for me, but I was glad to accept it. During many years I have the contacts with Prof. K.Singer by mail and was acquainted with his work and with work of some British research groups invoked in computer simulation of physical chemical systems on molecular level. With the help of E- mail the schedule of my two week journey was soon worked out. As I am engaged by developing and application of complex-valued Monte- Carlo method for simulation of real-time quantum dynamics and for for solving the stationary problems of quantum mechanics and the theory of wave propagation on random media, my schedule included the visit to Prof. K.Singer in Egham, to Dr. W.Smith in Daresbury Laboratory, to Prof M.Payne in Cavandish Laboratory and to Dr. M.Spivack in Department of Applied Mathematic and Theoretical Physics of Cambridge university, to Dr. M.Allen in H.H.Wills Physical Laboratory (Bristol university), to Prof. P.Madden in Oxford university and the meeting with Prof. E.Jakeman from Royal Signal and Radar Establishment and Prof. M.Gillan from Keele university. As I planed I came to Heathrow on the 4th of June, where Prof. K.Singer has met me. I spent Thursday, Friday and weekend with Prof. K.Singer and his colleagues in Egham and London in very intensive and stimulating discussions. The work performed by Prof. K.Singer and Dr. W.Smith are very close to my interests, as they are engaged in developing the the stochastic numerical method for solving Wigner-Liouville equation for simulation quantum dynamics. I have extended the Monte Carlo method for calculation the Feynman path integrals allowing to describe the dynamics of quantum particles. We had long discussions about problems related to the quantum dynamics. My schedule in London was very tough, so I had very little time for sight-seeing and cultural program, but with the help and due the care of Prof. K.Singer I have seen a lot of them. I am very appreciate to Prof. K.Singer for his hospitality during my staying in his beautiful house in Egham. On Sunday I went to the Daresbury laboratory. I was met by Dr. W.Smith at the railway station. He brought me at first to hostel and then to his home, where I met extremely cordial and hospitable. On the next evenings he brought me to Chester a small town full with historical monuments. Dr.W. Smith was wonderful guide during our visit to English pub. The visit to Daresbury Laboratory impressed me greatly. Such a variety of methods, approaches and subjects of investigation. In my lecture in Daresbury I spoke about real-time quantum dynamics, sign problem connected with calculation of the Feynman path integrals and ways to solve this problem. Proposed in my papers transformation of the Feynman path integrals resulted in the new representation of the Feynman path integrals having an explicit exponential decay of the modulus of the integrand outside the dominating region. The Metropolis algorithm can be used for the calculation the Feynman integrals by Monte Carlo method in this representation. This transformation may be also useful for constructive determination of the measure for the Feynman path integrals. The developed representation of the Feynman path integrals is already used for solving different problems of quantum physics, chemistry and the theory of wave propagation in random media. On Thursday I crossed half of Britain and left the train in Cambridge, where two hours late I gave a lecture in Cavandish Laboratory about my results on the application of developed complex-valued Monte Carlo method to the theory of quantum particles and classical wave localization in 1D, 2D and 3D random media. The Monte Carlo results showed that besides known the spatial scale of exponential decay of the mean intensity (localization length) the problem has a new spatial scale. The obtained MC results have shown that the exponential decay starts only when the distance from the source is more than this new length which is about five or six average distance between scatterers. I talked also about some other new results and the influence on the the large scale inhomogeneities on the classical wave localization and the influence of the external electrical field on the quantum electron localization. In the evening I was invited by Prof. M.Payne to the dinner in Pembroke college, where I can see the old British traditions and feel the breath of history. Next day I spent with Dr. M.Spivack, Prof. Uscinski and their colleagues in Department of Applied Mathematic and Theoretical Physics of Cambridge university. Subject of our fruitful discussions was the theory of wave propagation in random media and different approaches for solving related problems. The weekend I enjoyed the hospitality of Prof. K. Singer in his house and had wonderful excursion with him in London and country picturesque landscapes. We have also the long scientific discussions on the problem of quantum dynamics. Next two days I spent in Bristol. My host Dr.M.Allen showed me some of the sight-seeing of the town. It was very pleasant time to visit his house and met with his family. I have also many fruitful discussions with colleagues of Dr. M.Allen. After my lectures I had a meeting with Prof. E. Jakeman and we discussed some problems of the theory of wave propagation in random media and its application to the developing of the radio wave absorbers. In the evening I was invited in the Indian restaurant by Dr. M.Allen, Prof. B.Gyorffy and his colleagues, where we have a beautiful meeting. The last point of my visit was Oxford, I spent two wonderful days with my hosts Prof. P.Madden and Prof. D.Logan and their colleagues. Subject of the lectures was also the application of complex-valued Monte Carlo method and path integral technique to the problem of quantum particle localization in 1D, 2D and 3D disordered systems. I am very grateful to CCP5 project and to Prof. K.Singer and Dr. W.Smith who organized my unforgettable journey, to Prof. M.Payne, Dr. M.Spivack, Prof. E.Jakeman, Dr. M.Allen, Prof. P.Madden, Prof. D.Logan and all the colleagues for their hospitality and patience.

An other 'clever' idea down the drain ...

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As readers of this Newsletter know all too well, the efficient simulation of dense liquids is seriously hampered by the fact that the molecules diffuse rather slowly, instead they spend most of their time just rattling around in the cage of their neighbours. This is less of a problem for homogeneous liquids but more pronounced for mixtures.

The 'clever' idea referred to in the title was an attempt to used the cavity biased insertion, developed for grand-canonical ensemble simulation [1,2] in the canonical ensemble to perform simultaneously the removal and the insertion of a molecule. This idea grew out of the observation in [2] that the insertion - deletion feature of the grand-canonical ensemble simulations are mimicking large jumps. Such a pair of moves would be indistinguishable from a big jump - just the kind of move one would like to have. The idea appeared to be clever, because if one inserts the just removed molecule into a cavity, the removal also leaves behind a cavity and thus microscopic reversibility would be maintained without further corrections in the acceptance expression. To be rigorous, one should exlude from removal those molecules that have neighbours closer than the cavity radius.

This idea was put to test on 91 room-temperature SPC water molecules in a cubic box under periodic boundary conditions at experimental density. This system was shown to have sufficient number of cavities for the cavity-biased insertions [2]. Two million attempted Monte Carlo displacements were performed of the usual kind and after every 10-th conventional step a 'cavity jump' was also attempted. This, of course, required significant extra work since a grid whad to be maintained to track the location of cavities, as described in [2]. However, none of these attempted jumps were accepted, reflecting the fact that the algorithm also has to 'pay' for the removal of the molecule, and dearly, at that.

Naturally, one can still switch to the grand-canonical ensemble, but otherwise, until a truly clever idea comes along, we have to stay with the simulation moves of the kind we are used to.

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Modelling explosives

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Increasingly computer simulation techniques offer an attractive approach to the modelling of systems under extremes of temperature and pressure. An important example of this is the attention currently being paid to the behaviour of systems of geophysical importance, notably by Parker and Price [1]. Here we discuss briefly a related application, namely the ideal detonation of explosives. This requires accurate equations of state which can be obtained by simulation. The overall objective is the development of a code to solve chemical equilibrium problems arising from the detonation of explosives, as a part of suite of programs for estimating explosive rock-breaking performance. Such codes are essentially 'thermochemical' in nature, requiring as input the chemical formulation, heat of formation and density of the explosive together with thermodynamic data for allowed products. Effort has been directed towards the calculation of the final state of the explosive resulting from (a) a constant volume explosion (b) a Chapman-Jouguet detonation and (c) isentropic expansion from an initial (P,V) state.

The explosion problem

This involves determining the temperature T for a fixed volume V = V_0 of the explosive mixture such that

$$U(T, V, \mathbf{n_g}, \mathbf{n_s}) = U_0 \tag{1}$$

The mole vectors, $\mathbf{n}_g$ and $\mathbf{n}_s$, the numbers of moles of the various gaseous and solid species respectively, are the solution of the linearly constrained minimization problem

$$\min_{\mathbf{n_g},\mathbf{n_s}} A(T, V, \mathbf{n_g}, \mathbf{n_s}) \tag{2}$$

subject to the constraints

$$\mathbf{B_g n_g} + \mathbf{B_s n_s} = \mathbf{c} \tag{3}$$

and

$$\mathbf{n_g} > \mathbf{0}, \mathbf{n_s} > \mathbf{0} \tag{4}$$

Here U(T,V,$\mathbf{n}_g$,$\mathbf{n}_s$), is the internal energy of the system and A(T,V,$\mathbf{n}_g$,$\mathbf{n}_s$) the corresponding Helmholtz free energy of the total system, *including the solid*. The constraints reflect the atomic balance so that all the various elements present in the systems are conserved. V_0, U_0, the matrices $\mathbf{B}_g$ and $\mathbf{B}_s$ and the elemental mass c are input data.

The detonation problem

Here V is found such that

$$\min_{0 \le V \le V_0} (P - P_0)/(V - V_0) \tag{5}$$

where T satisfies

$$U(T, V, n_g, n_s) - U_0 = 1/2\ (P + P_0)(V_0 - V) \qquad (6)$$

where n_g and n_s are the solutions of the minimization procedure defined by the detonation problem. P_0 is one atmosphere, and U_0 and V_0 the quantities defined earlier. This last equation is the *Hugoniot* which relates the internal energy change to those in the pressure and the volume. The detonation problem is similar to the explosion problem with the additional minimisation, equation (5). The isentropic expansion is continued until either the temperature T, or the pressure p, achieves a specified lower bound.

