

DARESBUURY LABORATORY

INFORMATION QUARTERLY for COMPUTER SIMULATION OF CONDENSED PHASES

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

The coming months promise to be very active ones for CCP5. The visit by Professor B. J. Berne (see below) is very likely to be a great source of ideas and has been looked forward to eagerly for the past nine months. We hope all those who attend any of his venues will find the experience stimulating. Workshops too are very much in the news. There are three more being planned (below) that should generate some useful discussion in the areas of transport properties, graphics and ceramics. CCP5 members should note however that it is in the nature of a workshop that the numbers attending should be carefully controlled to encourage the essential informal discussion. It is therefore necessary to ask that those without a high degree of commitment to the subject matter refrain from applying. That way, hopefully, no-one with a real interest will be disappointed.

Once again your editor thanks those who have contributed to the present newsletter. It is gratifying that their interest in the survival of the newsletter is so strong. This does not mean however that we have ample authors available - far from it! We therefore request that our dedicated readers endeavour to fill our pages with the kind of articles everyone prefers to read: their own!

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General News.

a) The proposed CCP5 sponsored visit by Professor B. J. Berne is now imminent. As a result of replies to the recent questionnaire sent out by Daresbury, a clear idea of the requirements of CCP5 participants has emerged. In response to these requirements the itinerary of Professor Berne's visit is as follows:

Oxford - October 21st. to 22nd. Professor Berne will speak on the subject of 'Quantum Mechanical Computer Simulation' on the afternoon of 22nd. October. This will be followed by a workshop on the same subject. (Contact: Dr. M. P. Allen, Physical Chemistry Laboratory, Oxford).

Cambridge - October 23d. to 24th. Professor Berne will speak on the subject of 'The Computer Simulation of Rare (Activated) Events' on Wednesday 24th. October at 2:15 pm. (Contact: Dr. R. Lynden - Bell, Chemical Laboratories, Cambridge)

Birkbeck College, London - October 25th. to 26th. Professor Berne will speak on the subject of 'Water and Aqueous Solutions' on the morning of Friday 26th. October. This will be followed by a workshop on water in the afternoon. (Contact: Dr. J. L. Finney, Department of Crystallography, Birkbeck).

Interested parties should write the people indicated above to let them know of their intention to attend and to receive news of local plans. If sufficient time is available CCP5 will also circulate the final details. Some travel funds may be available, at the discretion of the CCP5 Executive Committee, upon application to Dr. W. Smith, TCS Division, S.E.R.C. Daresbury Laboratory, Warrington WA4 4AD.

b) CCP5 is to collaborate with the Statistical Mechanics and Thermodynamics Group of the Royal Society of Chemistry in organising a two day meeting on: 'Dense Fluids: Dynamic and Static Properties' at Bristol in April 1985 (10th. - 11th.). Papers will be welcome in any of the following areas:

The computer simulation of time dependent properties and complementary theory.

The gas-liquid interface and surface induced phenomena, such as wetting; (papers on phase transitions in adsorbed monolayers are inappropriate).

Equilibrium properties of molecularly simple liquids and their mixtures.

The speakers who have agreed to attend so far include G. Stell (University of New York at Stony Brook), W. Steele (University of Pennsylvania), J.-P. Hansen (University of Paris) and R. Evans (University of Bristol).

The conference organisers see a particular role for some papers dealing primarily with experimental results, provided that such work is directly related to theoretical development and/or to simulation studies. Those interested should write to Mr. A. J. B. Cruickshank, School of Chemistry, The University of Bristol, Cantock's Close, Bristol BS8 1TS.

Readers may also be interested to know that CCP5 is also planning a meeting on 'Large Molecules and Stochastic Methods', which will take place in York in September 1985.

c) CCP5 is to organise two workshops in the near future. The first is on the subject of transport properties (Royal Holloway College December or January 1984-85) and the second on the Simulation of Ceramics (ICI Runcorn December or January 1984-85). Interested readers should contact Professor K. Singer or Dr. D. Heyes, Department of Chemistry, Royal Holloway College, Egham, Surrey TW20 OEX in the first case and Dr. W. G. Mackrodt, ICI Corporate Laboratory, Runcorn, Cheshire in the second. Potential participants are warned that the nature of these workshops will mean that a restricted number of persons (maximum 15) will be able to attend.

d) CCP5 is also to organise a series of workshop sessions on graphics, with emphasis on its applicability to computer simulation and to the simulation of large molecules in particular. The series will begin with a one day meeting in November to discuss possible applications and learn about the available techniques. Subsequent meetings will develop software and discuss problems. A high degree of commitment is expected of all participants. Those interested should contact Dr. W. Smith, T.C.S. Division, S.E.R.C. Daresbury Laboratory, Warrington WA4 4AD, for information.

e) The CCP5 Steering Committee Meeting, which took place on Friday 21st. September 1984, has elected Dr. Julian Clarke (Department of Chemistry, U.M.I.S.T.) as the Chairman of CCP5. Dr. Clarke, has been Acting Chairman since the resignation of Professor J. G. Powles earlier this year. The Meeting also elected Dr. N. Quirke (B.P. Sunbury-on-Thames) and Dr. P. Madden (Oxford) to serve on the Executive Committee. The Executive Committee therefore consists of the following personnel:

Dr. J.H.R. Clarke (U.M.I.S.T.) Chairman,
Dr. C.R.A. Catlow (London),
Dr. M. Leslie (S.E.R.C.),
Dr. P.A. Madden (Oxford),
Dr. N. Quirke (British Petroleum),
Dr. W. Smith (S.E.R.C.) Secretary,
Dr. D. Tildesley (Southampton).

f) At the Rutherford and Appleton Laboratory, changes are to be made to the structure of the Computing Division; in response to the Central Computing Committee's Computer Review Working Party. From

July 1st. 1984 the division is to be split into the Central Computing Division (under Dr. G. J. Pavelin) and the Informatics Division (under Professor F. R. A. Hoggood). The Central Computing Division is to be responsible for the provision and maintenance of the mainframe services while the Informatics Division will be responsible for 'the Engineering Board's interactive computing facility, the single user system programme, the Alvey infrastructure and coordination/reasearch in I.K.B.S., software engineering and other related Alvey areas'.

R.A.L. reports that they have been running the ATLAS 10 as a front end recently to test its suitability in the role as well as to investigate previous MVT storage overwrites. Both of these objectives were achieved, though the performance as a front end was slower than hoped.

An item of news missed in our last report was the Central Computing Committee's decision to withdraw support from a number of multi user minicomputers (at Bradford, Cranfield, Glasgow, Heriot - Watt, Newcastle, Queen Mary College and Nottingham. This nominally occurred in May/June. Some of these centres are attempting to continue the services beyond the period of withdrawal using local funds, but most are looking elsewhere for alternative facilities.

The July issue of the R.A.L. newsletter FORUM84 contains a Graphics Supplement, which should be useful for graphics enthusiasts.

g) Users of the University of London Computing Centre should note that the 1983/84 block allocation of resources to S.E.R.C. supported users terminated in July 1984 along with the administration of this allocation at Daresbury. Users will, in future, have to be registered by their own institutions as are other University users. The administration of new allocations will be by the institution representative. Allocation of resources on the CRAY 1s and the AMDAHL V/8 will be in terms of 'shares' (see the U.L.C.C. newsletter for July 1984). The account numbers allocated for the 1983/84 period are now invalid.

Changes are also being made to the job scheduling. The number of AMDAHL jobs queued with a given account number will be limited in future and the job scheduling algorithm will take into account institutional and regional usage and therefore individual usage may affect the scheduling of jobs of other users in the same institution or region. A similar scheduler is planned for the CRAY 1s.

An operating system upgrade (MVS SPI.1 8101-G) is being prepared for the AMDAHL. Field trials were scheduled for late August. Similarly a new CRAY operating system (COS 1.12) was field trialled in July and has now been installed with the new CFT 1.11 FORTRAN compiler. These changes will have a significant impact on U.L.C.C. users, who should consult the U.L.C.C. August/September newsletter. The most important changes which may affect CCP5

program users are outlined below.

(1) The M parameter on the job card must be replaced by a MFL parameter, with the memory specified in decimal words instead of octal blocks.

(2) The RFL statement must be replaced by the MEMORY statement:
MEMORY,FL=words.
where words is the decimal number of words requested.

(3) FORTRAN users who obtain system information in the program using CALL SYSTEM will need to modify and recompile their programs. This will affect, in particular, any CRAY users of the suite of CCP5 programs written by S. Thompson. The calling sequence should now be as shown below:

For example, to obtain the job time;
DIMENSION IFAC(50)
DATA IFAC/50*0/,TCONVT/1.024E-9/

CALL ACTTABLE(IFAC,43)
JOBTIM=IFAC(12)*TCONVT

Similar changes will be needed to obtain other accounting information.

(4) It is now possible to use AUDIT to obtain information on an account other than the one on which the job is run.

h) The University of Manchester Regional Computing Centre has seen its fair share of troubles since the installation of the AMDAHL V/8 and CYBER 205 configuration but the situation is improving as time goes by. A number of improvements to the AMDAHL operating system are being implemented or are scheduled for the near future. These include the provision of job queue information, implementation of the latest version of MVS, provision of MASSTOR transparency and improved filestore management facilities. A new release of the Remote Host Facility software is planned for September. The new CYBER 205 operating system VSOS 2.1.5 will be installed as soon as possible, when it is expected to reduce the number of failures due to lack of RHF robustness. Improved disc management is also planned. U.M.R.C.C. is establishing a CYBER 205 Consultancy Unit and a CYBER 205 newsletter to improve user support.

The upgrade of the large core memory (LCM) of the CDC 7600's reported earlier has begun. One was completed in July and the second is scheduled for late August. The new CYBER 176 computer is expected to arrive before the end of September and will be commissioned in the first part of October. It will have the memory capacity of both the enhanced 7600's combined and a larger small core memory than either. It will be available to existing 7600 users. The ICL 1906A has departed after thirteen years of sterling service.

From the U.M.R.C.C. newsletter we learn that GAMM - the Committee for Numerical Methods in Fluid Mechanics is organising a

workshop on 'The Efficient Use of Vector Computers, with Emphasis on Computational Fluid Dynamics' in Karlsruhe, March 13/15th. 1985. This may be of interest to CCP5 members, who should contact Prof. Dr. W. Schoenauer, Rechenzentrum der Univeritaet, Postfach 6380, D-7500 KARLSRUHE 1, W. Germany.

i) Molecular dynamicists will be interested to know of a recent publication of the journal 'Computer Physics Reports' (Volume 1 Issue No. 6 July 1984. pp 298 - 343), which is dedicated to the subject of 'Non-Newtonian Molecular Dynamics' and is written by D.J. Evans and G.P. Morriss. The issue should provide a useful reference for anyone interested in the field.

We would be pleased to announce the appearance of any similar documents in future, should our readers provide advanced information.

j) Erratum. We regret to report some typographical errors in the article 'The Dynamics of Spherical Gaussian Wavepackets' by W. Smith and K. Singer, which appeared in the last issue of this newsletter (Number 13). The integral in equation <7> is missing the volume element $d^3\underline{r}_j$ and more importantly, the particle mass is missing from equation <10b>, which should read:

$$\left(\dot{P}_j^\alpha - 2 A_j \dot{R}_j^\alpha + 2 A_j P_j^\alpha / m \right) \left[\left(\frac{e_j^\alpha}{\underline{r}_j} \right)^2 \right] + \left[\frac{e_j^\alpha}{\underline{r}_j} V_j \right] = 0 \quad \langle 10b \rangle$$

$\alpha = x, y, z$

Our apologies go to all concerned.

