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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Contents

Editorial.

It must be some sort of achievement that the CCP5 Newsletter has reached 21 issues! When the idea of producing a newletter was first suggested to the editor five years ago he though that the pool of would-be contributors would dry up in a short while and thereafter the Newsletter would become sporadic and meagre. Happily this worry seems not to have materialised and it is good to be able to report that it is still marching on. This is due in no small part to the helpfulness of the participants in CCP5, who have been willing to contribute articles, sometimes at very short notice. Also, it has been one of the more satisfying aspects of producing the Newsletter that our overseas colleagues, presumably recognising its usefulness, have been prepared to submit interesting contributions without having been approached beforehand. To them and our home-grown contributors we extend our thanks.

In the last issue it was announced that discussions were in hand to decide the fate of the Cray XMP/48 that the Forty Committee had proposed as a research tool for scientific computing in the U.K.. A decision on this has now been announced. The machine will be housed at the ATLAS Centre in the Rutherford and Appleton Laboratory. This leaves us at Daresbury somewhat disappointed; having been a centre for the Cray 1S in the early 80's, we had hoped to capture the new machine on the strength of our existing expertise. However, the superior capabilities of the RAL mainframes to act as the front-end could not be gainsaid. Nevertheless, it cannot be denied that the availability of the Cray XMP/48 for scientific computing will have a marked effect on the U.K. simulation community and everyone involved with CCP5 must rejoice at the news. We have further news on this subject within.

Our thanks once again go to the contributors to this month's Newsletter.

Contributors:

A. Brass	Department of Physics, The King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, Scotland.
D.M. Heyes	Department of Chemistry, Royal Holloway and Bedford New College, Egham, Surrey TW20 0EX.
M. Leslie W. Smith	Theory and Computational Science Division, S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD.
J.G. Powles	The Physics Laboratory, The University of Kent, Canterbury CT2 7NR, Kent, England.

General News.

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

Enquiries regarding the conference should be addressed to Dr. J. Altmann, ISOC 87 Secretariat, Room 209, University of London Computer Centre, 20 Guildford Street, London WC1N 1DZ. (Telex 8953011).

b) We have received a notification of a working seminar on the subject of "Brownian Motion and Stochastic Mechanics", which has been planned for 7th-11th July 1986 at the Dublin Institute of Advanced Studies. Some of those attending will be Carlen, Elworthy, Lyons, Truman, Van Den Berg and Yor. Those interested in attending are asked to write to the organisers J.T. Lewis and P. McGill at the School of Theoretical Physics, Dublin Institute for Advanced Studies, 10 Burlington Road, Dublin 4, Ireland.

c) U.K. CCP5 participants are reminded that at Daresbury Laboratory the S.E.R.C. has available an FPS 164 attached processor, currently with 3 MAX (matrix accelerator) boards, which is available for grant supported computing within the Science Board Community. In the first year of its operation U.K. research groups are invited to apply informally to the Director of Daresbury Laboratory (Professor L.L. Green) for time on the FPS for benchmarking purposes. If the FPS proves viable for a given project, a formal application (using the familiar forms RG2 and AL54) may be made. Advice on using the FPS at Daresbury may be obtained from the User Interface Group (in the person of Dr. D. Taylor) or from the CCP5 representative Dr. W. Smith. A document entitled 'Using the FPS Attached Processor at the Daresbury Laboratory' by Dr. M.F. Guest is available from the User Interface Group.

d) The Rutherford and Appleton Computer Centre is to be the home of the Cray XMP/48 that was proposed by the Joint Working Party of the Advisory Board for Research Councils (The Forty Committee). The Cray XMP/48 is a 4-processor computer with 8Mwords of memory. When each processor is being driven, the machine is theoretically capable of a 1 GFlop rate. In addition to this impressive performance, the RAL machine will have a 32 Mword solid state

storage device and in the region of 14 Gbytes of disc storage. When the machine becomes operational it will be front ended by the RAL IBM 3081. The machine has been ordered but no delivery date is yet available. Speculations suggest that about six months will be required for delivery and a few additional weeks of installation and acceptance tests before the first few users will have access. Authorisation to use the Cray will be organised through a peer review system similar to those already used by SERC.