Isentropic expansion

For a sequence of increasing volumes, V, the temperature T is sought such that

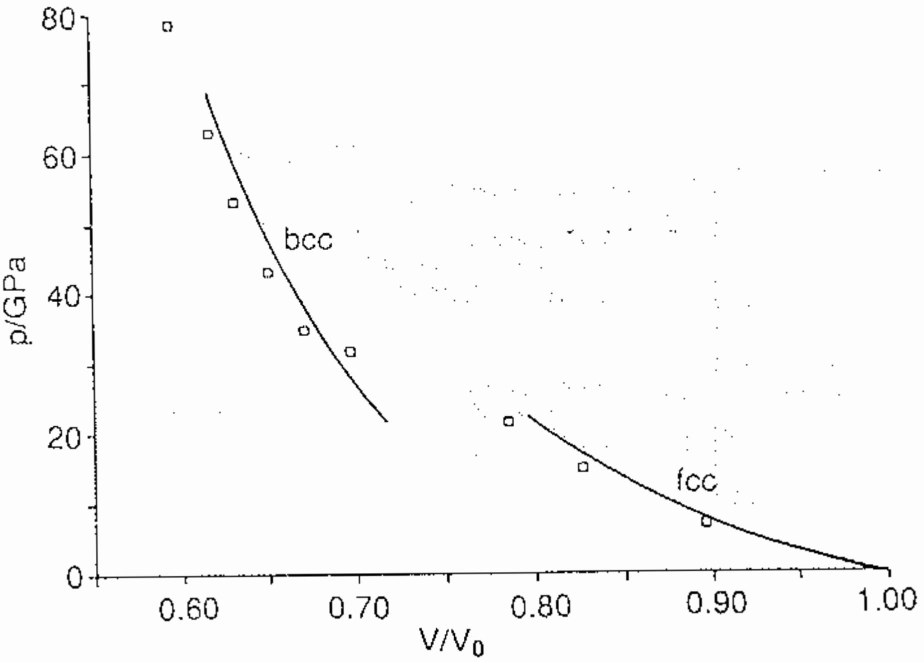
$$S(T, V, n_g, n_s) = S_{Det} \qquad (7)$$

where n_g and n_s are defined in the section on the explosion problem and S_{Det} is the entropy of the system at the converged solution of the detonation problem. Further details of the various formulations of this problem and the minimization techniques used are given in ref. [2]. For the present, however, it is sufficient to recognise that the success of the various procedures relies to a large extent on the existence of accurate equations of state for the materials of interest and here simulations can play a major role. For the gaseous phases, hard sphere perturbation theory is used to provide corrections to ideal gas behaviour. Our own recent work has concentrated on calculating equations of state for the solid phases as an alternative to other more approximate equations such as that due to Murnagahan.

To generate these we have used an combination of lattice statics and lattice dynamics within the quasiharmonic approximation based on two-body potentials incorporating the Dick-Overhauser shell model.The two-body, shell-model potentials, which represent the short-range interactions, have been taken without adjustment from recent static calculations of oxides and halides. They themselves were generated using a modified form of the Kim-Gordon electron-gas approach. For the binary rock-salt oxides and halides which we have considered so far, the experimental Hugoniot data can be reproduced satisfactorily, including the effects of phase changes from the B1 (NaCl) to the B2 (CsCl) structures. For example, Figure 1 shows calculated and experimental Hugoniots for NaF.

The quantity of principal concern in our approach is the Helmholtz free energy A(V,T) which is calculated directly from the potential energy of the lattice, U_{el}, and the normal mode frequencies, $\nu_j(k)$ for wavevectors k, evaluated from the dynamical matrix. In the quasiharmonic approximation, the normal mode frequencies $\nu_j(k)$ depend on the crystal volume but not on the temperature T explicitly. The

Figure 1. Comparison of calculated Hugoniot data for NaF with experiment[6]



Helmholtz free energy, A, is given by

$$A = U_{el} + \sum_{\mathbf{k},j} 1/2\ h\nu_j(\mathbf{k}) + k_B T ln[1 - exp(-h\nu_j(\mathbf{k})/k_B T)] \qquad (8)$$

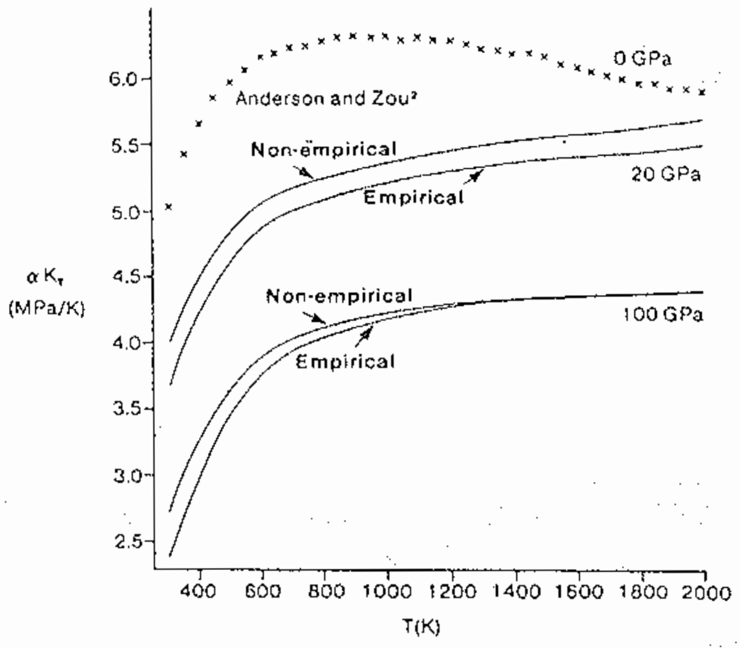
where k_B is Boltzmann's constant and the sum of k-vectors is over a uniform grid known as the Chadi-Cohen special points. Differentiation of A with respect to V, which is carried out numerically, gives the pressure, p(= -$(\partial A/\partial V)_T$). For the majority of cases considered so far pressures up to 100 GPa have been considered. The entropy, S (= -$(\partial A/\partial T)_V$), is determined directly from the normal mode frequencies from the expression

$$S = \sum_{\mathbf{k},j} h\nu_j(\mathbf{k})/T[exp(-h\nu_j(\mathbf{k})/k_B T) - 1]^{-1} - k_B ln[1 - exp(-h\nu_j(\mathbf{k})/k_B T)] \qquad (9)$$

Appropriate differentiation and algebraic manipulation gives other desired thermodynamic quantities.

Of course, the number of possible systems that could be of interest for this application is very large. Furthermore there are several structural types such as ammonium salts, nitrates, sulphates and hydroxides for which traditional ionic model simulations are problematical because of the presence of covalent bonds. However, this is not as severe as it might appear, since under the conditions of interest, these decompose to simpler systems, e.g. hydroxides to oxides and so on.

Figure 2. Variation with temperature of αK_T for MgO. Calculated results for empirical and nonempirical electron-gas potentials are shown, together with experimental values (crosses)[7]



In addition to the direct calculation of numerical equations of state, we are also currently exploring the use of other so called "universal" equations of state such as that due to Vinet [5]. Such approaches commonly make very restrictive assumptions as to the variation of the thermal pressure with respect to temperature and volume. For example, it is usual to assume that αK_T ($= (\partial p/\partial T)_V$) is independent of the temperature at high T, i.e. that the "thermal pressure" is proportional to T. In addition αK_T is often taken to be independent of the volume. The results of our simulations for a wide range of ionic oxides and halides indicate that the former is indeed remarkably accurate but that the latter is not necessarily so over the range of pressures important for geological applications. An example of this is given in Figure 2, which shows the calculated variation of αK_T with temperature for MgO. Over the considerably smaller pressure range that is important for explosives applications, the variation of αK_T with volume is not a serious problem. More importantly, the Debye temperature, Θ_D, above which αK_T is constant, can be quite high for simple oxides, e.g. Θ_D for MgO is $\sim$ 800 K. This presents two problems. The first is that equations of state below the Debye temperature are often needed. The second is that equations such as that due to Vinet require values of V, α, K_T and K_T' at a reference temperature which must itself lie above the Debye temperature. We have found that a simple approximation for αK_T below the Debye temperature using a cubic polynomial is remarkably succesful at alleviating both these problems and the resulting equations of state appear at this preliminary stage to work well down to temperatures typically around a quarter of the Debye temperature.

Another area which we are currently pursuing is the *ab initio* calculation of interionic potentials, which, as always, lie at the heart of most atomistic lattice simulations. Density functional theory, based on the electron gas model, has been widely used for over fifteen years for the evaluation of such potentials with considerable success; however, the theoretical foundations of this approach is somewhat questionable, and it is not clear why the most common formulations of the electron gas approach work as well as they do. More recent advances in electronic structure theory, such as the spin-coupled valence-bond approach, seem to offer alternative means of calculating potentials which is timely in view of the range of applications to which simulation methods are being applied. Initial results based on this approach are promising and will be reported in due course.