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

March 12-13, 1984

Oxford

Resume of Lectures.

1. Green's Function Monte Carlo

B. Wells, Physical Chemistry Laboratory, Oxford

The principle of Green's Function Monte Carlo (GFMC) rests on the formal analogy between the Schrödinger equation and the diffusion equation. Written in imaginary time the Schrödinger equation reads:

$$-\frac{\partial}{\partial t}\Phi(\underline{R},t) = [-D\nabla^2 + V(\underline{R}) - E_T] \Phi(\underline{R},t) \quad (1)$$

Here $D = \hbar^2/2m$, \underline{R} is a 3N-dimensional vector specifying the coordinates of the particles in our system and $V(\underline{R})$ is the potential energy. E_T is a constant which shifts the zero of energy. The introduction of this constant does not alter the time-independent solutions of (1). Let $\phi_n(\underline{R})$ and E_n denote the eigenfunctions and eigenvalues of the Hamiltonian. Then the solution to equation (1) may be written as:

$$\Phi(\underline{R},t) = \sum_n a_n \phi_n(\underline{R}) \exp(-(E_n - E_T)t) \quad (2)$$

If we choose $E_T = E_0$, the ground state energy, the asymptotic solution to eq.(1) becomes:

$$\Phi(\underline{R},\infty) = a_0 \phi_0(\underline{R}). \quad (3)$$

Equation (1) is formally identical to a diffusion equation in 3N-dimensional space. $\Phi(\underline{R},t)$ is then interpreted as the density of diffusing particles and $V(\underline{R}) - E_T$ represents an absorption probability. In GFMC this diffusion process is simulated in the computer. The diffusion equation is re-written as an integral equation

$$\Phi(\underline{R}_2, t_2) = \int d\underline{R}_1 \phi(\underline{R}_1, t_1) G(\underline{R}_2, t_2; \underline{R}_1, t_1) \quad (4)$$

where $G(\underline{R}_2, t_2; \underline{R}_1, t_1)$ is the Green's function which obeys the equation

$$-\frac{\partial}{\partial t_2} G(\underline{R}_2, t_2; \underline{R}_1, t_1) = - \left[D \nabla_{\underline{R}_2}^2 + V(\underline{R}_2) - E_T \right] G(\underline{R}_2, t_2; \underline{R}_1, t_1) \quad (5)$$

with the boundary condition

$$G(\underline{R}_2, t_2; \underline{R}_1, t_1) = \delta(\underline{R}_2 - \underline{R}_1) \quad (6)$$

Physically $G(\underline{R}_2, t_2; \underline{R}_1, t_1)$ can be interpreted as the average number of configurations arriving at \underline{R}_2 at time t_2 given a single configuration at \underline{R}_1 , and t_1 . For short times $\tau = t_2 - t_1$ eq.(5) can be solved approximately:

$$G(\underline{R}_2, t_2; \underline{R}_1, t_1) = \frac{1}{(4 D \tau)^{3N/2}} \exp\left[-\frac{(\underline{R}_2 - \underline{R}_1)^2}{4 D \tau}\right] \exp(-[V(\underline{R}_2) - E_T] \tau) \quad (7)$$

To simulate the diffusion process one starts with a number of configurations, distributed in space such that their density is proportional to $\psi_T(\underline{R})$, where $\psi_T(\underline{R})$ is a suitably chosen trial-wavefunction. The Gaussian distribution in eq.(7) is then used to move the particles in the system. The exponential factor in (7) grows or diminishes depending on the relative values of $V(\underline{R}_2)$ and E_T . This term arises as a consequence of the absorption term in eq.(1). It is used to create or destroy whole configurations with a probability such that the average number of configurations in the next time step is:

$$\exp(-[V(\underline{R}_2) - E_T] \tau) \quad (8)$$

In practice this procedure leads to a large statistical fluctuations and consequently a large statistical uncertainty. These fluctuations can be reduced considerably by using importance sampling. Multiplying eq.(4) on both sides by the trial-wavefunction $\psi_T(\underline{R}_2)$ yields:

$$f(\underline{R}_2, t_2) = \int K(\underline{R}_2, t; \underline{R}_1, t_1) f(\underline{R}_1, t_1) d\underline{R}_1 \quad (9)$$

$$f(\underline{R}, t) = \psi(\underline{R}, t) \psi_T(\underline{R}) \quad (10)$$

$$K(\underline{R}_2, t_2; \underline{R}_1, t_1) = \psi_T(\underline{R}_2) G(\underline{R}_2, t_2; \underline{R}_1, t_1) / \psi_T(\underline{R}_1) \quad (11)$$

For short times $\tau = t_2 - t_1$ the kernel may be approximated by:

$$K(\underline{R}_2, t_2; \underline{R}_1, t_1) = \frac{1}{(4\pi D\tau)^{3N/2}} \exp\left[-\tau \left[\frac{H\psi_T(\underline{R}_1)}{\psi_T(\underline{R}_1)} - E_T \right]\right] \\ \times \exp\left[\frac{(\underline{R}_2 - \underline{R}_1 + D\tau F_Q(\underline{R}_1))}{4D\tau}\right] \quad (12)$$

Here

$$F_Q(\underline{R}) = \nabla \ln |\psi_T(\underline{R})|^2 \quad (13)$$

is the quantum force. The Gaussian is now shifted towards regions where $\psi_T(\underline{R})$ is large. Further, if $\psi_T(\underline{R}_1)$ is a good trial wavefunction we nearly always find $H\psi_T(\underline{R})/\psi_T(\underline{R}) \approx E_0$, independent of \underline{R} . Thus when E_T is a good estimate for E_0 the exponential prefactor in eq.(9) will be close to unity and the number of configurations is almost constant.

The energy in the ground state is obtained from:

$$E_0 = \left\langle \frac{H\psi_T}{\psi_T} \right\rangle \quad (14)$$

where the averages $\langle \rangle$ are sampled from $f(\underline{R}, \infty)$. The diffusion equation formulation requires the density of diffusers to be non-negative, implying that the quantity $f(\underline{R}, t)$ must be non-negative. When dealing with a system composed of several fermions the wavefunction must have nodes, so that $f(\underline{R}, \infty)$ only can be made non-negative if the nodes in $\psi_T(\underline{R})$ coincide exactly with those in the ground-state wavefunction $\phi_0(\underline{R})$. This is generally not possible. In this case the GFMC procedure is applied to each nodally bounded volume of $\psi_T(\underline{R})$ separately with the boundary condition that $\psi(\underline{R}, t) = 0$ on the nodal surface. In this case the energy obtained from (11) is the best upper bound for the ground state energy with a given $\psi_T(\underline{R})$.

The method was illustrated with an application to the Helium ion He^+

using hydrogenic wavefunctions as trial functions. It was shown that the energy approached the exact value after a sufficient number of configurations had been generated.

2. Path Integral Monte Carlo

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The partition function for a single electron in an external potential $\phi(\underline{r})$ is:

$$Z = \text{Tr} e^{-\beta H} \quad (1)$$

where $H = -\frac{\hbar^2}{2m} \nabla^2 + \phi(\underline{r})$ and $\beta = 1/k_B T$.

Equation 1 can be re-written as:

$$Z = \text{Tr} [e^{-\beta H/P}]^P \quad (2)$$

Inserting a complete set of states we have:

$$Z = \int d\underline{r}_1 \dots \int d\underline{r}_P \langle \underline{r}_1 | e^{-\beta H/P} | \underline{r}_2 \rangle \dots \langle \underline{r}_P | e^{-\beta H/P} | \underline{r}_1 \rangle \quad (3)$$

When P is sufficiently large we can make the high temperature approximation

$$\langle \underline{r}_1 | e^{-\beta H/P} | \underline{r}_1 \rangle = \rho_0(\underline{r}_1, \underline{r}_2; \beta/P) \exp\left(-\frac{\beta}{2P} [\Phi(\underline{r}_1) + \Phi(\underline{r}_2)]\right) \quad (4)$$

where $\rho_0(\underline{r}_1, \underline{r}_2; \beta/P)$ is the free particle propagator:

$$\rho_0(\underline{r}_1, \underline{r}_2; \beta/P) = \left(\frac{Pm}{2\pi\hbar^2\beta}\right)^{3/2} \exp\left[-\frac{Pm}{2\hbar^2\beta} (\underline{r}_2 - \underline{r}_1)^2\right]$$

Inserting (4) into (3) we obtain an approximate expression for Z :

$$Z \approx Z_P = \left(\frac{Pm}{2\pi\hbar^2\beta}\right)^{3P/2} \int d\underline{r}_1 \dots \int d\underline{r}_P \exp(-\beta V_{\text{eff}}(\underline{r}_1, \dots, \underline{r}_P)) \quad (6a)$$

$$\text{where } V_{\text{eff}} = \sum_{i=1}^P \left[\frac{Pm}{2\hbar^2\beta} (\underline{r}_{i+1} - \underline{r}_i)^2 + \frac{1}{P} \Phi(\underline{r}_i) \right] \quad (6b)$$

Equation (6a) is now in the form of a Boltzmann distribution function, so that the usual simulation techniques can be applied to compute thermodynamic quantities. In eq.(6b) it is understood that, when $i = P$, $\underline{r}_{P+1} = \underline{r}_1$, reflecting

ting the fact that the trace has to be taken. We note that PIMC is a finite temperature technique, contrary to GFMC which is a zero temperature simulation.

The energy is obtained from:

$$E = -\frac{\partial}{\partial \beta} \ln Z = \frac{3P}{2\beta} - \frac{Pm}{2\hbar^2\beta^2} \langle \sum_{i=1}^P (r_i - r_{i+1})^2 \rangle + \frac{1}{P} \langle \sum_{i=1}^P \Phi(r_i) \rangle \quad (7)$$

The averages are taken over the Boltzmann distribution defined by eq.(6). The last term is obviously the estimator for the potential energy. Equation (7) is, however, not suited for a calculation of kinetic energy K since K would then be obtained from a difference of two large quantities with a fluctuation which increases with P . An alternative way of computing K is to use:

$$K = \frac{3}{2\beta} + \langle \sum_{i=1}^P \frac{r_{iP}}{r_{iP}} \cdot \frac{\partial \Phi}{\partial r_i} \rangle / 2P \quad (8)$$

The PIMC method was applied to study the properties of a single electron in molten KCl . The interaction between the electron and the Cl^- -ions was taken to be purely Coulombic whereas for the e^-/K^+ interaction a local pseudopotential was used. It was shown that the Feynman path of the electron was highly localised. This justifies the use of a F-center model. The local structure around the solute electron appears to be different from that around an F centre in the solid.

3. Molecular Dynamics Studies of a 2D-electron System in a Quasi-classical Approximation.

S.W. de Leeuw, Department of Theoretical Physics, Oxford.

