

LEADING COM  
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 and Lattice Simulations of Condensed Phases.

Number 20

March 1986

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PLANT AND ANIMAL KINGDOMS

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## Editorial.

As this newsletter leaves Daresbury, we wait to hear where the proposed Cray XMP 48 will go. The Cray XMP 48 was recommended by the Forty Report to help restore some of the vitality to British computer science. It is now certain that the computer will be housed in an SERC establishment, but at the time of writing, it is not known whether it will be stationed at Daresbury or Rutherford. Naturally, as Daresbury is the home of the nine Collaborative Computational Projects (CCP's) we hope it will come here. We believe that we are in the best position to exploit the computer scientifically. However there are other considerations, such as the suitability of the current mainframes to act as the front-end etc., which have a bearing on the quality of user service. We await the news of the decision with more than a little interest!

We extend our thanks to the contributors to this month's newsletter and we hope that our readers will find our combined efforts interesting.

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- |                                     |   |
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## General News.

a) The CCP5 conference on 'The Glass Transition' is imminent. It will be held in Oxford from April 9th. to 11th. 1986, at Wadham College. A circular giving more information, and including a registration form, is attached to the back of this Newsletter.

b) Readers may be interested to know of an international conference on 'The Impact of Supercomputers on Chemistry' is being organised and will take place in the University of London from 13 - 16 April 1987 (note: next year!). The conference will cover all aspects of the use of supercomputers; applications and methodology. Some of the areas to be covered include: the simulation of condensed matter, molecular mechanics, simulation of biological systems, protein crystallography and molecular collision processes. A session on hardware developments and a Computer Exhibition is also planned. Plenary lectures will be given by M.J. Gillan, H.J.C. Berendsen, D. Ceperley, E. Clementi and T.L. Blundell (some familiar names there!) among others. Further information will become available in the late summer of 1986.

Enquiries regarding the conference should be addressed to Dr. J. Altmann, ISOC 87 Secretariat, Room 209, University of London Computer Centre, 20 Guildford Street, London WC1N 10Z. (Telex 8953011).

c) U.K. CCP5 participants are reminded that at Daresbury Laboratory the S.E.R.C. has placed a FPS 164 attached processor, which is available for grant supported computing within the Science Board Community. In the first year of its operation U.K. research groups are invited to apply informally to the Director of Daresbury Laboratory (Professor L.L. Green) for time on the FPS for benchmarking purposes. If the FPS proves viable for a given project, a formal application (using the familiar forms RG2 and AL54) may be made. Advice on using the FPS at Daresbury may be obtained from the User Interface Group (in the person of Dr. D. Taylor) or from the CCP5 representative Dr. W. Smith. A document entitled 'Using the FPS Attached Processor at the Daresbury Laboratory' by Dr. M.F. Guest is available from the User Interface Group.

CCP5 members who are registered users of the Daresbury Computing facilities (including those using the FPS) should note that their representative on the Daresbury Computer Users Consultative Committee (DCUCC) is Dr. W. Smith of the Theory and Computational Science Division. Any matters (complaints, comments, recommendations etc.), which CCP5 users would like to be put before the Daresbury Computer Users Forum (DCUF) for discussion should be forwarded to Dr. W. Smith.

Daresbury recently implemented its own version of FTP, which enables users to transfer files to sites on the JANET network. The

system is working satisfactorily. Another recent implementation has resulted in a change in the way the ARCHIVE system works. From now on archived datasets will disappear immediately from the users' directory, and will no longer fill up the users' filestore for long periods.

d) The Rutherford and Appleton Computer Centre report that they intend to install the SLAC Batch system under VM. This will be completely independent of the MVS batch and run under CMS. It is hoped that the introduction of the SLAC Batch will lead to better use of the system's resources. Further information will be available on the online documentation USDOC 193. Other areas of work that are of general interest include a revamping of the useful RAL IBM library RHELIB (for FORTRAN 77) and the development work on the Graphics Kernel System (GKS), which RAL intend to make available on as many SERC machines as possible. GKS is a standardised graphics package, which will allow portability of graphics codes.

RAL is the JANET gateway for the long awaited European Academic Research Network (EARN), which connects about 250 computers Europe-wide for file transfer and mail communication between academic centres. All academic computing centres have been asked to join EARN, which currently implies no financial commitment, though users are required to use EARN in a responsible way. Already several people connected with CCP5 have used this facility to transfer software across Europe. Enquiries about EARN should be addressed to Paul Bryant at RAL.

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

On the AMDAHL 470/V8 ULCC intend to field trial a new version of the MVS operating system, MVS SP1.3 L8406B, in late March 1986. A host of changes (mostly minor) will result. Perhaps the most significant of these will be the partial implementation of the Disc Space Scheduler (DSS), which represents an important change in the management of disc space. In particular, users who have a penchant for exceeding their budgets will find that the system will prevent them from doing so. These changes were originally scheduled for last year. A new release (4.0) of the VS FORTRAN compiler will become the production version in April. One of the most useful features of this will be the automatic double precision option AUTODBL.

f) The University of Manchester Regional Computing Centre has announced that they intend to upgrade the AMDAHL 470/V8 operating system to MVS SP 1.3.3 and this is currently undergoing trials. Its introduction is not likely to cause users problems. On the CYBER 205 the operating system is to be upgraded to VSOS 2.2 following user trials in March 1986. The new operating system is expected to improve user - friendliness and system performance by allowing multiple jobs for each user, improving small job throughput and through a redesign of the file system. The VAST precompiler is now available at level 1.22 and the NAG Graphical Supplement Mark 2 is also available.

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

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

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

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

i) Anyone wishing to make use of the CCP5 Program Library is invited to do so. Documents and programs are available free of charge to academic centres upon application to Dr. M. Leslie (\*) at Daresbury Laboratory. Listings of programs are available if required but it is recommended that magnetic tapes (to be supplied by the applicant) be used. It may also be possible to transfer a small number of programs over the JANET network to other computer centres in the U.K.. Users wishing to send magnetic tapes are instructed to write to Dr. Leslie for information before sending the tape. PLEASE DO NOT SEND TAPES WITHOUT CONTACTING DR. LESLIE FIRST. Delays are caused by applicants sending new tapes which have to be initialised at Daresbury (i.e. tape marks have to be written

on them). Also tapes sent in padded bags have to be cleaned before use. Please do not use this form of packing. (A list of programs available follows in the next few pages.)

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

\* (Full address: S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.)

## List of Programs in the CCP5 Program Library.

MDATOM by S. M. Thompson.

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

HMDIAT by S. M. Thompson.

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

MDLIN by S. M. Thompson.

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

MDLINQ by S. M. Thompson.

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

MDTETRA by S. M. Thompson.

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



MDPOLY by S. M. Thompson.

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

ADMIXT by W. Smith.

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

MDMIXT by W. Smith.

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

MDMULP by W. Smith.

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

MDMPOL by W. Smith & D. Fincham.

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

DENCOR by W. Smith.

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

CURDEN by W. Smith.

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

HLJ1 by D. M. Heyes.

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

HLJ2 by D. M. Heyes.

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

HLJ3 by D. M. Heyes.

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

HLJ4 by D. M. Heyes.

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

displacements and radial distribution function.

HLJ5 by D. M. Heyes.

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

HLJ6 by D. M. Heyes.

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

MCRPM by D. M. Heyes.

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

SURF by D. M. Heyes.

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

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

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

MDATOM by D. Fincham.

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

MDDIAT by D. Fincham.

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

MDDIATQ by D. Fincham.

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

MDIONS by D. Fincham & N. Anastasiou.

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

MDMANY by D. Fincham & W. Smith.

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

CARLOS by B. Jonsson & S. Romano.

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

MCN by N. Corbin.

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

SCN by N. Corbin.

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

SMF by N. Corbin.

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

#### STATIC SIMULATION CODES

CASCADE by M. Leslie and W. Smith.

Calculates the structure and energy of a defect in an ionic crystal for a given potential model. Both two- and three-body potentials may be used. The properties of the perfect lattice are calculated as well by default. Use is made of symmetry only in the defect calculation and only for two-body potentials. A second derivative method using a Hessian update algorithm is used to minimise the defect energy. The program runs on the CRAY, AS7000 and FPS 164.

THBREL

Determines the minimum energy configuration of a perfect lattice for a given potential. Both two- and three-body potentials may be used. Relaxation to constant volume or zero bulk strain is possible. No use is made of symmetry to speed up the calculation.

THBFIT

Empirically fits a potential to experimentally observed properties of a perfect lattice. (Structure, elastic constants, dielectric constants.) Both two- and three-body potentials may be fitted.

#### SYMLAT

Determines the minimum energy configuration of a perfect lattice for a given potential. Only two-body potentials may be used. The program makes full use of symmetry to reduce time and memory requirements. The program runs on the CRAY, AS7000 and FPS 164.

#### THBPHON

Calculates phonon dispersion curves for ionic crystals with three-body terms in the potential.

CCP5 Working Group on Special Purpose Computers for Condensed Matter Simulations: Report on the meeting held at the Daresbury Laboratory on 4th. February 1986.

C.R.A. Catlow

The Steering Committee of CCP5 recommended at its meeting in September 1985, that the project should set up a small working party to examine the potential of dedicated, special purpose, simulation computers. A number of groups in the U.S.A. and Europe are building such machines; and their consideration by the U.K. computational science community is timely in view of the recent discussions concerning advanced computing following the publication of the Forty Report.

The group met for the first time on 4th. February at Daresbury. Dr. C.M. Moser (Orsay) presented a seminar on 'Special Purpose Computers', the main thrust of which was the enormous potential for simulation studies given that the computer architecture was designed for the specific class of simulation. With such machines, it was claimed, that it was possible to attack problems, via simulation, that would not be feasible, even with state-of-the-art supercomputers e.g. the CRAY XMP.

Following Dr. Moser's presentation, the meeting discussed the role that special purpose computers could have in the work of the U.K. condensed matter simulation community and came to the following conclusions and recommendations:

1. There is a strong scientific case for constructing a special purpose, molecular dynamics computer capable of undertaking simulations on large numbers of particles ( $> = 10,000$ ) for long time ( $> = 100$  picoseconds).
2. Such a computer could have a major impact in the areas of protein dynamics, materials science (including surface and bulk properties of solids) and the physical chemistry of fluids.
3. The construction of such a machine would lead to the establishment of U.K. expertise in an important area of computer hardware and software.
4. A special purpose computer initiative would be complementary to the Forty strategy of general purpose supercomputer facilities.
5. The construction of such a machine should be feasible using U.K. technology (although collaboration with European initiatives would be vital).
6. A special purpose computer project might be expected to receive commercial backing.
7. The working group needs additional expertise in the areas of electronics and computer hardware.

The group plans to meet again in March (date to be arranged) at Daresbury, when it is hoped to formulate more detailed plans concerning the scientific program, the funding, the location and the timetable for the proposed project.

REPORT ON THE VISIT TO JAPAN BY REPRESENTATIVES OF CCP5.

K. Singer and D. Fincham.

K. Singer writes:

In order to stimulate collaboration between Japanese and British scientists the SERC, with their Japanese counterpart, organised visits to Japan by groups of scientists from a number of research areas. One of these was organised by V. Saunders (Daresbury) and Professors Morokuma and Ohmine of the Institute of Molecular Sciences (IMS), Okazaki, in September 1985. The U.K. "team" consisted of V. Saunders plus six persons representing CCP1, CCP5 and CCP6. The plan was that we should visit one or two Japanese colleagues of our choice, two supercomputer installations at Tokyo and Kyoto Universities, and attend a three-day meeting at the IMS.

The IMS is an impressive modern complex of laboratories with pleasant living accommodation for visitors nearby. The meeting was attended by the Japanese colleagues whom we had visited, members of the IMS and by the seven U.K. scientists. For each of the three CCP areas there were four half-hour talks; in these our Japanese hosts and we were expected to talk about our own research and give a summary of work in progress at other laboratories.

Professor Nakanishi (Kyoto) reported MD simulations of a) urea, b) T.-butyl alcohol in ST2 water and showed illuminating graphics on the different arrangement of water around these solutes. Dr. Kataoka (Kyoto) gave an account of results obtained with both two- and three-dimensional models of water based on the work of Yamamoto. It is remarkable that good values for the transport coefficients have been obtained in the two-dimensional simulation.

A list of researchers and topics in the CCP5 area, compiled by Prof. Nakanishi is given below. It shows that there is a broad spectrum of interests and expertise in computer simulation in Japan, and that collaborative enterprises could be productive.

Although each of us could not expect to understand fully more than one third of the lectures, it was healthy to be forced to think about topics outside one's own specialisation; in addition the natural friendliness and generous hospitality of the colleagues at the IMS made the meeting a most enjoyable experience.

It was not expected that collaborations would follow such brief contacts between 4-5 persons in any of the CCP's. There is however scope for future collaborations generated by study visits, sponsored by the Royal Society and the Japan Society for the Promotion of Science. For details see the copy of the Royal Society document below. Applications for visiting fellowships are also considered by the IMS and should be directed to: Professor Keiji Morokuma, Institute for Molecular Science, Myodaiji, Okazaki 444,



Japan.

D. Fincham writes:

After the meeting at IMS I spent the best part of a week in Kyoto. Kyoto University has a large concentration of simulators, including Professors Nakanishi (Industrial Chemistry), Kataoka (Chemistry) and Ueda (Mathematics). Kyoto was the capital of Japan before the status was transferred to Tokyo, and is near to Nara, an even more ancient site of the capital. There are many fascinating sites to be visited in both Kyoto and Nara, and I thoroughly recommend Kyoto as a base for a visit to Japan. From Kyoto I went to Tokyo, really on my way home, but Professor Okada (Tokyo Institute of Technology) turned up on my doorstep and we spent a very pleasant day sightseeing, talking about simulation and visiting Tokyo University Computer Centre.

In Britain simulation tended to grow up as an adjunct to theory, but my impression of Japanese work is that it is used more by practical chemists as a tool in the interpretation of their experiments. This is a very valuable approach and complementary to our own and I very much hope that it will lead to fruitful cooperation. All the Japanese simulators I met were very appreciative of the CCP5 Newsletter.