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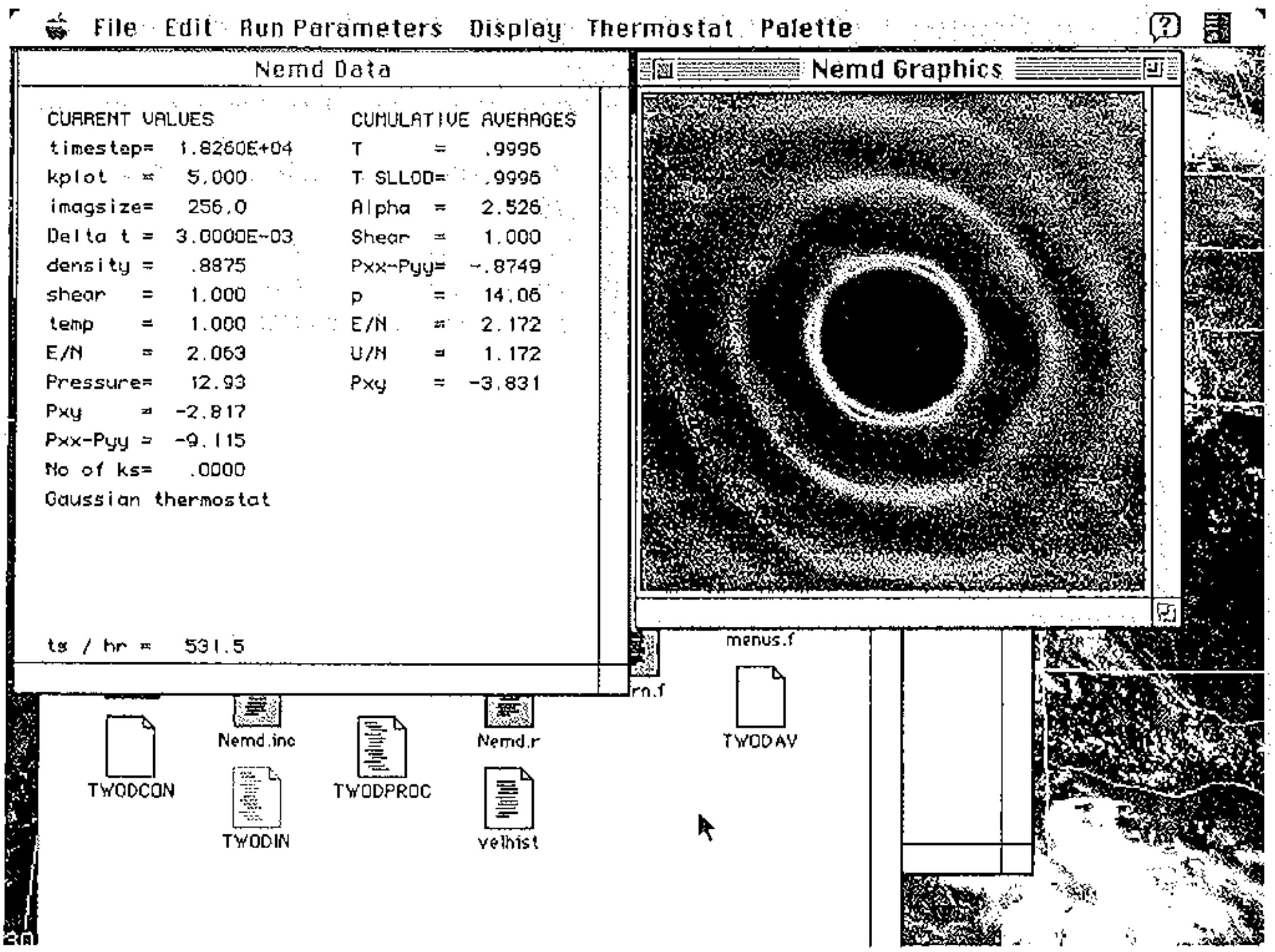


```
CURRENT VALUES                CUMULATIVE AVERAGES
timestep=  1.8260E+04         T        =   .9996
kplot    =  5.000             T SLLOD=     .9996
imagsize=   256.0             Alpha    =   2.526
Delta t =  3.0000E-03         Shear    =   1.000
density =    .8875            Pxx-Pyy=  -.8749
shear    =   1.000            p        =   14.06
temp     =   1.000            E/N      =   2.172
E/N      =   2.063            U/N      =   1.172
Pressure=    12.93            Pxy      =  -3.831
Pxy      =  -2.817
Pxx-Pyy =  -9.115
No of ks=   .0000
Gaussian thermostat



ts / hr =   531.5
```

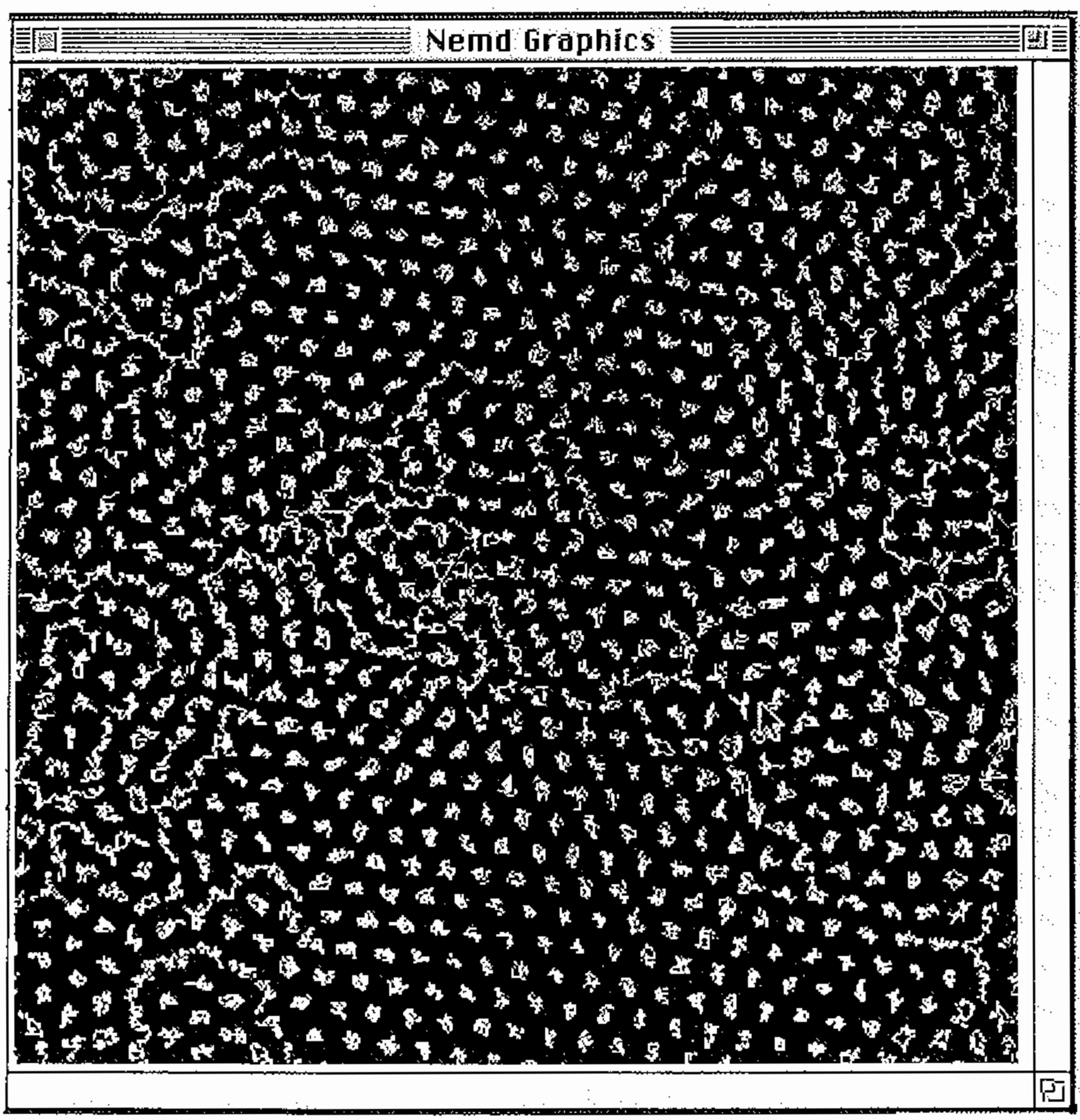
CONTENTS

§1. Introduction.

NonEquilibrium Molecular Dynamics is a computer programme that simulates a two-dimensional system of interacting atoms. The interactions between the atoms is purely repulsive. Depending upon the chosen temperature and density, the system can simulate fluids or solids (at a temperature of 1.0, the system freezes at a density ~0.9 - see display on next page for coexisting crystal and fluid). One can also apply a shear to the system to study the behaviour of a nonequilibrium system under the influence of a uniform applied shear rate. With a thermostat applied, you can the detailed behaviour and structure of a nonequilibrium steady state.

You can use the *mouse* to change either the conditions under which the fluid is simulated (temperature, density or shear rate), or to change the way in which you view the fluid. One can look at the instantaneous atomic positions, a trace of the past and present atomic positions, the distribution of atoms about any given atom and the distribution of x and y particle velocities. Other display modes show you the history of the pressure and the shear stress and the diffusion coefficient as a function of time.

For more detailed numerical work one can choose the precise state points for study, by editing an input ASCII file, *TWODIN*, and obtain outputs from a second ASCII file, *TWODPROC*. Time records of pressure and shear stress are available from tab delimited ASCII files which can then be read into graphing programmes. Similarly the velocity and pair distribution functions can be written to binary files which can be imported into image processing programmes for more detailed analysis.



Sample graphics screen using the *trace* display in the fluid - solid coexistence region.

§2. Driving the Programme

§2.1. menus

Apple

Allows you access to standard Macintosh Desk Accessories. It plays no direct role in the execution of *NonEquilibrium Molecular Dynamics*. You can however use this menus to find out the name and address of the programme's author.

File

Write out distribution
Writes out the near or far field pair distribution functions, the peculiar velocity distribution or the peculiar kinetic energy histogram depending on which of these distributions/histograms is being displayed in the current NEMD Graphics window. The pair and velocity distributions are written in single byte binary form and can be read by *NIH Image* or *NCSA Image*. In order for these programmes to read the image files produced by NEMD you will have to take note of *imagsize* given in the current values of the NEMD Data window. The peculiar kinetic energy histogram is exported as tab-delimitted ASCII text which can easily be read by *Cricket Graph, KaleidaGraph* or spreadsheeets for graphing. This permits an easy demonstration of the equilibrium Maxwell-Boltzmann distribution.