The properties of a two-dimensional electron system in a perpendicular magnetic field B were studied using a quasi-classical approximation to the partition function. In this approximation the partition function can be written as:

$$Z = A^N \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp(-\beta \sum_{i,j>i} v_{\text{eff}}(r_{ij})) \quad (1)$$

where

$$A = \left(\frac{m}{2\pi\beta\hbar^2} \right) \left(\frac{\frac{1}{2} \beta\hbar \omega_c}{\sinh \frac{1}{2} \beta\hbar \omega_c} \right) \quad (2)$$

and the effective potential can be written as:

$$v_{\text{eff}}(r) = \frac{\lambda^2}{2\pi} \int d\mathbf{s} v(|\mathbf{r} + \mathbf{s}|) e^{-1/2 \lambda^2 s^2} \quad (3)$$

where $v(r)$ denotes the pair potential.

Here ω_c denotes the cyclotron frequency: $\omega_c = eB/m$ and

$$\lambda^2 = \frac{\beta m \omega_c^2}{\frac{1}{2} \beta \hbar \omega_c \coth(\frac{1}{2} \beta \hbar \omega_c) - 1} \quad (4)$$

As $\omega_c \rightarrow 0$ we find that $\lambda^2 = 12m/\beta\hbar^2$ and we recover a result due to Feynman. Equation (1) has the same form as the classical partition function. The pair potential is replaced by an effective interaction $v_{\text{eff}}(\underline{r})$. Note that exchange effects have been neglected completely.

For a two-dimensional electron system integral (3) can be evaluated analytically to yield:

$$v_{\text{eff}}(r) = \left(\frac{\pi}{2}\right)^{1/2} e^{2\lambda} \exp\left(-\frac{1}{4} \lambda^2 r^2\right) I_0\left(\frac{1}{4} \lambda^2 r^2\right) \quad (5)$$

where $I_0(x)$ is a modified Bessel function of order zero.

We have studied a system of particles interacting through eq.(5) with the technique of molecular dynamics both with and without magnetic field.

In the absence of a magnetic field we observed that the system formed a Wigner crystal in a limited region of the p-T diagram. In particular there is an upper temperature T_c (ca 250 K) above which the system does not crystallize at any density. Below this temperature the solid phase is bounded on both the high and low density regions by fluids. In the low density region this corresponds of course to the classical result. The high value of T_c is of course due to the neglect of exchange effects.

The effect of switching on a magnetic field can be seen by noting that λ^2 increases with ω_c . This will decrease the width of the Gaussian in eq.(3), so that $v_{\text{eff}}(r)$ will be close to the pair potential $v(r)$. It follows that, as ω_c increases the system will behave in a more classical manner. This was indeed observed in the simulations and sufficiently high magnetic fields (10^6 Gauss or more) will crystallize the fluid in the high density region.

4. Semiclassical Molecular Dynamics using Gaussian Wave Packets.

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W. Smith, SERC Daresbury Laboratory, Warrington.

The work of E.J. Heller (1975-6) has suggested that the use of gaussian wave packets may afford a viable method for the semiclassical treatment of many-body systems. Following Heller, the authors have devised methods by which the molecular dynamics scheme may be adapted to treat an N-particle system of interacting gaussian wave packets.

The form of gaussian wave packet used contains time dependent parameters defining the width and shape of the gaussian (parameter \underline{A}), the spatial location of the centre of the gaussian (parameter \underline{R}), the momentum associated with the motion of the centre (parameter \underline{P}) and the phase and normalisation of the wave packet (parameter D). The N-particle wave function is assumed to be a Hartree product of the one-particle gaussians. The potential energy function describing the interaction between the gaussian wave packets is a pseudo-Lennard-Jones potential comprised of two gaussian functions and is due to K. Singer.

The equations of motion for the system of N gaussians may be produced in two different ways; both due to Heller. The Heller I method attempts to minimise the energy of the system through the variation of the gaussians defining the Hartree product (c.f. Hartree atomic theory). This leads to a set of one-particle equations, which are solved using the additional assumption that the local potential experienced by each gaussian is a quadratic function of the distance from the centre of the gaussian. This allows the separation of distinct equations of motion for the parameters \underline{A} , \underline{P} & \underline{R} and D respectively. The method appears to be suitable for low temperature solids (harmonic solid and Lennard-Jones solid ($T < 2$ K)), but at higher temperatures the quadratic approximation is inadequate for the L-J solid.

In the Heller II method, a variation principle due to Dirac, Frenkel and McLachlan (The DFM principle) is employed. This attempts to minimise the difference between the right and left hand sides of the time dependent Schrödinger equation. Singer has shown that for a system of gaussian wave

packets, this principle is equivalent to the requirement that the one-particle time dependent Schrödinger equation and its first and second moments be obeyed for each gaussian. The Heller II method once again allows the separation of distinct equations of motion for the time dependent parameters of the wave packets, though these equations are substantially more complicated than for the Heller I case.

In both the Heller I and Heller II methods the equations of motion for the momenta (\underline{P}) and position (\underline{R}) are integrable using the well-known Verlet leapfrog algorithm. The equations of motion for the gaussian width parameters (\underline{A}) may be integrated using Runge - Kutta algorithms. Alternatively the equations may be transformed using the so called Z algorithm described by Ter Haar and then integrated using the Verlet leapfrog algorithm. It has not proved necessary hitherto to integrate the equations of motion for the phase and normalisation parameters (\underline{D}) and it has been sufficient to rely on the normalisation condition for each gaussian to produce the required values.

The Heller II method is the more powerful method and permits the simulation of Lennard-Jones systems at liquid temperatures. Results for Neon show that, provided sufficient care is taken to parameterise the potential functions, the method affords a promising semiclassical treatment for liquids. The method is numerically stable over long simulations, giving a stable total energy and reasonable potential energies. However, there is a tendency for the wave packet to spread, resulting in gradually increasing potential energies, and this requires special treatment. Also, the single gaussian form for the wavepacket appears to permit inherently too high a contribution to the quantum component of the kinetic energy. Lastly, it must be said that the relationship between the system kinetic energy and the temperature is not as clearly defined in the semiclassical treatment and this creates difficulties in defining the state of the system being simulated.

(Note: See article by W. Smith and K. Singer in CCP5 Newsletter No.13 for a fuller description of the method as applied to spherical gaussian wavepackets.)

5. Molecular dynamics based on the first order correction in the Wigner-Kirkwood expansion.

J.V.L. Singer and K. Singer, Royal Holloway College, London.

In 1932 Wigner^(1,2) derived quantum mechanical versions of the Liouville equation and of the canonical distribution in phase space. Both can be written as power series in \hbar^2 which reduce to the classical expressions when $\hbar = 0$. The first few terms in the distribution function

$$f_w = f_0 (1 + \hbar^2 A_1 + \hbar^4 A_2 + \dots); \quad f_c = Q^{-1} \exp - \beta H_c \quad (1)$$

have served as a basis for the calculation of quantum corrections in almost classical systems⁽³⁻⁵⁾.

Putting the correction terms in (1) into the exponent, one obtains - to first order in \hbar^2 - the quantum corrected Hamiltonian

$$H_Q = H_c - \hbar^2 A_1 / \beta \equiv H_c + \Delta H_Q \quad (2)$$

where $H_c = \sum_j p_j^2 / 2m + U(\underline{r}_1, \dots, \underline{r}_N)$; $\beta = (kT)^{-1}$, $U =$ potential energy.

$$\Delta H_Q = \frac{\hbar^2}{24} \left\{ - \frac{\beta^2}{m^2} \left(\sum_j p_j \cdot \frac{\partial}{\partial \underline{r}_j} \right)^2 U + \frac{3\beta}{m} \sum_j \frac{\partial}{\partial \underline{r}_j} \cdot \frac{\partial}{\partial \underline{r}_j} U - \frac{\beta^2}{m} \sum_j \frac{\partial}{\partial \underline{r}_j} U \cdot \frac{\partial}{\partial \underline{r}_j} U \right\} \quad \text{Refs. (1,6,7)} \quad (3)$$

Corrections to the equilibrium properties can be obtained by first integration of (3) over the momenta and use of the effective potential so calculated in thermodynamic perturbation theory⁽²⁾. The effective potential can in principle also be used in MC simulations. Alternatively the first (and second) correction terms can be evaluated in classical MD simulations⁽⁵⁾.

In order to compute dynamical as well as equilibrium properties, it is necessary to use $H_c + \Delta H_Q$ as an effective Hamiltonian in the simulation with classical equations of motion. This can be justified by the following argument.

Since the system is in equilibrium we require that

$$\frac{dH_Q}{dt} = \sum_j \left(\dot{\underline{r}}_j \cdot \frac{\partial H_Q}{\partial \underline{r}_j} + \dot{\underline{p}}_j \cdot \frac{\partial H_Q}{\partial \underline{p}_j} \right) = 0 \quad (4)$$

(4) is satisfied if Hamilton's (classical) equations are valid:

$$\dot{\underline{r}}_j = \frac{\partial H_Q}{\partial \underline{p}_j}, \quad \dot{\underline{p}}_j = - \frac{\partial H_Q}{\partial \underline{r}_j} \quad (5)$$

$\ddot{\underline{r}}_j$ which is needed if one wishes to use the familiar Verlet or Leapfrog algorithms, is obtained from

$$\frac{d}{dt} \dot{\underline{r}}_i = \left(\sum_j \dot{\underline{r}}_j \cdot \frac{\partial}{\partial \underline{r}_j} + \dot{\underline{p}}_j \cdot \frac{\partial}{\partial \underline{p}_j} \right) \frac{\partial H_Q}{\partial \underline{p}_i} \quad (6)$$

Apart from the algebraic complexity, the simulation based on H_Q has some near-pathological properties resulting from the derivatives of the repulsive term in the Lennard-Jones 12-6 potential; particularly the derivative of the last term in (3) leads to a very rapid variation with distance in the repulsive range. To prevent occasional 'blow-ups' it proved necessary to incorporate a safety device whereby exceptionally large forces - say $20 \times$ larger than the mean - are reduced in magnitude. With a safety device coming into operation for $< 1\%$ of the pair forces and a time step of 0.4×10^{-14} s the simulation was still quite stable for neon near the triple point (LJ-12-6).

The principal results reported were:

1. For systems with a thermal de Broglie wavelength $\hbar/(mkT)^{1/2} > 2 \times 10^{-10}$ e.g. Ar, N_2 , Ne (not too close to the triple point) the energy correction calculated in a completely classical MD simulation agrees with that obtained in a simulation based on (3)-(6). This is not true for the pressures.
2. Even when λ (de Broglie) $\sim 0.5 \times 10^{-10}$, e.g. for Ar near the triple point, the quantum corrections are not negligible.
3. The quantum correction tends to reduce the diffusion constant.

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6. Methods for the Simulation of Quantum Rotors M.P. Allen and T.T. Hughes-Davies, Physical Chemistry Laboratory, Oxford

The work of this group has been the adaptation of established computer simulation techniques which yield quantum information directly for use with rotational systems. The techniques which have been examined and evaluated here are based upon the wave packet dynamics methods of E.J. Heller [1,2] and upon the discretization of the path integral formulation of quantum mechanics [3,4].

The wave packet method uses a highly localized wave packet to represent a one dimensional one particle rotor. The time dependent Schrödinger equation is applied to this function and the resulting equation of motion is simplified using one of two approximate methods. These methods yield a set of first order differential equations in the variables used to characterise each one particle wave function. These differential equations may then be integrated numerically using standard methods. This approach is essentially identical to that used by Corbin and Singer [5], and by Smith and Singer [6] for the simulation of translational systems. In order to treat rotational systems, it has been assumed that the wave packet is sufficiently localized as to obviate any problems concerned with overlap of the wave packet with itself in rotation space.

