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.

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Editorial.

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The eagerly awaited report on the 'Future Facilities for Advanced Research Computing' compiled by the Joint Working Party of the A.B.R.C., the U.G.C. and Computer Board appeared in June. It makes a number of recommendations highly important to the future of scientific (and other) computing in the United Kingdom. Of immediate interest is its recommendation of the purchase of a new supercomputer (a Cray X-MP/48) for the benefit of the U.K. research community (though we at Daresbury are somewhat disappointed to learn that the Rutherford and Appleton Laboratory is the favoured site). Taking a wider view the report offers a powerful scheme for enhancing and maintaining the computational expertise that exists in the U.K. and if it is acted upon should secure the position of the U.K. as a worthy competitor in a very important field of human endeavour. We must however await developments.

A brief summary of the main recommendations is presented within.

Once again we have pleasure in thanking our contributors for their efforts. It is particularly gratifying that we receive articles from our colleagues overseas. It undoubtedly indicates the value that is placed upon projects like CCP5. Thanks indeed !

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

b) Two further workshops are planned by CCP5 in the year ahead. These are on the subjects of 'Transport Properties' and 'Similation of Ceramics and High Temperature Materials'. The Transport Properties Workshop is scheduled for 26th. March 1986 at Royal Holloway and New Bedford College (note the different venue from previous announcements). Details can be obtained from Dr. David Heyes, Department of Chemistry, Royal Holloway and New Bedford College, Egham, Surrey TW20 OEX. The workshop on high temperature materials will take place in January 1986. The location has not yet been decided. Further information will be available from Dr. Maurice Leslie, TCS Division, SERC Daresbury Laboratory, Warrington WA4 4AD.

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

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

e) For the benefit of U.K. CCP5 participants we report briefly the principal recomendations of the Joint Working Party of the Advisory Board for the Research Councils (A.B.R.C.), the University Grants Committee (U.G.C.) and the Computer Board for Universities and Research Councils; otherwise known as the Forty Committee after the Chairman, Professor A.J. Forty (Warwick).

The Committee recommends the adoption of a National Strategy, funded centrally by A.B.R.C., U.G.C. and Computer Board, to ensure advanced computing facilities of sufficient capacity and continuity of funding for the very best computer science. To oversee this strategy an Advanced Research Computing Advisory Board (A.R.C.A.B.) with a full time director and reporting to the A.B.R.C. should be established. The National Strategy should embrace distributed

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computing as well as the centralised provision of powerful supercomputers for general research use. Good networking facilities are viewed as essential.

Proper emphasis on the support and development of the best algorithms and programs is required. High priority should be given to the initiatives of the CCP's and allied Engineering Board projects. The CCP's should be continued and extended. Collaboration with industry and with overseas scientific centres is viewed as highly important.

academic community should have access to a Cray X-MP/48 The system which should be established at the Rutherford and Appleton Atlas Computing Centre. A second machine should become available by 1990 (incorporating the advances in design over the period). This strategy should continue to operate into the 1990's, with a new facility becoming available three years into the six-year replacement cycle of each machine, thus keeping the hardware in the forefront of technology and yet allowing for continuity of software development. As an interim measure the facilities at ULCC amd UMRCC could be enhanced and also A.B.R.C. should consider buying computer time on bureau facilities to permit early development of software exploiting the architecture of the Cray X-MP.

A component of the National Strategy should be concentrated on distributed computing resources at selected sites. Areas such as graphics and special architecture computers (e.g. ICL DAP and GEC GRID) should be supported. Immediate enhancements of the JANET network is required, with megastream trunk lines between centres and fast local area networks. The Working Party endorses the current bid by Computer Board for network improvements.

A two-tier review procedure is required to regulate the use of the national facilities. The scientific merit of applications would be the concern of the Research Councils and the allocation of computing resources the concern of a broadly constituted Facility Board under the A.R.C.A.B.. Collaborations in computational science with industrial and overseas centres should be encouraged by A.R.C.A.B. through Fellowships in Computational Science and Overseas Exchange Fellowships.

f) The Institute of Physics is organising a Solid State Physics Conference at the University of Reading 18 th. to 20 th. December 1985. At this meeting CCP5 is sponsoring Professor K. Binder as a speaker. He will speak on the subject of "Finite size effects on phase transitions and their implication for computer simulations". Other speakers include H.J. Hiiorst ("Special purpose computers"), M. Parrinello ("Molecular dynamics and Kohn-Sham band structures"), E. Wimmer ("Surface electronic structure and energy minimization") and H. De Raedt ("Monte Carlo methods for quantum systems") among many others.

g) The S.E.R.C. are pleased to announce the appointment of

Professor E.W.J. Mitchell C.B.E., to be the new Chairman of the Science and Engineering Research Council from 1985 to 1990, begining from 1st. October. Professor Mitchell is currently Dr. Lee's Professor of Experimental Philosophy at Oxford. He replaces Sir John Kingman FRS, who will be taking up the post of Vice-Chancellor of the University of Bristol.

h) All readers of the CCP5 Newsletter and users of the CCP5 Program. Library are asked to take special notice of the following announcements.

1) 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.

2) In an issue of the CCP5 Newsletter earlier this year we regretfully announced that two of the CCP5 Prgram Library. programs had been found to be erroneous. The errors were in fact errors of specification rather than coding (i.e. the programs had been assumed to be applicable in areas where they were not), ... nevertheless users must have been dismayed to learn of them. This story highlights some of the difficulties of running a program library. While the programs we issue are to the best of our knowledge correct it has to be acknowledged that they are strictly only correct for those cases where test data are available. We therefore remind our readers that upon receiving. programs from us they should test them thoroughly themselves, in the situations in which they wish to use them (this is in fact a requirement the S.E.R.C. places upon recipients of any of its material). Also it should be understood that users have a moral obligation to report any errors they find as quickly as possible. No library of software can be guaranteed to be error free, but with the goodwill of its users, the problems can be minimised.

3) As the newsletter is now over four years old it is highly probable that our mailing list is in need of an overhaul. We therefore request that our readers inform us if they are receiving their copy indirectly through an incorrect address, or if they are reading someone else's and would like to be on our mailing list (there is no charge). Also it is very important for us to know if we have 'ghost' readers; that is people (usually research students) who have left the field. Perhaps readers aware of such cases would be kind enough to let us know.

Thank you for your attention to these matters.

i) At Daresbury Laboratory the promised conversion to the MVS operating system has taken place. The change-over has not taken place faultlessly however and there appear to be problems of loss of contact and difficulties with file tranfers between the mainframe and other machines. Users are requested to be patient while the inevitable bugs are ironed out. The MVS operating system offers considerable advantages over the old MVT system, not least the increased memory utilization of the NAS AS7000 and direct access to the FPS 164.

j) From the Rutherford and Appleton Computer Centre we learn that the CERN internetworking gateway was opened on August 1. This means that U.K. users with access to the JANET network will be able to send files through the DECnet at CERN or the CERNET and thus to many of the computers on the CERN network.

Also of practical interest is the fact that R.A.L. are to begin work on an online documentation system to replace the CIGAR and VS Reference manuals. This is part of a general move away from large manual production.

k) The University of London Computing Centre has scheduled a new version of the MVS Operating System (SPI.3) for the Amdahl 470/V8 for the Autumn. A field trial was scheduled for the end of July. A new Amdahl disc space scheduler is to be available to allow users better control and monitoring of their disc allocation and thus reduce problems of damaging datset deletion by the purger.

Similar changes are intended for the Cray. A compiler upgrade to CFT 1.14 is planned for September and an upgrade of the operating system to COS 1.12 BF1C is imminent. Associated with the latter is a new Resource Dataset Manager to allow more flexibility in file space usage and better job scheduling.

A molecular mechanics program MM2, which optimises the geometries of fairly complex organic molecules is available to U.L.C.C. users.