The Computer centres were very impressive. The Japanese scientists have available some extremely powerful vector processors with very high performance and huge amounts of memory and backing store. The centres are highly automated, with users mounting their own tapes. The IMS computers switch themselves off when they do not have much work to do, in order to save electricity. I did not see much use of personal computers except in the laboratories, nor many graphics workstations, and we may have a slight lead in the development of distributed computing.

## FELLOWSHIPS AND STUDY VISITS TO JAPAN

Grants in respect of visits to Japan by British scientists are administered by the Royal Society as follows:

### *Fellowships*

The Japan society for the Promotion of Science, in collaboration with the Royal Society, offers up to ten postdoctoral fellowships a year for British scientists to go to Japan for between one and two years (or exceptionally for a slightly shorter period). They are open to suitably qualified British scientists working in any field of the natural sciences (including biotechnology, engineering, mathematics, materials science, medical science and space science) in any scientific institution in the UK in which there are already close links with senior Japanese scientists and their departments.

Details and application forms are obtainable from:

The Executive Secretary (ref. F/1.Jap.BdeV)  
The Royal Society,  
6 Carlton House Terrace,  
London, SW1Y 5AG.

Telephone: 01-839 5561 (ext. 222)

### *Study Visits*

The Royal Society is able to consider applications for Study Visits for liaison and research for periods of between fourteen days and six months. The grants which are currently drawn from the Society's Parliamentary Grant-in-aid are designed to assist with travelling and subsistence expenses. Modifications to the scheme may occur in the financial year 1986/87.

Details and application forms are obtainable from:

The Executive Secretary (ref. SV/1.Jap.BdeV)  
The Royal Society,  
6 Carlton House Terrace,  
London, SW1Y 5AG.

Telephone: 01-839 5561 (ext. 222)

BdeV/September 1985

COMPUTER SIMULATION STUDIES IN JAPAN: CURRENT OF AREAS OF INTEREST.

THEORETICAL STUDIES.

1. Intermolecular Forces.

Kihara potential (Lennard-Jones plus hard core)  
Kihara (Tokyo)

2. Liquid State Theory

Morita-Hiroike (Tohoku University, Sendai)

3. Time Dependent Phenomena

Linear response theory, Kubo theorem.  
Kubo (Tokyo), Mori (Kyushu University, Fukuoka)

Kubo theory applied to chemical systems  
Yamamoto (Kyoto/Hiroshima)

MOLECULAR DYNAMICS AND MONTE CARLO SIMULATIONS

1. Simple Models

(a) Soft-core model;  $V(r)=E(z/r)^{12}$ ; RDF,  $D(\text{self})=f(T,P)$   
Ueda, Hiwatari et al. (Kyoto).

(b) Lennard-Jones Model;  $V(r)=4E((z/r)^{12}-(z/r)^6)$ ;  
liquid/glass transition, amorphous state.  
Hiwatari (Kanazawa), Yonezawa (Keio University, Yokohama).

(c) Liquid metals: metals, rapid quenching, 3-body  
distribution.  
Tanaka (Tohoku University, Sendai).

2. Methodology

(a) Nonequilibrium molecular dynamics  
Ono (Tokyo)

(b) Constant temperature and pressure molecular dynamics.  
Nose (Keio University, Yokohama).

3. Ionic Systems.

(a) Molten Salts: alkali halides, nitrates, chemla effect,  
structural analysis.  
I. Okada et al. (T.I.T.), Harada et al. (Kyoto).

(b) Silicate Melts: melts in earth interior.  
Matsui (Okayama), Kawamura (Hokkaido University, Sapporo), Hirao  
(Kyoto).

(c) Superionic conduction: alpha-AgI.  
Ueda et al. (Kyoto), Hiwatari (Kanazawa).

#### 4. Complex Models

(a) Diatomics (2-centre Lennard-Jones)  
H. Tanaka (Kyoto/IMS)

(b) Yamamoto Water: simplified model of water, wide ranges of properties and external conditions,  
Yamamoto, Kataoka, Okada et al. (Kyoto)

(c) Molecules with internal degrees of freedom: methane, sulphur dioxide etc., vibrational spectra.  
Hayashi, Machida, Oobatake, Ooi (Kyoto).

#### 5. Mixtures

(a) Lennard-Jones models: test-particle behaviour, local composition, free energy, PVT.  
Toukubo et al. (Kyoto), Adacki (NIT), Fujihara (Osaka), Iida (Nara)

(b) Nonpolar solutes in water: hydrophobic hydration and interaction.  
Lennard-Jones with ST2 water - S. Okazaki (Kyoto/Osaka)  
Lennard-Jones with Yamamoto water - Kataoka et al. (Kyoto).

(c) Aqueous solutions of nonelectrolytes: MO-based potential, dynamic hydration structure.  
Methanol, t-butanol - S. Okazaki (Kyoto/Osaka)  
Urea, purine - H. Tanaka (Kyoto/IMS)  
Ishibashi, Ikari (Kyoto).

#### 6. Chemical Reactions in Solution

Dynamic behaviour of excited molecules in solution.  
Ohimine (IMS)

#### RELATED TOPICS

##### 1. Biopolymers

Conformation and dynamics:  
Proteins - Go et al. (Kyushu University, Fukuoka)  
DNA - Mikami (Fujitsu, Tokyo)

##### 2. Molecular Mechanics

Simplified MO for large molecules, non-bond interaction.  
Osawa (Hokkaido University, Sappore)

## Optimisation by simulated annealing.

### - An overview and some case studies -

L. T. Wille

#### 1. Introduction.

It is only four years ago since algorithms based on thermodynamic concepts were introduced to solve approximately large-dimensional optimisation problems. In this short lifetime, these techniques, amongst which the most famous one is the simulated annealing method, have attracted a good deal of attention. These methods have already found very important practical applications in such areas as chip design, image processing, etc. Several theoretical physicists as well are working in this field and recent work suggests for example that simulated annealing might very well revolutionise electronic structure calculations. On the other hand these methods have also given rise to controversy and criticism. Some authors have claimed that the simulated annealing method is inferior to classical search techniques, while others have argued that this method is not the best implementation and that it should be combined with evolutionary strategies. Obviously, much has still to be discovered in this field and the question of the best annealing scheme for example remains unsettled so far. However, it is equally clear that these techniques are here to stay for at least some time and that hopefully through some process of evolutionary selection some descendant (or mutant) will survive.

It was felt that there might be sufficient interest in this subject among the readers of this quarterly, hence this contribution, which consists of two parts. In the first one an overview of thermodynamic optimisation methods is given, as well as a short description of some work the author has done using the simulated annealing method. The second part consists of a bibliography of papers dealing with these subjects. An attempt has been made to make this list reasonably complete, but I would of course be glad to receive any additional information, which will be published in a forthcoming issue of this newsletter. The papers in this list will be referred to as Xyz@@ where Xyz is an acronym for the first author's name and @@ denotes the year of publication, if necessary with an additional a,b,c, ... to label the references uniquely. The other references in this overview will be indicated by Arabic numerals.

#### 2. Thermodynamic optimisation methods.

It occasionally occurs in scientific research that discoveries are made almost simultaneously by two or more independent groups or individuals. The same has happened in the early eighties, when the applicability of the concepts of statistical mechanics to combinatorial optimisation problems was investigated independently by Cerny in Bratislava and by Kirkpatrick, Gelatt and Vecchi in IBM Yorktown Heights. Unfortunately, it took some time before articles describing

this work appeared (Kir83, Cer85), but the subject received a fair amount of attention in the popular press [1,2,3]. Some preliminary results had also been mentioned by Kirkpatrick in a paper on spin glasses [4]. At about the same time a method in the same spirit was proposed to determine crystal structures from X-ray diffraction patterns (Kha81, Sem85).

An important motivation for the work of the IBM-group was an analysis of the computational complexity of the frustration model for spin glasses. It had been realised for some time that the frustration model belongs to a class of problems known to computer scientists as NP-complete. Loosely speaking, NP stands for non-polynomial (time) and indicates that the execution time of the most efficient algorithms grows exponentially with the input size. The term complete means that all problems in this class are equivalent in the sense that a polynomial time algorithm for one problem can be mapped into a polynomial time algorithm for any other problem in this class. The list of such problems is very long (almost 100 pages in the standard work by Garey and Johnson [5]). Many important optimisation problems belong to it, the most famous one being the travelling salesman problem. In it one asks for a closed tour of minimal length for a salesman who has to visit  $N$  cities. Obviously the number of distinct tours is  $(N-1)!/2$  and it is very surprising that there is no known algorithm which is substantially better than an exhaustive search of all these possibilities. In spite of extensive investigations, polynomial time algorithms have not been found and if anybody in this readership can devise such an algorithm, instant fame is guaranteed. It is generally believed that such algorithms do not exist - although this conjecture has not been proved - and therefore this problem and the others in the class NP are considered intractable. Consequently much effort has been concentrated on finding good heuristics, which give a near optimal solution in polynomial time.

The important breakthrough of the IBM-group consisted in suggesting the use of thermodynamic concepts to treat not only the spin-glass problem but for all other NP-complete optimisation problems. As already mentioned, a similar suggestion was made by Cerny (Cer85) and in a more specific case by Khachaturyan et al (Kha81). Here, I will mainly concentrate on the IBM-work.

Optimisation problems typically involve a cost function which has to be minimised (for a maximisation problem one simply takes the negative function). A well known heuristic for the approximate solution of such problems is iterative improvement, where one starts with a given configuration and defines a rearrangement operation to explore "neighbouring" configurations. If a configuration with a lower cost function is found the previous set of operations is repeated with the new configuration as starting point. This process is iterated until no further improvements can be made. To be specific, take the travelling salesman problem and define the following rearrangement operation: for any segment of the tour visiting the cities a-b-c-d in this order, consider the replacement a-c-b-d. This is a very unsophisticated heuristic - much better ones exist - but it will do as an illustration. The main problem of such schemes is that they usually get stuck in local minima (local, that is with respect to the notion of neighbourhood we

have introduced). For example in the travelling salesman problem (with the Euclidean metric) one can easily check that any tour without intersecting lines is a local minimum with respect to the earlier defined operation. In most cases the local minima are a bad approximation to the global one and in order to find acceptable solutions one would have to repeat this scheme a number of times starting from different random initial configurations.

Kirkpatrick et al observed that minimising the cost function in an optimisation problem is not unlike growing a crystal from the melt by slowly cooling it. In order to grow a reasonably pure crystal one has to use a process of very slow annealing, otherwise the resulting sample will have many defects or it may form a glass, i.e. the physical system is stuck in a local minimum of the total energy surface. This powerful analogy can now be further pursued by introducing an effective temperature for optimisation and carrying out a process of simulated annealing using the Metropolis procedure and taking the cost function as the energy. In this way rearrangements that increase the cost function will be accepted at sufficiently high temperatures and the system can be frozen into the global minimum (or a good approximation to it).

In the Metropolis algorithm an atomic system in equilibrium at a temperature  $T$  (in reduced units) is simulated by giving each atom in turn a small, random displacement  $\Delta r$  and considering the resulting change in energy  $\Delta E$ . If  $\Delta E \leq 0$  this displacement is accepted and the process is repeated with the atom in its new position. If  $\Delta E > 0$  the new configuration is accepted with a probability

$$p = \exp(-\Delta E/T) \quad (1)$$

This choice ensures that the system evolves into a Boltzmann distribution.

In the simulated annealing method one considers a neighbouring configuration, accepts it if it has a lower cost or with a probability similar to (1) if it has a higher cost. Obviously, in this way the system can escape from local minima. The temperature is merely a control parameter, for which reasonable initial and final values can be obtained from general observations on the nature of the cost function, or from a preliminary simulation. The reader might notice that in the optimisation problem there is no a priori reason for choosing an exponentially decaying probability in the analog of (1). In fact any reasonable function which goes from 1 at  $\Delta E = 0$  to zero may be used and can be chosen to be computationally more efficient. As already mentioned, great care (i.e. slow cooling) is needed when the system is "freezing" into a minimum. Kirkpatrick et al suggested a neat way of detecting freezing by considering the thermodynamic analogy and defining a parameter similar to the specific heat:

$$C(T) = \frac{\langle E(T)^2 \rangle - \langle E(T) \rangle^2}{T^2} \quad (2)$$

where the brackets denote configurational averages. A large value of  $C$

indicates a change in the state of order of the system and signals that slow cooling is needed. In the next section I will briefly describe some of the problems which have been studied using this method, and which illustrate just what an important breakthrough it really is.

Most of the early applications focussed on discrete optimisation problems. There is of course no need to restrict applications to NP-complete problems and complicated polynomial time problems can be studied just as well. An extension of the method to continuous optimisation problems was first given by Vanderbilt and Louie (Van84) and used to solve a non-linear least squares fitting problem. Their method is quite sophisticated, for example it uses the simulation itself to generate optimal step distributions. They point out that in the simulation one actually performs a (biased) random walk in the  $n$ -dimensional parameter space and that the excursion of the random walker can be used to detect the (local) topology of the cost-function surface. Their method has been compared with other global minimisation algorithms on a set of test problems. The overall conclusion is that simulated annealing is comparable in efficiency to other (non-stochastic) methods although the performance is somewhat problem dependent. For example in cases where the barriers between minima are low, simulated annealing works excellently, whereas if there are two minima quite close together in energy and with the global minimum the narrower one, trapping in the wrong minimum can easily occur. Also they limited their investigations to low-dimensional systems ( $n < 10$ ).

Shortly afterwards I suggested the application of simulated annealing to study the structural stability of condensed phases [6]. Strictly speaking there is no such notion as NP-completeness for continuous optimisation problems. However in [6] some plausible arguments were presented which indicated that a discretised version of the energy minimisation problem for a condensed system has many of the characteristics of an NP-complete problem. To be specific, I focussed on atomic clusters interacting under two-body forces, but my remarks apply quite generally. The problem of the minimum energy configuration of a cluster of atoms interacting under Lennard-Jones forces is a very topical one, in particular since the observation of "magic numbers" in rare gas clusters [7]. The ground state geometries are usually determined by a steepest descent algorithm starting from a randomly generated initial configuration and repeating this process many times with different initialisation [8]. With the analogy to iterative improvement methods in mind the application of the simulated annealing algorithm to this class of problems is a logical step. An additional impetus was the fact that steepest descent methods become too time-consuming for clusters with more than 13 atoms (the very stable icosahedral structure) and in fact the number of local minima seems to grow exponentially with the cluster size. For larger clusters one tries to deduce growth sequences and applies steepest descent only to these. Some results for a similar system will also be discussed in the next section.