To prepare potential users of the Cray RAL are organising an Open Meeting on Tuesday 8 July in the Great Hall at Imperial College London. Information on the hardware available and the peer review procedure will be discussed. Questions raised by the audience will also be dealt with. About 600 people will be permitted to attend. Readers should contact Mrs. Jacky Hutchinson at RAL (Tel: 0235-21900x6193) or, if she is unobtainable, Mrs Mary Shepherd (Tel: 0235-445635), if possible before June 23.

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

e) The University of London Computing Centre is another beneficiary of the recommendations of the Fort Committee. At a meeting of the Advisory Board for the Research Councils at which the purchase of the Cray XMP/48 was decided, it was also agreed to install a Cray 1S at ULCC with a 2 Mword memory. This machine will be additional to the Cray 1S already operated by ULCC and will be delivered during the summer.

Meanwhile, on the existing Cray 1s the operating system is to be upgraded to COS level 1.14 BF2A. A similar upgrade of the compiler to CFT 1.14 BF4 is scheduled. Users should note that binary (load) modules compiled with the previous compiler 1.13 cannot be combined with newly compiled codes due to a change in the calling sequence. When the COS 1.14 is installed, users must recompile any modules compiled under CFT 1.13.

On the AMDAHL 470/V8 ULCC there is a new version of the MVS operating system, MVS SP1.3 L8406B, installed in late March. The promised the Disc Space Scheduler also became operational.

f) 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.

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

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

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

List of Programs in the CCP5 Program Library.

MDATOM by S. M. Thompson.

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

HMDIAT by S. M. Thompson.

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

MDLIN by S. M. Thompson.

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

MDLINQ by S. M. Thompson.

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

MDTETRA by S. M. Thompson.

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

MDPOLY by S. M. Thompson.

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

ADMIXT by W. Smith.

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

MDMIXT by W. Smith.

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

MDMULP by W. Smith.

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

MDMPOL by W. Smith & D. Fincham.

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

DENCOR by W. Smith.

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

CURDEN by W. Smith.

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

HLJ1 by D. M. Heyes.

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

HLJ2 by D. M. Heyes.

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

HLJ3 by D. M. Heyes.

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

HLJ4 by D. M. Heyes.

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

displacements and radial distribution function.

HLJ5 by D. M. Heyes.

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

HLJ6 by D. M. Heyes.

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

MCRPM by D. M. Heyes.

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

SURF by D. M. Heyes.

M.D. simulation of model 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.

MDDIATQ by D. Fincham.

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

MDIONS by D. Fincham & N. Anastasiou.

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

MDMANY by D. Fincham & W. Smith.

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

CARLOS by B. Jonsson & S. Romano.

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

MCN by N. Corbin.

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

SCN by N. Corbin.

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

SMF by N. Corbin.

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

STATIC SIMULATION CODES

CASCADE by M. Leslie and W. Smith.

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

THBREL

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

THBFIT

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

SYMLAT

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

THBPHON

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

THE GLASS TRANSITION

M. Leslie

Meeting held at Wadham College, Oxford.

April 10th-11th 1986

The meeting was well attended by overseas visitors, who almost outnumbered the U.K. participants. A broad spectrum of interests was covered; theoretical, MD simulation and experimental aspects.