1) The University of Manchester Regional Computing Centre has announced the withdrawal of FTN compiler at the end of 1985. Users are being advised to begin conversion to the FTN5 compiler immediately. The FTN5 compiler meanwhile, was upgraded in July along with the associated library and PMD (Level 614). Two useful documents to look out for are the ROSCOE Commands Handbook and the Introduction to the Amdahl (Terminal Users).

m) Readers may be interested to know of two conferences. The first is the 1985 Materials Research Society Symposium on Computer-Based Microscopic Description of the Structure and Properties of Materials to be held at Boston, Massachusetts December 2-6 1985. The speakers include A. Angell (Purdue), A. Bakker (Delft), B.

Berne (Columbia), J. Haile (Clemson) and W. Hoover (U.C. Davís), to mention a few. Additional information is available from W. Krakow or S.T. Pantelides at the IBM Thomas J. Watson Research Centre, P.O. Box 218, Yorktown Heights, N.Y. 10598.

The second conference is the Faraday Symposium No.20 on the Phase Transitions in Adsorbed Layers to be held at the University of Oxford 17-18 December 1985. The contributors to the meeting include J.S. Rowlinson (Oxford), M. Fisher (Cornell), D. J. Tildesley (Southampton), D. Nicholson and N.G. Parsonage (Imperial), F. van Swol (Oxford) and R. Evans (Bristol), among others. The fee is expected to be £25 for RSC members and £45 for non-members (fee includes a set of preprints and papers). Students studying for a degree will not be charged the conference fee. The cost for accommodation is expected to be about £35. Enquiries regarding attendance at the conference should be referred to Mrs. Y.A. Fish, The Royal Society of Chemistry, Burlington House, Piccadily, London WIV OBN. A final programme will be available in October 1985.

n) Anyone wishing to make use of the CCP5 Program Library is invited to do so. Documents and programs are available free of charge to academic centres upon application to Dr. M. Leslie (*) at Daresbury Laboratory. Listings of programs are available if required but it is recommended that magnetic tapes (to be supplied by the applicant) be used. Users wishing to send magnetic tapes are instructed to write to Dr. Leslie for information before sending the tape. PLEASE DO NOT SEND TAPES WITHOUT CONTACTING DR. LESLIE FIRST. Delays are caused by applicants sending new tapes which have to be initialised at Daresbury (i.e. tape marks have to be written on them). Also tapes sent in padded bags have to be cleaned before use. Please do not use this form of packing. (A list of programs available follows in the next few pages.)

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

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

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List of Programs in the CCP5 Program Library. ary, The second se

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, displacement, quantum corrections and radial mean square distribution function.

HMDIAT by S. M. Thompson. An anti-Merselectron with the state of the the the second s

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. and a start and the start of the An effective start of the start of

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. 2

CURDEN by W. Smith.

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

HLJ1 by D. M. Heyes.

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

HLJ2 by D. M. Heyes.

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

HLJ3 by D. M. Heyes.

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

HLJ4 by D. M. Heyes.

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

displacements and radial distribution function.

HLJ5 by D. M. Heyes.

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

HLJ6 by D. M. Heyes.

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

MCRPM by D. M. Heyes.

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

SURF by D. M. Heyes.

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

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

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

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 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.

MDDIATO 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.

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CARLOS by B. Jonsson & S. Romano.

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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. sees and approximation and the object of the conditioned and the set of the set of the en al franciska franciska se se standar fra Antonia 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. general de la complete de la complet SMF by N. Corbin. M.C. simulation of atomic fluids. Standard (path integral method) Monte Carlo program for atomic fluids.

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REPORT ON THE ITALIAN PHYSICAL SOCIETY'S SUMMER COURSE (23rd July / 2nd August, 1985)

MOLECULAR DYNAMICS SIMULATION OF STATISTICAL MECHANICAL SYSTEMS

by D.M. Heyes

An Enrico Fermi International Summer School of Physics was held recently at the Villa Monastero, Varenna, idyllically situated on the shores of Lake Como, N. Italy. The directors Giovanni Ciccotti and Bill Hoover, and secretary Paolo Giaquinta with staff, are to be thanked for the work they put in to make this a very worthwhile meeting to attend. The Varenna School system was established in 1953 and has provided a forum where internationally famous scientists can discuss their work and ideas at length to the benefit of young scientists. The meeting is named after Enrico Fermi in tribute to his contribution to science and his association with Varenna (where he gave a number of famous lectures prior to his untimely death in 1954).

There are seminars on many topics of interest to the Molecular Dynamics community. Though, I can only hope to give you a subjective flavour of the meeting.

M.L. Klein (Chemistry Division, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6) described techniques and results relevant to simulating molecular crystals and ionic salts by molecular dynamics. He gave a comprehensive account of the formalism needed to characterise the ordering in the solid phase (which is compatible with neutron scattering, for example). It is possible (and most convenient) to express favoured molecular orientations in terms of the sub-groups of the space group of the lattice. The mechanisms of translational and re-orientational dynamics were discussed in terms of their effects on the acoustic and optic phonon branches of the dispersion curve. Techniques for following phase changes, forced by external conditions which involve a time variation of the size and shape of the MD replicated cell, were also considered. Compounds dealt with in his presentation were $\text{Li}_2SO_{\rm h}$, NH₄Br, KCN, NaNO₂, CF₄, N₂ and Bicylo (2.2.2) octane.

M. Meyer (Laboratoire de Phyqiue des Matériaux, C.N.R.S. 1, Place Aristide Briand, F-92195 Meudon, Cedex, France) continued this theme by discussing the orientational order in a plastic crystal phase of adamantane, which is tricyclo (3,3,1,1) decame or $C_{10}H_{16}$. (A plastic phase is one in which the molecules have translational order corresponding to a crystal but the molecules are more or less free to rotate about their fixed average lattice positions). The temperature dependence of the structure and the orientational probability density (expressed in terms of the cubic harmonics of the lattice) were investigated. The most probable orientations of the molecules were almost equally distributed between two degenerate sub-groups of the lattice. There was also evidence of other structures derived from occasional re-orientations about available four-fold and three-fold axes.

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J.P. Ryckaert (Université Libre de Bruxelles, Pool de Physique - CP 223, Campus Plaine - bvd. du Triomphe, B-1050 Brussels, Belgium) described the constraint method for simulating polyatomic molecules. The high frequency (generally irrelevant) intramolecular vibrations are omitted by constraining bond lengths and (more dangerously) bond angles to their average values in the actual molecule. The Verlet algorithm was used to produce an algorithm which updates molecular positions as normal for a monatomic liquid or solid and then re-adjusts them in an iterative fashion so as to maintain the constraints. Alkanes were considered as specific examples.

H.J.C. Berendsen (Laboratory of Physical Chemistry, University of Groningen, Nyenborgh 16, 9749 AG Groningen, The Netherlands) reviewed the algorithms that can be used to integrate the equations of motion in molecular dynamics. Systems from a simple harmonic oscillator to a protein containing 458 atoms were considered. For general purpose use a low order algorithm such as the Verlet algorithm (which is the same as the Beeman algorithm!) was recommended. Although higher order predictor-corrector (Gear) algorithms do produce more accurate dynamics at small time steps, stability can be a problem at the usual values chosen ($\approx 10^{-14}$ sec). Some interesting comments concerning the solution of the stochastic Langevin equation were also made. In a separate talk he described some recent results of these techniques applied to biological molecules and membranes. The objective being to understand and even predict functional properties in terms of their behaviour on the molecular scale. Ultimately drug design could benefit from of this work. He showed

how it was possible to produce a stable macromolecule solely from the pairpotentials independently derived. The thermodynamic stability of these states can be determined by calculating the configurational free energy using the multidimensional configurational distribution function. These calculations are very important for comparing the relative stability of conformers. Some startling pictures of biological membranes were shown. The chains exhibit a collective tilt, explaining the experimentally observed decrease in order parameter. The water-hydrocarbon interface in the region of the head groups is remarkably disordered and shows evidence of subtle charge cancellation between water, free ions and head groups in this region.