Before closing this section I must mention some recent work by Brady (Bra85). In the scheme developed by this author for the travelling salesman problem one performs  $n$  iterative improvement calculations in



parallel (this can of course be emulated on a sequential machine). After a number of iterations the  $n$  trial solutions are compared and good subroutes from different solutions are combined in a process reminiscent of biological evolution. Brady claims that his method is superior to simulated annealing for this problem. However, it must be pointed out that he only considered relatively small problems (64 cities, whereas simulated annealing has been applied to problems with thousands of cities). Nevertheless this is certainly a very promising approach and further experience is eagerly awaited. A similar technique has recently been described by Dewdney (Dew85, Gre85).

### 3. Applications.

It was already clear from the first publication on the subject that Kirkpatrick and his colleagues had not invented simulated annealing as a theoretical curiosity. In their Science paper (Kir83) they applied the method to the physical design of computers, in particular to the three stages: logic partitioning, placement and wiring. For each of these steps a constrained optimisation problem has to be solved. (Note that constraints can easily be included by augmenting the cost function.) Using simulated annealing the authors obtained a 10% improvement in the wiring of a multilayer ceramic module used in the IBM 3081 processor. A more convincing proof of the viability of a new computational technique is hard to imagine! As a perhaps more fanciful application, results for a 400-city travelling salesman problem were also presented. In this particular problem the cities were clustered in more or less densely populated regions. It turned out that in the simulation the large scale order is first visible (at higher  $T$ 's) and that the minimisation problem within a cluster of cities is only optimised at lower temperatures. This is reminiscent of another well known heuristic, "divide and conquer", where the problem is divided in subproblems which are solved independently and whose solutions are then patched together.

Almost inevitably much of the later work has used the travelling salesman problem, either for benchmarking or for general investigations. The first, somewhat disappointing, results in this direction came from Golden and Skiscim (Ski83a, Gol84). These authors made an extensive, comparative study of several heuristics for relatively small problems (maximum 318 cities) and found that simulated annealing was clearly inferior to the best heuristic known, both in speed and accuracy. However, a more optimistic tone came soon from Bonomi and Lutton (Bon84). These authors studied much larger problems (1000 - 10000 cities) and also took explicitly advantage of possible clustering in the distribution of the cities. They concluded that in this way solutions within a few percent of the optimal one were obtained in better than quadratic time. Further work on the theoretical aspects of the travelling salesman problem and its deep relation with the spin glass problem can be found in Van84 and Kir85.

It is hardly conceivable that real salespersons will benefit from these studies, but that even this problem has practical relevance is nicely illustrated in a paper by Kirkpatrick (Kir84) where an optimised tour is found for an automatically positioned laser which has to drill

6406 holes in a printed circuit board. Much further work has been done on the computer design problem as can be seen from the following list of references: Vec83, Jep83, Lin84, Sec84, Sia84, Sec85. One final technological area in which simulated annealing has been successfully used is image processing (Smi83, Smi85, Car85a), where one wants to restore objects from coded or noisy images.

Applied mathematicians have used simulated annealing to solve a variety of NP-complete problems (Bon85, Bur84, Lut85a, Lut85b, Sch85a, Sch85b). Again many practical applications can be found. The warehouse problem (Lut85a), for example, consists in finding the best places for switching centres and concentrators in telephone, videocommunication or computer networks. More recently, I have applied simulated annealing to the so-called "football pool problem", which is a notoriously difficult combinatorial problem studied theoretically by several mathematicians in the last decade. The problem asks for a minimal subset of all ternary codes of length  $n$ , such that all codes lie on a maximum Hamming distance of 1 from at least one code in the subset. Only upper bounds for the number of elements in the optimal subsets are known and in one case ( $n=6$ ) I have succeeded in reducing the best bound from 79 [9] to 74 [10]. Work in this direction is relevant to the design of optimal codes for data transfer (in this context see also Elg85).

As already mentioned in the previous section I suggested the application of simulated annealing to structural energy optimisation problems [6]. Although I originally had applications to Lennard-Jones clusters in mind, an interesting opportunity presented itself when a letter by Berezin appeared in Nature [11]. This author pointed out that the minimum energy configuration of  $N$  equal point charges confined to a circle is not necessarily obtained by putting all charges on the circumference. In fact, from  $N = 12$  on, a configuration with one charge in the centre has lower energy. It was subsequently realised [12] that this peculiarity arose because of the use of the three dimensional  $(1/r)$ , rather than the two dimensional  $(\ln r)$ , Coulomb potential in a two dimensional problem. Nevertheless, this problem was a tempting test case to study the performance of simulated annealing. However, it must be borne in mind that this was a difficult test case, since a near optimal solution would not be satisfactory, but I was aiming at finding the true ground state. An account of my results can be found in Wil85. Unfortunately, I later discovered that some of the results (in the range  $N = 16-23$ ) corresponded to local minima with an energy close to the global one [13]. On the other hand the more difficult case of  $N = 50$  was optimised correctly. In my original letter I used a very slow annealing scheme which nevertheless occasionally got stuck in a local minimum. It was found afterwards that it was better to use a faster annealing, but perform a number of independent runs instead. Also an important speed improvement was obtained by using a steepest descent routine in the later stages of the anneals. This scheme is now completely satisfactory and is currently applied to study a variety of interactions and boundary conditions in the charge confinement problem [14]. The same algorithm has also been used to study Lennard-Jones clusters with up to 25 atoms. In general, Hoare's results [8,15,16] are reproduced, but the algorithm has also found two recently reported improvements (for  $N = 17$  ref. [17] and for  $N = 23$  ref. [18]) as well as

a new minimum for  $N = 24$  [19]. For these  $N$  values the running time is approximately 25 mins. on the FPS-164 attached processor at Daresbury Laboratory.

Finally, I cannot leave this section without briefly discussing the recent very exciting work by Car and Parrinello (Car85b). These authors have constructed a new scheme which combines the density functional theory used in electronic structure calculations with a molecular dynamics simulation. The starting point is the density functional result that each point of the Born-Oppenheimer potential energy surface can be obtained from a minimum principle for the energy functional. Conventionally, this variational principle is recast in the form of a set of differential equations whose solution requires repeated matrix diagonalisations. Car and Parrinello suggested that the energy functional be considered as the cost function and that a molecular dynamics simulated annealing could be used to optimise this functional (under appropriate orthonormality constraints). The optimisation is with respect to the ionic positions, the single particle orbitals and all external constraints (such as volume, strain, etc.). The dynamics associated with the last two parameters is of course fictitious but that for the ionic positions has a real physical meaning. First of all, for large systems, this scheme is more efficient than standard diagonalisation techniques. Secondly and much more importantly, in the Car-Parrinello approach diagonalisation, self-consistency, atomic relaxation and volume and strain relaxation are all obtained simultaneously. Traditionally, in electronic structure calculations one solves the density functional equations for the ions in a given configuration and then investigates several possible lattices (and lattice constants). This can be considered as an optimisation method where one optimises parallel to two "axes", first along the "electronic axis" and then along the "ionic axis". Car and Parrinello used their method to determine the static and dynamic properties of silicon, using a self-consistent pseudopotential method. Certainly, this is a very promising line and if the method can be made to work for more complex solids (or for clusters) it will completely alter the fields of electronic structure calculations and molecular dynamics simulations.

#### 4. Conclusions.

I hope to have shown in the previous pages that simulated annealing and methods derived from it can be applied to a large variety of problems. These do not necessarily have to be NP-complete, but other discrete or continuous optimisation problems can be investigated as well. In fact many problems can be formulated as an optimisation problem which makes them amenable to one of these methods. For example, non-linear equations, differential and integral equations all can be written in the form

$$\mathcal{E}(f(\underline{x})) = c \quad (3)$$

where  $\mathcal{E}$  is an appropriate operator, and consequently one can define a cost function

$$[\mathcal{E}(f(\underline{x})) - c]^2 \quad (4)$$

whose minimum value is obtained when (3) is satisfied. Constraints can be implemented in a number of ways: one can augment the cost function so that moves that do not satisfy the constraints will be rejected or, alternatively, one can introduce Lagrange multipliers. One last possibility is to include the constraints in such a manner that they are not necessarily obeyed during the simulation, but so that they are correctly taken into account as  $T \rightarrow 0$ .

Most of these methods are suitable for parallel computation. There has in fact been some speculation that the brain works in a similar way and the importance for artificial intelligence has been noted by several authors. Obviously, the last word has not been said in this matter and the following years promise to be highly exciting.

An overview like this one is necessarily limited and biased. Several important concepts, such as frustration and ultrametricity, have hardly been mentioned at all. The interested reader is strongly urged to consult some of the references, in particular the original paper (Kir83) which is exceptionally lucid. As far as applications are concerned, I have given somewhat more attention to my own work, not because it is a much better illustration, but merely because I am more familiar with it. In the bibliography the titles of the papers have been included so that further information can be found there.

#### Acknowledgments.

It is a pleasure to thank a number of authors for useful correspondence and preprints of their work. In particular I am grateful to E. Bonomi, R. Burkard, V. Cerny, S. Kirkpatrick, A. Lobstein and J.L. Lutton. I also want to thank Ian Sharp for an on-line literature search which constitutes the backbone of the bibliography. Finally the stimulating atmosphere of the T.C.S. Division at Daresbury cannot be left unmentioned.

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## What is the temperature in leapfrog MD?

### A cautionary tale of using algorithms with large timesteps

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#### Introduction

The importance of using as large a timestep as possible in molecular dynamics (MD) simulations has recently been emphasised in the pages of this newsletter. This note is primarily aimed at explaining an apparent discrepancy between the conclusions of two recent contributions on this subject by Fincham [1] and Heyes [2]. A number of related points will be mentioned incidentally.

The two main competing classes of MD algorithm are the leapfrog and Gear predictor-corrector methods. Both are easily applied to standard (isoenergetic) MD, i.e. solution of the coupled differential equations

$$\ddot{\underline{r}}_i = \underline{a}_i(\{\underline{r}_j\}), \quad \underline{a}_i = \underline{F}_i/m, \quad (1)$$

where  $\underline{F}_i$  represents the resultant force on particle  $i$ , and it is well known that Gear methods have the advantage in accuracy for low timesteps but that the leapfrog algorithm is stable for higher timesteps [3]. The crucial question is whether and to what extent leapfrog accuracy is sufficient at higher timesteps.

In this note I shall, however, deal directly only with the isokinetic algorithms discussed in [1,2]. The elementary form of the leapfrog algorithm cannot be applied to velocity dependent fictitious forces such as those arising in Gaussian thermostating:

$$\ddot{\underline{r}}_i = \underline{a}_i(\{\underline{r}_j\}) - \lambda \dot{\underline{r}}_i, \quad (2)$$

$$\lambda = \mu/\kappa \quad (3)$$

where

$$\mu = \sum \underline{a}_i \cdot \dot{\underline{r}}_i, \quad (4)$$

$$\kappa = \sum \dot{\underline{r}}_i^2. \quad (5)$$

Therefore isokinetic MD was originally done with Gear algorithms [4]. More recently, the leapfrog algorithm has been modified in two different ways by Brown and Clarke (BC) [5] and Heyes et al. (HEM) [6] for use with isokinetic equations. Fincham [1] used the BC method and found systematic changes in thermodynamic properties with increasing timestep. Heyes [2] used the HEM method and found no such changes within statistical errors. (Both authors agreed that radial distribution functions and time correlation functions were unaffected by timestep but the poorer statistics for these mean that this is not a very strict test.) Heyes [2] attributed the discrepancy between his conclusion and that of Fincham to the different state point he studied but I shall argue that it is in fact a consequence of the different algorithms used.

### Algorithms and results

I begin by giving a brief summary of the two algorithms as I applied them (not guaranteed to be exactly as in [1,2]) with special emphasis on the startup procedure which turns out to be quite important. The simulations were done for a (one-component) system with a Lennard-Jones potential (parameters  $\epsilon$  and  $\sigma$ ). The potential was cutoff and shifted to be zero at  $2.5\sigma$ .  $N=108$  particles were simulated in a cubic box with the usual periodic boundary conditions at temperature  $T=0.75$  and density  $\rho=0.8$ . Here and subsequently results are quoted in Lennard-Jones reduced units without any particular symbol being used to denote these.

For both simulations the initial values input were positions  $\underline{r}_i(0)$  and velocities  $\underline{w}_i(-h) = \dot{\underline{r}}_i(-\frac{1}{2}h)$ ,  $i=1, \dots, N$ , where  $h$  is the timestep. For conciseness in the sequel, we omit the particle index  $i$  and denote the time argument  $(nh)$  simply by a subscript  $n$ . Any summations are always understood to be over the suppressed particle index  $i$ . The initial positions were an fcc lattice and the random initial velocities gave zero total momentum and satisfied

$$\sum w_{-1}^2 = (3N-4)k_B T/m = 8. \quad (6)$$

The system was equilibrated (separately using BC and HEM algorithms) for 500 timesteps with  $h=0.025$  and then the resulting outputs stored as common starting states for the subsequent equilibrium averaging runs.

The usual leapfrog algorithm used to solve equations (1) is most simply written in the form

$$\underline{r}_{n+1} = 2\underline{r}_n - \underline{r}_{n-1} + h^2 \underline{a}_n \quad (7)$$

but it is often seen in the "half timestep velocity" form

$$\underline{r}_{n+1} = \underline{r}_n + h \underline{w}_n \quad (8)$$

$$\underline{w}_n = \underline{w}_{n-1} + h \underline{a}_n \quad (9)$$

(8) can be regarded as the definition of an auxiliary variable  $\underline{w}_n$  and is retained throughout this note.  $\underline{w}_n$  is an approximation to the half timestep velocity  $\dot{\underline{r}}_{n+\frac{1}{2}}$  with truncation error of  $O(h^2)$ .