The two approximate methods that have been used to simplify the equations of motion for the wave packets are a harmonic expansion of the potential about the instantaneous centre of the wave packet [1], and a time dependent variational principle due to Dirac, Frenkel and McLachlan [2]. The harmonic approximation yields the classical equations of motion for both the centre and momentum of the wave packet: there is thus a classical simulation 'built in' to this simulation, which proves useful when comparing quantum and classical results.

The path integral method is based upon the division of the partition function for a quantum mechanical many body system into discrete states. This yields an isomorphism with the statistical mechanics of a classical 'polymer' [3]: in this each rotor may be visualised as a 'bundle' of 'rods', each 'rod' free to rotate in one dimension about the common centre, and in-

interacting with the other 'rods' in the 'bundle' via a harmonic potential. This isomorphism is exploited by performing a classical Monte Carlo simulation of the polymer, the results from which yield quantum information. As the number of 'rods' into which the partition function is divided approaches infinity, and as the temperature increases, the isomorphism yields the exact quantum results. There is also evidence that the results, as a function of the number of 'rods' converge relatively quickly at temperatures of chemical interest [4].

The model system which has been used to test these methods is a set of rotors, confined to a plane on a triangular net, interacting via an electrostatic quadrupole-quadrupole potential. This simplified model has been used, with some success, to simulate the low temperature behaviour of nitrogen adsorbed upon a graphite surface. This system shows a first order phase transition at 28K, and it was hoped to observe this transition and also to see the relative importance of quantum effects upon this transition.

The results from the molecular dynamics runs using the wave packet method have in general been disappointing. It was found that at relatively low temperatures, and below the phase transition region, the wave packets rapidly spread out, i.e. they could no longer be considered to be highly localized. This rendered invalid the assumptions used to propagate the wave packet, notably that concerned with the overlap of the wave function. At very low temperatures the method was more successful.

The Monte Carlo path integral method was far more successful. It was stable at all temperatures attempted. The phase transition has not yet been observed, as the runs have so far been confined to short runs of a small system. However the expected convergence of the results, as a function of the number of 'rods' and as the temperature increased, was observed. It seems likely that a relatively small number of 'rods' may be sufficient to give reasonable quantum information. Indications are that as few as 4 'rods' may be sufficient. This would mean that approximate quantum results could be obtained for a many body system using computer runs that would take four times as long as conventional simulations.

Programs were written in double precision Fortran 77, and run on the

Oxford PCL Norsk Data ND-520 32 bit processor. Simulations were run for 50000 steps for the molecular dynamics programs, and for approximately 2500 successful moves per 'rod' for the path integral programs. A system of 64 rotors was used for the MD programs, and 16 rotors for the path integral programs.

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MODELLING POTENTIALS WITH SHIFTED FORCE FUNCTIONS.

W. Smith and J. H. R. Clarke.

Most readers are probably familiar with the definition and use of the so - called 'shifted force' potential; it is merely a standard potential, such as the Lennard - Jones 12 - 6 potential, which has been carefully adjusted so that both the potential and its first derivative (and hence the force) are zero at the prescribed cut - off (1). In the normal course of things the adjustment made to the potential is small in comparison to the average force or potential and can be corrected for thermodynamically using perturbation theory (2). Our use of shifted force functions however is different from the usual application. We are not so much concerned to adjust the standard potential to remove unwanted discontinuities at the cut - off (though we do exploit this advantage) as to distort the standard potential into an acceptable model of a more complicated potential. This aspect of shifted force potentials; i.e. their use as modelling potentials, has not, to our knowledge, received much attention. We therefore wish to use the CCP5 newsletter to introduce this aspect as well as talk about shifted force functions in general.

The general form for a shifted force potential is given by <1>, in which $U(r)$ represents the shifted force potential, $V(r)$ the standard potential and $P(r)$ is a polynomial, which is designed to give the potential function the desired properties at the designated cut - off.

$$U(r) = V(r) + P(r)$$

<1>

It should be noted that the coefficients of $P(r)$ are dependent upon the chosen cut - off as well as on the nature of the function $V(r)$ and are not therefore transportable. Also the polynomial $P(r)$ is not to be regarded as a mere 'tail correction' even though it is in the tail that its influence is most noticeable. It alters the entire functional form of the standard potential. This is most easily seen in the use of these functions as modelling potentials, since then the polynomial $P(r)$ may be large in relation to the standard potential and greatly alter its functional behaviour.

As we have mentioned above, in the usual application of shifted force potentials we attempt to ensure that the potential function and its first derivative are both zero at the cut - off

(i.e. at $r = c$). To fulfil these requirements it is sufficient for the polynomial $P(r)$ to be a simple linear form <2>, with just two coefficients a and b .

$$P(r) = a + b.r \quad \langle 2 \rangle$$

The coefficients a and b are easily determined using the equations <3a> and <3b>, which are the algebraic expressions of the cut - off requirements.

$$U(c) = V(c) + a + b.c \quad \langle 3a \rangle$$

$$U'(c) = V'(c) + b \quad \langle 3b \rangle$$

It is easy to see from these expressions that no matter what function is used as the standard potential, a simple pair of simultaneous equations will give the desired coefficients. It is also worth noting the effect that the polynomial $P(r)$ has in this simple case; it is in effect both shifting and rotating the standard potential to satisfy the cut - off requirements.

As an example of this procedure, consider the standard $N - M$ potential <4>, in which E represents the potential well - depth and d the value of r for which the potential is at the minimum value $-E$.

$$V(r) = \frac{E}{(n-m)} \left\{ m \left[\frac{d}{r} \right]^n - n \left[\frac{d}{r} \right]^m \right\} \quad \langle 4 \rangle$$

The first derivative of this function is <5>:

$$V'(r) = -\frac{Enm}{r(n-m)} \left\{ \left[\frac{d}{r} \right]^n - \left[\frac{d}{r} \right]^m \right\} \quad \langle 5 \rangle$$

Setting $r = c$ and substituting $\langle 4 \rangle$ and $\langle 5 \rangle$ into $\langle 3a \rangle$ and $\langle 3b \rangle$ readily gives the desired linear coefficients as $\langle 6a \rangle$ and $\langle 6b \rangle$:

$$b = \frac{Enm}{c(n-m)} \left\{ \left[\frac{d}{c} \right]^n - \left[\frac{d}{c} \right]^m \right\} \quad \langle 6a \rangle$$

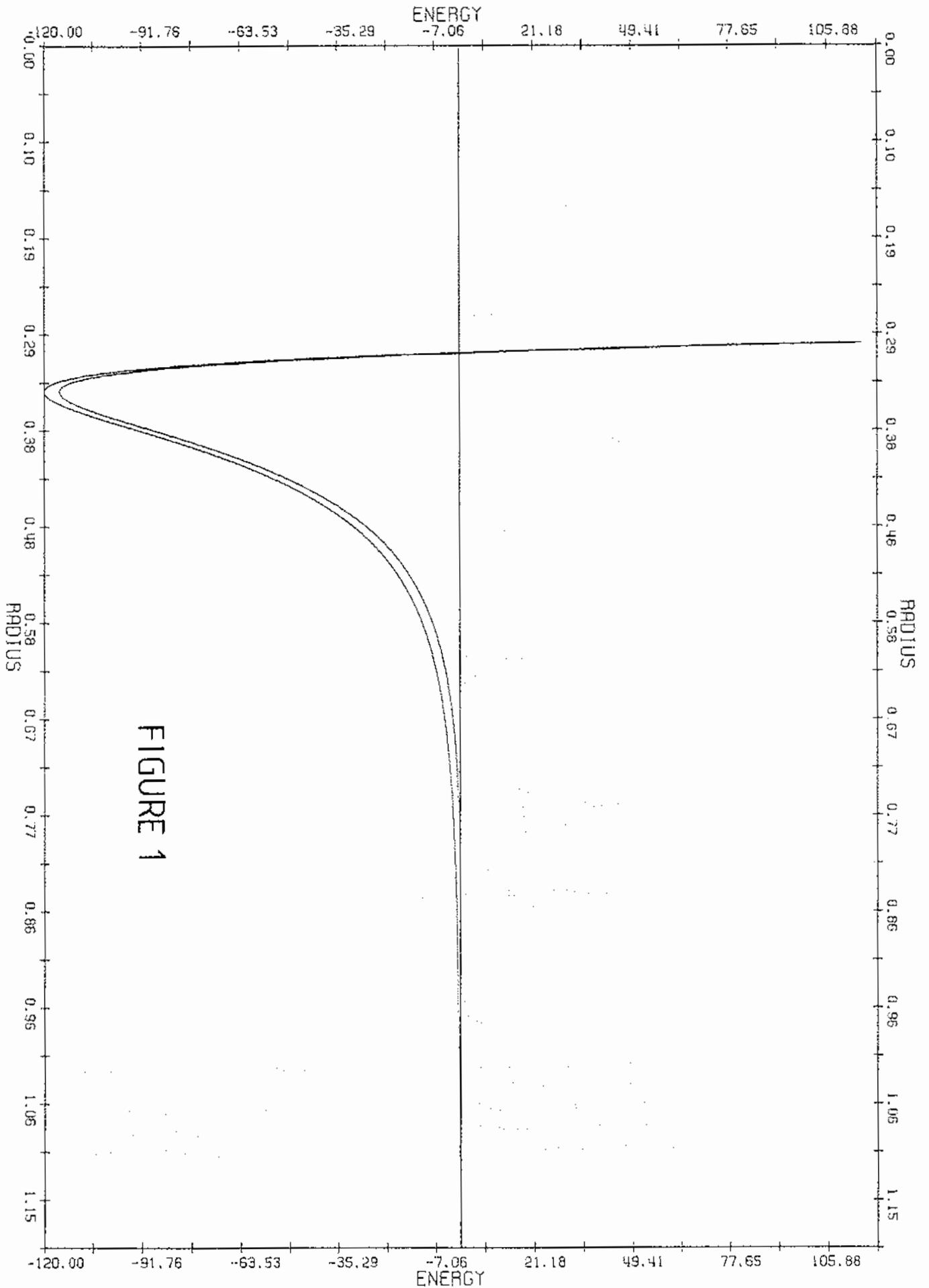
$$a = -\frac{E}{(n-m)} \left\{ m \left[\frac{d}{c} \right]^n - n \left[\frac{d}{c} \right]^m \right\} - b \cdot c \quad \langle 6b \rangle$$

Needless to say, these terms need only be evaluated once in any given simulation, a fact obscured somewhat in the full expression for the shifted force $N - M$ potential $\langle 7 \rangle$.

$$U(r) = \frac{E}{(n-m)} \left\{ m \left[\frac{d}{r} \right]^n - \left[\frac{d}{c} \right]^n \right\} - n \left\{ \left[\frac{d}{r} \right]^m - \left[\frac{d}{c} \right]^m \right\} + \frac{nm(r-c)}{c} \left\{ \left[\frac{d}{c} \right]^n - \left[\frac{d}{c} \right]^m \right\} \quad \langle 7 \rangle$$

In Figure 1 we show an example $N - M$ potential with $n = 12$, $m = 6$, $E = 120K$ and $d = 0.345nm$, together with the corresponding shifted force function in which $c = 2.5 \times d$. Clearly, in this application, the polynomial $P(r)$ is having a small (but significant) effect on the form of the potential.