Dr. A. Angell set the scene with an introductory talk on Thermodynamic and Dynamical properties at the glass transition. He described some recent Brillouin scattering work on glasses. (C. A. Angell and L. M. Torell, J. Chem. Phys. 78 937 1983). In the liquid. two narrow longitudinal peaks are seen. As the liquid is cooled, the peaks broaden but narrow again as transverse peaks appear. The transition to the glass is gradual over a wide temperature range. rather than the usual sudden transition observed by calorimetry. The reason for this is the time scale over which the experiments are performed, the Brillouin scattering being the response to a very rapidly alternating field. In this respect, the Brillouin scattering

experiment resembles an M.D. simulation, where very rapid quench rates are used, and again a gradual transition to the glass is observed. Dr. Angell then went on to distinguish two classes of glass-forming material which he terms strong and fragile. The distinction may be seen from an Arrhenius plot of the logarithm of the relaxation time or viscosity against the inverse temperature. For fragile liquids at high T, the slope is small corresponding to a low activation energy E_A in the high fluidity region. Approaching the glass transition the slope and activation energy increase. Strong liquids have the same slope over all T range. Materials of this type would be tetrahedral network forming such as BeF_2, SiO_2

Two theoretical contributions then followed from T. Geszti (Budapest) and A. Sjolander (Gotenburg). Both dealt with aspects of LBGS theory. (Leutheusser. Z. Phys. B. 55 235, Bengtzelius, Gotze, Sjolander J. Phys. C. 17. 5915). Dr. Geszti discussed the role of the shear viscosity in the glass transition feedback. Dr. Sjolander gave some of the properties a successful theory would need to predict. These were

(1) Discontinuous changes in the compressibility, thermal expansion and heat capacity.

(2) Non-Arrhenius T dependence of viscosity and self diffusion.

(3) Two different slow relaxation processes α and β (α remains on the glass side).

(4) Strong non-exponential decay in relaxation time, proportional to $\exp(-t/\tau)^\beta$ with $0<\beta<1$.

Dr. Sjolander then went on to emphasise that the static structure factor enter enters into LBGS theory as an adjustable

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parameter, and that the integral under the first peak appeared to be most important. He then described dynamical predictions of LBGS theory.

Dr. Pusey (Malvern) reported some interesting experimental observations on a real hard sphere system consisting of uniform spherical PMMA particles suspended in a liquid. He described the behavoir of initially homogeneous samples of varying concentration. The most dilute failed to crystallise after 24 hours. In order of increasing concentration the other samples showed crystals which segregated under gravity; crystals dispersed in the liquid; heterogeneous nucleation at the surface and meniscus; no crystallization. The most concentrated sample eventually crystallised at the meniscus and proceeded down into the liquid very slowly. (the samples have been left for 1 year.) The concentrated samples form a glassy like phase. This work has been published in Nature vol 27 March 1986.

M. Baus (Brussels) then described computation of the free energy of a hard sphere solid and liquid, starting from an exact expression for the free energy difference. He emphasised the problem of approximating the direct correlation function of the solid and discussed the method used to do this. This work has been recently published. (M. Baus and J. L. Colot J. Phys. C. 18 L365 (1985), Mol. Phys. 55 653 (1985), Mol. Phys. 56 807 (1985), Mol. Phys. 57 809 (1985).

R. Cotterill (Lyngby, Denmark) then discussed entropy and the glass transition with reference to the shape of the energy

hypersurface of the material. This was carried out by computing the dynamical matrix from a M.D. simulation and investigating the shape of the surface in the orthogonal directions given by the eigenvectors of the dynamical matrix. For a solid and a glass these cross sections through the E hypersurface all have U shaped sections corresponding to real modes. For liquids, some W shaped modes appear, more appear as T increases. (Note that W shaped modes do not imply jumps because it is possible to move in phase space from one side to the other.)

Dr. D. Chokappa (Cornell) then gave a talk on M.D. simulation aspects of the glass transition. He has used both constant T (damped force method) and constant P (Andersens method) simulations. The time step was $8.6 * 10^{-15}$ s, 2000 steps were used to equilibrate followed by 4000 steps to calculate properties. Melting runs showed a constant apparent melting T as system size increased except for the largest system. Cooling runs showed formation of a glass for sufficiently fast quench rates as shown by a plot of density against T. Small systems tended to crystallise more easily than large.