The necessity to know the full timestep velocity in the Gaussian isokinetic equations (2)-(5) prevents the use of (8) and (9). Both BC and HEM approximate the full timestep velocity initially by

$$\underline{u}_n^* = \underline{w}_{n-1} + \frac{1}{2} h \underline{a}_n \quad (10)$$

and then incorporate the thermostat term by

$$\underline{u}_n = \underline{u}_n^* - \frac{1}{2} h \lambda \underline{u}_{n-n} \quad (11)$$

or

$$\underline{u}_n = f_n \underline{u}_n^*, \quad f_n = 1 / (1 + \frac{1}{2} h \lambda_n) \quad (12)$$

At this point BC use the required temperature at every timestep by setting

$$f_n = \sqrt{[\theta / (\sum u_n^{*2})]}, \quad (13)$$

whereas HEM maintain constant temperature by solving the implicit equations (12) to give

$$\lambda_n = u_n^* / (\kappa_n^* - \frac{1}{2} h u_n^*), \quad (14)$$

where

$$u_n^* = \sum a_n \cdot u_n^* \quad \text{and} \quad \kappa_n^* = \sum u_n^{*2}.$$

Equation (9) is now replaced by

$$w_n = (2f_n - 1)w_{n-1} + hf_{n-n} \quad (15)$$

for the BC algorithm or, for the HEM algorithm,

$$w_n = w_{n-1} + h(a_n - \lambda_n u_n). \quad (16)$$

(Although (15) and (16) are equivalent their forms are best suited to the respective algorithms indicated.)

We now define any approximate temperature  $T_n^x$  by

$$(3N-4)k_B T_n^x = m \sum x_n^2, \quad (17)$$

where  $x_n$  is some approximation to the velocities at timestep  $n$ . It is clear that the BC algorithm ensures  $T_n^u = T$  identically. On the other hand, HEM used as described above tends to lead to  $T_n^w = T$  because of the input data given by (6), though in this case there will be a slight drift of this value due to roundoff errors. As I understand it, it is for this reason that HEM

introduce their temperature adjustment parameter  $\beta$  [6] (not to be confused with the inverse temperature). This permits an adjustment of the temperatures in the HEM simulation so that  $T_n^u = T$  as in the BC simulation.

As an aside I wish to point out an improved method of temperature adjustment, just as simple and more useful in practice than that proposed by HEM. Instead of causing  $T^u$  to vary linearly from its current value to the required  $T$ , it is preferable to let it relax exponentially to  $T$ . Then it is not necessary to switch off the temperature adjustment at any particular time. Equation (2) is still used but equation (3) which ensures  $\dot{\kappa} = 0$  is replaced by

$$\lambda = [\mu + \alpha(\kappa - \theta)]/\kappa \quad (18)$$

which arises from  $\dot{\kappa} = -2\alpha(\kappa - \theta)$ . Here  $\alpha$  is an arbitrary relaxation rate. Specifically for the modified leapfrog algorithm, the velocity update is still given by equation (16) but (14) is replaced by

$$\lambda_n = \frac{2[\mu_n^* + \alpha(\kappa_n^* - \theta)]}{\kappa_n^* - \frac{1}{2}h(\mu_n^* - \alpha\theta) + \sqrt{[\kappa_n^* - h\kappa_n^*(\mu_n^* - 2\alpha\theta) + h^2(\frac{1}{4}\mu_n^* + \alpha^2\theta\kappa_n^*)]}} \quad (19)$$

Any positive value of  $\alpha$  causes  $T^u$  to relax toward  $T$ . Once this is attained,  $\alpha$  can be set to zero and the temperature remains stable. Slight drift in a very long simulation could be avoided by keeping  $\alpha$  small but non-zero. Any temperature adjustment of this type is of course not possible within the framework of the BC algorithm.

In addition to the temperatures  $T^u$  and  $T^w$ ,  $T^v$  is also considered, where

$$\frac{v}{n} = [7(\frac{w}{-n} + \frac{w}{-n-1}) - (\frac{w}{-n+1} + \frac{w}{-n-2})]/12 \quad (20)$$

is the higher order [truncation error  $O(h^4)$ ] approximation to the full timestep velocity advocated in [3]. Actually, (20) represents unnecessary overkill,  $\underline{v}_n$  having higher order truncation error than the positions from which it is calculated. It is preferable to avoid  $\underline{w}_{n+1}$  which slightly complicates the programming and use, instead of (20),

$$\underline{v}_n = (2\underline{w}_n + 5\underline{w}_{n-1} - \underline{w}_{n-2})/6 \quad (21)$$

which has  $O(h^3)$  truncation error, the highest order compatible with the truncation error of the positions. It has been checked that the  $T^V$ 's obtained from (20) and (21) agree within statistical error; the tabulated numbers below were actually obtained from (20). For comparison purposes we note that

$$\underline{u}_n = (\underline{w}_n + \underline{w}_{n-1})/2 \quad (22)$$

has truncation error of  $O(h^2)$  with a coefficient four times that for the truncation error in  $\underline{w}_n$  (regarded as an approximation to the half timestep velocity).

Tables 1 and 2 show the results of equilibrium simulations, started as described above, with various timesteps  $h$  but each of total time 60.  $U^C$  and  $p^C$  represent the configurational parts of the internal energy and pressure respectively. The errors (shown in parentheses when non-negligible) are obtained from the formulae given by Fincham [1] but the statistical inefficiency has not been obtained directly but rather approximated by  $1/(10h)$  which reproduces the statistical inefficiencies of Fincham with reasonable accuracy. (In Fincham's real units, 20fs corresponds to  $h=0.01$ .)



In view of the preceding comments, it is not surprising that the BC simulations all give  $T^u = T$  whereas the HEM simulations (with  $\alpha=0$ ) give  $T^w = T$ . It is my contention that  $T^v$  represents the true temperature of the system better than  $T^u$  or  $T^w$ . Clearly  $T^w$  is quite close to  $T^v$  whilst  $T^u$  is consistently lower (by ~5% for  $h=0.025$ ). The relative values of the different temperatures are consistent for small  $h$  with  $T^v$  being essentially exact and  $T^u$  having an error four times as great as  $T^w$ . For larger  $h$ , higher order corrections distort this simple relation.

Before considering the implications of these results for the work of Fincham [1] and Heyes [2] we should note that the temperatures reported by Heyes are not in fact constant but vary with timestep. This indicates that the results in [2] were obtained without the use of the temperature adjustment parameter  $\beta$  introduced in [6]. Thus the ( $T^u$ ) results quoted in [2] which decrease as  $h$  increases correspond, in the light of the present simulations, to very nearly constant values of  $T^w$ , a good approximation to the real system temperature. On the other hand, the results of [1] have  $T^u$  exactly the same for all  $h$  which corresponds to an increase in the real system temperature as  $h$  increases.

It is of interest to see whether the changing  $T^v$  in [1] is sufficient to account for the changes in thermodynamic properties observed. To this end I carried out several BC simulations with the required input temperature (equal to  $T^u$ ) scaled down from 0.75 in an attempt to produce  $T^v=0.75$  almost exactly, independent of  $h$ . The starting configuration for these runs was the equilibrated HEM configuration used for Table 1 and the results are shown in Table 3. The change in values with  $h$  is essentially eliminated except for  $h=0.03$  where  $T^w$  has very large fluctuations.

Discussion

The implications of this work are as follows. It is perhaps surprising that  $T^u$  is systematically lower than  $T^v$  (the true temperature) but in fact this is true even for small  $h$  though the difference is only substantial for larger  $h$ . It indicates that, for a dense liquid state, the average value of  $\ddot{\underline{r}}_i(t) \cdot \dot{\underline{r}}_i(t)$  is noticeably negative. Expression (21) [or (20)] should be used to determine the velocities in leapfrog simulations (whether isokinetic or isoenergetic, since similar ratios between the different temperatures also occur in standard MD). Previous simulations where lower order accuracy has been used for the velocities are generally still quite valid because they have used small timesteps but use of (21) should be preferred in all future leapfrog MD work even although the error resulting from not doing so only becomes important for large  $h$ .

Since  $T^w \approx T^v$ , the HEM temperature adjustment parameter  $\beta$  should definitely not be used as proposed in [6]. It will move  $T^w$  away from  $T$  which also moves  $T^v$  away from  $T$ . If it is for any reason felt necessary to eliminate the small discrepancy between  $T^w$  and  $T^v$  this should be done with equations (16) and (19) of this note in preference to the HEM method. This entails using an input temperature  $T'$  different from the intended output temperature  $T$ . The ratio  $T'/T$  can be approximated by  $T^u/T^v$  from an initial short run with  $\alpha=0$ . Strictly this procedure may have to be iterated but in practice  $T'/T$  varies only slowly with  $T$ .

It is well known that the ordinary leapfrog algorithm can be cast in various more convenient predictor-corrector forms [7,8] but it is not at all clear that these can be modified for isokinetic MD without loss of stability. In particular, equations (28) of [8] with  $c=\frac{1}{2}$  do not work stably

for Gaussian isokinetic MD contrary to what might be deduced from the throwaway remark following equations (28). This is presumably because the stability analysis used in [8] refers specifically to velocity independent forces. A test was made of algorithms similar to those of BC and HEM aimed at directly producing a prescribed  $T^V$  [from equation (21)] rather than a prescribed  $T^U$ . The instability of the resulting algorithms was attributed to the inclusion of  $r_{n-2}$  in the resultant position updating equation which replaces (7).

In conclusion, the results here show that both the BC and HEM isokinetic leapfrog algorithms give stable and consistent results for any  $h \leq 0.025$  at the state point studied, provided the system temperature is obtained accurately. The HEM method is to be preferred to that of BC because the former does not use a prescribed temperature at each timestep and also because the latter seems to give severe fluctuations of  $T^W$  at  $h=0.03$ . Although the maximum allowed value of  $h$  in the HEM method may not be as high as 0.03 for higher temperatures or potentials other than the Lennard-Jones, it is reasonable to expect that  $h$  can be increased significantly from the values up to 0.01 usually employed in past leapfrog simulations, with consequent savings in computer time. When high accuracy of trajectories is unimportant, as is the case in most MD work (including all properties determined as simple time averages), the HEM leapfrog algorithm as modified here for use with large  $h$  provides considerable gains in efficiency over Gear algorithms which are stable only for  $h \leq 0.005$ .

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Table 1 HEM simulations with  $T^W=0.75$ 

| h     | $T^U$      | $T^W$   | $T^V$      | $U^C/N$   | $p^C$      |
|-------|------------|---------|------------|-----------|------------|
| 0.010 | 0.74550(4) | 0.75002 | 0.75144(1) | -5.354(3) | -0.288(14) |
| 0.015 | 0.73981(9) | 0.75002 | 0.75299(3) | -5.352(3) | -0.253(15) |
| 0.020 | 0.7317(2)  | 0.75002 | 0.75469(8) | -5.355(3) | -0.290(15) |
| 0.025 | 0.7206(3)  | 0.75002 | 0.7561(2)  | -5.355(3) | -0.298(15) |
| 0.030 | 0.7064(4)  | 0.75002 | 0.7559(4)  | -5.356(3) | -0.290(15) |

Table 2 BC simulations with  $T^U=0.75$ 

| h     | $T^U$   | $T^W$      | $T^V$      | $U^C/N$   | $p^C$      |
|-------|---------|------------|------------|-----------|------------|
| 0.010 | 0.75000 | 0.7548(10) | 0.75604(5) | -5.347(3) | -0.235(15) |
| 0.015 | 0.75000 | 0.7608(11) | 0.7636(1)  | -5.343(3) | -0.225(15) |
| 0.020 | 0.75000 | 0.7693(12) | 0.7739(2)  | -5.333(3) | -0.167(15) |
| 0.025 | 0.75000 | 0.7821(19) | 0.7877(2)  | -5.321(3) | -0.139(15) |
| 0.030 | 0.75000 | 0.7995(32) | 0.8040(3)  | -5.315(3) | -0.106(16) |

Table 3 BC simulations with  $T^V=0.75$ 

| h     | $T^U$      | $T^W$      | $T^V$      | $U^C/N$   | $p^C$      |
|-------|------------|------------|------------|-----------|------------|
| 0.010 | 0.74400(1) | 0.74852(8) | 0.74994(5) | -5.356(3) | -0.265(14) |
| 0.015 | 0.73660(1) | 0.7469(5)  | 0.74976(9) | -5.352(3) | -0.265(16) |
| 0.020 | 0.72680(1) | 0.7457(20) | 0.7497(1)  | -5.359(3) | -0.290(15) |
| 0.025 | 0.71410(1) | 0.7438(21) | 0.7490(2)  | -5.359(3) | -0.293(15) |
| 0.030 | 0.70200(1) | 0.7466(29) | 0.7512(3)  | -5.363(3) | -0.319(15) |

GRAPHICS AND NON-EQUILIBRIUM MOLECULAR DYNAMICS.

D.M. Heyes.

CCP5 has sponsored a number of half-day discussions on the role of computer graphics in MD. In particular, the question was often raised: What extra information does graphical portrayal of MD results give? Basically, there were three types of graphical display presented.

(a) Simple line plots which are coupled to the ends of MD runs. These provide an effortless way of keeping track of the progress of your simulation, especially equilibration. This form is very useful when performing simulations of ionic liquid and solid interfaces [1]. The appearance of the density (and other property) profiles was particularly useful in this respect. One could run the simulation until it looked aesthetically pleasing. Therefore valuable computer time is not wasted in unnecessary continuation of the simulation. You have to watch the build-up of mounds of graph plots though!

(b) Interactive graphics in various forms were presented. This is beginning to find a role in many areas of chemistry, such as in the design of drugs which couple effectively to enzymes. The ability to explore the effects of changing the position of a molecule in part of a molecular grouping is proving invaluable. The expense of such an apparatus is at present a limiting factor.

(c) Movies of MD configurations I find to be the most appealing and informative recent development. A number of films were shown in these sessions. One obtained insights into the many-body correlations involved in the collective dynamics of liquid states. A number of the national computer centres have the equipment for making films. I am sure this will be an increasingly popular addition to the armoury of peripherals used with MD.

In this short note I would like to bring to your attention a form of graphics which I find very useful in unravelling the consequences of large perturbations on liquids and solids, which go under the broad banner of Non-Equilibrium Molecular Dynamics (NEMD). It could be considered to be a sub-branch of category (c) above, but in fact can be obtained much more easily and cheaply using a conventional pen plotter. The technique is to plot the instantaneous positions of the molecules projected onto a two-dimensional surface. An example of such has been given in a previous CCP5 Newsletter article [2]. There the destructive effects of ion bombardment of solid surfaces was considered. Each surface atom was represented by a circle with a number within it, so one could keep track of it from frame to frame separated by many time steps. Another area in which strong structural changes result from the external field is in shear flow. A recent example demonstrating the power of such graphics to extract new effects from the simulation is in shear flow of soft discs [3]. The existence of co-existing phases during rapid shear thinning comes out of the

instantaneous configuration plots. It is a very simple modification to an MD program to get it to write out a configuration to a file at some point during the sub-average. It can be plotted later at leisure.