Write out time record
Writes out a time record containing:
time Pxy p Pxx-Pyy $<\Delta x(t)^2>$ $<\Delta x(t)^2>$ $<\Delta x(t) \cdot \Delta y(t)>$
where $\Delta x(t)=x(t)-x(0)$ and <...> denotes an average taken over all the particles in the system. The time origin for the displacements is set when the Einstein display is called up from the *Display* menu. When the shear is nonzero the coordinate displacements are not laboratory displacements but are instead integrals of the SLLOD momenta appearing in the equations of motion for shear flow, $\Delta x(t) = {}_0\int^t ds\ p_x(s)/m$, where $dx/dt = p_x/m + \gamma y$. The time record is written out as tab delimited text and can be read by word processors and graphics programmes.

Quit
Enables you to exit from the programme.

Edit
Is only included to allow the *Apple* menu to function. It serves no purpose in the execution of *NonEquilibrium Molecular Dynamics.*

Run Parameters
Most of the items under this menu are self explanatory.

The *timestep* is the time increment used to solve the differential equations of motion for the system. A typical value for this variable is 0.001-0.003. If the shear rate is increased to values larger than unity the *timestep* will have to be decreased otherwise the programme will not conserve energy or maintain a constant temperature correctly. If this problem becomes severe the programme can ***bomb*** with a series of messages stating that there are too many particles in a cell.

Kplot is the number of timesteps between updates of the graphics and text windows. The programme runs faster for larger values of *kplot.* The number of timesteps per hour is indicated under *Current Values* as *ts / hr =* in the *NEMD Data* window.

Restart simulation

Enables the user to start the programme from a crystal. This same result can be achieved by editing the ASCII file *TWODIN* and changing the value of *NTYPE* from 3 to 1. If the programme ***bombs*** this is the most efficient way of restarting the programme. If this is the case remember to decrease the shear rate (*SHEAR*), temperature (*TR*), density (*DR*) or timestep (*DELTA*) that initially caused the programme to ***bomb***.

Reverse direction of time

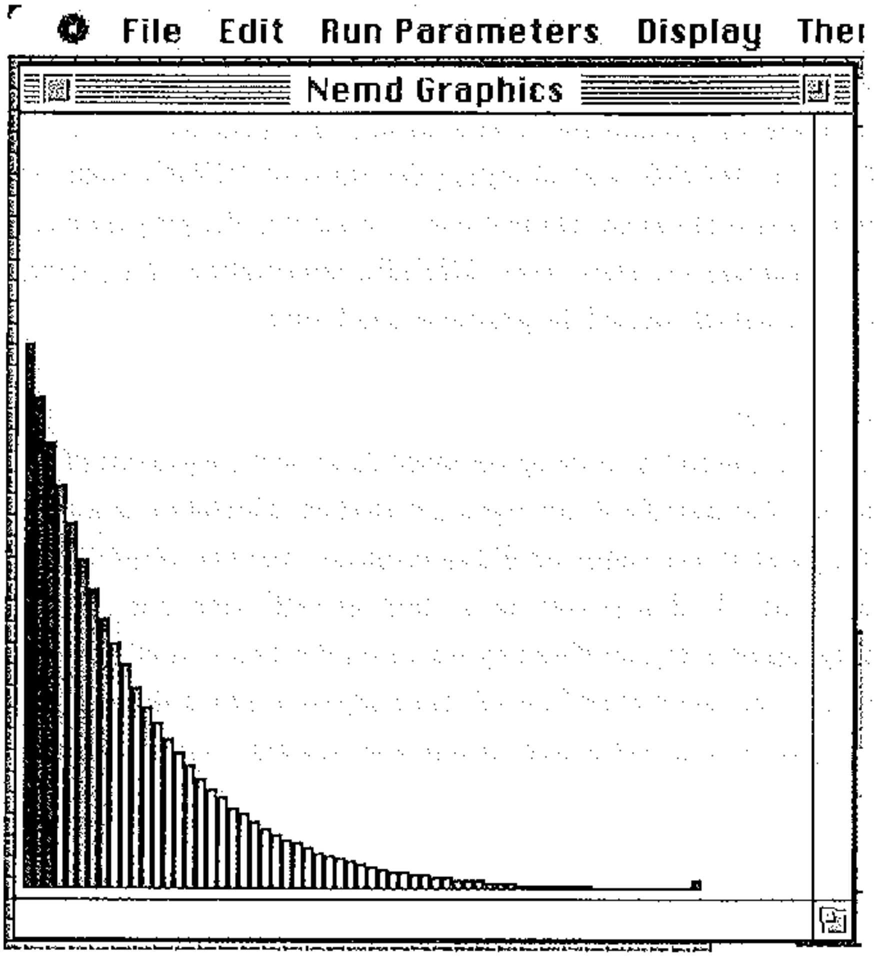
Does what it says. This is useful in teaching the reversibility of the equations of motion with or without a thermostat. For example if one starts a zero shear simulation at a temperature and density where the fluid is the stable equilibrium phase, one can observe that the initial crystalline phase melts. If this occurs in a short enough time one can return to the thermodynamically unstable crystal phase by reversing the direction of time. Likewise in a shearing fluid one can defy the Second Law of Thermodynamics for a short while generating a negative viscosity phase where heat is converted into work using *reverse direction of time.*

Display

Atoms

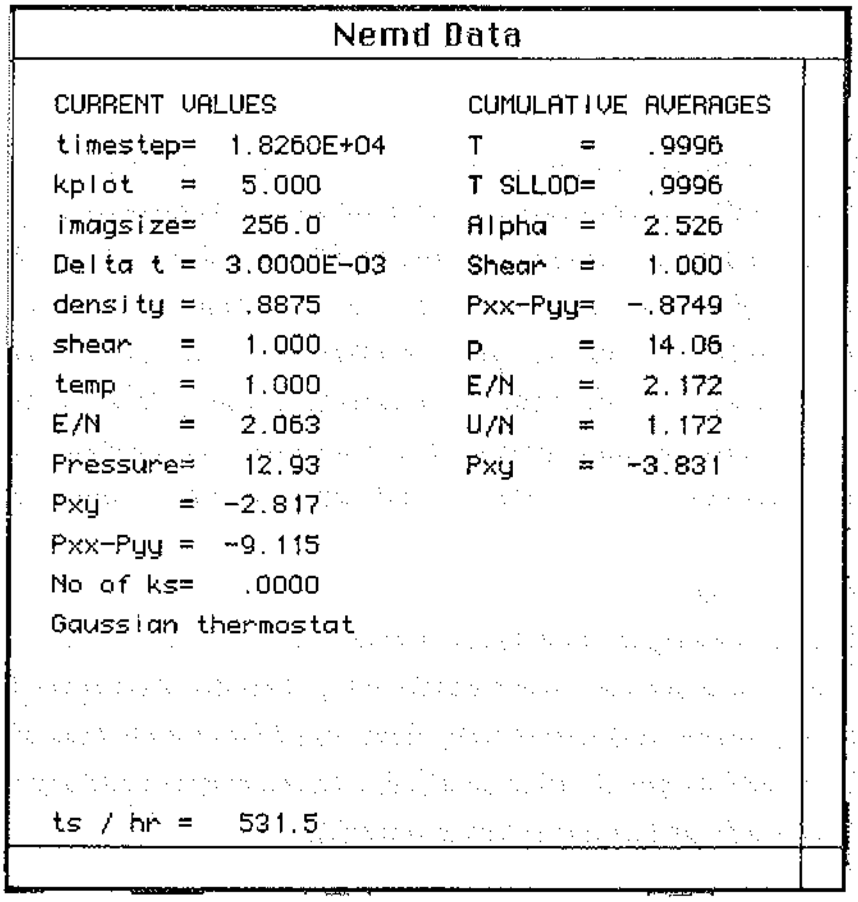
Shows the atomic positions as a (slow!) movie. The positions are updated at a rate that you choose by setting the value of *kplot* in the *Run Parameters* menu. The atoms are coloured according to their individual peculiar kinetic energies, those with higher kinetic energy (relative to the local average velocity) are shown in red). The *peculiar* velocity of a particle is the velocity measured with respect top the *local streaming velocity* . One can change the definition of the streaming velocity used for this purpose from within the *Thermostat* menu. The colour map for the *Atoms* and the *Trace* display is linear in the peculiar kinetic energy of the particles. There are 13 bins each $k_BT/6$ wide covering the range of kinetic energies from 0 to $2.166k_BT$.

Trace
Plots the atomic positions a pixels which are coloured according to their individual peculiar velocities.. These pixels are not erased as time progresses so that one can trace the past positions of individual atoms. This is very useful for showing the difference between the diffusive behaviour of atoms in the fluid phase and the trapped oscillatory behaviour of atoms in solids.



Sample *Kinetic Energy Histogram* display. This display also shows the colour palette used for the other displays.

Kinetic Energy Histogram
Displays the distribution of the peculiar kinetic energies of the atoms. As time evolves the displayed distribution denotes the cumulative time average. At equilibrium the average distribution should be the exponential Boltzmann distribution exp(kinetic energy/temperature). The colours used in the histogram use a different colour map from that used in the *atoms* and *trace* displays. For the peculiar kinetic energy histogram there are 62 bins which covering the range of kinetic energies from 0 to 6.2k_BT. These bins are coloured with 14 different colours.