L. Woodcock (Bradford) then gave a talk on rheological aspects of the glass transition. He emphasised that all materials exhibit Non-Newtonian behavoir at sufficiently high shear rate and that this depends on the Weissenberg number N_W which equals the products of the structural relaxation time and the velocity gradient. The viscosity plotted as a function of log N_W shows a linear Newtonian region for low N_W, followed by a shear thinning region of decreasing viscosity, followed by a

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shear thickening region when the viscosity increases, followed by a second Newtonian region of constant viscosity. He then described modelling of a soft sphere system suspended in a solvent, and the three possible choices of dynamics. (Newtonian, Stokesian or Brownian). For concentrated suspensions it is just as plausible to use Newtonian rather than a continuum approach. The phase behavoir found in these systems shows three phases as the shear rate increases. Increasing the shear rate across the liquid crystal phase boundary causes an ordering transition ordered in 2 of 3 dimensions only. At higher still shear rates a disordering transition occurs with a glass-like phase frozen in 2 of 3 dimensions.

J.P. Hansen (Paris) reported on some recently published work (J. Phys. C. 18 L371 1985). This investigated glass formation in an M.D. simulation of a binary mixture of soft spheres. The soft sphere potential was

$$v_{\alpha\beta}(r) = \varepsilon(\sigma_{\alpha\beta}/r)^{12}$$

$$\sigma_{\alpha\beta} = 1/2(\sigma_\alpha + \sigma_\beta)$$

The diameter ratio $\sigma_2/\sigma_1 = 1.4$ and mass ratios m_2/m_1 of 2 and 4 were simulated. The integration algorithm used was a very accurate one due to B. Bernu (Physica 122A 129 (1983)). Among other properties the partial pair distribution functions were derived from the simulations. For sufficiently strong coupling the familiar splitting of the second peak was observed, characteristic of a glassy material. The partial structure

factor had an interesting feature. The oscillations beyond the second peak are strongly damped, but then reappear at large wavenumber.

Dr. J. Clarke gave an appraisal of the Grest-Cohen theory from the simulation standpoint. In this the atoms are assumed to occupy a cell of volume v, with p atoms in liquid like cells with $v > v_c$ and 1-p atoms in solid-like cells with $v < v_c$ The cell volumes are assumed to have a certain distribution.

A. Geiger (Aachen) presented an M.D. simulation of water under negative pressure. The structures thus obtained resemble the clathrate compounds with large cavities.

S. Yip (M.I.T) discussed other routes to vitrification, in particular a simulation analogue of irradiation. This involved a random introduction of interstitials at a constant rate (1 every 30 time steps) followed by annealing. At low interstitial concentrations the simulated material annealed back to a crystal, at intermediate concentrations a crystal was again formed but with a grain boundary. Only at the highest concentration did a glassy-like phase appear. The pair distribution function in this case showed the characteristic splitting second peak.

HIGH TEMPERATURE PROPERTIES OF SOLIDS

M. Leslie

Workshop held at Coseners house, Abingdon.

20-21 Feb 1986

The workshop began with a talk by Dr. J. H. Harding (Harwell) on the static lattice calculation of defect free energies. He focused on three aspects of the calculation

(1) The importance of good interatomic potentials.

(2) Methods of calculating defect entropies.

(3) Prediction of local modes.

The criteria used to decide the merits of an interatomic potential were discussed. Potentials used have all been fully ionic pair potentials. They have been derived either empirically from a fit to the bulk lattice properties, or by using quantum mechanical methods. The calculation of high temperature properties provides a more stringent test of the quality of a potential. For example, the free energy may be calculated as a function of volume to derive the thermal expansion. For CaF_2 , KCl the agreement was good. However for UO_2 with the empirical potential the agreement was poor due to X point phonons going imaginary as the lattice expands. The use of splined potentials

was also discussed. Since properties were being calculated which depend on volume derivatives it is important to have splined functions continuous in 3 derivatives instead of the usual 2.