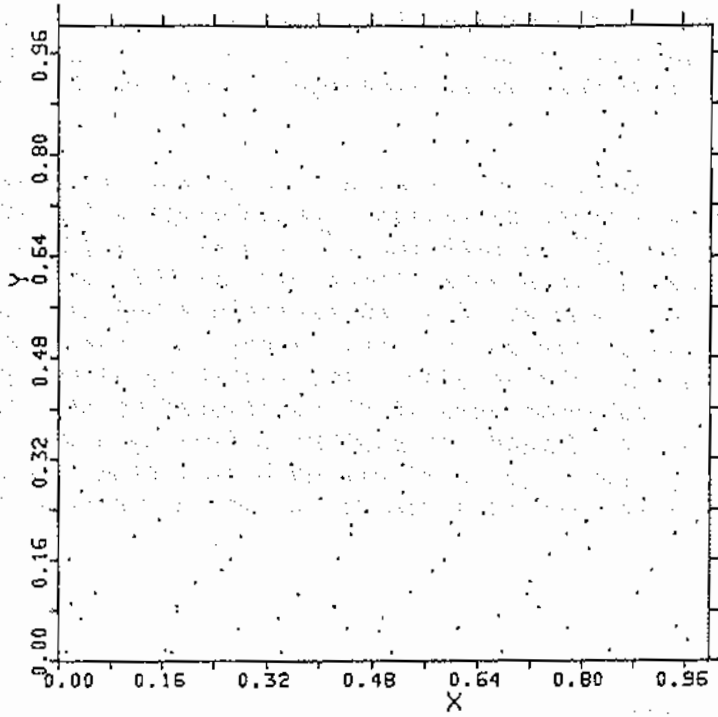
Another example of similar structural alignment created by shear flow in a three-dimensional Lennard-Jones liquid close to its triple point ( $\rho^* = 0.8442$  and  $T^* = 0.722$ ) is given in the figure which accompanies this note. There you see the projection of all the molecular centres of a 256 particle simulation onto the three orthogonal planes formed by the sides of the cubic MD cell. Shearing is in the XZ plane. The streaming velocity is along the X-direction. The shear rate is 90 LJ reduced units. The plots were performed on a CALCOMP 81 plotter driven by a VAX 11/780 at this college. They took about a minute each to create. Such a program can easily be written in a few hours, which includes debugging.

#### References

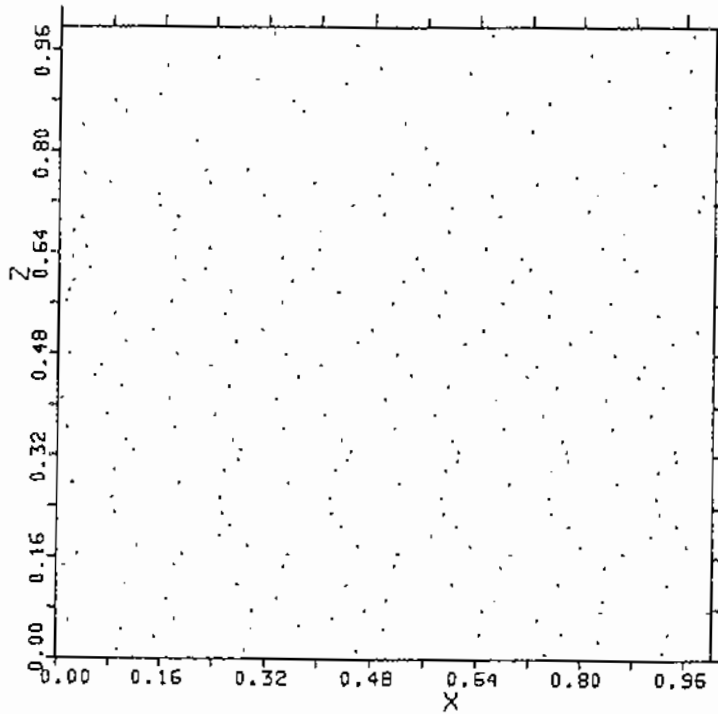
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(a)

$$\underline{\gamma = 90}$$



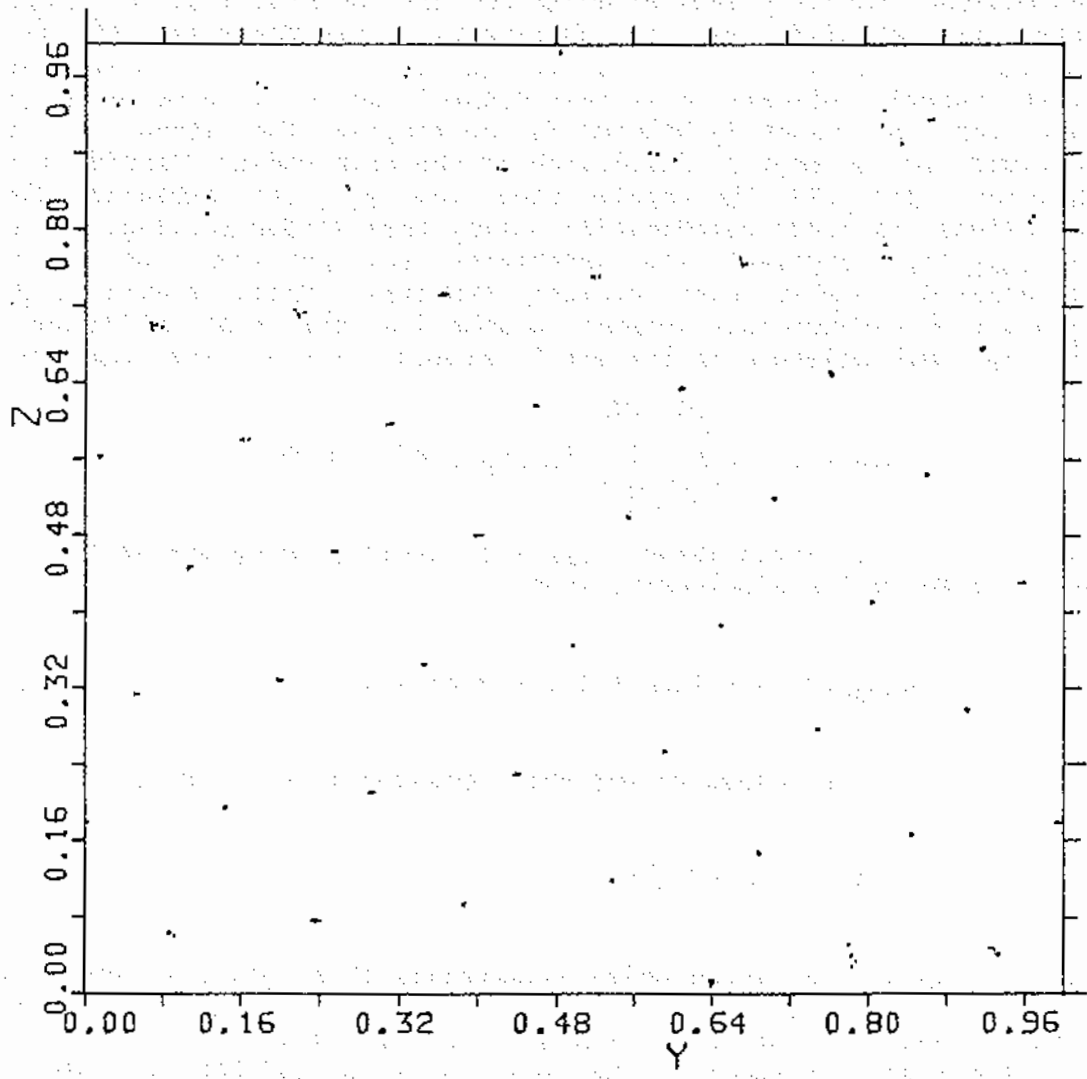
(b)





(C)

$\gamma = 90$



ANGULAR PAIR RADIAL DISTRIBUTION FUNCTION - THE FORTRAN CODE

D.M. Heyes

As is evident in another article in this issue on "Graphics and Non-Equilibrium Molecular Dynamics" the presentation of NEMD data is crucial to a successful interpretation of the non-equilibrium state. The relative disposition of the molecules gives useful information in this respect for the effects of shear flow. One probe which is helpful in portraying the structure is provided by an angular resolution of the pair radial distribution function,  $g(r)$  [1]. The angular component,  $g_{\alpha\beta}(r)$ , measures the deviations in local coordination number from random packing. Peaks in  $g_{\alpha\beta}(r)$  represent the importance and position of pair coordination shells with certain symmetry. Space around each molecule is divided into concentric spherical shells of thickness,  $\delta r$ . For each molecule in the shell between  $r \pm \delta r$  the function

$$f_{\alpha\beta}(r) = \left[ \sum_{i \neq j}^N \sum_{j}^N \langle R_{\alpha ij} R_{\beta ij} / R_{ij}^2 \rangle \right] / N \quad (1)$$

is added into accumulator  $f_{\alpha\beta}(r)$ , usually going out as far as half the MD cell's sidelength. Then

$$g_{\alpha\beta}(r) = V f_{\alpha\beta}(r) / (V(r) N) \quad (2)$$

where  $V(r)$  is the volume of the shell bounded by  $r \pm \delta r$ ,

$$V(r) = 4 \pi r^2 \delta r \quad (3)$$

As an example, the figure which accompanies this article presents the  $g_{\alpha\alpha}(r)$  for a  $\gamma = 20$ ,  $\rho^* = 0.8442$  and  $T^* = 0.722$  Lennard-Jones simulation. To assist other MD simulators to evaluate this function, I present in the Table the essential FORTRAN code to perform the evaluation.

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## TABLE

SHOWS HOW TO CALCULATE THE ANGULAR PAIR RADIAL DISTRIBUTION FUNCTION FOR A SIMPLE SPHERICALLY SYMMETRIC MOLECULAR FLUID

```

C
C   RHO IS THE LENNARD-JONES REDUCED DENSITY
C   NDIST IS THE NUMBER OF ELEMENTS IN THE PAIR
C   DISTRIBUTION ARRAYS
C   CUT IS THE INTERACTION CUT-OFF DISTANCE IN LJ SIGMA
C   FIX=FLOAT(NDIST)/CUT**2
C
C   INITIALISE ACCUMULATORS (SEE EQUATION (1))
C
C   NT=0
C   DO 5011 I=1,NDIST
C   GIN(I)=0.0
C   XXRR(I)=0.0
C   YYRR(I)=0.0
C   ZZRR(I)=0.0
C   XYRR(I)=0.0
C   XZRR(I)=0.0
C   YZRR(I)=0.0
5011 CONTINUE
C
C   MAIN PROGRAM STARTS HERE
C
C   CONTINUE
C   N1=N-1
C   DO 1062 I=1,N1
C   THE COORDINATES OF THE PARTICLES ARE IN ARRAYS
C   RX(N),RY(N) AND RZ(N)
C
C   I1=I+1
C   DO 1053 J=I1,N
C
C   PERFORM NEAREST IMAGE CONVENTION
C
C   SG2I=1.0/(SIGMA**2) WHERE SIGMA IS IN MD BOX UNITS
C   X, Y AND Z ARE THE COMPONENT RELATIVE SEPARATIONS BETWEEN
C   THE MOLECULAR PAIR I,J IN UNITS OF THE BOX SIDELENGTH.
C   RR=(X*X+Y*Y+Z*Z)*SG2I
C   CU2 IS THE CUT-OFF SQUARED IN LJ SIGMA UNITS
C   IF(RR.GT.CU2)GOTO 1099
C   XX=X*X
C   YY=Y*Y
C   ZZ=Z*Z
C   IRR=(FIX*RR+0.5)
C   IF(IRR.GT.NDIST)GO TO 7510
C   RRI=1.0/RR
C
C   NOTE THAT THE RADIAL FUNCTIONS ARE ACCUMULATED
C   IN TERMS OF THE SQUARE OF THE PAIR SEPARATION
C   TO AVOID TAKING A SQUARE ROOT IN THIS TWO-PARTICLE
C   DOUBLE LOOP.
C   GIN(..) ACCUMULATES THE PAIR RADIAL DISTRIBUTION FUNCTION.