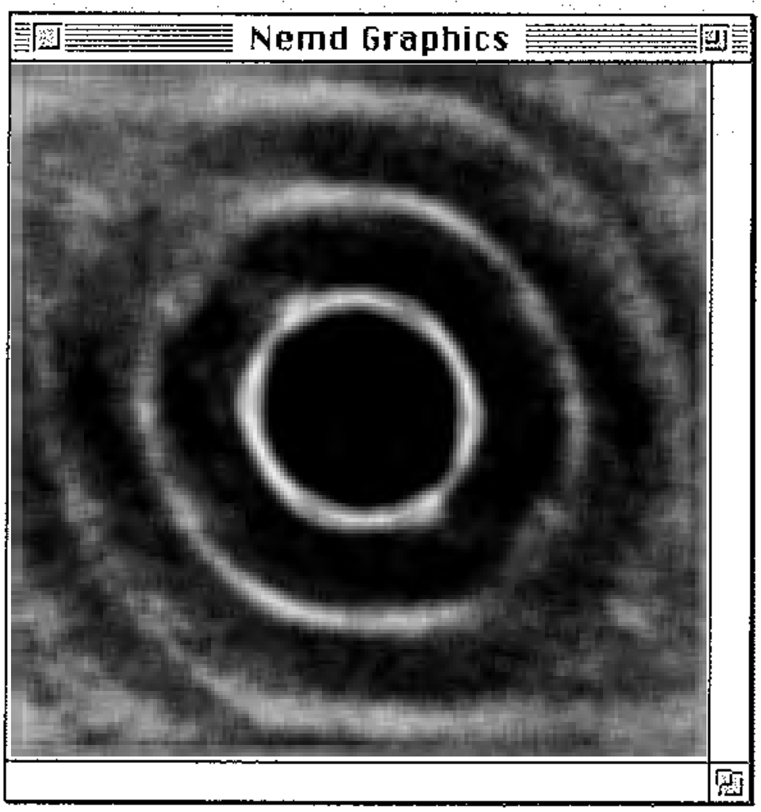
```
                          Nemd Data

CURRENT VALUES                    CUMULATIVE AVERAGES
timestep=  1.8260E+04             T        =    .9996
kplot    =   5.000                T SLLOD=     .9996
imagsize=   256.0                 Alpha    =   2.526
Delta t =  3.0000E-03             Shear    =   1.000
density =    .8875                Pxx-Pyy=   -.8749
shear    =   1.000                p        =   14.06
temp     =   1.000                E/N      =   2.172
E/N      =   2.063                U/N      =   1.172
Pressure=   12.93                 Pxy      =  -3.831
Pxy      =  -2.817
Pxx-Pyy =  -9.115
No of ks=    .0000
Gaussian thermostat




ts / hr =   531.5
```

Sample *Nemd Data* window. These parameters were used to generate the pair distribution shown below.



Sample *Pair distribution wide field* display.

Pair distribution near field

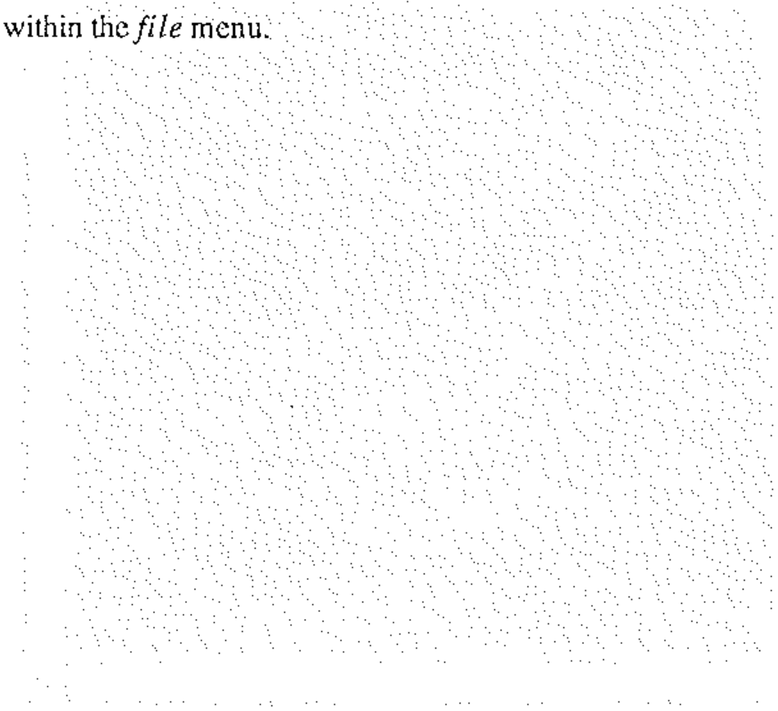
Shows the relative positions of particles in the system. If any given particle is located at the centre of the screen the other particles pack around it generating the so-called pair distribution. Neighbours are excluded from coming too close to the central particle by the repulsive interatomic forces. The plot is coloured according to the probability density - red denotes the highest probability while blue denotes the lowest. In a fluid phase the pair distribution function is isotropic while in the solid a sixfold pattern of spots is revealed. This distribution can be written to disk for importing into image programmes using *Write out Distribution* from within the *file* menu. *Near field* refers to the fact that we only show the first coordination shell.

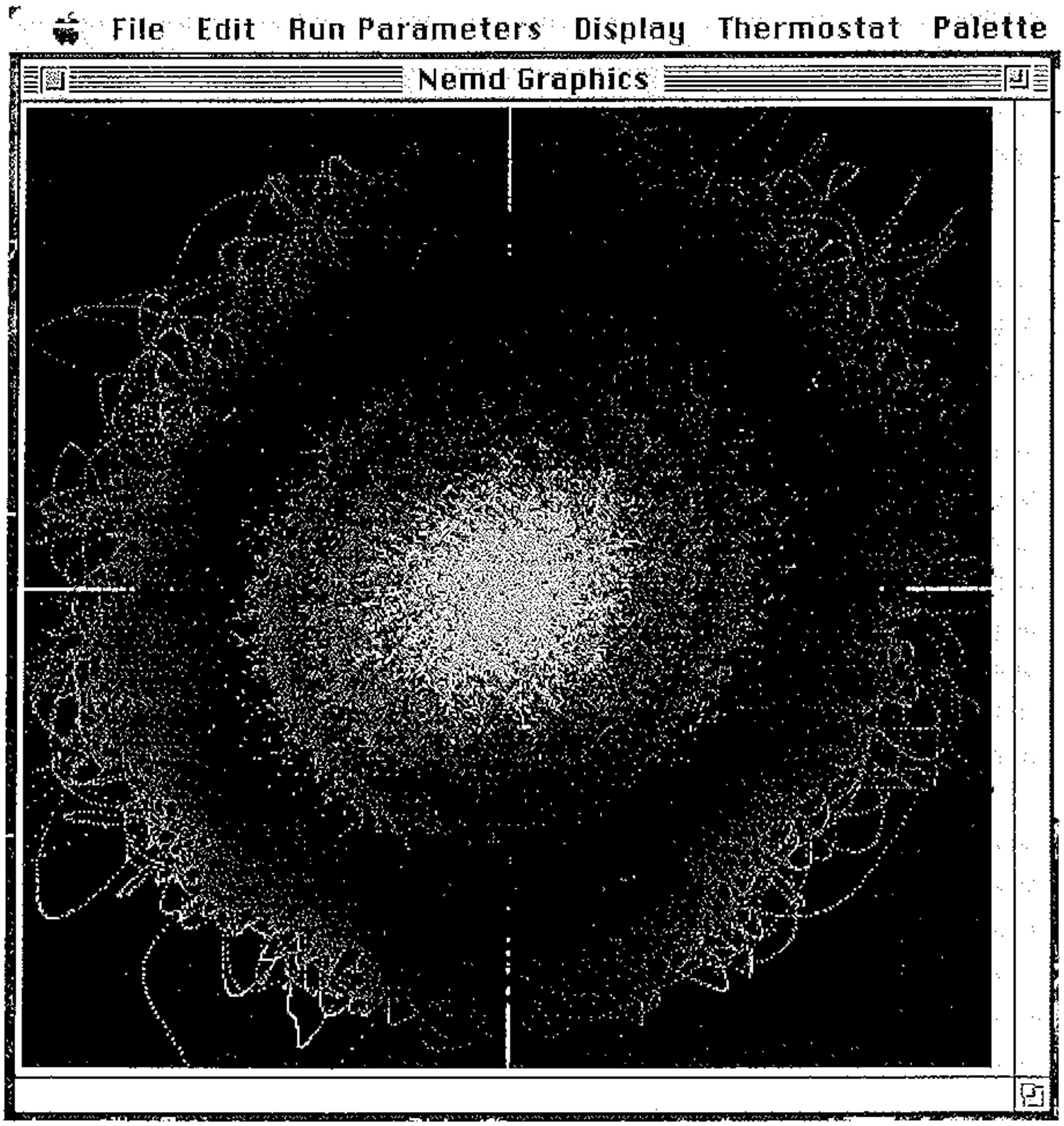
Pair distribution wide field

Same as above, but but showing the first three coordination shells. The increased range in the pair distribution slows the programme down considerably. This distribution can be written to disk for importing into image programmes using *Write out Distribution* from within the *file* menu. Using NIH IMAGE the pair distribution function can be Fourier transformed to give the static structure factor which can be measured experimentally.

Velocity Distribution

Shows the probability distribution of peculiar velocity. The white lines show the zeros of the x and y velocities.The range of peculiar velocities displayed in this window is ±4$\sqrt{(k_B T/m)}$. This distribution can be written to disk for importing into image programmes using *Write out Distribution* from within the *file* menu.