Turning to methods of calculation, Dr. Harding outlined three alternatives to calculate the phonon contribution to the defect entropy. These were the Green's function method, which need a very large inner region, supercell methods and large crystallite methods. The large crystallite method needs a boundary correction to ensure good convergence with increasing region size. The calculated entropy is then linear with N^{-1} and can be extrapolated to infinity. In general for 100-200 ions, the calculated entropy is within 1/10k of the extrapolated value.

The comparison of calculated local modes with experiment is a very good method of testing the quality of a potential and the accuracy of the phonon mode calculation. Dr. Harding presented results of such a comparison recently carried out with Dr. M. J. Sangster (Reading) given in the table below.

Defect	Calculated	Experimental
H^- substitutional in KI	12.1	11.5
H^- interstitial in KI	21.5	21.6
Cl^- substitutional in KI	2.34	2.31
H^- interstitial in KBr	2.95	2.96
Br^- substitutional in KI	2.86	2.66

Dr. Harding then showed how h_p for a defect is thermodynamically approximated very well by u_v at 0^oK. Indeed,

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all of the static lattice calculations of defect energies rely
on this approximation since h_p is the experimentally measured
quantity. He then stressed that the same approximation does not
work for entropies. Indeed, for a Schottky defect in KCl s_v is
negative but s_p is positive. The biggest contribution to s_p is
the variation of u_v with V. Approximating h_p with u_v will not
necessarily work at a surface, indeed the whole question of the
thermodynamics of surface defects needs careful examination.

Dr. A. D. Murray (UCL) presented more details of the UO_2
potentials discussed by J. H. Harding. The earlier calculations
with an empirical UO_2 potential fitted to room temperature data
gave poor results. u_v of a Frenkel defect plotted as a function
of V was linear over a range of V but then rapidly dropped. s_v
was not even linear over the same V range. Further calculations
are in hand using a new potential which reproduces the lattice
expansion far better. Dr. Murray then presented some results of
the experimental and calculated elastic constants. In the
ensuing discussion the need was stressed to be careful making
comparisons of this type, since elastic constants may be
measured isothermally or adiabatically. The contribution of the
entropy to the elastic constants was also discussed.

Dr. Leslie (Daresbury) then presented some calculations of
defect entropies using a supercell method. Here the entropy of
the defect is calculated as the difference between a perfect
lattice and a supercell containing a defect. The superlattice is
allowed to relax around the defect at constant volume. The sum
of the phonon frequencies is carried out only over the zone

centre modes of the supercell. Results were presented for the
Schottky defect in KCl. The entropies extrapolated linearly as a
function of N^{-1}, but on different straight lines according to
the defect configuration. (sc, bcc or fcc). The extrapolation
goes back to the same point in each case, and also agrees with
the extrapolated value obtained by the large crystallite method.
The convergence with increasing system size was at least as
good. The extrapolated entropy is the same taking the sum of two
charged defects as for a superlattice with both types of defect
in. There was some discussion of the validity of this method for
charged defects.

D. Tildesley then reviewed the methods available for
calculating the free energy from a simulation. There was some
discussion as to there applicability to ionic solids, and it was
felt that simulation methods would be of use where anharmonicity
was felt to be important. The reader is referred to an earlier
CCP5 newsletter article by Frenkel and Ladd (March 1984).

Finally M. Gillan presented some simulation results of
calcium fluoride. These had been used to make a direct
comparison with experimental coherent inelastic neutron
scattering. The simulation showed that all jumps in CaF_2 were
between regular lattice sites, 80% were 100 hops and 20% were
110 hops. Motion of defects can be seen as a chain of hops. The
quasielastic scattering is essentially seeing the distortion
field about the defect.

REVIEW OF THE CCP5 WORKSHOP ON "TRANSPORT PROCESSES" HELD AT ROYAL HOLLOWAY AND BEDFORD NEW COLLEGE 25/26TH MARCH 1986.