```

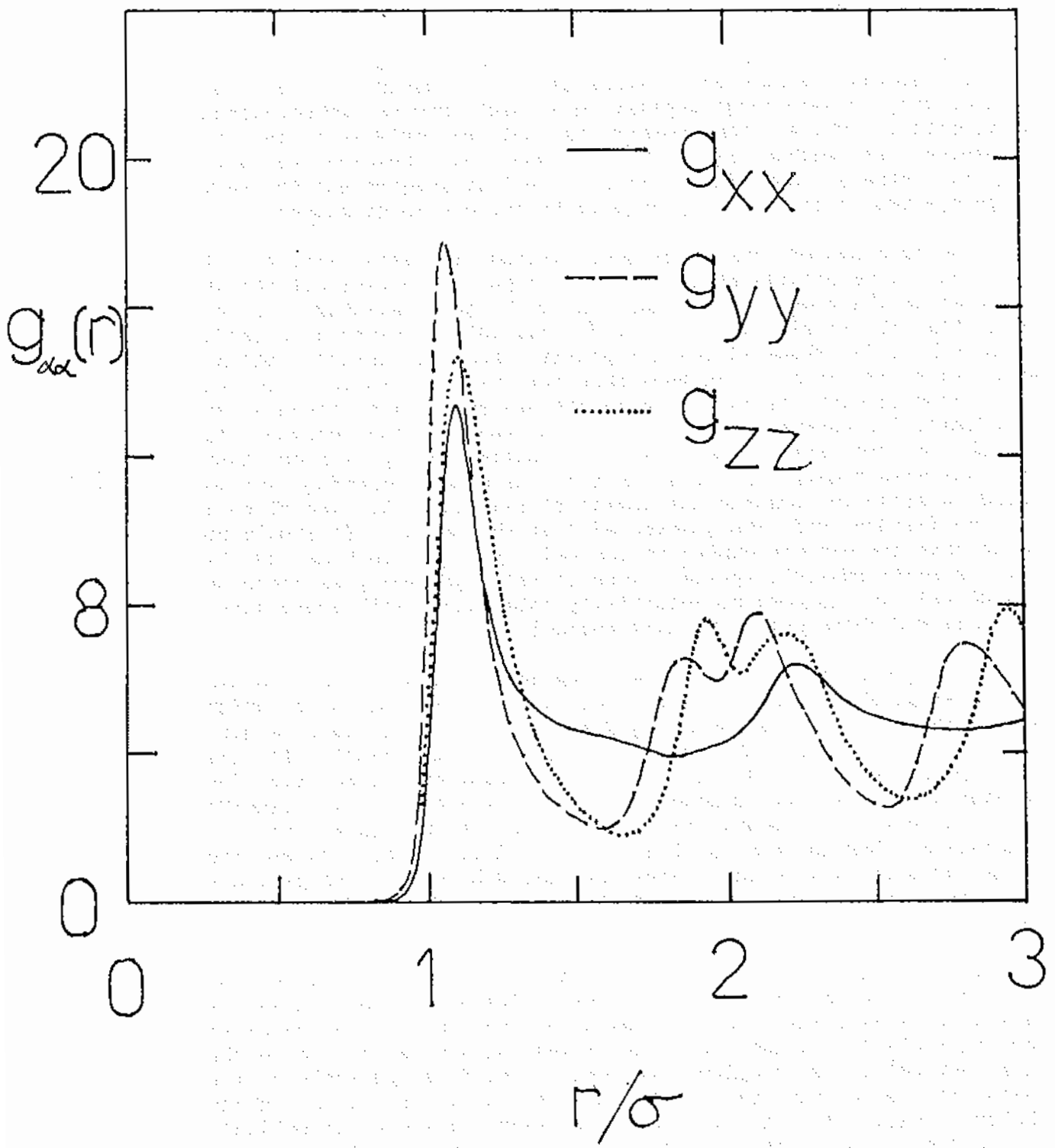
```

GIN(IRR)=GIN(IRR)+1.0
XYRR(IRR)=XYRR(IRR)+X*Y*RR1
XZRR(IRR)=XZRR(IRR)+X*Z*RR1
YZRR(IRR)=YZRR(IRR)+Y*Z*RR1
XXRR(IRR)=XXRR(IRR)+X*X*RR1
YYRR(IRR)=YYRR(IRR)+Y*Y*RR1
ZZRR(IRR)=ZZRR(IRR)+Z*Z*RR1
7510 CONTINUE
1099 CONTINUE
1063 CONTINUE
1062 CONTINUE
C
C      NT=NT+1
C      NRUN IS THE NUMBER OF TIMESTEPS IN THE RUN
      IF(NT.LT.NRUN)GO TO 6
C
C      END OF RUN
C
      WRITE(6,2299)
2299  FORMAT(6X,'R',9X,'G(R)',9X,'GXX',9X,'GYY',9X,'GZZ',
18X,'GYY',8X,'GXZ',8X,'GYZ',/)
      DO 9346 I=1,NDIST
      FI=FLOAT(I)
      DR=SQRT((FI+0.5)/FIX)-SQRT((FI-0.5)/FIX)
      R=SQRT(FI/FIX)
C      FNT=FLOAT(NT)
C      FN=FLOAT(N)
      DEN=2.0*3.1415926536*R*R*FNT*FN*RHO*DR
      IF(I.EQ.NDIST)DEN=0.5*DEN
      GR=GIN(I)/DEN
C      SG2=SIGMA*SIGMA
      G1=XXRR(I)/(DEN*SG2)
      G2=YYRR(I)/(DEN*SG2)
      G3=ZZRR(I)/(DEN*SG2)
      G4=XYRR(I)/(DEN*SG2)
      G5=XZRR(I)/(DEN*SG2)
      G6=YZRR(I)/(DEN*SG2)
      WRITE(6,3951)R,GR,G1,G2,G3,G4,G5,G6
3951  FORMAT(8(1X,G11.5))
9346  CONTINUE
      STOP
      END

```

$N = 256$

$\gamma = 20$



FORTTRAN Code for the LINK-CELL MD Method.

W. Smith

The LINK-CELL method [1,2] is one of the techniques available to the molecular dynamicist by means of which computer simulations, particularly of very large systems ( $N > 1000$ ), may be accomplished efficiently. While the method is not as efficient as the neighbour-list method [2,3,4,5] it does not require as much computer memory, nor is it as difficult to program and for very large systems it is generally held to be the preferred method.

The idea behind the LINK-CELL method is very simple; it exploits the relatively small size of the pair potential cut-off in relation to the dimensions of the system being simulated. To do this the MD simulation cell is divided into a number of equally sized sub-cells, whose widths are greater than the cutoff radius. When this is done, it is then apparent that a given particle can only interact with the particles in its own sub-cell or those in an immediately neighbouring sub-cell. It is therefore not necessary to search over the entire MD cell to locate the particles that interact with a given particle. This is where the computing time is saved. Clearly the greater the number of sub-cells that the MD cell can be divided into, the greater will be the saving. (It should be noted that the minimum number of sub-cells that can be used is 27 i.e. a  $3 \times 3 \times 3$  sub-cell system - even in this case every particle in the MD cell is regarded as potentially interacting with every other particle and there can be no time saving).

Having partitioned the MD cell, we need to know, from timestep to timestep, which sub-cell each particle is in and also which particles are in the neighbouring sub-cells. (At some stage we must also take into account the periodic boundary condition). In the LINK-CELLS method, this is done with the help of a link list. The concept of a link list is simple. First we define an array LINK(N) with a dimension equal to the number of particles in the simulation. Then an entry of the array, LINK(J), say, gives the index of a particle which shares the same sub-cell as the particle with the index J. Thus if we write  $I = \text{LINK}(J)$ , then particle 'I' is in the same sub-cell as particle 'J'. Similarly,  $K = \text{LINK}(I)$  identifies particle 'K' as yet another particle in the same sub-cell - and so on. By following the indices in this way, we can identify all the particles in a sub-cell. The end of the chain is marked by a zero entry in the LINK array; thus  $\text{LINK}(L) = 0$  indicates that particle 'L' is the last link in the chain of particles in the same sub-cell. To complete the chain, the first particle in the chain, for each sub-cell, is recorded in an auxiliary array (LCT(M), say). If any of the sub-cells is empty (an unlikely occurrence in the condensed phase), the LCT entry is set to zero. Thus once we have such a catalogue of the contents of each sub-cell, it is easy to locate all the particles we must consider when evaluating the interactions. The construction of the LINK and LCT arrays, as we shall see, is very simple, and can be calculated

afresh for each timestep, without incurring a severe cost in computing time.

Table 1 presents a FORTRAN 77 listing of the LINK-CELLS method. It should not be imagined that this is the most effective coding of the method, but it should suffice as an introduction. (It would be pleasing if it encourages the kind of response the previous articles on the neighbour list method engendered. Does anyone have a vectorised version for instance?). The coding given is for a  $4 \times 4 \times 4$  partition of the MD cell and a 864 particle system, but extensions to larger systems are trivial. The internal unit of length has been defined so that the width of the MD cell is 2 units and also, the apparent Lennard-Jones parameters EPSILON and SIGMA correspond to  $24 \times \text{Epsilon}$  and  $\text{Sigma}^2$  respectively. PLRC and VLRC are the long range corrections to the potential energy and virial respectively. The variable RCUT, which corresponds to the potential cut-off, is set to  $\text{RCUT} < 2.0/\text{AMAX0}(\text{NLX}, \text{NLY}, \text{NLZ})$ , where  $\text{NLX} \times \text{NLY} \times \text{NLZ}$  specifies the total number of sub-cells.

The LINK and LCT arrays are calculated in lines 33 to 46. For each particle the index of its sub-cell is calculated. The previous particle found in the same sub-cell is indicated in the LCT array. The new particle index is stored in LCT to mark the new chain start while the old particle index is put into the LINK array at the location specified by the new index. Since the LCT array is initialised to zero, this procedure will automatically enter a zero in LINK at the end of a chain.

The main loop of the forces calculation begins at line 54 and runs over all the sub-cells in the system. (The sub-cells indicated by this outer loop I call primary sub-cells). For each (non-empty) primary sub-cell, a secondary loop, beginning at line 61 runs over the primary sub-cell and 13 of the nearest neighbour sub-cells. (The sub-cells indicated by this loop I call secondary sub-cells). The loop runs over just 13 neighbour sub-cells (out of 26 possible) to avoid double counting of interactions in the MD cell as a whole. The identity of the secondary sub-cell is determined with the help of three short arrays NIX, NIY and NIZ, which define the X, Y and Z index displacements of the secondary sub-cell relative to the primary sub-cell. (Their role is seen in lines 66 to 68). The periodic boundary condition (as used to calculate the minimum image of each particle) is determined between lines 71 and 91, in which the values of the additive displacements CX, CY and CZ are calculated. These are applied later when the atom-atom separations are calculated. Notice that these displacements are only non-zero when the secondary sub-cell is found to be 'outside' the MD cell; a situation that can only arise when the primary sub-cell has indices indicating that it is at the edge of the MD cell.

If the secondary sub-cell is not empty, the calculation of the potential energy and the particle-particle forces is begun. Line 101 is the start of the loop over the contents of the primary sub-cell, and line 108 is the start of the loop over the secondary sub-cell contents. The actual calculation of the potential and the forces is unremarkable, but three aspects of the coding are worth

noting. Firstly, notice how the LINK array is exploited to identify the next particle in both the primary and secondary particle loops (lines 130 and 126 respectively) and how the start of the chain of particles for the secondary loop is reset using the LCT array at line 129. Secondly, note how the aforementioned variables CX, CY and CZ are used in calculating the minimum image (lines 109 to 111). Finally, note how the chain start for the secondary loop is reset, when it transpires that the primary and secondary sub-cells are the same (line 105). This is necessary to prevent double-counting of interactions within the primary sub-cell.

The loop over secondary sub-cells ends at line 133. Following this is a short section which generates the indices of the next primary sub-cell. The primary loop over sub-cells ends at line 146.

Readers with an aversion to using IF statements to control loops (and I am usually one of them) will no doubt wonder why the loops over the particles are controlled in this way. Certainly, it is not necessary to do this, and a DO loop structure may be devised - based on a count of the number of particles in each sub-cell for example. Such strategy would be a pre-requisite to vectorisation, which would also require GATHER and SCATTER stages [6]. However, I have retained the IF loop structure since I believe that the role of the LINK and LCT arrays is better exemplified. The present code is quite adequate for scalar machines.

Table 2 presents some timings for runs of a LINK-CELLS program called MDLINK. The results were obtained on the Daresbury FPS 164, though no effort was made to optimise the code for that particular machine. The table shows clearly how the LINK-CELLS method greatly improves the efficiency of a molecular dynamics simulation of large systems. The larger the number of sub-cells, the more efficient the method becomes.

#### References

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- [2] D.M. Heyes, CCP5 Info. Quart. No.2 (1981) p11.
- [3] D. Adams, CCP5 Info. Quart. No.3 (1982) p32.
- [4] S.M. Thompson, CCP5 Info. Quart. No.8 (1983) p20.
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- [6] D. Fincham and B.J. Ralston, Comp. Phys. Comm. V23 (1981) P127.



TABLE 1. FORTRAN 77 Code for the LINK-CELLS Method.

```

SUBROUTINE FORCES                                001
C                                                002
C*****003
C                                                004
C   CALCULATE SHORT RANGED FORCES ON EACH PARTICLE 005
C                                                006
C*****007
C                                                008
C   PARAMETER (NSP=864,NLX=4,NLY=4,NLZ=4)          009
C   PARAMETER (NCELLS=NLX*NLY*NLZ)                010
C   COMMON/CMSYST/SIGMA, EPSLON, RCUT, PLRC, VLRC  011
C   COMMON/CMVECT/XX(NSP), YY(NSP), ZZ(NSP)       012
C   COMMON/CMPOTL/CPE, CVR, FRX(NSP), FRY(NSP), FRZ(NSP) 013
C   COMMON/CMINDX/LCT(NCELLS), LINK(NSP)         014
C   DIMENSION NIX(14), NIY(14), NIZ(14)         015
C   DATA NIX/ 0,-1,-1,-1, 0, 0,-1, 1,-1, 0, 1,-1, 0, 1/ 016
C   DATA NIY/ 0, 0,-1, 1, 1, 0, 0, 0,-1,-1,-1, 1, 1, 1/ 017
C   DATA NIZ/ 0, 0, 0, 0, 0, 1, 1, 1, 1, 1, 1, 1, 1, 1/ 018
C   RRC=1.0/RCUT**2                               019
C                                                020
C   INITIALISE POTENTIAL ENERGY AND VIRIAL      021
C   CPE=0.0                                        022
C   CVR=0.0                                        023
C                                                024
C   INITIALISE FORCE ARRAYS                       025
C   DO 100 I=1,NSP                                026
C   FRX(I)=0.0                                    027
C   FRY(I)=0.0                                    028
C   FRZ(I)=0.0                                    029
C 100 CONTINUE                                    030
C                                                031
C   CALCULATE LINK CELL INDICES                  032
C   DO 110 L=1,NCELLS                             033
C 110 LCT(L)=0                                     034
C   XDC=0.5*FLOAT(NLX)                           035
C   YDC=0.5*FLOAT(NLY)                           036
C   ZDC=0.5*FLOAT(NLZ)                           037
C   DO 120 I=1,NSP                                038
C   IX=INT(XDC*(XX(I)+1.0))                       039
C   IY=INT(YDC*(YY(I)+1.0))                       040
C   IZ=INT(ZDC*(ZZ(I)+1.0))                       041
C   ICELL=1+IX+NLX*(IY+NLY*IZ)                   042
C   J=LCT(ICELL)                                  043
C   LCT(ICELL)=I                                  044
C   LINK(I)=J                                     045
C 120 CONTINUE                                    046
C                                                047
C   SET CONTROL VARIABLES FOR LOOP OVER SUB-CELLS 048
C   IX=1                                          049
C   IY=1                                          050
C   IZ=1                                          051
C                                                052