D. Frenkel (Physical Laboratory, Rijksuniversiteit Utrecht, P.O. Box 80000, 3508 TA Utrecht, The Netherlands) reviewed the methods available for calculating the (Helmholtz) free energy of simulation systems. Being a "thermal" property it depends on the total volume of phase space accessible to the system. Various manipulations of Metropolis sampling have created a number of methods for determining the free energy. These include particle insertion (usefully generalised here for microcononical ensembles), its biased sampling derivatives to improve the efficiency at high density and the cavity distribution method. Grand cononical Monte Carlo, overlapping distributions, Umbrella Sampling and formal direct integration were also considered. Applications towards locating the point of first order phase transitions were described. The relative merits of the different approaches were discussed. Daan finished with some sound advice to the novice (and not-so-novice!) simulator: Always look for the simplest method available. It is often better to adopt a formally more "time-consuming" but straightforward approach than a sophisticated method which involves considerable programming efforts at least at first.

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W.W. Wood (Carroll College, Helena, Montana 59625, USA) gave a fascinating description of the early days of Monte Carlo and its formulation including the metropolis sample scheme. This now routine technique was the subject of much controversy in the early fifties. The repeated counting of a state from which a trial move was rejected, was a particular point of contention. It is easy to overlook the work that has gone into the techniques which we now tend to take for granted.

I.R. McDonald (Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, UK) gave an overview of the work performed at characterising the structural correlations in simple molecular liquids since the first simulation of Harp and Berne (1970) on diatomics. For diatomics there are a number of schemes for representing the molecular pair distribution function which include the relative orientations of the molecules. One can project the orientations of linear molecules in spherical harmonics, about their inter-molecular bond axis or alternatively the orientations of the two molecules can be referred to a laboratory-fixed frame of reference. The latter approach is particularly useful when it comes to evaluating laboratory coordinate related properties such as Fourier transforms. Angular correlation parameters, which are useful in interpreting a variety of spectroscopic experiments, are difficult to determine unambiguously because of the slow decay with distance of their defining integrals. This has a bearing on ways for establishing dielectric properties, where cut-offs can induce spurious long range orientational correlations of dipoles. However, this is less of a problem than it might first appear as the dielectric constant can be calculated in a variety of ways that are mutually consistent, as the defining formulae are different in each case. Dielectric relaxation was also considered.

P.A. Madden (Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK) demonstrated the value of molecular dynamics simulations in aiding the interpretation of spectroscopic line shapes. He outlined the formidable problems involved in this because there are many processes (interaction-induced effects) which go on within a liquid which contribute to the spectra. These are complex functions of the molecular motions, which can also be obscured by collision-induced effects which marr our ability to evaluate re-orientational correlation times, for example. The merits of a low order cumulant expansion in describing the relationship between the angular displacement and angular velocity correlation functions were demonstrated. Some interesting observations were made concerning the form of intermolecular encounters (cage and rebound effects). Using the Hutchinson and Lynden-Bell decomposition of successive particle moves, it was suggested that the structure in the velocity autocorrelation function is due to a small number of 'rattling' encounters, the rest being rather damped and featureless. The general re-orientational behaviour of a number of liquids such as CS2, CH3CN, N2, Br2, CO2 was described, and comments were made on the

relationship between collective and single particle motion.

J.-P. Hansen (Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, F-75230 Paris 05, France) presented a review of MD simulations of one and two component Coulomb systems in the fields of plasma physics and condensed matter (e.g., metals, molten salts) physics. Using plasma notation he defined a number of parameters which can be used to characterise the Coulomb system in any application. There are two length scales, the size of the charged species and the mean separation. There is a coupling parameter which measures the strength of the interaction when compared with There is a parameter called the Debye screening length, which governs k_T. the importance of collective motion. After reviewing methods for treating the long-range forces in MD he concentrated on the dimensionality and its impact on the properties of strongly coupled plasmas, the one component plasma, binary ionic mixtures (molten salts, macro-ionic solutions), two component plasmas such as electrons and protons. Although these latter two components relax over very different time scales it is still possible to use MD to come to some interesting conclusions about the electric current auto correlation function and thermal conductivity. A novel way of simulating a 2D system, wrapped around a sphere, was also discussed.

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The area of two-dimensional phase transitions was introduced by F.F. Abraham (IBM Research Laboratory, San José, California 95193, USA). He found that for a Lennard-Jones system with full periodicity two-dimensional melting occurs by a first order phase transition at a higher temperature than the thermodynamically predicted temperature (although still compatible with the mechanical stability criteria of Kosterlitz-Thouless-Feynman). This is rectified by the incorporation of surfaces in the model (i.e. periodic boundary conditions on one direction only for 2D). He also talked about the related behaviour of quasi-two-dimensional physisorbed LI films. These are models for Xe, Kr, and Ar on graphite. Xe is influenced least by the sublattice whereas Kr, being commensurate (i.e. in some form of registry) with the sublattice has its 2D melting temperature raised. Ar is more complex because it is the liquid which is commensurate with the sublattice, not the This causes a "conflict of interests" resulting in a continuous meltsolid. ing transition. Some outstanding films were shown. One of spinodal decomposition in the 2D LJ fluid and another of the incommensurate phase of Krypton

on graphite. The latter is created by increasing the density of Kr above a value at which it can form a continuous commensurate layer. Calculations performed on up to 161,604 Krypton atoms (!) produced a honeycombe pattern of commensurate areas separated by incommensurate boundaries which have fascinating dynamical properties.

Other forms of phase transition were discussed by many speakers: M. Parrinello (Istituto di Fisica Teorica, Strada Costiera 11, Miramare, I-341000 Trieste, italy) described what has now come to be known as the Rahman-Parrinello technique for following phase changes in solids by allowing the MD cell to vary in shape under the conditions of stress or change in temperature etc. The system seeks out its preferred crystal structure, governed by the pair potential, amongst other parameters. He gave some examples: the polymorphic transition of KCl from fcc to bcc under pressure; the transformation of α -AgI to β -AgI and mechanical failure of Ni under uniaxial stress.

S. Yip (Department of Nuclear Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139; USA) looked at self-diffusion in grain boundaries. A Lennard-Jones kite-shaped configuration was set-up and vacancy migration in this volume was followed. One vacancy was introduced in about 500 atoms (small, but still larger than in real systems!). The Arrherius behaviour activation energy for jumping (~ 0.5 eV) is close to typical experimentally determined values (~ 1 eV). The mechanism of diffusion and its characterisation are quite different to those encountered in liquid state studies. These "rare-events" were also discussed by G. Jacucci, C. Centro del Consiglio Nazionale delle Ricerche e Dipartimento di Fisica, Universita di Trento, I-38050 Povo, Italy). He said that in order to develop a theory for atomic diffusion in crystals (due to the migration of point defects) it is necessary to know the N-body thermodynamics of the system. Using a Lattice Dynamics formulation of a LJ system he demonstrated how useful information on lattice vacancies can be obtained which can lead on to rate theories for vacancy migration.

Shock waves were aluded to on a number of occasions. B.L. Holian (Los Alamos National Laboratory, Los Alamos, New Mexico 87545,USA) talked about a NEMD method of studying the transfer of energy from translational degrees of

freedom into internal vibrations of molecules, using N₂ as a test case. By thermostating the vibrational degree of freedom (preferably by the Nosé-Hoover scheme) and the other degrees of freedom at a higher temperature the vibrational relaxation rate constant can be reuced to the evaluation of a steady-state non-equilibrium property.

E. Presutti (Dipartimento di Matematica, Università La Sapienza, P. Le Aldo Moro 2, I-00185 Roma, Italy) presented models of random interacting particle systems which can be induced to exhibit shock wave and other interfacial phenomena.

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D.M. Ceperley (Lawrence Livermore National Laboratory, University of California, P.O.Box 808, Livermore, California 94505, USA) discussed simulation methods for quantum mechanical systems at finite temperatures. The path integral method was described. The applications to helium produced energy and specific heat values which were in very good agreement with experiment. There were a series of talks on the underlying statistical mechanical foundations for transport coefficient evaluation. B.J. Alder (Lawrence Livermore National Laboratory, University of California, P.O. Box 808, Livermore, California 94550, USA) described the various types of long-time tails that come out of simulation and their relationships to hydrodynamic and viscoelasticity. If a I might be premitted some small advertisements (1), a velocity auto-correlation function which goes positive again after its minimum (discussed in the talk) was observed in ref.[1]. Also some attempts at following the form of structural relaxation which gives rise to the "molasses" tail were made in ref.[2].