D.M. Heyes

Another rewarding CCP5 workshop was held recently on "Transport Processes". This one differed from a previous workshop on the same topic, held also at this College in January 1985, in a number of respects. The main one being that it followed from and overlapped with a British Society of Rheology workshop on "Molecular Approaches to Rheology" (24/25th March). Many MD simulators have been working in rheology for years without even realising it! Anyone calculating viscosity by Green-Kubo or Non-Equilibrium Molecular Dynamics (NEMD), techniques can justifiably claim to be called a rheologist. Rheology, for the unaware, is the all-encompassing name given to the study of the flow and deformation of materials. It is very much an interdisciplinary subject, with people entering the field from a variety of backgrounds, from chemical engineering to theoretical physics, for example.

Traditionally theoretical treatments in this area have been the preserve of continuum mechanics approaches and the molecular theories (such as the Rouse and Doi-Edwards models) which are applicable to macromolecules. The purpose of the BSR workshop was to discuss the the NEMD technique in some depth, to introduce it to the rheology community and to discuss its potential, together with the other molecular theories. These spirited discussions certainly set the scene for the CCP5 meeting.

It was heartening to note the great interest there is in CCP5 from our European neighbours and we welcome future participation and collaboration in the areas of simulation between us. The meeting was especially rewarding for those interested in NEMD and shear flow!

First to speak was Gisele Marechal (University of Brussels) [a], who talked about the determination of the shear viscosity coefficient of fluid butane. The Green-Kubo and NEMD subtraction technique were applied to the same systems. These were 128 n-butane molecules constructed according to the model of J.-P. Ryckaert <1>. Both methods were described in detail. A number of interesting and freely given observations were made, which will save the NEMD community much wasted effort. The theme was continued with another revealing talk by Jean-Paul Ryckaert (University of Brussels) [b]. Kurt Kremer (University of Johannes Gutenberg - Universitat Mainz) [c] gave a lucid talk on the phase diagram and dynamics of a Yukawa fluid. Werner Loose (Technische Universitat Berlin) [d] described fascinating results on shear flow of gases, which certainly made an impact on the participants. Martin Dare-Edwards of Shell (Thornton Research Centre) [e] described results of NEMD shear flow of simple molecules (performed in collaboration with D. Brown and J.H.R. Clarke of U.M.I.S.T.) with various mass distributions, again coming to some important conclusions. D. Brown [f] described calculations

of plastic flow in model crystals using revolutionary techniques developed by him. M.J. Gillan [g] presented in detail some results of NEMD simulations of thermo-transport of hydrogen in metals, which proved to be very successful. D.M. Heyes [h] talked about NEMD calculations of shear in 2D soft discs (performed with D.J. Evans and G.P. Morriss of the Australian National University, Canberra, Australia), NEMD in 3D Lennard-Jones liquids at low and high shear rates, and shear flow in gases. The talks were interspersed with much informal discussion. Geoffrey Ansell (University of Leeds) [i] outlined details of the Brownian Dynamics technique for shared systems. All the participants made important contributions in the many discussion sessions held.

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PARTICIPANTS

Mr. G.C. Ansell [i],
Department of Food Science,
University of Leeds,
Leeds LS2 9JT, U.K.

Dr. M.P. Dare-Edwards [e],
Shell Research Limited,
Thornton Research Centre,
P.O. Box 1,
Chester CH1 3SH, U.K.

Dr. D. Brown [f],
Department of Chemistry,
U.M.I.S.T.,
Sackville Street,
P.O. Box 88,
Manchester M60 1QD, U.K.

Dr. M.J. Gillan [g],
Theoretical Physics Division,
AERE Harwell,
Didcot
Oxon OX11 ORA, U.K.

Dr. D.M. Heyes [h],
Department of Chemistry,
Royal Holloway & Bedford New
College,
University of London,
Egham,
Surrey TW20 0EX, U.K.

Mr. A. Hopkins,
School of Studies in Chemical
Engineering,
University of Bradford,
W. Yorkshire,
Bradford BD7 1DP, U.K.