```

```

C     PRIMARY LOOP OVER ALL SUB-CELLS                                053
C     DO 500 IC=1,NCELLS                                           054
C     II=LCT(IC)                                                    055
C     .                                                                056
C     BYPASS SUB-CELL IF EMPTY                                     057
C     IF(II.GT.0)THEN                                              058
C     .                                                                059
C     SECONDARY LOOP OVER SUB-CELLS                                060
C     DO 400 KC=1,14                                               061
C     I=II                                                            062
C     CX=0.0                                                         063
C     CY=0.0                                                         064
C     CZ=0.0                                                         065
C     JX=IX+NIX(KC)                                                 066
C     JY=IY+NIY(KC)                                                 067
C     JZ=IZ+NIZ(KC)                                                 068
C     .                                                                069
C     MINIMUM IMAGE CONVENTION                                     070
C     IF((IX.EQ.NLX).AND.(JX.GT.IX))THEN                            071
C     JX=1                                                            072
C     CX=2.0                                                         073
C     ELSEIF((IX.EQ.1).AND.(JX.LT.IX))THEN                          074
C     JX=NLX                                                         075
C     CX=-2.0                                                        076
C     ENDIF                                                           077
C     IF((IY.EQ.NLY).AND.(JY.GT.IY))THEN                            078
C     JY=1                                                            079
C     CY=2.0                                                         080
C     ELSEIF((IY.EQ.1).AND.(JY.LT.IY))THEN                          081
C     JY=NLY                                                         082
C     CY=-2.0                                                        083
C     ENDIF                                                           084
C     IF((IZ.EQ.NLZ).AND.(JZ.GT.IZ))THEN                            085
C     JZ=1                                                            086
C     CZ=2.0                                                         087
C     ELSEIF((IZ.EQ.1).AND.(JZ.LT.IZ))THEN                          088
C     JZ=NLZ                                                         089
C     CZ=-2.0                                                        090
C     ENDIF                                                           091
C     .                                                                092
C     INDEX OF NEIGHBOURING SUB-CELL                               093
C     JC=JX+NLX*((JY-1)+NLY*(JZ-1))                                094
C     J=LCT(JC)                                                      095
C     .                                                                096
C     BYPASS SUB-CELL IF EMPTY                                     097
C     IF(J.GT.0)THEN                                                098
C     .                                                                099
C     LOOP OVER PRIMARY SUB-CELL CONTENTS                           100
200  IF(IC.EQ.JC)J=LINK(I)                                           101
C     IF(J.GT.0)THEN                                                102
C     XI=XX(I)                                                       103
C     YI=YY(I)                                                       104
C     ZI=ZZ(I)                                                       105
C     .                                                                106
C     LOOP OVER SECONDARY SUB-CELL CONTENTS                          107

```

|     |   |     |
|-----|---|-----|
| 300 | CONTINUE                                | 108 |
|     | XDIF=(XX(J)-XI+CX)                      | 109 |
|     | YDIF=(YY(J)-YI+CY)                      | 110 |
|     | ZDIF=(ZZ(J)-ZI+CZ)                      | 111 |
|     | RIV=1.0/(XDIF*XDIF+YDIF*YDIF+ZDIF*ZDIF) | 112 |
|     | IF(RIV.GT.RRC)THEN                      | 113 |
|     | SR3=(SIGMA*RIV)**3                      | 114 |
|     | SR6=SR3*SR3                             | 115 |
|     | GAMMA=RIV*EPSLON*(SR6+SR6-SR3)          | 116 |
|     | CPE=CPE+EPSLON*(SR6-SR3)                | 117 |
|     | CVR=CVR-GAMMA/RIV                       | 118 |
|     | FRX(I)=FRX(I)-GAMMA*XDIF                | 119 |
|     | FRX(J)=FRX(J)+GAMMA*XDIF                | 120 |
|     | FRY(I)=FRY(I)-GAMMA*YDIF                | 121 |
|     | FRY(J)=FRY(J)+GAMMA*YDIF                | 122 |
|     | FRZ(I)=FRZ(I)-GAMMA*ZDIF                | 123 |
|     | FRZ(J)=FRZ(J)+GAMMA*ZDIF                | 124 |
|     | ENDIF                                   | 125 |
|     | J=LINK(J)                               | 126 |
|     | IF(J.NE.0)GO TO 300                     | 127 |
|     | ENDIF                                   | 128 |
|     | J=LCT(JC)                               | 129 |
|     | I=LINK(I)                               | 130 |
|     | IF(I.NE.0)GO TO 200                     | 131 |
|     | ENDIF                                   | 132 |
| 400 | CONTINUE                                | 133 |
|     | ENDIF                                   | 134 |
| C   |   | 135 |
| C   | PRIMARY SUB-CELL INDEX CONTROL SECTION  | 136 |
|     | IX=IX+1                                 | 137 |
|     | IF(IX.GT.NLX)THEN                       | 138 |
|     | IX=1                                    | 139 |
|     | IY=IY+1                                 | 140 |
|     | IF(IY.GT.NLY)THEN                       | 141 |
|     | IY=1                                    | 142 |
|     | IZ=IZ+1                                 | 143 |
|     | ENDIF                                   | 144 |
|     | ENDIF                                   | 145 |
| 500 | CONTINUE                                | 146 |
| C   |   | 147 |
| C   | ADD LONG RANGE CORRECTIONS              | 148 |
|     | CPE=CPE/6.0+PLRC                        | 149 |
|     | CVR=CVR+VLRC                            | 150 |
|     | RETURN                                  | 151 |
|     | END                                     | 152 |

TABLE 2.

Typical Timings for a Single Timestep with the LINK-CELLS Method.

| No. Ples. | Number of Sub-cells |       |       |      |      |
|-----------|---------------------|-------|-------|------|------|
|           | 64                  | 125   | 216   | 343  | 512  |
| 864       | 2.25                |       |       |      |      |
| 1372      | 5.55                | 2.97  |       |      |      |
| 2048      | 12.35               | 6.54  | 3.88  |      |      |
| 2916      | 24.86               | 12.67 | 7.58  | 4.96 |      |
| 4000      | 46.80!              | 24.09 | 14.13 | 9.23 | 6.42 |

Note: All timings are in seconds per MD timestep.

! = Estimated time.

## The migration of interstitial cations in $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

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Ireland.

Because iron and chromium are constituents in many high temperature steels there is considerable technological importance in understanding fully the growth mechanisms of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> during oxidation. In common with some other high temperature corrosion reactions the migration of the cations through the oxide layer is thought to be a vital part of these growth processes and a comprehensive atomistic simulation study of these materials has been undertaken [1]. The present report concerns one aspect of this work, namely the migration of interstitial cations in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the calculations were made using the CASCADE program.

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has the corundum structure and the available experimental evidence suggests that cation interstitials migrate by an interstitialcy mechanism. This involves the initial interstitial ion knocking a lattice cation into another interstitial position while taking up the empty lattice site itself. Four such interstitialcy pathways were identified in the corundum structure: each of them is more complicated than the type of interstitialcy migration which has been modelled previously [2] in that their two sections are not symmetrical. Interstitialcy motion is modelled by fixing the first interstitial at a series of points along an approach direction to the lattice cation which it will displace while allowing that cation, as well as the remainder of the crystal, to relax in the energy minimization procedure.

The interionic potentials used for the main part of the project have been published [3]. When these were used in the present work the cations suffered excessive polarization and a new interionic potential was derived in which  $\text{Fe}^{3+}$  was treated as a rigid ion. This potential was fitted to the crystal properties in the usual way and proved to be only negligibly different from the original potential when used to calculate the basic defect energies. Activation energies were first calculated for all the four interstitialcy mechanisms as well as for a direct interstitial jump. With the exception of one interstitialcy pathway all gave unacceptably high migration energies ( $\sim 10\text{eV}$ ) and thus, on the basis of these calculations, would appear to be unlikely to occur in  $\alpha\text{-Fe}_2\text{O}_3$ . The one mechanism which gave a much lower calculated migration energy,  $\sim 2.0\text{eV}$ , involved a movement of the interstitial ion in the c-direction with the displaced lattice cation then moving away at an angle so that it had a component in the horizontal plane. The calculated energy profile for this motion is shown in the Figure as a function of the distance along the line of approach.

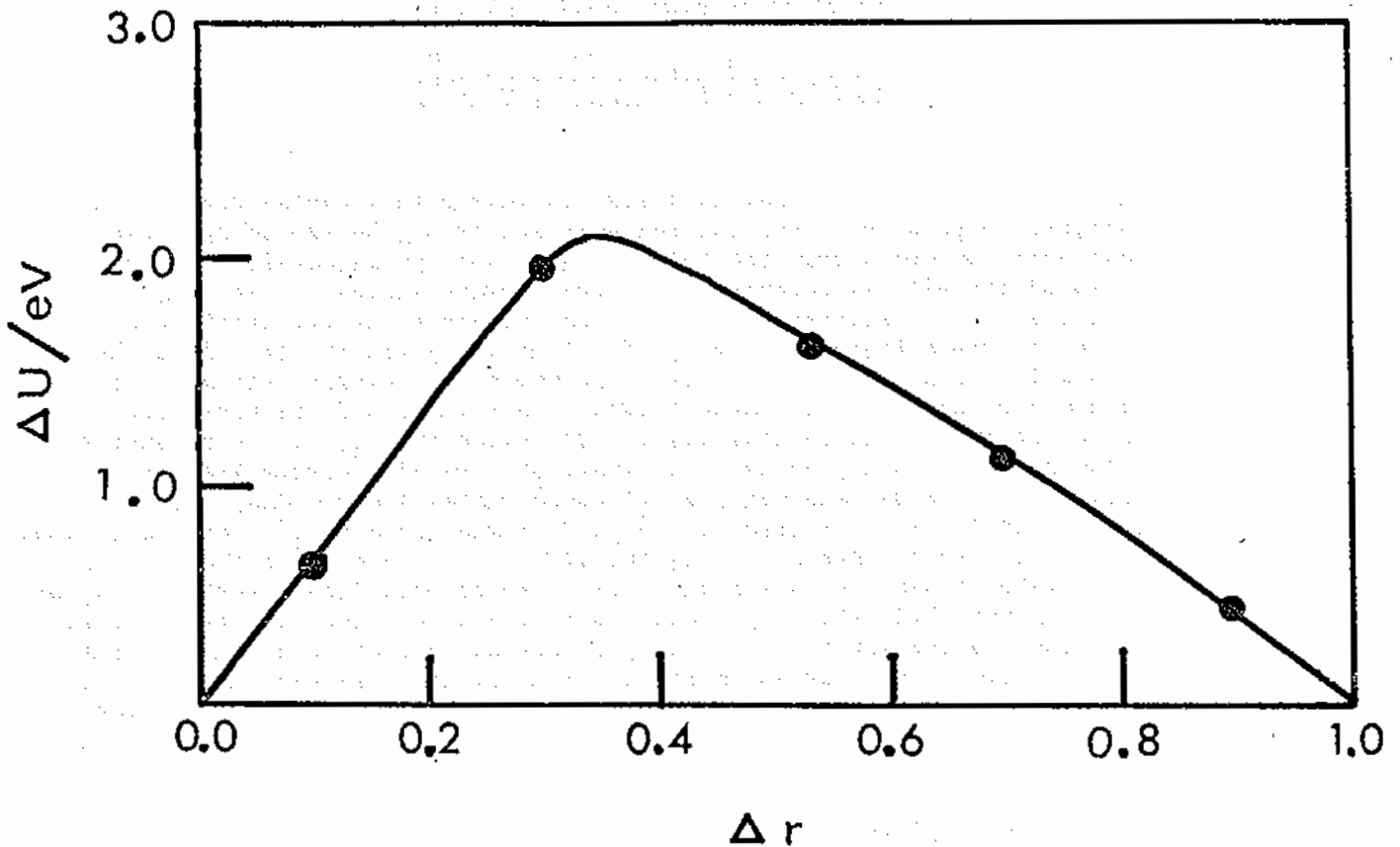
These results are encouraging and the calculations suggest that this interstitialcy motion may be feasible in  $\alpha\text{-Fe}_2\text{O}_3$ . The experimental Arrhenius energies, for which the mechanism has not been confirmed, are of the order of  $6\text{eV}$ . When defect formation energies are taken into account and an estimate is made of the effect of crystal field stabilization energies, our result appears to be quite reasonable. The work has also provided valuable experience in the type of calculations which are necessary to explore fully these more complicated interstitialcy migration pathways.

#### Acknowledgements

JC gratefully acknowledges the provision of financial assistance by CC P5 which made it possible for him to visit the SERC Laboratory at Daresbury.

## References

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- [2] Jacobs P.W.M., Corish J. and Catlow C.R.A. J. Phys. C., 13 (1980) 1977.
- [3] Mackrodt W.C. and Stewart R.F. in 'Handbook of Interatomic Potentials' A.M.Stoneham, AERE Harwell Report 9598 (1979)



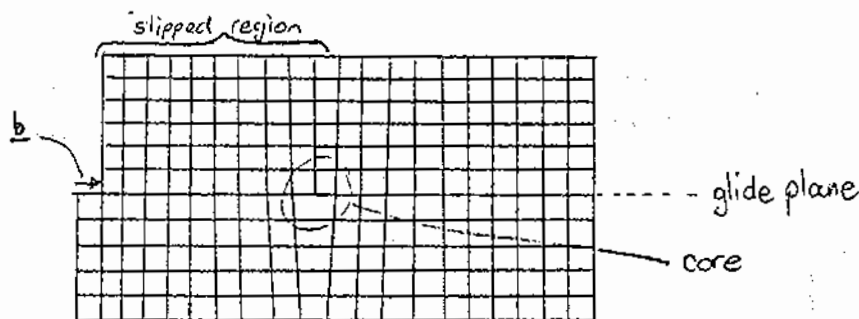
Profile of the calculated activation energy,  $\Delta U$ , for the most favourable interstitialcy mechanism as a function of the distance along the line of approach of the interstitial ion that initiates the migration.

## Plasticity - A suitable case for treatment ?

M. Heggie (Exeter)

The theoretical study of plasticity has recently been in the doldrums, particularly in Britain. This article has been written to renew interest in an exciting field that now offers new opportunities for understanding materials and it totally rejects the popular view that the theory of dislocations was wrapped up thirty years ago.