D.J. Evans (Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia) presented a detailed account of the theory of non-equilibrium molecular dynamics. Formulations of linear isothermal responses were made using a non-Liouville equation. A useful summary of the various NEMD algorithms for various transport coefficients was given.

J.R. Dorfman (Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, USA) gave an excellent account of what to an outsider seems an extremely complicated field! He reviewed the

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state of play in the kinetic theory of hard sphere fluids. He showed how recent developments in mode coupling theory, which lead to a "softening of the heat mode", can now bring kinetic theory and simulation data into close agreement. Such properties as the "molasses" tail can be accounted for (leading to possible extensions to predict the glass transition). Also the $\dot{\gamma}^{1/2}$ non-Newtonian correction to the shear viscosity ($\dot{\gamma}$ is the shear rate) comes out of the theory.

J.W. Dufty (Department of Physics, University of Florida, Gainesville, Florida, USA) presented a statistical mechanical formulation of a fluid under shear by the Lees-Edwards time-dependent boundary conditions. He systematically revealed that there were a number of "sources" for the non-equilibrium state e.g. inertial forces due to the boundary conditions, viscous heating and the non-conservative force. It was shown that the effects of non-conservative forces on transport processes are difficult to predict, although in practice the system seems to be resilient to a number of nominally equivalent thermostating procedures.

G. Benettin (Dipartimento di Fisica del'Università di Padova and Centro Interuniversitario di Struttura della Materia, Via Marzolo S, Padova, Italy) addressed the ergodic problem for classical non-linear oscillators. These weakly coupled harmonic oscillators exhibit unexpected paths of energy equilibration between modes, which demonstrate a limited exploration of phase space. "Thermalisation" can be extremely slow.

H. Spohn (Universität München, Theoretische Physik, Theresienstrasse 37, D-8000 München 2, FRG) reviewed the progress in understanding the segregation transition in a driven diffusive system. In particular what is the influence of a perturbation on an equilibrium (second order) phase transition such as demixing of a two-component system under shear? The critical temperature is increased due to the suppression of fluctuations by the driving force.

E. Marinari (Dipartimento di Fisica, Università Roma, 2 via Orazio Raimondo, I-00173 Roma, Italy) talked about a numerical approach to the theory of strong interactions. The area of the presentation was to apply statistical mechanics to lattice Gauge theories.

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R. Impey (National Research Council) Division of Chemistry, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada) reviewed the work performed on water simulations and those on ionic solutions. Various models for water (e.g.MCY) were discussed and their impact on the hydration shell of ions was summarised. Li⁺ and Cl⁻ has a coordination number (up to the first minimum of g(r)) of 5.3 and 7.2, for example, in one simulation.

In addition to the talks, they were interleaved with round-table discussions on a number of topics. Carl Moser (CECAM, Université Paris-Sud, F-91405 Orsay, France) hosted one on the introduction and best use of "New Computers for Molecular Dynamics". The main theme that seemed to come out of the discussion was that the simulator can no longer tackle a problem without being aware of the architecture of the machine to be used. The variety of machines available from micros to super computers, with broadly equivalent computer power, do things most efficiently in different ways.

V. Pontikis (Section des Recherches de Métallugie Physique, CEN-Saclay, F-91191 Gif-Sur-Yvette, Cedex, France) hosted a round-table discussion on pair potentials which included a contribution from H.J.C. Berendsen on the use of simulation of large molecules to determine functional group specificity. Also Dr. Pontikis showed a very impressive film of ad-atom surface diffusion. There was also an interesting talk on the structure and dynamics of water in zeolites (by MD). (Apologies, but I did not catch the speaker's name!). The water molecules went quickly to charged sites on the zeolite surface, evident in a diminishing self-diffusion coefficient with equilibrium.

Howard J.M. Hanley (National Bureau of Standards, Boulder, Colorado 80303, USA) chaired a round-table discussion on non-equilibrium molecular dynamics. It was clear that, although the NEMD calculations are surprisingly efficient at deriving transport coefficients with a small N-dependence (when compared with Green-Kubo integrals), the foundations upon which they are based are theoretically somewhat shakey at times.

Denis Evans showed that non-neutonian shear viscosities obtained by SSLOD using a variety of thermostating methods are identical within statistics. So that there is a weak coupling there. Evans and Morriss have sorted out the NEMD schemes and made them compatible with isothermal linear response

theory. This and the just non-newtonian regime are the main preserves of theoreticians (e.g. J. Dufty) at the moment. Substantial extensions to microscopically finite shear rates, which produce extreme shear thinning are still lacking. Gary Morriss talked about a two-particle gas under shear, for which analytic solutions for non-linear behaviour are possible. There were also contributions from J. Dufty and M. Mareschal (Chemie Physique II, C.P.231, Université Libre de Bruxelles, Bld. du Triomphe, B-1050 Brussels, Belgium) who talked about a stochastic model for the influence of boundaries (socalled "local" boundary conditions) in NEMD. Bill Hoover talked about MD calculations of the diffusion coefficients of 2 and 3 particle systems. David Heyes talked about the shear-thickening phenomenon in the LJ liquids, a la Les Woodcock.

There were also informal gatherings on other topics. Sidney Yip hosted a series of contributions on the glass transition. This included an interesting talk on glass-forming mixtures of simple liquids using MD by Y. Hiwatari (Department of Physics, Faculty of Science, Kanazawa University, Kanazawa 920, Japan). J. van Opheusden and M. van Waveren chaired an interesting session on the use of parallel and vector computers for molecular dynamics.

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THE MONTE CARLO TECHNIQUE FOR EVALUATING AVERAGES IN

STATISTICAL MECHANICS SIMPLY EXPLAINED

Jack G. Powles, Canterbury, England

The explanation of this technique is very poorly covered in the textbooks [1,2,3,4] on liquids and is elegant but obscure in the original papers [5,6].

The object is to evaluate expectation values (or ensemble averages, or averages over phase space) of a function of the coordinates, e.g. the configurational energy, for a thermodynamic system in equilibrium at temperature T. We consider only a canonical ensemble. Extension to grand canonical and other ensembles, e.g. (P,T) instead of (p,T) is possible.

Let the function be $f(\underline{r}_1, \dots, \underline{r}_N)$, although it is not necessarily dependent on all the coordinates of all the N particles. Strictly speaking we have to take the thermodynamic limit, $N \neq \infty$, $V \neq \infty$ with $N/V = \rho$.

If $U_{N}(r_{1}, \dots, r_{N})$ is configurational potential energy then,

 $\langle \mathbf{f} \rangle = \int \mathbf{f}(\mathbf{r}_1, \dots, \mathbf{r}_N) \exp[-\mathbf{U}_N(\mathbf{r}_1, \dots, \mathbf{r}_N)/k\mathbf{T}] d\mathbf{r}_1 \dots d\mathbf{r}_N / \int \exp(-\mathbf{U}_N/k\mathbf{T}) d\mathbf{r}_1 \dots d\mathbf{r}_N$ (1)

for a classical canonical ensemble. The simplest case is where f is U itself.

This is a multiple integral of multiplicity ~ 10²³ for a macroscopic sample. However, even if we approximate this for N particles where N is say 200, using appropriate boundary conditions, it is a formidable object to evaluate by brute force methods even with present day computers.

The conventional Monte Carlo (MC) (brute force) method of evaluation of $\langle f \rangle$ by equation (1) is to choose points in phase space (i.e. a set of values of $r_1 \cdots r_N$), which we label i (for i = 1 to \mathcal{N}). However this is hopelessly inefficient because virtually all choices of i will result in a large value of U(i)/kT. We are quite likely to have two particles 'overlap' and this involves a large value of U(i)/kT and virtually zero contribution to the

integral. In other words we get a sum of terms, $\langle f \rangle = \sum_{i=1}^{\infty} f(i) e^{-U(i)/kT} / \sum_{i=1}^{\infty} e^{-U(i)/kT}$ (2) and the second second where most of the terms are zero.

What we need is a systematic way of finding all the large terms in (2) i.e. we need to introduce a bias to configurations (i) for which exp-U(i)/kTis large. This is a biased MC and it is extremely difficult to find these configurations by any analytic procedure.