Sample output in the velocity distribution window for a shearing fluid.

Time Record

Shows the past history of the indicated elements of the pressure tensor as a function of time. This is very useful in studying the transient behaviour of systems to a suddenly applied shear rate. One can easily study stress overshoot by this means. The time record can be written out as a tab delimited text file which can be read by word processors and graphics programmes - use *write out time record* in the *file* menu.

Einstein Diffusion

Enables you to use Einstein's method of calculating the self diffusion coefficient for a fluid. You can verify that the diffusion coefficient is zero for a solid. In an equilibrium fluid the diffusion process is isotropic and $D_{xx}=D_{yy}$ while $D_{xy}=0$. In a fluid under shear neither of these conditions is satisfied. In high density fluids under shear the diffusion tensor is anisotropic but very nearly diagonal. At lower densities, D_{xy} can become quite large. When this display is active the time record which is written out to disk under the *File* menu includes the mean square displacements of the particles as a function of time.

Thermostat

Allows you to change the thermostats used in the simulation. The thermostat which is currently operating is shown in the *Nemd Data* window.

None

Is self explanatory. In the absence of an applied shear rate one can observe that Newton's equations of motion conserve energy. This can be used to check whether the current timestep is sufficiently small for energy to be conserved satisfactorily - typically < 0.2% drift in say 2,000 timesteps. If no thermostat is used for a system under shear, one can observe that the work done by the shear is converted into heat, raising the temperature of the system. At equilibrium, time averaging along an unthermostatted trajectory is equivalent to a microcanonical ensemble average.

Gauss

Runs at constant peculiar kinetic energy. In this case the streaming velocity at a point $\mathbf{r} = (x,y)$, is assumed to be $\mathbf{i}\gamma y$ where $\mathbf{i}$ is the x unit vector, γ is the value of the strain rate. At equilibrium, time averaging along a Gaussian isokinetic trajectory is equivalent to a microcanonical ensemble average for the kinetic part of phase functions and a canonical ensemble average for the configurational part of phase functions.

Nosé-Hoover

Uses an integral feedback mechanism to constrain the average peculiar kinetic energy. In this case the streaming velocity at a point $\mathbf{r} = (x,y)$, is assumed to be $\mathbf{i}\gamma y$ where $\mathbf{i}$ is the x unit vector, γ is the value of the strain rate. At equilibrium, time averaging along a Nosé-Hoover thermostatted trajectory is equivalent to a canonical ensemble average.

Nosé-Hoover k=1, k=2, k=3, k=4

Employs the Nosé-Hoover integral feedback thermostatting mechanism but uses a Fourier series technique to compute the instantaneous streaming velocity. Within Lees-Edwards shearing periodic boundary conditions if $\mathbf{v}$ is the laboratory velocity of any particle then $\mathbf{v}-\mathbf{i}\gamma y$ is a periodic function and can therefore be represented by a Fourier series. *k=1,2,3,4* refers to how many Fourier harmonics are used to represent this periodic function. The peculiar velocity of any particle is then defined as the instantaneous difference of $\mathbf{v}-\mathbf{i}\gamma y$ from the harmonic representation of the periodic velocity field. In this case the streaming velocity is associated with the instantaneous long wavelength velocity modes while the peculiar velocity is assumed to be given by the short wavelength modes. Choosing different values of k allows the user to choose the breakpoint between the 'long' and the short' wavelength modes. At equilibrium the time averages of phase functions and time correlation functions are independent of k. The value of k chosen from this menu is shown under the Current Values in the *NEMD Data* window.

Palette

Enables you to changes the colour palette for the programme. These changes are not saved to disk.

§2.2. INPUT FILE *TWODIN*

The programme can be driven by editing the input ASCII file *TWODIN*. A typical input looks like:

```
    1.00000   .900000  3.500000E-03
    1.12246  1  .000000  100.000  0
    1093076  3  0  1
    50  20  20  1.00000  .300000


TR,DR,DELTA
RCUT,NTIME,SHEAR,TAU,Nklim
KBMAX,NTYPE,NON,NGAUS
KSCAL,KPROC,KPLOT,scal,RDEL
```

Thus precise values of the set temperature density and shear rate may be chosen by using an ASCII editor. A dictionary of variable names used in this file follows:

TR	desired temperature
DR	desired density
DELTA	timestep for integration of equations of motion
RCUT	cutoff distance for interaction potential. If this is near $2^{1/6}$ the programme employs a WCA potential. If it is set at a larger value say, 2.5, the programme will employ a Lennard-Jones potential with the specified cutoff distance. Clearly a Lennard-Jones potential will run more slowly than a WCA potential.
NTIME	unused
SHEAR	the strain rate, $\partial u_x/\partial y$
TAU	the Nosé-Hoover time constant τ, used in the equation of motion for the thermostatting multiplier, α

$$d\alpha/dt = [\Sigma p_i^2/2m]/Nk_BT - 1)/\tau$$

NKLIM Number of harmonics, N_k, used to define the streaming velocity. The number of degrees of freedom in the system is $2N-2-(2N_k+1)^2$. N is the number of particles moving in 2 dimensions. For example the temperature should be calculated from the equation,

$$k_BT = \Sigma p_i^2/\{m[2N-2-(2N_k+1)^2]\}$$

KBMAX The max number of timesteps before the programmes stops.

NTYPE Control parameter: 1. means start from crystal **This is very important for restarts when the programme is bombing.**

2. means reinitialise the averages contained in the TWODPROC file.

3. is the normal setting. It just means continue the present run from the end-point of the previous and continue to accumulate averages of thermodynamic properties.

NON control parameter: leave set to zero.

NGAUS control parameter: 0. means turn off thermostats

1. means use Gaussian isokinetic thermostat.

2. means use Nosé-Hoover thermostat for some N_k.

KSCAL not used

KPROC frequency of writing to disk. Note quitting from the programme automatically invokes a full write to disk of all restart and averaging files.

KPLOT frequency of drawing the screen, in timesteps

SCAL not used

RDEL thickness of neighbour list shell. 0.3 works reasonably well but programme speed may be improved by tuning this value and monitoring programme speed in timesteps/hr in the *NEMD DATA* window.

§2.3. OUTPUT FILE *TWODPROC*

This file can be opened with a word processor or ASCII file editor to show the accumulated thermodynamic averages. a typical output might be:

```
     SIMULATION PARAMETERS

Set Temperature           =     1.0000000
Density                   =      .9000000
Current timestep          =      .0035000
Potential Cutoff distance =     1.1224620
Number of Particles       =           224
Simulation Cell Length    =    15.7762120
Simulation Cell Area      =   248.8889000

NTYPE  =     3
NON    =     0          NGAUS  =     1
No of wavevectors defining streaming velocity  =     0


KB =    12980     No of steps  =        12980     TIME =        45.4300

     Simulation Averages

Temp using Nk-vectors for streaming velocity =   1.00000
Temp using 0k-vectors for streaming velocity =   1.00000
Thermostat Mutiplier, Alpha   =   -.00009
Shear Rate                    =    .00000
Pxx - Pyy                     =    .06965
Pressure, 0.5*(Pxx +Pyy)      =   9.93919
Internal  Energy per Particle =   1.78405
Potential Energy per Particle =    .78403
xy-element of pressure tensor =   -.05467

     Diffusion Coefficients
D(t)  =<(delr(t))**2>/4t     = none
Dxx(t)=<(delx(t))**2>/4t     = none
Dyy(t)=<(dely(t))**2>/4t     = none
Dxy(t)=<(delx(t))*dely(t)>/4t= none
```

This is all fairly self explanatory. To obtain estimates of the various elements of the diffusion tensor, *Einstein Diffusion* under the *Display* menu must have been selected.

§2.4. Exporting raster files to NIH Image

The default size of the *NEMD Graphics* windows is 256*256. This is convenient for using Fast Fourier Transform routines and computing the static structure factor since 256 is a power of 2. The size of these images can however be changed by the usual method of 'stretching' windows. For exporting image files to NIH Image or NCSA Image, you will need to take note of the value of *imagsize* as reported in the *NEMD Data* window.

We will now give the instructions for exporting an image to NIH Image for computing the structure factor. After the image generation is complete, choose *Write out Distribution* from the *File* menu. At the prompt for choosing a name for the raster file we suggest that you use the value of *imagsize* in the file name so that you will not forget it. Then quit from *NEMD*. Open NIH Image and select *import* from its *file* menu. At the prompt select *special, 8bit* and fill in the value of imagesize in the dialog box. Click *OK* and the image will be displayed.

If *imagsize* is a power of 2 you can compute the Fourier Transform yielding the static structure factor.

§3. Technical Details

§3.1. Equations of Motion

The 224 particles interact via the WCA pair potential $\phi(r)=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$, $r<2^{1/6}$; $\phi(r)=0$, $r>2^{1/6}$. The readouts are given in reduced units for which the potential parameters ε, σ are unity as is the atomic mass, m. The system is subject to a shear rate $\gamma = \partial u_x/\partial y$ and the equations of motion are given by the thermostatted SLLOD equations[1].