It is clear from $\langle 1 \rangle$ that, in general, we are not confined to a linear form for the polynomial $P(r)$ and that a higher order polynomial may be used. If this is done we can obtain values for



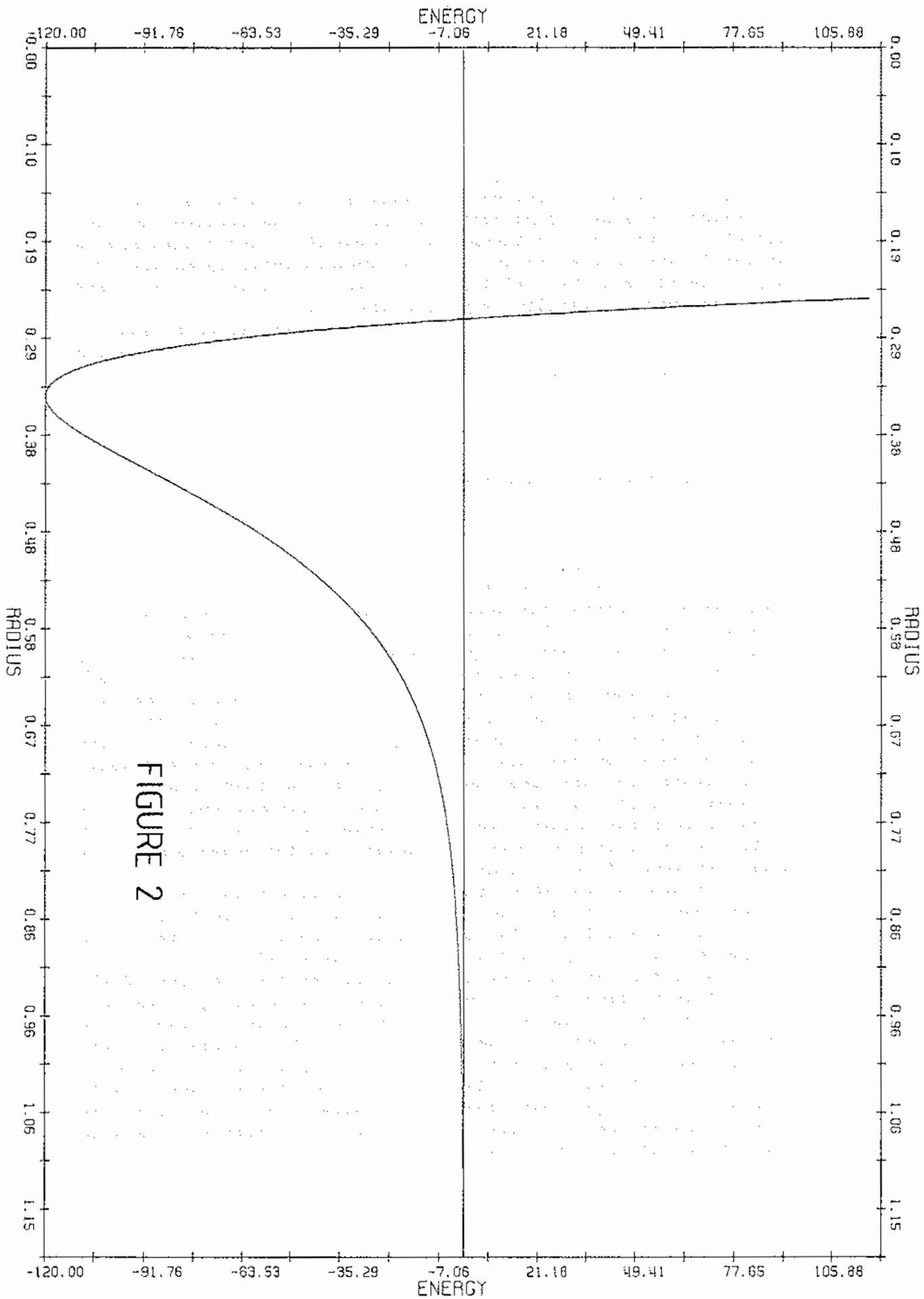


FIGURE 2

the coefficients of the polynomial by insisting that successively higher derivatives of the shifted force function are zero at the cut - off. Such a strategy may be required, for instance, where it is necessary to ensure continuity of the first derivative of the force at the cut - off. Alternatively, some the coefficients may be arbitrarily set to zero to obtain some computational advantage. For example, we may set the coefficients of odd powers of r to zero and remove the need to calculate square roots (3).

Our interest in shifted force potentials arose because we required a simple potential function that had the same basic features as the Morse potential (8).

$$V(r) = E \left((1 - \exp(-b(r/d-1)))^2 - 1 \right) \quad (8)$$

Principally we required a 'soft' repulsive potential at short distances, a broad potential energy well near the minimum and a quickly decaying attractive potential for longer distances (see Figure 2). A simple $N - M$ potential (1), with $n = 8$ and $m = 4$ to 1, fulfilled some of these requirements, but the decay of the attractive part was too slow. A simple cut - off was not acceptable in this case because of the large 'step' it introduced for all practical values of the cut - off. We then had the idea of using the shifted force method to impose the behaviour we wanted on the attractive part of the potential. Despite the large discontinuity in the truncated standard potential, the problem was still sufficiently well defined for the method to produce the result we wanted. We therefore considered the shifted force $N - M$ function (7) to be a suitable model potential with the added bonus of a complete absence of discontinuities.

In Figure 3 we show the $N - M$ function with $n = 8$, $m = 3$, $E = 120K$ and $d = .345nm$, and the corresponding shifted force function with $c = 2.5 \times d$. The large discontinuity in the truncated $N - M$ potential is only too obvious (c.f. Figure 1).

There is however one aspect of the shifted force potential (7) however, that we found to be inconvenient. In dealing with the standard $N - M$ potential (and for that matter, the Morse potential), we found it helpful that the potential was characterised by a prescribed well depth (E) and the location of the potential minimum (d). In the shifted force form, these parameters no longer had the same physical significance, as the potential minimum was now displaced from its original position (note this effect in Figure 3).