Suppose however we are able to choose the configuration, i, with probability, exp-U(i)/kT, then (2) becomes,

There is no unique way of doing this, but one which experience shows to work is the following. This is a 'recipe' for doing MC. Those who want to do it without understanding why can just use the recipe and read no further!

 $\langle \mathbf{f} \rangle = \sum_{i} \mathbf{f}(\mathbf{i}) / \sum_{i} \mathbf{1} = \frac{1}{\mathcal{F}} \sum_{i=1}^{\mathcal{F}} \mathbf{f}(\mathbf{i})$ (3)

The_recipe

We choose a configuration, i, say. Choose a particle at random; say, N, = Int(ξ_1 N+1) where ξ_1 is a random number 0 < ξ < 1.

Move this particle a random distance i.e. $x(j) = x(i) + (1-2\xi_2)\Delta x$, where j = i+1 and similarly for y and z, where ξ_2 (and ξ_3 and ξ_4) are random in the interval 0 to 1. For the new configuration, j, evaluate,

$$\Delta U_{ij} = U(j) - U(i) \qquad (4).$$

(N.B. This is fast because it only involves neighbours of the one particle moved.)

If $\Delta U < 0$ the move is accepted, because it is a more probable configura-

tion, and we wish to bias towards probable configurations which contribute materially to the sum in (3). However, we must not get trapped in one region of high probability and we must provide some means of escape. Thus if $\Delta U > 0$ we do not reject the move necessarily. We decide whether to move or not with probability exp- $\Delta U/kT$. In order to do this we choose a random number ξ_5 and compare it with exp- $\Delta U/kT$ (N.B. 0 < exp- $\Delta U/kT$ < 1 since $\Delta U > 0$). If $\xi_5 < \exp{-\Delta U/kT}$ we accept the new configuration j. If $\xi_5 > \exp{-\Delta U/kT}$ we reject the move and return to configuration i but count this as a move by including this term in the sums of (3) - this is essential and must not be omitted.

Repeat for long enough!

Of course initial configuration will be chosen with as low a U(i) as possible, e.g., f.c.c. so that atoms overlap least, but this system is not in equilibrium. We must continue therefore for a sufficient number of configurations to get to 'equilibrium'. This may need some tens of thousands of moves, depending on the system being studied, on the initial state, on N and on Δx . The attainment of equilibrium can be judged by the fluctuations be ing 'random' e.g. by evaluating the instantaneous pressure or some other property. The average of a suitable number of steps must be 'constant enough'.

Once in equilibrium we begin to count moves for the production run and start accumulating the sum in (3). When the statistics are good enough for the accuracy desired we have a large enough \mathcal{N}_{\circ} . The value of \mathcal{N} required may depend on the property. Any number of properties, i.e. different f's, may be evaluated simultaneously or the configurations stored and used afterwards to evaluate any desired f.

The value of Δx is arbitrary but is usually chosen to give a 'success' rate of order 50%, which means we stay a reasonable 'time' in a given high probability configuration. Δx would be say $\frac{1}{20}$ of a particle 'diameter'. If Δx is too small we sample significant regions of phase space too slowly and also we may get round-off error accumulation, depending on the computer. End of recipe

The subtle and difficult part is why this recipe works. This may be seen by considering not just the probability of a configuration $\pi_i^{\alpha} \exp^{-U(i)/kT}$ but the probability of the configuration i changing to j which we call p_{ij} . (N.B. The steps do NOT correspond to any real physical motion of the particles, that is Molecular Dynamics, which is quite different).

Clearly if we start from i we must end up in some j so that,

$$\Sigma p_{i,j} = 1 \quad \text{for all i } (p_{i,j} > 0) . \tag{5}$$

In the steady state,

$$\sum_{i} \pi_{i} p_{ij} = \pi_{j} \quad \text{for all } j \ (\pi_{j} > 0) \ . \tag{6}$$

Moreover if the state j is realised from i in n steps then,

$$p_{\pm j}^{(n)} \neq \pi_{j}$$
 for $n \neq \infty$ (7)

Equilibrium statistical mechanics only specifies the π_i and the p_{ij} are therefore arbitrary (we are not doing Physics we are evaluating an integral i.e. (1)). However the p_{ij} must satisfy (5), (6) and (7) by virtue of the meaning of p_{ij} as a transition probability.

Although the choice of p_{ij} is 'arbitrary' a possible one is suggested by the analogue of the microscopic reversibility conditions i.e.,

 $\pi_{i} p_{j} = \pi_{j} p_{j}, \quad \text{all i and } j (N.B. no sum). \quad (8)$

This is almost universally used but is, in mathematical parlance, sufficient but not necessary.

It is easy to see that (8) is consistent with (5) and (6). From (8)

$$\sum_{i} \pi_{i} p_{ij} = \sum_{i} \pi_{j} p_{j1} = \pi_{j} \sum_{i} p_{j1} = \pi_{j}$$

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i.e. (6), after using (5) with the arbitrary labels i and j interchanged. The formal proof that $p_{ij}^{(n)} \neq \pi_j$, $n \neq \infty$, is more difficult but can easily be seen to be satisfied, if (6) is true, and is independent of (8) - as we expect since (8) is claimed not to be unique.

$$p_{ij}^{(n)} = \Sigma p_{ik} p_{kl} \cdots p_{qr} p_{rj}$$

k,l,m....q,r
n-1 symbols

But $\Sigma p_{1k} \dots p_{qr}$ is the probability of getting to r from i in a large number $k, 1 \dots q$ of steps. Evidently in the limit, $n \neq \infty$, there is no memory of i, i.e. the starting point, and the probability of getting to r is just π_r , the absolute probability. Thus

$$p_{ij}^{(n)} \neq \sum_{r}^{\pi} r^{p}rj$$

Hence by (6) $p_{ij}^{(n)} \neq \pi_j$.

It only remains to show that the recipe is consistent with (8) and that we will get to equilibrium from any starting point. These are very poorly discussed in the books - the second one is poorly discussed even here!

We have chosen p_{ij} so that it is a certain move (prob.1) if $\pi_j > \pi_i$. Also if $\pi_j < \pi_i$ we move if $\pi_j/\pi_i = e^{-\Delta U/kT}$ is > ξ_5 , (0 < ξ_5 < 1), i.e. we accept with a prob. π_j/π_i (< 1). Now suppose P_{ij} is the probability that $\pi_j > \pi_i$ so that the probability that $\pi_j < \pi_i$ is (1- P_{ij}). Then

$$p_{ij} = P_{ij} \times 1 + (1 - P_{ij}) \times \pi_j / \pi_i$$

i.e. $\pi_i p_{ij} = P_{ij} \pi_i + (1 - P_{ij}) \pi_j$ (9)

Now consider in the same way a transition from j to i. $p_{ji} \propto 1$ for $\pi_i > \pi_j$ which has prob. $(1 - P_{ij})$ and $p_{ji} \propto \pi_i / \pi_j$ for $\pi_i < \pi_j$ which has prob. P_{ij}

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From (9) and (10)

$$\mathbf{i}^{\mathbf{p}}\mathbf{i}\mathbf{j} = \pi_{\mathbf{j}}^{\mathbf{p}}\mathbf{j}\mathbf{i}$$

i.e. (8) is satisfied by the recipe, which is consistent with all other requirements on π_i and p_{ij} , all i and j.

π

Hence the procedure is valid at least in 'equilibrium', It is difficult to show formally that we <u>get</u> to equilibrium. But this surely is assured because wherever we start we tend to explore probable configurations and this is just what we <u>mean</u> by equilibrium. In practice it seems no problem arises. The formal proof involves the theory of Markov chains which is not straightforward [7].

It is interesting to speculate whether there is any other criterion than (8) which is more efficient (there are some in the literature which are claimed to be) and also whether there is any systematic way of choosing Δx . Since this is a mixture of numerical analysis and computer technology it seems unlikely that alternatives can be evaluated other than by trial and error. Since the procedure is dependent on the problem in hand this investigation is likely to use more computer time than the evaluation of the averages of interest in any particular case using the conventional recipe.

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THE APPLICATION OF ISOKINETIC SLLOD TO MOLECULAR SYSTEMS EMPLOYING

QUATERNION ALGORITHMS.