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i + \mathbf{i}\gamma y_i \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{i}\gamma p_{y_i} - \alpha \mathbf{p}_i \end{aligned} \qquad (1)$$

Using the reduced units $\mathbf{q}_i$ stands for $\mathbf{q}_i/\sigma$, $\mathbf{p}_i$ for $\mathbf{p}_i/(m\varepsilon)^{1/2}$, t for $t\,(\varepsilon/m\sigma^2)^{1/2}$ with $(\varepsilon/m\sigma^2)^{1/2}$ ($\approx 5 \times 10^{11}$Hz for argon) and γ for $\gamma(m\sigma^2/\varepsilon)^{1/2}$. $\mathbf{i}$ is a unit vector in the x-direction. The $\mathbf{p}_i$ are peculiar momenta, defined in terms of the peculiar velocities, i.e., the velocities of the particles with respect to the (local) fluid velocity $u_x(y)=\gamma y$. The last term in (1) represents an thermostat which removes heat from the system so as to keep the kinetic temperature, $T_k=(1/Nk_B)\Sigma_i(p_i^2/2m)$ constant. P_{xy} is the xy–element of the pressure tensor[1], $P_{xy}V = \Sigma_i[p_{xi}p_{yi}/m + F_{xi}y_i]$. The equations (1) are equivalent to Newton's equations of motion in the presence of frictional forces $-\alpha\mathbf{p}_i$, if a constant shear rate γ is imposed on the fluid at $t = 0^+$. This is illustrated in the figure below.

The equations of motion (1) are supplemented by Lees-Edwards periodic boundary conditions.[1]. In their adiabatic form the SLLOD equations of motion give an exact description of adiabatic planar Couette flow arbitrarily far from equilibrium.

These time varying periodic boundary conditions can be represented in a number of apparently different but equivalent ways. One such diagrammatic representation is shown below. The blue hatched square is the primitive cell (i.e. represents the coordinates of the set of N particles that we arbitrarily choose to define the N-particle system configuration. The red hatched square is the Minimum image cell of particle (1,j). It is a cell of the same size as the primitive cell but it is centred on particle (1,j). Within the infinite array of periodic images of particles, it contains those that are closest to (1,j). The particles that can interact with (1,j) are chosen from those within the minimum image cell of (1,j). Thus (1,j) can interact with (9,i) but not with (1,i) even though (1,i) is in the primitive cell.

The SLLOD equations of motion give an exact representation of planar Couette Flow

Assume the strain rate is a step function of time.

$$\frac{d\mathbf{q}_i}{dt} = \frac{\mathbf{p}_i}{m} + \mathbf{i}\gamma y_i$$

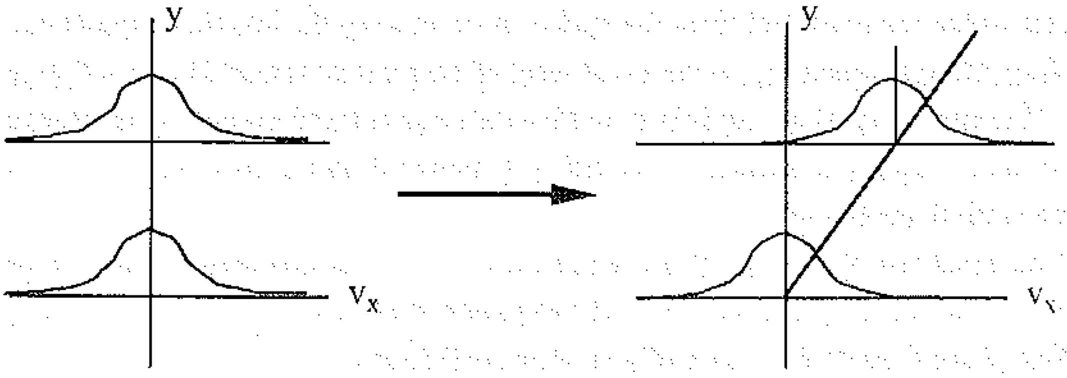
$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \mathbf{i}\gamma p_{yi}$$

SLLOD applied to the equilibrium ensemble is equivalent to Newton applied to the local equilibrium ensemble

$$m\frac{d^2\mathbf{q}_i}{dt^2} = \mathbf{F}_i + \mathbf{i}m\frac{d\gamma(t)}{dt}y_i$$

$$= \mathbf{F}_i + \mathbf{i}m\gamma\delta(t)y_i$$

Probability of v_x as a function of y

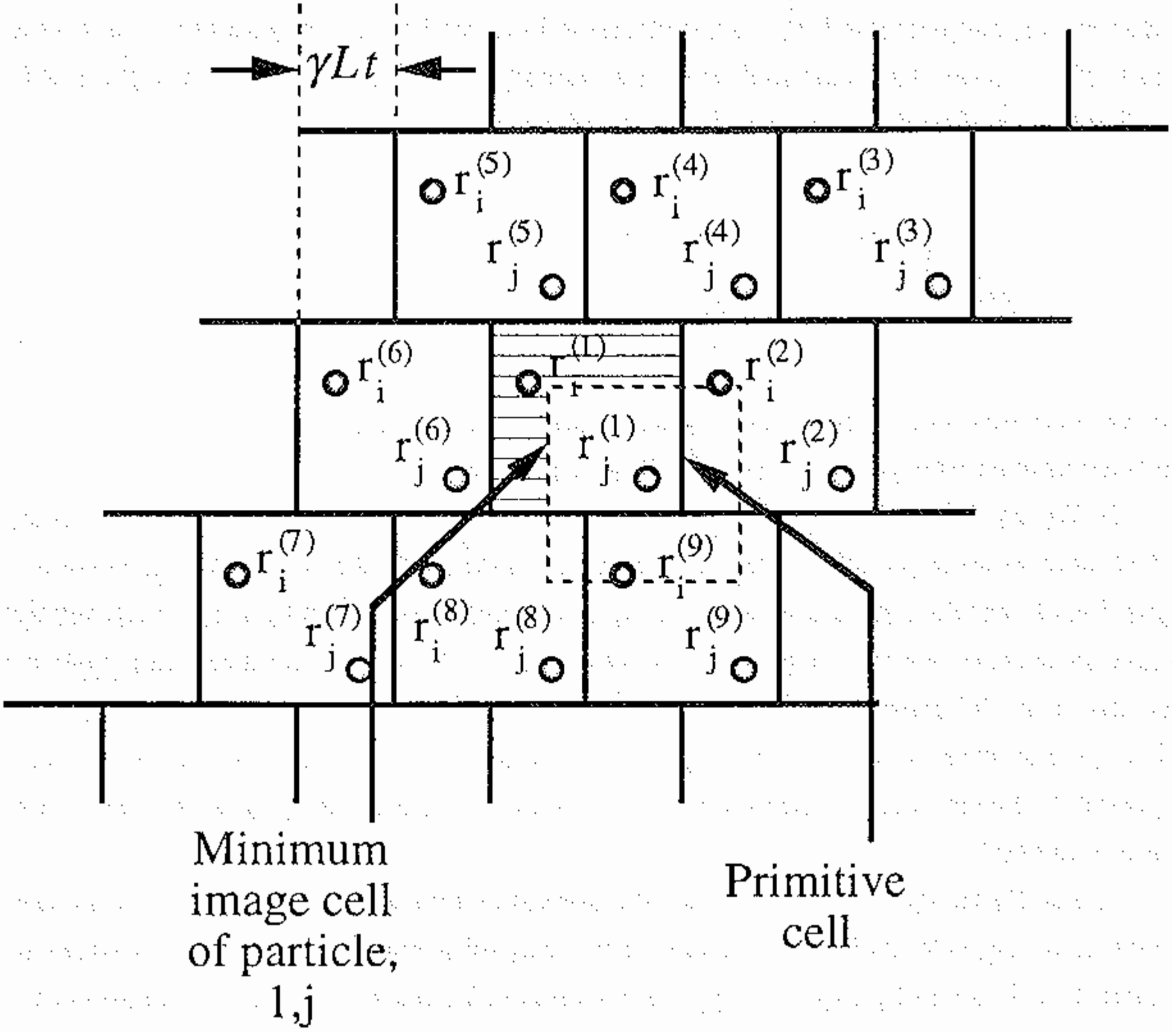


Equilibrium distribution at $t = 0^-$

Local equilibrium distribution at $t = 0^+$

During the course of time particles diffuse and convect through the system. If a particle moves through a vertical face of the primitive cell it is replaced in the primitive cell by one of its images moving with the same SLLOD and laboratory velocities, with the same y coordinate but with an x-coordinate ±L different from its own x-coordinate. If a particle moves out of the primitive cell through an horizontal face, matters are more complex. It will be replaced by an image of itself but in this case the image particle differs in y by ±L. Because however of the time dependent horizontal motion of the cells above and below the primitive cell, the x-coordinate can also be different from that of the particle in the primitive cell that it replaces.

Further, although it enters the primitive cell with the same SLLOD momentum as its image its laboratory momentum will be different. From the figure you can deduce that the SLLOD momentum of any particle is identical to that of each of its images. This is obviously not so for the laboratory velocities.



Lees-Edwards periodic boundary conditions.

§3.2. The Nosé-Hoover k=1,k=2,k=3,k=4 Thermostats

Consider a fluid of N particles of mass, m, interacting via a pair potential, $\phi(r)$, in volume V (density, n = N/V) in planar Couette flow. The properties of the system can be simulated with the SLLOD algorithm[1], supplemented by Lees-Edwards periodic boundary conditions, which are known to give an exact description of adiabatic planar Couette flow. If the algorithm is supplemented with a thermostat to keep the kinetic temperature, T, constant, the SLLOD equations for isothermal flow in a Cartesian coordinate system with a gradient in the y-direction and flow in the x-direction can be written;

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m} + \mathbf{i}\gamma y_i$$
$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \mathbf{i}\gamma p_{iy} - \alpha m\left(\frac{\mathbf{p}_i}{m} - \mathbf{u}_S(\mathbf{r}_i)\right) \tag{2}$$

where the term involving a thermostatting multiplier, α, in (2) represents the thermostat whose form is determined from Gauss' principle of least constraint.