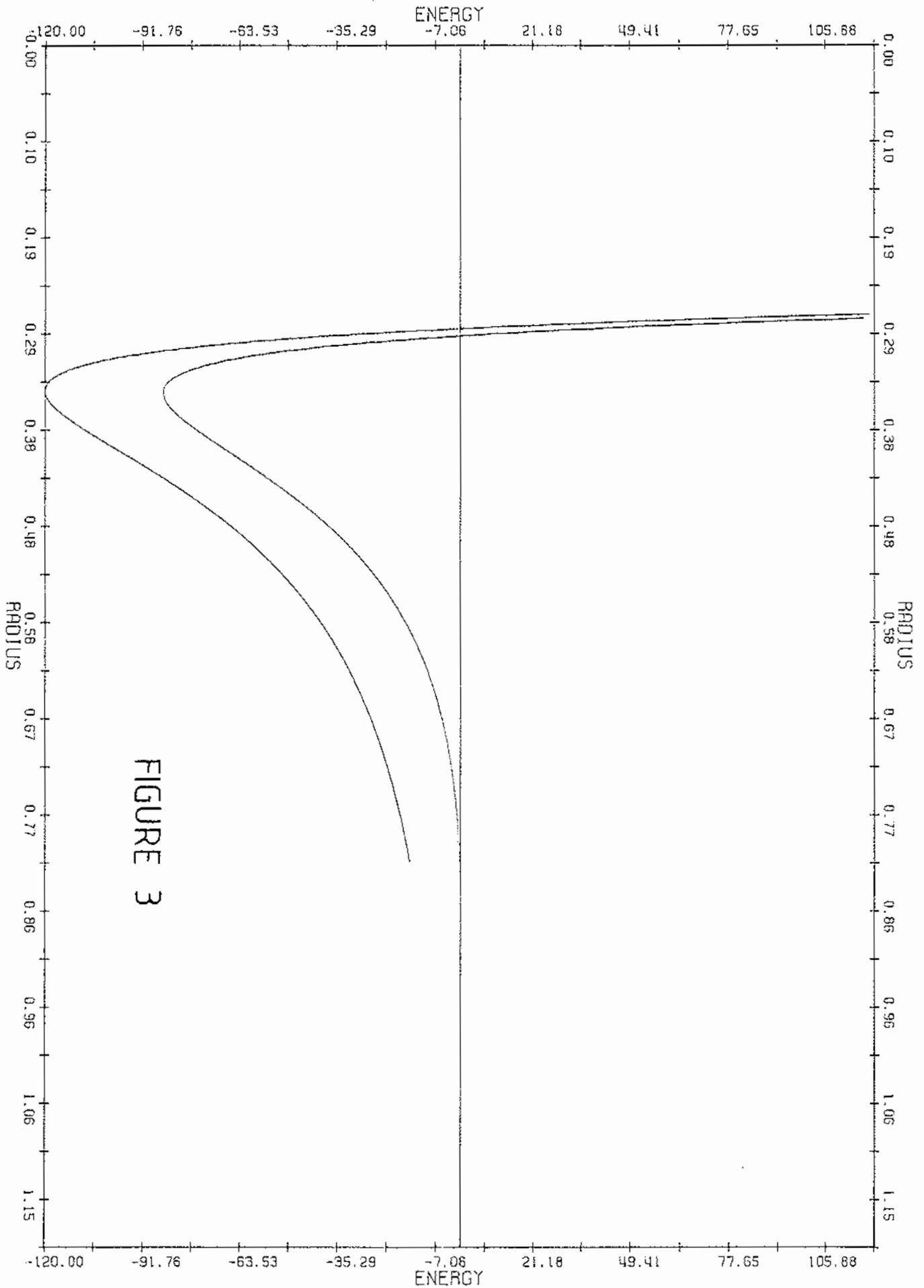


FIGURE 3

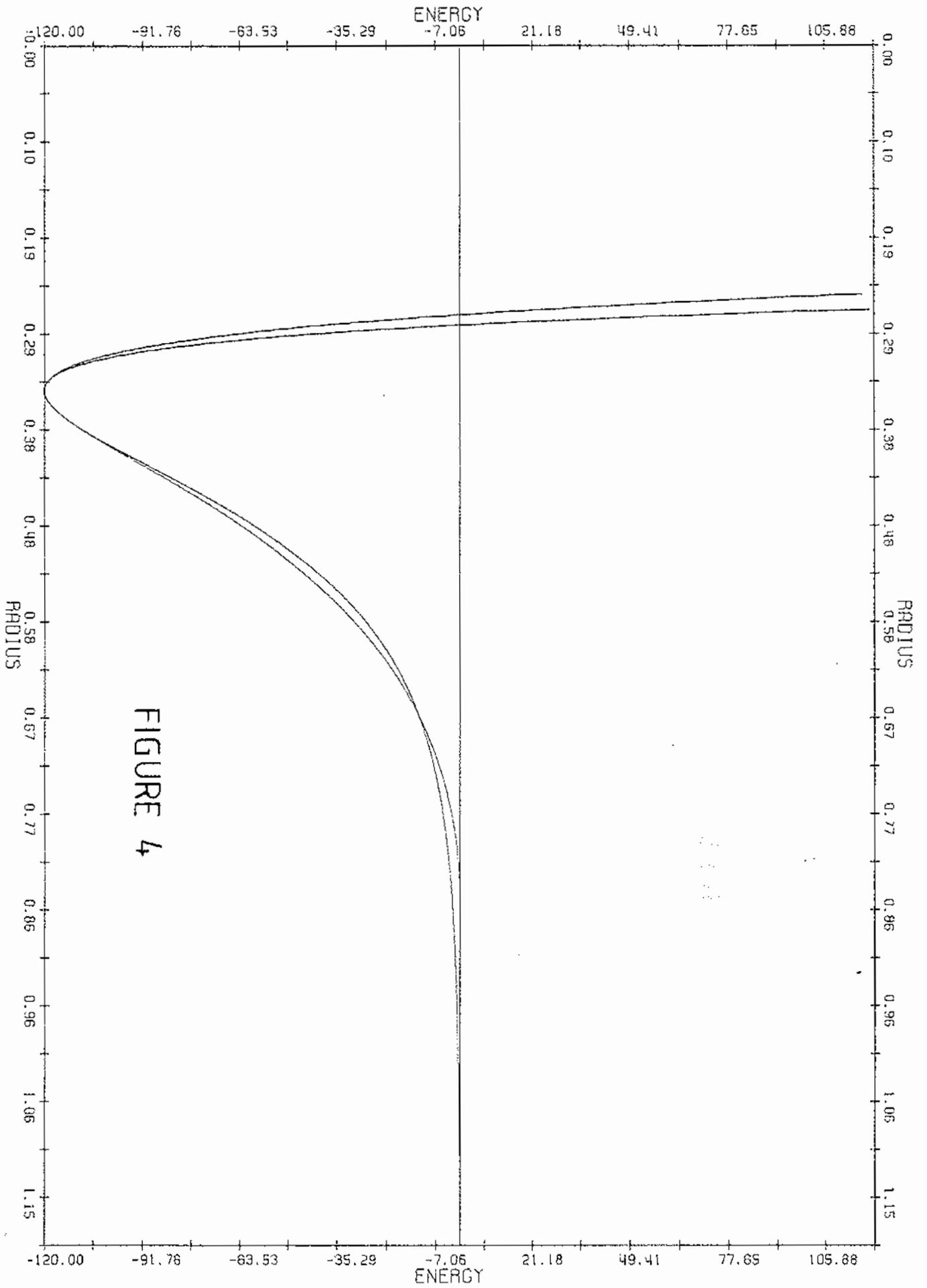


FIGURE 4

We overcame this difficulty by first finding the location (d') of the true potential minimum ($-E'$) (by equating the first derivative of <7> to zero). This gave the relationship between d' and d as <9>:

$$d = d'q \quad \text{<9>}$$

where:

$$q = g \left(\frac{g^{m+1} - 1}{g^{n+1} - 1} \right)^{1/(n-m)} \quad \text{<10>}$$

and $g = c/d'$ and c is the cut - off radius. Knowing that when $r = d'$ then $U(d') = -E'$ gave us the relation <11>:

$$E = eE' \quad \text{<11>}$$

where:

$$e = -\frac{(n-m)}{mq} \left(1 + \frac{n}{g} - n - 1 \right) / g^{-n} - nq \left(1 + \frac{m}{g} - m - 1 \right) g^m \quad \text{<12>}$$

Substituting eE' for E and qd' for d in <7> provided the potential energy function <13>:

$$U(r) = \frac{eE'}{(n-m)} \left\{ mq \left[\left(\frac{d'}{r} \right)^n - g^{-n} \right] - nq \left[\left(\frac{d'}{r} \right)^m - g^{-m} \right] \right. \\ \left. + nm \left[\frac{r}{gd'} - 1 \right] \left\{ \left[\frac{q}{g} \right]^n - \left[\frac{q}{g} \right]^m \right\} \right\} \quad \text{<13>}$$

This formula allows the potential to be described in terms of three easily understood parameters; the well depth E' , the position of the minimum d' (i.e. the particle 'diameter') and the ratio of the cut - off to the position of the minimum. We therefore propose <13> as a particularly versatile modelling potential.

In Figure 4 we present the N - M shifted force potential function <13> (with $n = 8$ and $m = 1$) and the Morse function <8> with $E' = E(\text{Morse}) = 120\text{k}$, $d' = d(\text{Morse}) = .345\text{nm}$ and $b(\text{Morse}) = 3.169$. The cut - off for the N - M potential was chosen to permit a reasonable fit of the Morse function.

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NON-EQUILIBRIUM MOLECULAR DYNAMICS USED TO OBTAIN SECOND ORDER
THERMODYNAMIC PROPERTIES

D.M. HEYES

Second-order thermodynamic properties of MD systems have traditionally been evaluated from appropriate expressions involving fluctuations in first order thermodynamic quantities. These values can be subject to considerable uncertainty and spurious N-dependent effects. Consequently differentiation of a fitted equation of state has often been used as a more reliable alternative route. In this note the use of Non-Equilibrium Molecular Dynamics, NEMD, is explored as another method to obtain these second order quantities.

The specific heat per molecule at constant volume, C_v , and the thermal pressure coefficient, $\gamma_v = (\partial P / \partial T)_v$ are considered specifically (although the approach should be quite generally applicable). The NEMD technique as used here employs the "differences-in-trajectories" modification introduced by Ciccotti and Jacucci [1]. The MD simulation is run twice from the same collection of N coordinates and velocities. In one half of this "segment" a specified perturbation is applied to the system so that it modifies the dynamics slightly; in the other half this perturbation is not employed and the system is allowed to continue at equilibrium. Effectively the only limit to the small magnitude of this perturbation is governed by the number of significant figures carried by the computer because one takes the difference between system properties at the same time in both parts of the segment.

C_v :

In order to evaluate, c_v , all the molecular velocities are multiplied by a factor $(1 + \lambda)$ (i.e., the perturbation mentioned above). There is an instantaneous (equivalent) temperature rise from T to $T + \delta T$. Let m_i be the mass of molecule i and v_i its velocity then,

$$T = \left(\sum_{i=1}^N m_i v_i^2 \right) / 3Nk_B, \quad (1)$$

$$T + \delta T = \left(\sum_{i=1}^N m_i v_i^2 (1 + \lambda)^2 \right) / 3Nk_B, \quad (2)$$

where k_B is Boltzmanns constant. This leads to,

$$\delta T \approx 2\lambda T, \quad (3)$$

for $\lambda \ll 1$.

Here we only consider spherical molecules.

Now,

$$C_v = \left(\frac{\partial u}{\partial T} \right)_v, \quad (4)$$

where

$$U = \frac{1}{2N} \sum_{i=1}^N m_i v_i^2 + \frac{1}{2N} \sum_{i \neq j} \theta_{ij} = 1.5 k_B T + U_c, \quad (5)$$

where θ_{ij} is the pair potential between molecules i and j .

Hence

$$\frac{C_v}{k_B} = 1.5 + \frac{\delta U_c(t \rightarrow \infty)}{k_B \delta T(t \rightarrow \infty)} \quad (6)$$

$$= 1.5 \frac{\delta T(t=0)}{\delta T(t \rightarrow \infty)}, \quad (7)$$

Therefore by monitoring the time dependence of $\delta T(t)$ after the application of the velocity scaling at $t = 0$ C_v can be obtained.

γ_v :

Similarly, the same MD "experiment" can be used to obtain γ_v as the associated rise in pressure $\delta P(t)$ is also evaluated,

$$\gamma_v = \frac{\delta P(t \rightarrow \infty)}{\delta T(t \rightarrow \infty)}. \quad (8)$$

The advantage of this NEMD approach is that extra insights into other aspects of thermal re-equilibration are also obtained "for free".

As illustrative examples of equations (7) and (8) certain test calculations have been performed on Lennard-Jones states close to T^* ($= Tk_B/\epsilon$) = 2.5 using a CRAY-1S computer. The velocity scaling factor $\lambda = 6 \times 10^{-6}$ and 256 ($= N$) molecules were simulated. Three states were considered. (a) $\rho^* = 0.6$, $T^* = 2.50$, run for 150 segments; (b) $\rho^* = 0.9094$, $T^* = 2.53$, run for 200 segments; and (c) $\rho^* = 1.0397$, $T^* = 2.50$, run for 150 segments. All quantities are in Lennard-Jones, LJ, reduced units.

In figure 1 the time dependent excess kinetic energy profiles,

$$\delta k^*(t) = 1.5 \delta T^*(t) \quad (9)$$

are shown for the above states. The satisfactory nature of this method is demonstrated by comparison of the long time limit $\delta k^*(t \rightarrow \infty)$ with the prediction using equation (7) and the Nicolas et al. LJ equation of state [2] for C_v . The arrows denote these predictions, which are indistinguishable from the NEMD results within the small statistical uncertainty. (The large oscillations at long times ($t^* \gtrsim 0.4$) reflect insufficient averaging.) The $t \rightarrow \infty$ limit, in fact, is reached between $0.15 \lesssim t^* \lesssim 0.35$, well before the noise starts to dominate.

Similar excess total pressure profiles $\delta P(t)$ are also shown, in figure 2. Again the use of equation (8) (here) and equation of state γ_v predict limiting δP as $t \rightarrow \infty$ which are in excellent agreement with those of the NEMD technique.

To conclude, NEMD is a promising alternative route to thermodynamic data as well as to the more usually studied transport coefficients [3].

Acknowledgement

The Royal Society is thanked for a Research Fellowship.