D.Brown

Introduction

In some recently commissioned MD simulations the need to apply a steady state shear to a system of rigid triatomic molecules arose. In the past Evans' method [1] has generally been used by myself [2,3] and others [4] but having recently discovered the merits of the Sllod method [5,6] for monatomic systems I was keen to use it also in this case. As it turned out the application of Sllod proved quite simple to implement within a quaternion type algorithm but the details seem novel enough to warrant at least a brief mention.

<u>Method</u> Mathematical Action of the following coupled first order equations of second motion of the following coupled first order equations (first order) (

$$\dot{R} = P/M + R \dot{\gamma} \hat{x}$$
(1)

$$\underline{P} = \underline{F} - \alpha \underline{P} - \dot{\gamma} P_{z} \hat{x}$$
(2)

where M is the mass, $\underline{\mathbf{R}}^{\pm}(\mathbf{R}_{\mathbf{X}},\mathbf{R}_{\mathbf{y}},\mathbf{R}_{\mathbf{Z}})$ is the position of, \underline{P} is the momentum and $\underline{\mathbf{F}}$ is the force on the COM of a molecule and $\dot{\mathbf{y}}$ is the shear rate applied in the x-direction with the gradient in the z-direction. The multiplier α is determined from the constraint that the total kinetic energy is a constant of the motion. These equations are integrated in conjunction with the usual Lees-Edwards shearing boundary conditions as with all previous homogeneous methods.

For rigid molecules I prefer to use a rotational algorithm that uses quaternions to specify orientations. This also involves the integration of coupled first order equations of motion and so is compatible with the Silod equations. The equations relevant to the rotational motion involving the four quaternions q_1 , q_2 , q_3 and q_4 defined by the Euler angles are

$$\dot{\mathbf{j}} = \mathbf{\underline{T}} \tag{3}$$

$$\underline{J}_{\mathbf{p}} = \underline{\underline{A}} \ \underline{J} \tag{4}$$

$$\omega_{p\beta} = J_{p\beta} / I_{\beta\beta} \qquad \beta = x, y, z$$
 (5)

						_		1
i	Ġэ		q4	-q1	q ₂	q3	ω_{p_X}	
	ά ₂	$=\frac{1}{2}$	qı	$-q_4$	$^{+q}$ з	q2	$\omega_{\rm Py}$	
	ġ4	4	Чз	q ₂	ġ ₁	94	ω _{Pz}	
	ġ1		-q2	qэ	-q 4	q1	0	an a
(or ģ	= Q 4	2p				8. S.	(6)

where \underline{J} and \underline{T} are the angular momentum and torque in the lab. frame, \underline{J}_p and $\underline{\omega}_p$ are the angular momentum and angular velocity in the body fixed frame, $I_{\beta\beta}$ is the principal moment of inertia of the β (=x,y,z) principal axis and \underline{A} is the rotation matrix. Now as the shear is applied via the COM, eqns. (1) and (2), the rotational equations do not require any changes involving $\dot{\gamma}$, however, to maintain constant total kinetic energy the α parameter does have to be included. It can be simply shown that by using the same equations of motion for the sites as for the COM, eqns. (1) and (2), but excluding the terms involving $\dot{\gamma}$ results in the following modified equation for the rotational motion

$$\underline{\mathbf{J}} = \underline{\mathbf{T}} - \alpha \, \underline{\mathbf{J}} \tag{7}$$

To evaluate α the condition that the total kinetic energy, K_e, is fixed is invoked. Now K_e is given by

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$$K_{e} = \frac{1}{2} M \Sigma \left(\frac{P}{M}\right)^{2} + \frac{1}{2} \Sigma \Sigma_{\beta} I_{\beta\beta} \omega_{P\beta}^{2}$$
(8)

, where here E refers to a sum over all N molecules and Σ_{β} refers to a sum over all three principal axes, so the condition that K_e is fixed implies that $\dot{K}_e = 0$ which in turn means that

$$M^{-1}\Sigma \underline{P} \cdot \underline{\dot{P}} + \Sigma \Sigma_{\beta} I_{\beta\beta} \omega_{p\beta} \dot{\omega}_{p\beta} = 0$$
(9)

For the first term substituting eqn. (2) in (9) gives

$$M^{-1} \Sigma \underline{P} \cdot \underline{\dot{P}} = M^{-1} \Sigma \left(\underline{P} \cdot \underline{F} - \alpha \underline{P}^2 - \dot{\gamma} P_x P_z \right)$$
(10)

For the second term differentiating eqn. (5) w.r.t time and substituting into (9) gives

$$\Sigma \Sigma_{\beta} I_{\beta\beta} \omega_{p\beta} \dot{\omega}_{p\beta} = \Sigma \Sigma_{\beta} \omega_{p\beta} \dot{J}_{p\beta} = \Sigma \omega_{p} \cdot \dot{J}_{p} \qquad (11)$$

Now in the principal axis reference frame the equilibrium equation of motion is

$$\dot{\mathbf{j}}_{\mathbf{p}} = \underline{\mathbf{T}}_{\mathbf{p}} - \underline{\boldsymbol{\omega}}_{\mathbf{p}} \mathbf{x} \underline{\mathbf{J}}_{\mathbf{p}}$$
(12)

SO

$$\underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{j}}_{\mathbf{p}} = \underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{T}}_{\mathbf{p}} - \underline{\omega}_{\mathbf{p}} \cdot (\underline{\omega}_{\mathbf{p}} \mathbf{x} \underline{\mathbf{j}}_{\mathbf{p}})$$

which by the rules of vector products is the same as

$$\underline{\omega}_{p} \cdot \underline{j}_{p} = \underline{\omega}_{p} \cdot \underline{T}_{p} - (\underline{\omega}_{p} \times \underline{\omega}_{p}) \cdot \underline{j}_{p}$$

 $= \underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{T}}_{\mathbf{p}}$ (13)

as $\underline{\omega}_p \mathbf{x} \underline{\omega}_p$ is identically zero. It follows from (13) and (3) that

as $\underline{T}_p = \underline{A} \ \underline{T}$

$$\underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{j}}_{\mathbf{p}} = \underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{A}} \ \underline{\mathbf{j}}$$
(14)

Now substituting eqn. (7) into (14) gives

$$\underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{j}}_{\mathbf{p}} = \underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{T}}_{\mathbf{p}} - \alpha \underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{J}}_{\mathbf{p}}$$

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$$= \underline{\omega}_{\mathbf{p}} \cdot \underline{\mathbf{T}}_{\mathbf{p}} - \alpha \, \boldsymbol{\Sigma}_{\boldsymbol{\beta}} \, \mathbf{I}_{\boldsymbol{\beta}\boldsymbol{\beta}} \, \boldsymbol{\omega}_{\mathbf{p}\boldsymbol{\beta}}^{2} \qquad (15)$$

Recombining equations (15) and (10) and rearranging gives

$$\alpha = \frac{M^{-1}\Sigma \left(\underline{P} \cdot \underline{F} - \dot{\gamma} P_{X} P_{Z}\right) + \Sigma \omega_{p} \cdot \underline{T}_{p}}{M^{-1}\Sigma \underline{P}^{2} + \Sigma \Sigma_{\beta} I_{\beta\beta} \omega_{p\beta}^{2}}$$
(16)

With an expression for α it is possible to integrate eqns. (1), (2), (4), (5), (6) and (7) using standard Gear predictor-corrector algorithms for coupled first order differential equations [6] and these were implemented in a triatomic program.

By using eqn. (7) the need for *ad hoc* rescaling is avoided and so one retains the advantages of the Sllod method of a consistent set of equations of motion which includes the constraint on the kinetic energy and the ability to estimate the viscosity from the α parameter by the equation

$$n = 2 \propto K_e / \dot{\gamma}^2 V$$
 (17)

as for monatomic systems (see apology). This result can be simply verified by substituting eqns. (1), (2) and (7) into the equation for the rate of change of the total energy which for a system at steady state is zero as the heat generated by the shear is removed by α .