In Eq.(2), $\mathbf{F}_i = -\Sigma_j\, \partial\phi(r_{ij})/\partial\mathbf{r}_i$, $\mathbf{i}$ is the unit vector in the flow direction and $\mathbf{p}_i$ is the SLLOD momentum of particle i. The velocity $\mathbf{u}_S(\mathbf{r}_i)$ is the local SLLOD streaming velocity at the position of particle i, defined in terms of the local number density, $n(\mathbf{r}) \equiv \Sigma_i\delta(\mathbf{r}-\mathbf{r}_i)$, and the momentum current, $\mathbf{J}_S(\mathbf{r}) \equiv \Sigma_i\mathbf{p}_i\delta(\mathbf{r}-\mathbf{r}_i) \equiv mn(\mathbf{r})\mathbf{u}_S(\mathbf{r})$. Note that the streaming velocity measured in the laboratory coordinate frame, $\mathbf{u}_L(\mathbf{r})$, is the sum of nonzero and the zero wavevector components: viz, $\mathbf{u}_L(\mathbf{r}) = \mathbf{u}_S(\mathbf{r}) + \mathbf{i}\gamma y$, where γ is formally the zero wavevector component of the strain rate which governs the motion of the infinite array of shearing Lees-Edwards[1] unit cells.

At low Reynolds number the stable laboratory streaming velocity is $\mathbf{i}\gamma y$ and the average SLLOD streaming velocity is zero. Hence, at low Reynolds number, the peculiar velocity of any particle, i, is given by $d\mathbf{r}_i/dt - \mathbf{i}\gamma y_i = \mathbf{p}_i/m$, and the kinetic temperature is defined in the usual way, namely; $T = \Sigma_i(\mathbf{p}_i^2)/2mNk_B$, where k_B is Boltzmann's constant.

At higher Reynolds number we cannot make *a priori* any prediction about the finite wavevector components of the streaming velocity, it is clear that the SLLOD momenta, $\{\mathbf{p}_i\}$, defined in Eq.(2), are periodic functions of displacement along the time dependent Lees-Edwards axes. The Lees-Edwards periodic boundary condition implies that the SLLOD momentum of any particle is identical to the SLLOD momentum of any image of that same particle. Thus the instantaneous finite wavevector components of the streaming velocity can be computed from a Fourier series analysis as the simulation evolves in time.

The number density, $n(\mathbf{r})$, and SLLOD momentum current, $\mathbf{J}_S(\mathbf{r})$, are periodic functions of the primitive lattice vectors describing the instantaneous alignment of the Lees-Edwards periodic boundaries. These lattice vectors are time dependent and non-orthogonal. We compute $n(\mathbf{k})$ and $\mathbf{J}_S(\mathbf{k})$ for a number of $\mathbf{k}$-vectors given by $(N_x,\ N_y) = (2i_{max}+1,$

$2j_{max}+1$). On transforming from the **k**-domain back to real space, the SLLOD streaming velocity $\mathbf{u}_S(\mathbf{r})$ is evaluated from its defining equation. If i_{max}, j_{max} are equal and nonzero for each Cartesian component of $\mathbf{u}_S$, the algorithm allows the system to take on any possible form for the instantaneous streaming velocity as a function of position as long as the length scale for variations in the streaming velocity is greater than $L/(2i_{max}) \equiv \lambda_{min}$.

In this programme we set, $i_{max} = j_{max}$ for both Cartesian components of $\mathbf{u}_S$. Thus *Nosé-Hoover k=1* refers to the situation where $i_{max} = i_{max} = 1$, *Nosé-Hoover k=2* refers to the situation where $i_{max} = i_{max} = 2$,... etc.

Once the local streaming velocity is known, the kinetic temperature follows;

$$(N - N_k)k_B T = \sum_{i=1}^{N} \frac{1}{2} m\left(\frac{\mathbf{p}_i}{m} - \mathbf{u}_S(\mathbf{r}_i)\right)^2 = \sum_{i=1}^{N} \frac{1}{2} m(\dot{\mathbf{r}}_i - \mathbf{u}_L(\mathbf{r}_i))^2 \qquad (3)$$

where $N_k = N_x.N_y$ is the total number of k-vectors used to determine the local streaming velocity. We use the identity at equilibrium of the temperature from (3) with the usual equipartition relation for the temperature, to verify our coding of the PUT algorithm.

The simulations use a Nosé-Hoover thermostat to keep the temperature constant; that is, the multiplier, α, of Eq. (2) fixed the average peculiar kinetic energy, defined by Eq. (3), to the preset value, T_s, from the feedback equation,

$$\frac{d\alpha}{dt} = \frac{(T / T_s - 1)}{{\tau_s}^2} \qquad (4)$$

where the reciprocal of τ the feedback time, is set in the ASCII file *TWODIN*.

§3.3. Diffusion Under Shear

The self diffusion coefficient describes the diffusive flux, **J**, of labelled atoms induced to flow by the presence of a concentration gradient, ∇n, in the number density of those labelled atoms. The convective contributions to the flux are removed. Thus the macroscopic equations describing diffusion under shear are the defining constitutive relation,

$$\mathbf{J} = -\mathbf{D} \bullet \nabla n \tag{5}$$

and the convective diffusion equation,

$$\frac{\partial n}{\partial t} + \mathbf{u} \bullet \nabla n = -\nabla \bullet \mathbf{D} \bullet \nabla n \tag{6}$$

When a single component fluid is subject to steady planar Couette flow, $\gamma=\partial u_x/\partial y$, the self diffusion coefficient becomes a self diffusion tensor (SDT) with shear rate dependent components. In Cartesian coordinates the steady state diffusion tensor can be written as,

$$\mathbf{D} = \begin{pmatrix} D_{xx} & D_{xy} & 0 \\ D_{yx} & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}. \tag{7}$$

The xz,yz,zx and zy are identically zero because of symmetry. In previous work[2] the following Green-Kubo relations for the various components of this tensor were derived.

$$D_{\alpha\beta} = \int_0^\infty \left\langle p_\alpha(t) p_\beta(0) \right\rangle_\gamma dt \tag{8}$$

where α,β=x,y,z. The ensemble average is taken over shearing steady states, hence the subscript γ. We can operationally define this ensemble by considering some equilibrium ensemble at $t = -\infty$, being subject for all subsequent time, to thermostatted planar Couette flow (equations (1,2)). At $t=0$ the system is assumed to have completely relaxed to a steady state. Thus the time correlation function referred to in (8) correlates the Cartesian components of momentum at times 0,t long after the transients leading to the establishment of the steady state, have decayed.

Note that the p_α in this equation are the SLLOD momenta of (1). These relations can be integrated to give the Einstein relations for the mean square displacement. The diagonal components become

$$\left\langle q_\alpha(t)^2 \right\rangle_\gamma = 2D_{\alpha\alpha}t \tag{9}$$

where

$$\mathbf{q}_i(t) \equiv \mathbf{r}_i(0) + \int_0^t ds \frac{\mathbf{p}_i(s)}{m} \tag{10}$$

is the convected, Lagrangian position of particle **i**. It is not possible to obtain separate Einstein relations for the two nonzero off diagonal elements of the diffusion tensor[3] it is only possible to obtain an Einstein relation for the sum of these two elements,

$$\left\langle q_x(t) q_y(t) \right\rangle_\gamma = \left(D_{xy} + D_{yx}\right)t \tag{11}$$

In general the self diffusion tensor for a fluid under Couette flow is non symmetric. The x–mass current generated by a y-concentration gradient is not necessarily equal to the y-current generated by an x-gradient. However, it is easy to prove that by measuring the time dependence of concentrations alone, it is only possible to determine the symmetric part of the diffusion tensor[3].

An alternative route to the Green-Kubo relations for the diagonal components of the Self Diffusion Tensor is to derive the above Mean Square Displacements from the macroscopic convective diffusion equation[3,4,5]. One then assumes that the macroscopic and microscopic MSDs are the same and GK relations are thus recovered from the MSDs instead of the the other way around. Unfortunately, it is not possible to derive any GK relations for the off diagonal elements by this method.

Final remarks: at equilibrium (γ=0), the relations given above reduce to the standard equilibrium Green-Kubo and Einstein relations for the self diffusion tensor. When any of the *Nosé-Hoover k=1,k=2,k=3,k=4* Thermostats are selected the expressions given above for the diffusion tensor are evaluated with the $\mathbf{p}_i$ above being peculiar momenta evaluated relative to the streaming velocity obtained from the Fourier-Series fit of the streaming velocity using k=1,2,3 or 4.

§4. Availability

Write to:

Prof. Denis J. Evans,
Research School of Chemistry, Australian National University, GPO Box 4 Canberra, A.C.T., 2601, Australia. Phone 61-6-249 3767, Fax: 61-6-249 0750. Please include high density (i.e. 1.44MB floppy disk).

You may find it much easier (and faster!) to retrieve the programme under anonymous ftp from a UNIX file server at ANU. The machine's name is: *rschp1.anu.edu.au*, (IP number is 150.203.35.20). The binhexed programme is available in the subdirectory */pub* and the name of the file is *Nemd_v.8.sit.hqx*. Within this file there are two of items: *About NEMD* and *NEMDII v.8 distribution*. *About NEMD* contains the documentation written as a MacWrite II file, while the actual programmes are contained within *NEMDII v.8 distribution*. There are 3 subdirectories containing programmes for 56, 224 and 896 particles. Each of these subdirectories contains a second programme called *Drawpict*. This programme can be used to produce LaserWriter quality images of the atomic configurations. The other files are data files of one sort or another. In order for the programme to execute properly do not move or rename these data files.

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