Dr. K. Kremer [c],
Fachbereich Physik,
Insitut fur Physik,
Johannes Gutenberg-Universitat
Mainz,
Postfach 3980,
6500 Mainz 1,
West Germany.

Mr. W. Loose [d],
Fachbereich 4 Physik,
Institut fur Theoretische Physik,
Technische Universitat Berlin,
Sekr. PN 7 - 1,
Hardenbergstrasse 36,
D-1000 Berlin 12,
West Germany.

Dr. G. Marechal [a],
Faculte des Sciences,
Universite Libre de Bruxelles,
Campus de la Plaine (C.P. 223),
Boulevard du Triomphe,

Dr. M. Rex,
Iwan-N.-Stranski-Institut fur
Physikalische und Theoretische
Chemie der TU Berlin,
Sekretariat TEL 33,

B-1050 Bruxelles,
Belgium.

Professor K. Singer,
Department of Chemistry,
Royal Holloway & Bedford New
College,
University of London,
Egham,

Dr. J.-P. Ryckaert [b],
Faculte des Sciences,
Universite Libre de Bruxelles,
Campus de la Plaine (C.P. 223),
Boulevard du Triomphe,
B-1050 Bruxelles,
Belgium.

Ernst-Reuter-Platz 7,
D-1000 Berlin 10,
Germany.

Dr. L.F. Rull,
Facultad de Fisica,
Universidad de Sevilla,
Aptdo 1065,
41080 Sevilla,
Spain. Surrey TW20 0EX, U.K.

What Henri might have said to Nigel!
==

J.G. Powles

An explanation is given of the paradox recently posed by N. Corbin.

In a recent issue of this Newsletter Nigel Corbin (1985) discussed the accuracy of molecular dynamics trajectories. He studied a Lennard-Jones 12-6 liquid for N=108 using the leapfrog algorithm. He analysed the results for two different time steps, 5 fs and 2.5 fs and considered the correlation of the forces and the velocities, averaged over the particles, for the two trajectories. He showed that the difference in the trajectories was not due to the accuracy of the computer and appeared to conclude that these time steps (although the ones conventionally used) are too long to yield trajectories that are effectively identical for more than about 2 ps. His results for the correlation of the forces for the two trajectories are given in figure 1 (reproduced from figure 2 of Corbin 1985). The correlation is virtually perfect up to about 1.5 ps and then falls suddenly and precipitously. He does not give the correlation function for times longer than about 3.5 ps but presumably the behaviour is as illustrated in my figure 2.

I believe that these results would have been understood by Henri Poincaré in 1892! I believe that they are an example of the 'exponential' divergence of trajectories resulting from vanishingly small variations of the initial conditions.

Consider the simpler, but still moderately realistic, mechanical system which is a simple case of what is normally called Brownian motion as used in computer simulation (Turq et al. 1977).

The equation of motion is

$$dv/dt = -v/\tau_v + f(t),$$

where τ_v is the correlation time of the velocity (N.B. the usual velocity autocorrelation - not the correlations we are to be concerned with here), f(t) is proportional to the random force. The principal requirement on f(t) is that it should have a Gaussian probability distribution with zero correlation time. $< f^2 >$ then determines the temperature in equilibrium. Normally the values of f(t) are taken as constant for periods, Δt, and they change discontinuously. Δt is analogous to the time step in a conventional simulation. The correlation time of the force is $\Delta t/2$, which ---> 0 as Δt ---> 0. $f(n + \Delta t)$ is usually obtained using any convenient 'library' pseudo random-number generator. However all conventional generators - of course! - produce sets of random numbers where the sets are uncorrelated for different 'seeds'. We require here sets of random numbers which are initially

correlated to a quantitatively determined extent. I have not been able to find such a recipe in the literature (perhaps someone can give me a reference?) and I use the following procedure.