Details of the Simulations

To test this method simulations were performed on a system composed of triatomic molecules each modelled as three Lennard-Jones interaction sites of equal mass with bond lengths and bond angle σ and 109° 28' respectively. Other details are given below

Number of molecules	N = 108
L-J diameter	$\sigma = 0.392$ nm
L-J well depth	$\epsilon = 300 k_{\rm B} J$
Total mass	$M = 0.2612417 \text{ Kg mol}^{-1}$
Reduced volume	V [#] = V/σ ³ = 373.248
Reduced density	$\rho^* = N/V^* = 0.289352$
Potential truncation radius	$r_c = 3.6\sigma \equiv half a box length$
Timestep	$\Delta t = 0.002$ ps
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In all this system was aged for ~100 ps from an initial face centred cubic configuration before ensemble averages were accumulated.

Results and Discussion

Altogether four simulations are briefly reported here. Firstly a normal equilibrium constant energy (α =0, $\dot{\gamma}$ =0) simulation was performed at a temperature of ~300 K. This was then compared with a constant 'temperature' simulation ($\dot{\gamma}$ =0) of the same duration as the first and starting from the same initial configuration with a temperature fixed at the mean of that obtained at constant energy. Two other simulations are also reported at shear rates of 10^{11} s⁻¹ and $2*10^{11}$ s⁻¹. A summary of some of the results obtained are given in tables 1 and 2.

With the timestep used of 2 fs the integration of the equations of

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motion in all cases is quite stable with no perceptible drift in either the total energy at constant energy or the temperature at constant temperature. To the significant figures quoted in table 1 there is no fluctuation in either of these quantities but the actual errors were estimated to be $-9*10^{-4}$ % and $-3*10^{-4}$ % for the total energy and the temperature respectively. The larger fluctuations in the total energy is attributed to the errors caused by truncating the potential.

From table 1 it can be seen that at equilibrium ($\dot{y}=0$) the mean value of the potential energy and the pressure are the same , within the errors, in both simulations. This was confirmed by the coincidence of the site-site radial distribution function , not shown here. In figs. 1 and 2 the auto-correlation functions for the COM velocity and the angular velocity are given and they can be seen to agree reasonably well out to ~1 ps beyond which the statistics become increasingly poor.

For the shear calculations the added perturbation presented no problems as the method maintained the same degree of constancy in the kinetic energy as at equilibrium. From table 2 it can be seen that there is good agreement between the viscosity evaluated from the stress and from α .

Conclusions

It has been demonstrated that a simple alteration to the rotational equations of motion allows the isokinetic Sllod method to be used for molecular systems where quaternion algorithms are employed. At equilibrium there is no indication that the isokinetic method greatly affects the rotational motion. Under shear the agreement between the values obtained for the viscosity from the stress and from α confirm the consistency of eqn. (7) with respect to eqn. (17).

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Apology In a previous related article [8] I credited David Heyes with the derivation of eqn. (17). What I omitted to say was that he had in turn the been shown the derivation by one D.J.Evans whilst on his recent trip to Australia, Sorry Denis, and the second and the second statement of the statement of the second statement of the second statement of References D.J.Evans, Mol.Phys. <u>37</u> (1979), 1745. [1]D.Brown and J.H.R.Clarke, Chem. Phys. Letts. <u>98</u> (1983), 579. [2]D.Brown, Ph.d. Thesis, (1985). [3]M.P.Allen and D.Kivelson, Mol.Phys. <u>44</u> (1981), 945. [4]A.J.C.Ladd, preprint. [5] D.J.Evans and G.P.Morriss, Comp.Phys.Rep. 1 (1984), 297. [6] D.Fincham, CCP5 Newsletter 17 (1985), 43. States and states and states and [7] D.Brown, CCP5 Newsletter 16 (1985), 70. " Standard States and States Activ [8]

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<u>TABLE 1</u>. The mean total energy (U), total potential energy (Φ) , temperature (T), translational temperature (T_t), rotational temperature (T_r) and pressure (P) from simulations of the rigid triatomic fluid at equilibrium and under steady state shear. The errors quoted are the standard errors determined in the fashion described in a very useful newsletter article by Fincham [7]. The length of the run is that time over which averages have been calculated, the figures in parentheses give the total time of the simulation.

У /10 ¹⁰ s ⁻¹	U. /Jmol ⁻¹	Φ	T /K	T _t . ∕K.	T _r /K	P: /bar	Length of run /ps
		· · · · · · · · · · · · · · · · · · ·			· ·		· · · · · · · · · · · · · · · · · · ·
0	-32680	-40280	304.55	304.79	304.30	360	30
	±0	±30	±1.35	±2.78	±2.09	±30	(30)
0	~32640	-40240	304.55	304.04	305.05	380	30
	±50	±50	±0;00	±2.11	±2.11	±40	(30)
						sa a shi	n. Arter
	** ** ** ** **						-
10	-32350	-39840	300.00	298.40	301.61	530	36
	±50	±50	±0.00	±1.63	±1.63	±30	(45)
20	-32740	-39230	300.00	304.55	295.45	860	27
	±70	±70	±0.00	±2.33	±2.33	±40	(33)

(1,1,1)

<u>TABLE 2</u>. The mean symmetrised XZ component of the stress tensor (σ_{XZ}^S) , normal pressure components (P_{XX}, P_{YY}, P_{ZZ}) , value of the α parameter used in the Sllod equations, viscosity determined from the stress (η) and from α (η_{α}) for the same steady state shear simulations referred to in table 1.

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Ý	$\sigma_{\rm XZ}^{\rm S}$	P _{xx}	Pyy	P _{ZZ}	α	n	nα
/10 ¹⁰ s ⁻¹	/bar	/bar	/bar	/bar	/10 ¹⁰ s ⁻¹	/mPa's	/mPa s
10	820 ±27	380 ±60	560 ±40	650 ±40	6.94 ±1.25	0.820 ±0.027	0.829 ±0.149
20	1344 ±39	720 ±60	790 ±70	1080 ±60	22.65 ±1.38	0.672 ±0.020	0.676 ±0.041
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Legends to Figures

In both figures the solid line (----) indicates results obtained at constant total energy and the broken line (---) indicates results obtained at constant 'temperature'.

- Fig.l The normalised COM velocity auto-correlation function, $\hat{C}_{\mathbf{v}}(t)$ vs. time.
- Fig.2 The normalised angular velocity auto-correlation function, $\hat{C}_{\mathbf{r}}(t)$ vs. time.



FCC → BCC → CLOSE-PACKED STRUCTURE PHASE TRANSFORMATION IN A LOW TEMPERATURE LENNARD-JONES SOLID

John R. Ray

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Recently we have studied a structural phase transformation using the isothermal-isotension ensemble or (TtN) ensemble form of molecular dynamics. This version of molecular dynamics combines the Parrinello-Rahman theory with Nosé's theory and allows one to perform molecular dynamics calculations at constant temperature and tension (stress). The phase transformation is produced by applying uniaxial compression to an FCC crystal along, say, the [100] direction until the crystal becomes unstable; the crystal then transforms to a more stable crystal structure. Figure (1) shows the mean square displacement of the crystal during such a molecular dynamics calculation. To the left of OAt in Figure (1) the system is a zero pressure FCC (Lennard-Jones) solid at a reduced temperature and density of 0.15 and 1.05 respectively. To the right of 7000At in Figure (1) the system is a zero pressure solid at the same temperature and density but with a different structure; in particular the system has transformed into a polytypic close-packed structure. The phase transformation may be seen to occur

at around time step $3500\Delta t$ in Figure (1). The stress applied to the system at this time is approximately 125MPa for argon. The average rate of increase of stress over the period between $0\Delta t$ and $3500\Delta t$ is 3.6 x 10^9 GPa/sec for argon. Although this is a very large rate of increase of stress the simulation remains stable.

In order to better understand this transformation we made low temperature quenches of the particle positions starting from various points along the trajectory around time step 35004t. Figure (2) shows the pair correlation function and coordination number constructed by quenching the configuration of the system at time step 3659At. This figure shows clearly that the system at this particular instant is in a nearly perfect BCC structure. Also the molecular dynamics cell, which contains 500 particles, is very close to a right angle parallelopiped at this instant; the sides of the parallelopiped are in the ratio 1:1: $\frac{1}{\sqrt{2}}$ which also implies a BCC structure. Therefore, the transformation is initiated when we force, by compressive loading, the crystal into a BCC structure, which is unstable for the Lennard-Jones potential. The system transforms away from this unstable structure into a close-packed polytypic structure. . The precise final configuration that is obtained is a complicated problem since it involves the motion of the system away from a point of unstable equilibrium. We are still studying the details of this problem.