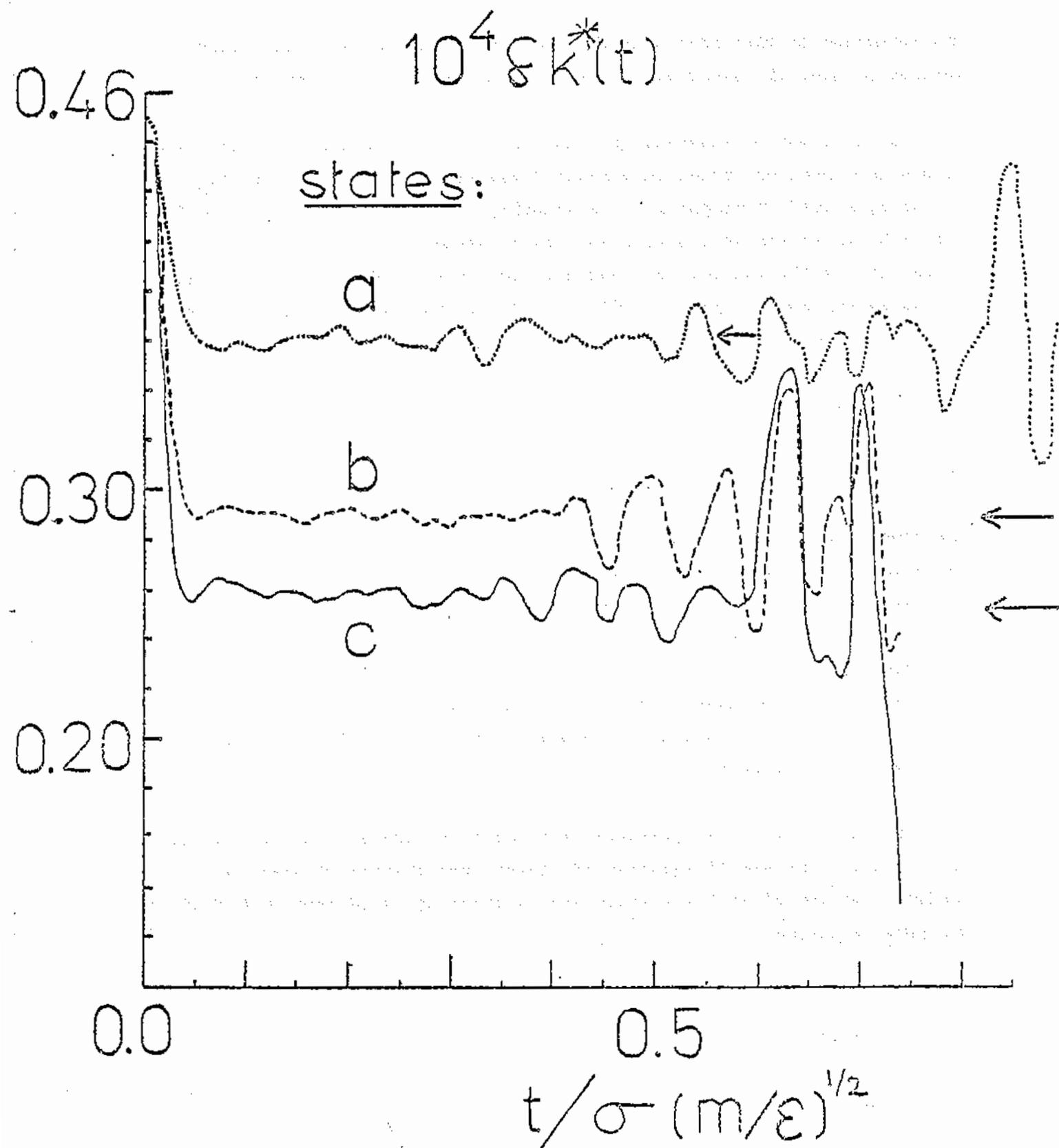


Fig.1

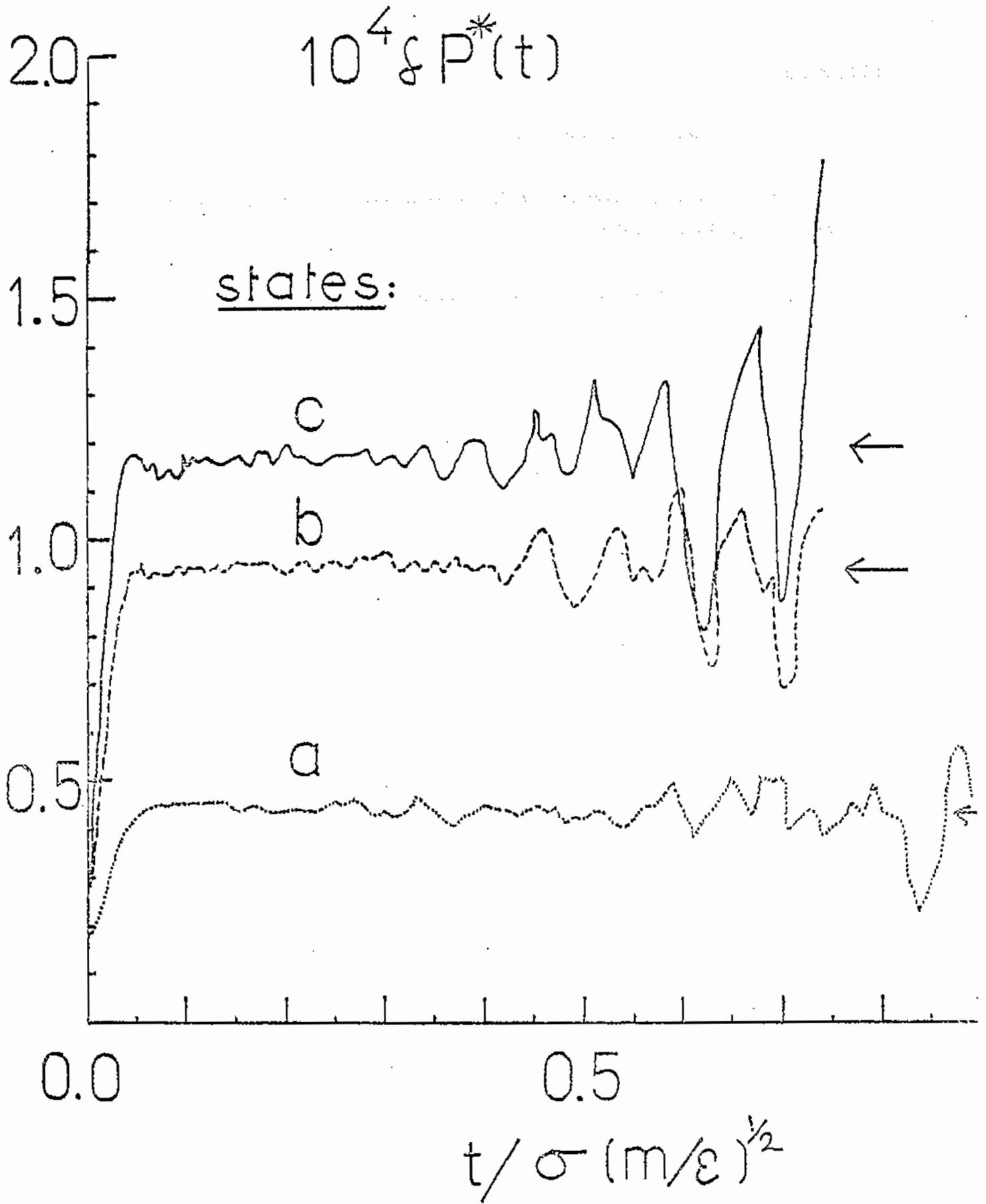


Fig. 2

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A VARIABLE TIMESTEP ALGORITHM.

M. Whittle

In an equilibrium M.D. simulation the timestep is chosen small enough to ensure sufficient accuracy - usually synonymous with adequate energy conservation, whilst the largest possible timestep is desirable to maximise efficiency. One prescription for the Verlet algorithm might be <1>,

$$\Delta t \leq \alpha \sigma \left(\frac{m}{k_B T} \right)^{1/2} \quad \langle 1 \rangle$$

where σ is the Lennard - Jones interaction diameter, m the particle mass and α is a constant, typically 0.01 - 0.1. This ensures that for a given temperature the distance moved by any particle should not involve changes in the force large enough to introduce significant non-linear terms (i.e. higher derivatives of the potential) in the Verlet expansion.

In certain non-equilibrium simulations it is sometimes advantageous for reasons of efficiency to employ a variable timestep (1). In our case this applies to a sputtering routine where a fast moving particle collides with a surface causing cascades of lower energy particles. A much shorter timestep is appropriate for the initial collision than for later stages of the simulation. Rapid quenching of a liquid configuration to simulate glass formation is another situation where a variable timestep may be useful. A simple interpolation of the Verlet formula is all that is required. We start with the algorithm in the form,

$$R(t_0 + \Delta t) = R(t_0) + v(t_0 + \Delta t/2) \quad \langle 2a \rangle$$

$$v(t_0 + \Delta t/2) = v(t_0 - \Delta t/2) + F(t_0) \Delta t / m \quad \langle 2b \rangle$$

$$v(t_0) = \frac{1}{2} [v(t_0 - \Delta t/2) + v(t_0 + \Delta t/2)] \quad \langle 2c \rangle$$

knowing $R(t_0)$, $v(t_0 - \Delta t/2)$ and $F(t_0)$. Instead of $R(t_0 + \Delta t/2)$ we now require the position at some other time, $R(t_0 + \Delta t'/2)$, where $\Delta t'$ is not too different from Δt , say, $0 < \Delta t' < 2\Delta t$. We can get this from,

$$R(t_0 + \Delta t') = R(t_0) + v(t_0 + \Delta t'/2) \Delta t' \quad \langle 3 \rangle$$

where by linear interpolation from $\langle 2c \rangle$ we have,

$$v(t_0 + \Delta t'/2) = v(t_0) \left[1 - \frac{\Delta t'}{\Delta t} \right] + v(t_0 - \Delta t/2) \left[\frac{\Delta t'}{\Delta t} \right] \quad \langle 4 \rangle$$

For the next cycle we now store $v(t_0 + \Delta t'/2)$ as $v(t_1 - \Delta t'/2)$ along with $\Delta t'$ and $R(t_0 + \Delta t')$ and proceed as before with next increment $\Delta t''$,

$$v(t_1 + \Delta t'/2) = v(t_1 - \Delta t'/2) + F(t_1) \Delta t' / m \quad \langle 5 \rangle$$

etc. In time honoured fashion, it is 'easily shown' that, in terms of positions this is a quadratic interpolation:

$$\begin{aligned} R(t + \Delta t') &= R(t - \Delta t) \left[\left(\frac{\Delta t'}{\Delta t} \right)^2 - \frac{\Delta t'}{2\Delta t} \left(1 + \frac{\Delta t'}{\Delta t} \right) \right] \\ &+ R(t) \left[1 - \left(\frac{\Delta t'}{\Delta t} \right)^2 \right] \\ &+ R(t + \Delta t) \left[\frac{\Delta t'}{2\Delta t} \left(1 + \frac{\Delta t'}{\Delta t} \right) \right] \quad \langle 6 \rangle \end{aligned}$$

To use the algorithm one needs to apply a criterion analogous to <1> to define the timestep sizes at each increment. In our case this is set by restricting displacement of the fastest moving particle to 0.05 atomic diameters. Using this scheme we have obtained energy conservation of around 1 percent for sputtering particle energies up to 2keV.

It is worth noting that this type of algorithm is readily adapted to constant temperature work (2), where eq. <2a> is replaced by <7>.

$$v(t + \Delta t/2) = (2\beta - 1)v(t - \Delta t/2) + \beta F(t)\Delta t/m \quad \langle 7 \rangle$$

$$\beta = (T_0/T)^{1/2}$$

with T_0 the required temperature. However, the calculation of time correlation functions poses a few problems!

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Acknowledgement.

Useful discussions with D. Brown leading to eq. <6> are gratefully acknowledged.

REPORT ON THE VISIT OF DR. A. N. CORMACK TO
TWENTE, UNIVERSITY OF TECHNOLOGY, HOLLAND

The main aim of this visit was to complete a collaborative project in which static lattice simulation methods have been used to investigate ion transport mechanisms in pyrochlore structured oxides. The Twente group (supervised by Prof. A. J. Burgraaf) has undertaken a detailed experimental study of ionic conductivity in these important superionic materials. The aim of the calculations is to identify the mechanisms of ionic transport. Indeed, owing to the complexity of the system, guidance from reliable calculations is necessary if detailed models of the transport processes are to be developed.

Pyrochlores are essentially anion deficient fluorite oxides of general formula $A_2B_2O_7$ (A = tetravalent cation, B = trivalent cation) in which both the cation and anion vacancies are ordered. The work of the Twente group has concentrated on the rare earth zirconates especially for the rare earths Gd and Nd. Neutron diffraction studies have been performed on these compounds. Thus the first aim of our collaborative project was to develop a set of interionic potential models which would reproduce the crystallographic data. This was successfully achieved. We also carefully examined the shell model parameters describing ionic polarisation, as preliminary defect calculations revealed a very high sensitivity of the results to these parameters. As a result of this work we have now constructed reliable interionic potentials for these materials.