Starting mainly with the three independent seminal papers by Orowan, Polanyi and Taylor [1,2,3] it gradually became established through theory and later direct observation [4] that dislocation creation and movement dominates the plasticity of solids under most conditions. Instead of rational planes maintaining their integrity while slipping over one another, one part of such a plane and all the atoms above it will slip with respect to the plane below. This incomplete slip is illustrated below.



When the slip is about equal to a lattice vector this configuration - a dislocated crystal - is not too unstable and it may be frozen-in. Thus local shear occurs across the "glide plane" and the magnitude and direction of the slip is referred to as the Burgers vector,  $\underline{b}$ . The region where the slip is neither nearly zero nor nearly a lattice translation vector, i.e. where bonding in the glide plane is difficult, is called the dislocation core. The dislocation line, which runs through the core is the boundary in the glide plane between the slipped and the unslipped region. If a dislocation line changes its direction,  $\underline{l}$ , then the character of the dislocation may change. For instance, the edge dislocation of the first figure ( $\underline{b}$  perpendicular to  $\underline{l}$ ) would become a screw dislocation ( $\underline{b}$  parallel to  $\underline{l}$ ) if it turned in the glide plane through  $90^\circ$ . This is because the Burgers vector characterising the slip stays constant in the absence of other dislocations. The dislocation line cannot move "conservatively" up or down from the glide plane - it must emit or absorb point defects to do so (non-conservative motion). The easy, conservative motion, known as glide, occurs by simple bond-swapping in the glide plane to advance the slipped region and hence the dislocation. More involved rearrangements of bonds across the glide plane have been postulated for some core structures and termed "shuffle".

The process of glide is the predominant mechanism of plastic deformation under most normal conditions (say  $T = 0.6 \times$  melting temperature,  $T_m$ , shear stress resolved into the slip plane,  $s < 0.01 \times$  shear modulus,  $\mu$ , applied for less than a day). The dislocation line feels an effective force per unit of its length of  $sb$ , as the shear stress tries to extend the slipped region. At



low stresses and temperatures the dislocation will not move - the effective force is not sufficient to break the bonds in the dislocation core and so the bond rearrangements necessary for glide cannot occur (tunneling does not seem to be important). As the stress is raised to the "Peierls stress" this condition is no longer true and the dislocations can glide, so the material yields. The dislocation can glide more or less as a whole because the effective force acts nearly uniformly over its whole length. Ductile materials like metals generally have low Peierls stresses, while strong, covalent solids have very high Peierls stresses, which tend to diminish with increasing ionic or metallic character.

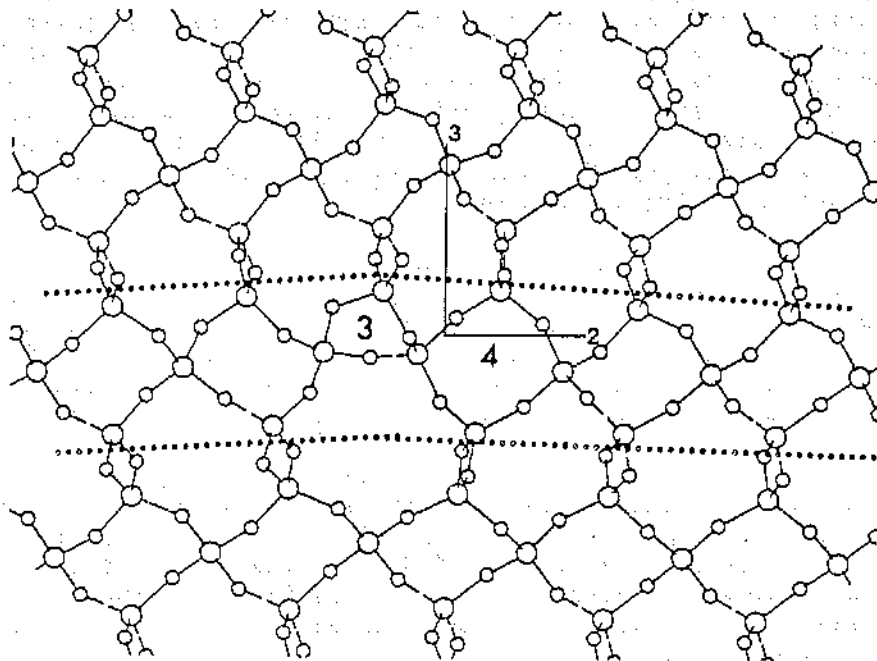
The Peierls stress can be estimated by computer modelling in a way similar to the methods to be described later and in ionic solids and metals [5] such a calculation is useful and may be the only sort of calculation possible. But in covalent solids its usefulness is very limited. This is because dislocations in these materials under moderate stresses (much less than the Peierls stress) move by thermal activation, with the stress providing the thermodynamic force. The most likely mechanism for thermal activation will involve least energy and the least energy process will involve only a small part of the dislocation in each step. The Peierls stress would cause the long, straight dislocation lying in its potential valley ("Peierls valley") to move as a whole to the next one (normally a lattice vector away in the glide plane) But at lower stresses and finite temperature a small segment of dislocation might jump to the next valley, being bounded at each end by "kinks" in the dislocation line where the line mounts the Peierls energy barrier ("of the first kind") separating the valleys. Bearing in mind the atomistic nature of the solid, the smallest possible kink pair has a width of about a lattice vector. The applied stress and temperature then act further on the kink pair, once it has been nucleated, causing it to expand (or be ripped apart at high stresses) leaving the dislocation in the next valley. If the kink pair cannot reach a critical width dependent on stress then it will collapse instead of expanding. The atomistic nature of the problem means that kinks have stable positions on the dislocation line, normally a lattice vector apart, separated from each other by another energy barrier (the "Peierls barrier of the second kind"). The barrier of the first kind gives rise to a kink pair formation energy,  $F_{kp}$ , while the barrier of the second kind gives rise to a kink migration energy,  $W$ . The reason why kink pairs tend to collapse at small widths is that the kinks in a pair act like short segments of dislocation of opposite Burgers vectors and so they attract each other with an elastic Peach-Koehler force [6,7]. This force falls off as the inverse square separation of the kinks and is roughly balanced by the force on the kinks due to the applied stress at the critical width [7]. Modelling of dislocation mobility aims at estimating the values of  $F_{kp}(x)$  - the kink pair formation energy as a function of its width,  $x$  - and  $W$ .

Several factors conspire to make this sort of calculation feasible and worthwhile for covalent solids. Firstly, observations of dislocations in an electron microscope reveal that dislocation motion at moderately high stresses must be limited by the rate of nucleation of kink pairs of a critical width less than 5 lattice vectors. This means that the formation and migration energy for the rate-determining step may be estimated from clusters of, say, 6000 atoms, which contain the appropriately kinked dislocation. Secondly, modern mainframes can easily cope with minimising the energy of 6000 atoms if a simple valence force potential is used with either a "steepest descent" or "conjugate gradient" algorithm. Such a calculation is a natural progression from the early modelling of dislocations using linear continuum elasticity, which said little of the dislocation core. The valence force potential expresses the energy of a cluster of atoms as a sum of contributions from constituent atoms, each contribution being a simple function of the atom's

valence coordinates (ie bond lengths and bonds angles). Normally these contributions are proportional to the square of the difference between the actual valence coordinate and its value in an ideal, reference crystal structure. The constants of proportionality are fixed so as to reproduce, for example, the elastic constants, the measured phonon spectrum and/or the movements of atoms in the unit cell occurring under high hydrostatic pressure (monitored by X-ray diffraction) for the perfect crystal.

The fascinating aspect of these calculations, apart from the "getting to grips" with the intricacies of the dislocation and kink structures, is that this first-order approach to the atomistic nature of solids draws information from the elastic properties of the material and yields important information about its plastic behaviour. The project that led to the writing of this article concerned plasticity in  $\alpha$ -quartz and it was prosecuted with a 3 year Research Assistantship from the SERC. In those three years the prescription above was followed and additional calculations were made to account for the effect of water on dislocations. Unlike earlier research into dislocations in silicon [8] there was little theoretical work to build on, but some very useful results were obtained - this is very encouraging for future work on other materials.

This lack of background material meant that the ground state structures of the cores of dislocations had to be found by examining all reasonable possibilities [9]. The unit cell of  $\alpha$ -quartz ( $\text{SiO}_2$ ) contains nine atoms - a fact that gives rise to many possible dislocation core structures. The number of structures examined was limited to 15 by assuming that the strain in the dislocation core was insufficient to cause broken bonds or valence alternation. (This assumption appeared justified, a posteriori, because of the low dislocation core energies found). One low energy dislocation in the basal plane of the trigonal  $\alpha$ -quartz structure was studied in detail in order to find  $F_{kp}(x)$  and  $W$ . An axial view of this dislocation is given below (oxygen atoms are illustrated as small spheres, twofold coordinated and silicon atoms are larger and tetrahedrally coordinated). This dislocation has line direction  $\underline{a}_1$  and Burgers vector  $\underline{a}_2$  (whose projection is marked with a small 2). The glide plane is  $c$  (the  $c$  axis is denoted by a small 3) and the glide plane atoms are those between the dotted lines.



Looking along a in perfect  $\alpha$ -quartz one sees channels bounded by either 4 or 6 silicon atoms, which are in fact helices. However, in the dislocation core there are two channels bounded by 3 and 4 silicon atoms (marked 3 and 4 in the diagram) which were originally right-handed helices like the other 4-fold channels, but may be ring-like in the dislocation core. The formation of rings seems to reduce the strain due to the screw component in this "60°" dislocation (the angle quoted is the angle between the Burgers vector and the line direction, i.e. it is 90° for an edge and 0° for screw). The ground state of this dislocation had a ring structure in the four-fold channel and a right-handed helix in the three-fold channel. The movement of this dislocation is rather complicated to describe but it will be published in detail later - the picture of the dislocation above was included to give a feeling for the complexity of this problem.

In essence what the computer modelling revealed was that the dislocation would be highly immobile in dry  $\alpha$ -quartz, because  $F_{kp}(x) = 5$  eV (for  $x=1$  to 5 lattice vectors and  $W > 4$  eV. The kink-kink interaction was very small, since  $F_{kp}$  was more or less a constant and hence the critical width would be about  $x=1$  lattice vector. However the large strains in the kinks that gave rise to these values could be released by breaking some Si-O-Si bonds in the core of the kinks. The presence of water should allow Si-O-Si bonds to hydrolyse into Si-OH HO-Si configurations and it was found that these could separate, allowing one -OH group to associate with each side of the kink pair. This reduced  $F_{kp}$  to less than 1 eV [10], with probably a similar change in  $W$  (it was not possible to calculate  $W$  for wet quartz). Thus it was shown theoretically why wet quartz is so much less brittle and hard than dry quartz and that one of the earliest hypotheses concerning this experimentally observed fact [11] (i.e. the hydrolysis above) is most credible. It should be noted that another mechanism, due to Hirsch [12], that invoked charge transfer between water in the lattice and kinks was investigated by using ab-initio calculations [10,13] of the electronic levels of dislocations and kinks. This mechanism seemed unreasonable in the light of these calculations.

More calculations will be necessary to shore-up the conclusions that have been stated here, but these initial findings are very exciting.

The study of dislocations in this fashion and with more refined models will intensify in the coming years because of the need to understand dislocation mobility. It offers the hope of a quantitative explanation of the hardness of solids and of hardening and softening mechanisms. Combined with similar studies of crack propagation it will show why the brittle/ductile transition occurs and how it can be moved by, for instance, adding or removing impurities. Fundamental geology, particularly the behaviour of the earth's crust, stimulated the modelling of  $\alpha$ -quartz and it will spawn other studies on, for example, feldspars and ice. The demands of reactor technology and the increasing structural use of carbon fibres will be supported theoretically by an understanding of dislocation movement in graphite.

Finally, and of equal importance, is the idea that dislocation cores can be models for the short range (defect) properties of amorphous or glassy solids. These materials are very difficult to study because of their lack of long range order, but nevertheless the conventional current approach involves experiments on amorphous materials themselves and theoretical modelling of hand- or computer-built amorphous networks. Little has been done to ameliorate the complexity, while retaining the essential features of the amorphous state. In a dislocation core probably all of the bonding defects postulated to exist in the amorphous state can exist. Examples in silica glass are the rings of atoms  $(-\text{Si-O-Si-})_n$ ,  $n=3$  to 5, evident in the last figure, valence

alternation defects ( $O_2, O_3, Si_3$ ) and peroxy defects. The advantage is that both experiment and theory/computational modelling can be applied to well-characterised dislocations and they would not be hindered by the "dirty" background (eg. band-tailing) found in amorphous structures. In building a huge continuous random network of atoms the number of possible configurations is almost limitless, but a dislocation core is more or less well defined by

the dislocation direction and character. Computer modelling of dislocations with different directions and Burgers vectors would reveal differences in structure and these structure properties could then be correlated with differences in electronic and physical properties observed by, for instance, the various forms of electron microscopy applied to exactly the same set of dislocations. This would allow the characteristics of each bonding defect to be isolated and described - a process of "dissection" that is fundamental to scientific method.

This argument applies to the whole range of elements and compounds that form an amorphous phase and should revitalise the study of dislocations. However it does involve stepping back from the problem in hand to more fundamental physics - a step that some people are reluctant to take.

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CCPS LITERATURE SURVEY 1985.

W. Smith

We present below the result of our 1985 literature survey. In truth the response to our appeal was disappointing, but a sufficient number of readers responded to make further efforts worthwhile. Thanks to the Library Services at Daresbury, we were able to conduct a search of the periodicals that the Daresbury Laboratory subscribes to! Such a survey cannot of course compete with a computer search, but we hope we have produced something that will be of use.

Our special thanks go to everyone who responded to our appeal.

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

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

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

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

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

OXFORD CCP5 MEETING - REGISTRATION FORM

Name: .....

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Accompanying members:

I will be accompanied by (name):

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Student requesting reduced fee:

I am a registered student and am submitting a contribution

Contribution:

I hope to present a talk  poster

Title:

For a talk - I enclose a short abstract

Conference Fee:

I enclose a cheque for £ payable to "The Glass Transition"

I will pay later  on arrival.