Here the main point we wish to make is the very clear signature of the unstable BCC phase shown in Fig. (2).

ACKNOWLEDGEMENT

I thank the Research Corporation for a research grant in support of this work.

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Figure 1. The mean square displacement as a function of time during the compressive loading of an FCC crystal. The phase transformation occurs around time 3500At.



Figure 2. The pair correlation function and coordination number divided by ten at time step $3659\Delta t$ into the simulation as determined by a low temperature quench using the configuration at time step $3659\Delta t$ as initial conditions. The arrows show the coordination numbers for the filled shells at the values of R pointed to by the arrows. The structure is BCC.

COMMENT ON: "ERROR IN CCP5 PROGRAMS....." BY D.J. TILDESLEY AND M.P. ALLEN.

D. J. Evans.

1

CCP5 owes thanks to Tildesley and Allen for pointing out the unfortunate error in the library programs MDTETRA and MDPOLY. However upon reading their article I felt compelled to point out that I had no role in the development of those programs. Indeed, I have never even seen a listing of them. This is not meant as a criticism of Tildesley and Allen. They were probably unaware of the history of those programs. They may have assumed that since I developed the quaternion algorithm that I had been involved in the development of the library programs. This was not the case. It may be that a version of the original program developed by Murad and myself for spherical top molecules was subsequently used as a basis for MDTETRA and MDPOLY. However I had no hand in this process.

As far as I know there are no errors in either of my papers cited by Tildesley and Allen. Taken together these papers provide essentially complete information on how to write programs for simulations of rigid bodies of arbitrary symmetry. Furthermore I know of no errors in any of my applications of the quaternionic formulation of rigid body dynamics in either MD simulations or lattice calculations. I am happy to supply interested parties with copies of my quaternion MD programs. Although they are correct

potential users may find the total absence of comment cards more than a trifle annoying.

2

My personal view is that libraries of MD programs are dangerous. This danger is highlighted by the length of time it took before these straightforward errors were discovered. MD programs are simple both structurally and conceptually. Writing such a program should only take a couple of weeks and it serves the excellent purpose of educating the user in MD and statistical mechanics.

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In order to improve the "quality control" aspect of bur work, people should compare simulations of standard systems at standard state points. Many workers feel this an unnecessary waste of computer time but I am sure that the users of MDTETRA and MDPOLY, who have now published incorrect results, are wishing that they could have cross-checked their programs against standard systems. Perhaps CCP5 should report some results in this newsletter which could be used as a standard for MD on assymetric top molecules.

Much of my recent work has been in NEMD. Workers in this field have used triple point Lennard-Jonesium as a standard. New algorithms are always tested on this system. It is important that these tests should be performed on precisely the same system at precisely the same state point. All too often we see "near" comparisons at almost, but not quite the same state point. The reader is always left with the question, "why didn't they do it at T=0.722 instead of T=0.85" ?

Another technique we employ is to compare the results of a number of different algorithms in attempts to calculate a given property. We have now compared three different methods for calculating the self diffusion coefficient: Green-Kubo, Gaussian NEMD in the Thevenin ensemble and Gaussian NEMD in the Norton ensemble (D.J. Evans and G.P. Morriss, Phys. Rev. <u>A31</u>,3817(1985)). In calculations of vortex viscosity (Phys. Rev. <u>A25</u>,1771(1980)) Hanley and I reported results obtained using different algorithms (NEMD and GK) because no previous standard existed. These computer experiments are doubly satisfying because they test our understanding of statistical mechanics as well as our ability to code in FORTRAN.

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Further comments by D.J. Tildesley and M.P. Allen.

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In our article, we did not suggest that any equation or statement in either of the two papers sited was incorrect or incomplete. We did not assume or imply that Denis Evans played any part in developing either of the two library programs. We support the view that properly tested simulation results on specific fluids constitute an essential benchmark for new programs.

SELF-CONSISTENT CALCULATION OF LATTICE RELAXATION AND ELECTRONIC STRUCTURE OF DEFECTS.

1

J.M. Vail, J.H. Harding and A.H. Harker

For many years it has been possible to make very accurate calculations either of the electronic structure or of the lattice relaxation for a defect in a crystalline material. The techniques used for the two types of calculation are quite different: our aim in this work has been to develop a satisfactory marriage between the them.

Electronic structure calculations tend to use quantum mechanical methods. For simple defects it is often possible to use a one-electron theory in which the effects of the ions surrounding the defect are replaced by model potentials. For more complicated defects the 'molecular cluster' scheme is often used, in which a region containing several atoms around the defect is treated as though it were a large molecule, using standard Hartree-Fock methods.

Lattice relaxation is frequently calculated using pair potential models. Here the form of the potential is chosen with quantum mechanical considerations in mind - for example the Born-Mayer form - but the parameters are fitted empirically.

In our approach we write the total energy of a defective crystal in terms of the coordinates of the atoms in a molecular cluster, <u>C</u>, the variational parameters of the electronic structure of the cluster, <u>A</u>, and the coordinates of the rest of the crystal, <u>R</u>:

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. 1

$E(\underline{C},\underline{A},\underline{R}) = E_{\underline{C}}(\underline{C},\underline{A}) + V(\underline{C},\underline{A},\underline{R}) + E_{\underline{L}}(\underline{C},\underline{R})$

Here the terms represent the total energy of their cluster are the second seco

Our self-consistent procedure hinges on simplifying the interaction V. When calculating the lattice coordinates \underline{R} the cluster is replaced by a set of point charges which has the same multipole moments as the quantum mechanical charge distribution. The resulting positions of the ions of the surrounding lattice define a potential which acts on the cluster, and is incorporated in the quantum mechanical calculation. We can then use a slight modification of the ATMOL Hartree-Fock programs (1) to calculate the parameters \underline{A} . The optimization of the lattice coordinates \underline{R} is done by the HADES program (2), leaving only the cluster coordinates \underline{C} to be optimized by hand to find the minimum total energy E.

We have applied this method to the F^+ centre in magnesium oxide, which has an optical absorption energy of 4.96eV. In a one-electron approximation, with only the single electron of the centre treated quantum mechanically, this energy is calculated to be 5.96eV if lattice distortion is ignored, 4.94eV with self-consistent lattice distortion. This shows the accuracy of the method.

Further developments will reduce the amount of hand calculation required, and so make the procedure feasible for more complicated defects. It is also intended to incorporate pseudopotential methods for more distant ions, and to make better use of symmetry in the calculation.

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CERFACS: A new European computer center

During the last 1-2 years effort have been performed in order to create a common "super computer center" in Toulouse, France. The center is named CERFACS (<u>Centre European de</u> Recherche et de Formation Avanceé en Calcul Scientifique).

The basic idea is that there is a need in Europe for a common center where the new generation of computers can be presented and new ideas (hardware and software) developed in cooperation with the European high technology industries. It is by no means a <u>computer</u> center, emphazis are placed on development, and thus it is no alternative to the national centre. Another basic idea is that the development is best ensured by that scientists perform basic research, but in open teams, where also people from industri as well as scientists with another background can join.

The present status is shortly this: It is likely that the center will be established as a part of the Eureca Program. A European supporting comunity has met and, among other subjects for consideration we have chosen particle pushing codes as one of 4-5 starting projects on the center. The projects should be initiated already in 1986.

In a short notice in Nature (316, 5, (1985)), the center is commented, but not much has appeared about the plans. An European supporting committee was established in 1983-84 and have met twice. If the plans are followed, however, the center could soon be a reality and of great interest for the CCP5 members.

Søren Toxværd

ADDENDUM TO THE CCP5 LITERATURE SURVEY 1985 (CNTD.)

Studies of Liquid Water by Computer Simulations III. Dynamical Properties of a 2-D Model.

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