We then proceeded to calculate defect energies using the CASCADE code. Since we are interested in oxygen transport, defects on the oxygen sublattice are the most important. Two types of vacancy - at the 48(f) and 8(a) sites - are possible; there are similarly two types of interstitial - at the 8(b) and 32(e) sites. Table 1 gives the calculated energies for these defects.

DEFECT	ENERGY (eV)
O (8a) Vacancy	19.86
O (48f) Vacancy	18.38
O (8b) Interstitial	-14.45
O (32e) Interstitial	-11.70

We conclude from these results that the predominant defects will be O 48(f) vacancies created by deviations from stoichiometric composition. We then undertook a detailed examination of possible migration mechanisms. The most

favourable appears to be a $\langle 100 \rangle$ jump between 48(f) sites. An activation energy of 0.9 eV was calculated which accords well with the experimental Arrhenius energy for conductivity of 0.85eV.

The main conclusions of this project were therefore

- (i) It is possible to model complex ternary oxides provided care is taken with shell model parameterisation.
- (ii) Oxygen transport in pyrochlores is effected by migration of 48(f) vacancies.

The visit to Twente was an essential component of this collaborative project. It was also of considerable interest to learn of the range of projects currently in progress in Burgraaf's group. I was able to enlighten their group about our computer modelling studies in the seminar I gave on Computer Modelling of Solids.

The financial support from CCP5 is gratefully acknowledged.

A. N. Cormack. University College London

A. HYBRID SCHEME OF COMPUTER SIMULATION BASED ON
HADES AND MONTE CARLO: APPLICATION TO CONDUCTIVITY
IN Y3+ DOPED CeO2.

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Static relaxation codes, e.g. HADES, can provide reliable estimates of defect formation and migration energies in massively disordered solids for various postulated local environments encountered by the defect [1]. However it has been impossible to use these energies for the calculation of ensemble average quantities like the chemical potential or long time averaged transport quantities such as the d.c. ionic conductivity or the tracer diffusion coefficient without making grossly simplifying assumptions about the distribution of defects and correlation effects. The reason for good agreement or lack of it with experiment can then be virtually impossible to locate.

Monte Carlo lattice calculations have been used to calculate the chemical potential and various transport quantities in solids [2]. Two kinds of calculation can be identified. In the first, interaction energies are used to generate transition probabilities (jump frequencies) which are then used to calculate rigorously the above quantities in a thermally equilibrated lattice. The weak point of such calculations centre upon (a) the interaction energies themselves which must always be treated as rigid lattice quantities and (b) the relatively free choices possible for the jump frequencies (although these must be consistent with the interaction energies). In the second kind of Monte Carlo calculation, the jump frequencies are taken as input. The Monte Carlo calculation then provides rigorous calculation of transport quantities by statistically sampling the jump frequencies in the long time limit. Up till now the latter calculations have been quite rare because it was thought that the jump frequencies must come from experiment or be treated as adjustable parameters. But the required jump frequencies can, in fact, come from a HADES calculation. Thus a powerful new kind of hybrid calculation becomes possible.

Accordingly, one uses HADES to calculate migration energies for the local environments encountered by a defect. Assuming the same attempt frequency everywhere, one uses these energies to define explicit jump frequencies for the same environments as input for a Monte Carlo calculation. By statistically sampling, the latter now serves to calculate the long time averaged tracer diffusion coefficient and d.c. ionic conductivity and their components.

The approach has been applied to a long-standing problem in the field of solid electrolytes, namely the variation of ionic conductivity with dopant concentration in Y^{3+} doped CeO_2 [2]. In this system a pronounced maximum is observed in the conductivity versus dopant concentration at a concentration of approximately 8 mole % Y_2O_3 in CeO_2 - an observation that has not received a satisfactory quantitative explanation. We therefore calculated the migration energies for defects in a wide range of environments, and fed these into the Monte Carlo program. Both random and ordered configurations of immobile Y^{3+} were studied. The results for the random distribution agree well with experimental data given in reference [2]. A much lower conductivity is found when an ordered Y distribution is assumed - a result that again ties in well with experiment, as ageing of the solid solution (which leads to ordering of the dopants) causes a reduction in the conductivity.

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CALCULATIONS OF THE ENERGIES OF POINT DEFECTS
IN QUARTZ

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Defects in quartz are of great technological importance. Quartz crystal controlled resonators are widely used in communications systems, where stringent requirements for frequency stability have to be met. Frequency instability, which may be radiation induced, is known to be caused by changes in the configuration of point defects in the crystal.

Commercially grown and natural quartz both contain Al^{3+} substituting for Si^{4+} as an important impurity. This is compensated for by an interstitial M^+ ion, where $M = Li$ or Na . One M^+ ion in quartz may be replaced by the other by the technique of electrodiffusion or sweeping. Thus it is possible to produce quartz crystals containing virtually pure Li^+ or Na^+ as the compensating alkali metal cation. It is known experimentally [1] that irradiation above 200K liberates the M^+ cation and replaces it with either a proton H^+ or a hole h^+ . The proton binds to a neighbouring oxygen and may be studied by infrared absorption [2]. The $Al^{3+} - h^+$ centre has been studied by electron spin resonance [3]. The $M^+ - Al^{3+}$ centre itself is less easy to study experimentally. The $Na^+ - Al^{3+}$ centre may be detected by anelastic relaxation [4] and by dielectric relaxation [5], where it shows up as a characteristic pair of peaks. No such peaks are observed for the $Al^{3+} - Li^+$ defect. Finally the electrical conductivity of quartz may be studied [6] as a probe of the unbound M^+ cations.

Our calculations have been concerned with the $M^+ - Al^{3+}$ centre. A peak in the dielectric relaxation corresponds to the defect switching between two symmetry related structures. In this case there is a C_2 axis through the Al^{3+} ion in the $z=0$ plane of the crystal. Figure 1 shows the structure of alpha quartz viewed at a slight angle to the z axis. The conclusion of the dielectric relaxation experiment is therefore that in the $Na^+ - Al^{3+}$ centre the Na^+ ion lies off the C_2 axis. The dielectric loss peak is observed when the Na^+ ion switches between the two equivalent sites on either side of the C_2 axis. The absence of any peak for the Li^+ swept samples shows that the Li^+ ion lies on the C_2 axis. The presence of two peaks in the Na^+ swept samples shows that the Na^+ ion can sit in two inequivalent sites, both of which have a pair of equivalent positions. An examination of Figure 1 shows that there are two channels in the z direction, which we shall call α and β , into which the M^+ ion may go. If the M^+ ion is bound to an Al^{3+} ion these channels are not equivalent. This explains the two peaks in the dielectric relaxation experiment. (It

is important to note that the two sites are equivalent if the M^{+} ion is bound to a Si^{4+} ion instead of Al^{3+} . This is because the M^{+} ion does not need to cross from one channel to another to reach the alternate site, but only move across the channel in the $z=0$ plane to another Si^{4+} ion). Quantitative information about the defect may also be obtained from the dielectric relaxation. Thus the activation energy for the transition between two equivalent sites is determined by the temperature at which the dielectric relaxation is observed. The free energy for the transition from an α to a β site may also be estimated. The ratio of the dipole of the defect in the z direction and in the $z = 0$ plane normal to the C2 axis may be determined from the peak intensities for samples cut in different directions. The variation of electrical conductivity with temperature gives an Arrhenius energy. As shown in [6], this is the sum of the free energy of migration E_m and of activation E_a . Both Li^{+} and Na^{+} swept samples may be studied.

Preliminary calculations have been carried out in order to simulate these processes. The host quartz lattice is simulated with a classical Born model with additional three body, angle dependent terms [7]. The angle dependent terms act about the $O-Si-O$ bond. This model has also been described in issue 12 of this newsletter. The potentials for the interaction of the substitutional Al^{3+} with the host lattice were obtained from a best fit to the structure and properties of Al_2O_3 . The aluminium oxygen potential was then corrected to allow for the change in coordination number of the aluminium from 6 fold in Al_2O_3 to 4 fold in SiO_2 . As a check on the aluminium oxygen potential, the structure and properties of the mineral sillimanite (Al_2SiO_5), which contains both 4 fold and 6 fold coordinated Al^{3+} ions, were simulated and found to be in reasonable agreement with experiment. For the four fold coordinated aluminium, the same angle dependent force constant was used as for silicon. No such angle dependent terms were used for the 6 fold coordinate Al^{3+} in sillimanite. The alkali oxygen potentials were taken from [8].

The calculations show that the Na^{+} ion bound to Al^{3+} , in both the α and β sites, relaxes off the two fold axis. In contrast, the Li^{+} ion remains on the 2 fold axis. Thus our calculations give the correct qualitative behaviour for the $M^{+}-Al^{3+}$ defect. The activation energy for the transition between the two equivalent sites was then calculated by restricting the Na^{+} ion to lie on the C2 axis and finding the minimum energy configuration. The results of these calculations are presented in table 1. The dipole ratio of the defect was also estimated from the simulations. As can be seen, while the α configuration is in very good agreement with experiment, the agreement for the β configuration is poor. Finally the activation energy for the α to β transition was calculated, assuming that the saddle point lies on the z axis between the Al^{3+} substitutional and the nearest Si^{4+} ion. The activation and migration energies of both the Li^{+} and Na^{+} ion were then calculated to compare with the Arrhenius energy obtained from electrical conductivity measurements. The simulation of the unbound Na^{+} ion defect showed that in the relaxed configuration the Na^{+} ion lies on a C2 axis which cuts the z axis at $z = 1/6$. (This is not crystallographically equivalent to the C2 axis passing through the Si^{4+} ion at the origin.) In contrast, the free Li^{+} ion still prefers the C2 axis at $z=0$ as the stable configuration. The migration

energies for the free ions were determined by calculating the minimum energy constraining the ion to lie along the C2 axis which is not equivalent to that adopted in the relaxed configuration ($z=0$ for Na^+ and $z=1/6$ for Li^+). The results are presented in table 1 together with the experimental values for $E_a + E_m$.

In conclusion, our simulations reproduce the experimental results reasonably well. Further work is in progress on the potentials, particularly the alkali oxygen potentials, to attempt to improve the quantitative agreement.

Acknowledgements

I am grateful to Prof. A. S. Nowick, Dr. C. R. A. Catlow and Dr. A. Cormack for useful discussions.

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TABLE 1

Na+

	CALCULATED	OBSERVED
$\alpha - \alpha$ Transition		
Activation energy eV	0.02	0.057
Dipole ratio dz/dy	5	4
$\beta - \beta$ Transition		
Activation energy eV	0.26	0.135
Dipole Ratio dz/dy	1	4
$\alpha - \beta$ Transition		
Energy eV	-0.12	0.045
Activation Energy eV	1.4	---
E_m eV	0.29	--
E_a eV	0.85	--
$E_m + E_a$	1.14	1.3

Li+

$\alpha - \beta$ Transition		
Energy eV	-0.047	---
Activation Energy eV	1.2	---
E_m eV	0.085	---
E_a eV	1.31	---
$E_m + E_a$	1.40	1.4

FIGURE 1