The iteration, or mapping,

$$u_{n+1} = (1/2) - 2 |u_n| \quad ,$$

gives a uniform distribution in $(-1/2, 1/2)$. The set of random numbers, u_n, depends on the seed, u_1, and u_1 may be chosen almost at will in $(-1/2, 1/2)$. It is prudent however to avoid pathological cases such as; 0, $\pm 1/2$, etc. Try a nice irrational number such as 0.5 ln(2). Adjacent pairs of sets of random numbers are generated with seeds, u_1 and $u_1 + \Delta u$. The uniform distribution in u can be transformed to a Gaussian by any convenient approximation for erf^{-1}. I used (Abramovitz and Stegun, para. 26.2.23),

$$f = \left\{ s - \frac{c_0 + c_1 s + c_2 s^2}{1 + d_1 s + d_2 s^2 + d_3 s^3} \right\} sgn(u) \quad ,$$

where $s = [ln(1/u^2)]^{1/2}$; for the c's and d's see the table.

This gives,

$$p(f) = (2\pi)^{-1/2} exp(-f^2 /2), \text{ i.e. } < f > = 0 \text{ \& } < f^2 > = 1.$$

We still have a corbinous problem because the equation of motion cannot be solved exactly to get the exact forces and velocities. However it is instructive to study the random forces, f.

Consider the correlation function, C_{ff}, of the f's for pairs of trajectories with seeds u_{1m} and $u_{1m} + \Delta u$ for a uniform distribution of the u_{1m} and a range of values of Δu. Δu is a quantitative measure of the 'contiguity' of the trajectories.

$$C_{ff}(\Delta u, n) = < f_1(n) f_2(n) >_m / [< f_1^2(n) >_m < f_2^2(n) >_m] \quad ,$$

where n is the time step index, i.e. $n = t / \Delta t$. Of course $< f^2(n) >_m \longrightarrow 1$, for $m \longrightarrow \infty$, any n. The average over m is the analogue of the average over particles.

A 'typical' result, for m = 20 and $\Delta u = 10^{-5}$ is given in figure 2. Note the striking resemblance to Corbin's result given in figure 1. In this case the correlation is almost perfect for thirteen steps and then falls in two or three steps to a value which fluctuates around zero for all longer times. This is also illustrated in the table.

We define the inter-trajectory force-correlation time, τ_{ff}, as the time when $C_{ff}(\Delta u,n) = 1/2$, e.g. for $\Delta u = 10^{-5}$, $\tau_{ff} = 14.4$. Similar results are obtained for values of Δu from 10^{-1} to 10^{-7}. The transition remains sharp and just moves to the left or right. These calculations were done one afternoon on a Commodore PET 8083, whose accuracy is claimed to be nine significant figures. For this problem round-off becomes a problem for $\Delta u \lesssim 10^{-7.5}$. For $\Delta u \gtrsim 10^{-1}$ the trajectories are uncorrelated at all times.

The values of the trajectory-pair correlation time, τ_{ff}, are plotted as a function of, $-\log_{10} \Delta u$, in figure 3. The almost linear plot obtained is presumably what is meant by the phrase, 'exponential divergence of trajectories as a function of the initial conditions'.

I suggest that the loss of correlation of trajectories observed by Corbin arises from the errors in the algorithm. These are presumably related to the size of the time step employed. These errors in the initial steps are equivalent to a small change in the initial conditions which eventually result in an 'exponential divergence' which causes the sudden loss of correlation. I agree with him that this extreme dependence of trajectories on the accuracy of the algorithm throws some doubt on the validity of time autocorrelation functions for very long times.

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Turq, P., Lantelme, F. and Friedman, H.F., 1977, J.Chem.Phys., V66, p3039.

Table

The correlation of 'random' forces for adjacent trajectories for $u = 10$.

Time Step	1 to 10	11	12	13	14	15	16	17
C_{55}	>0.9999	0.9987	0.9951	0.9768	0.9034	-0.1328	-0.3566	+0.3011

Erf^{-1} constants:

$c_0 = 2.515517$ $c_1 = 0.802853$ $c_2 = 0.010328$

$d_1 = 1.432788$ $d_2 = 0.189269$ $d_3 = 0.001308$
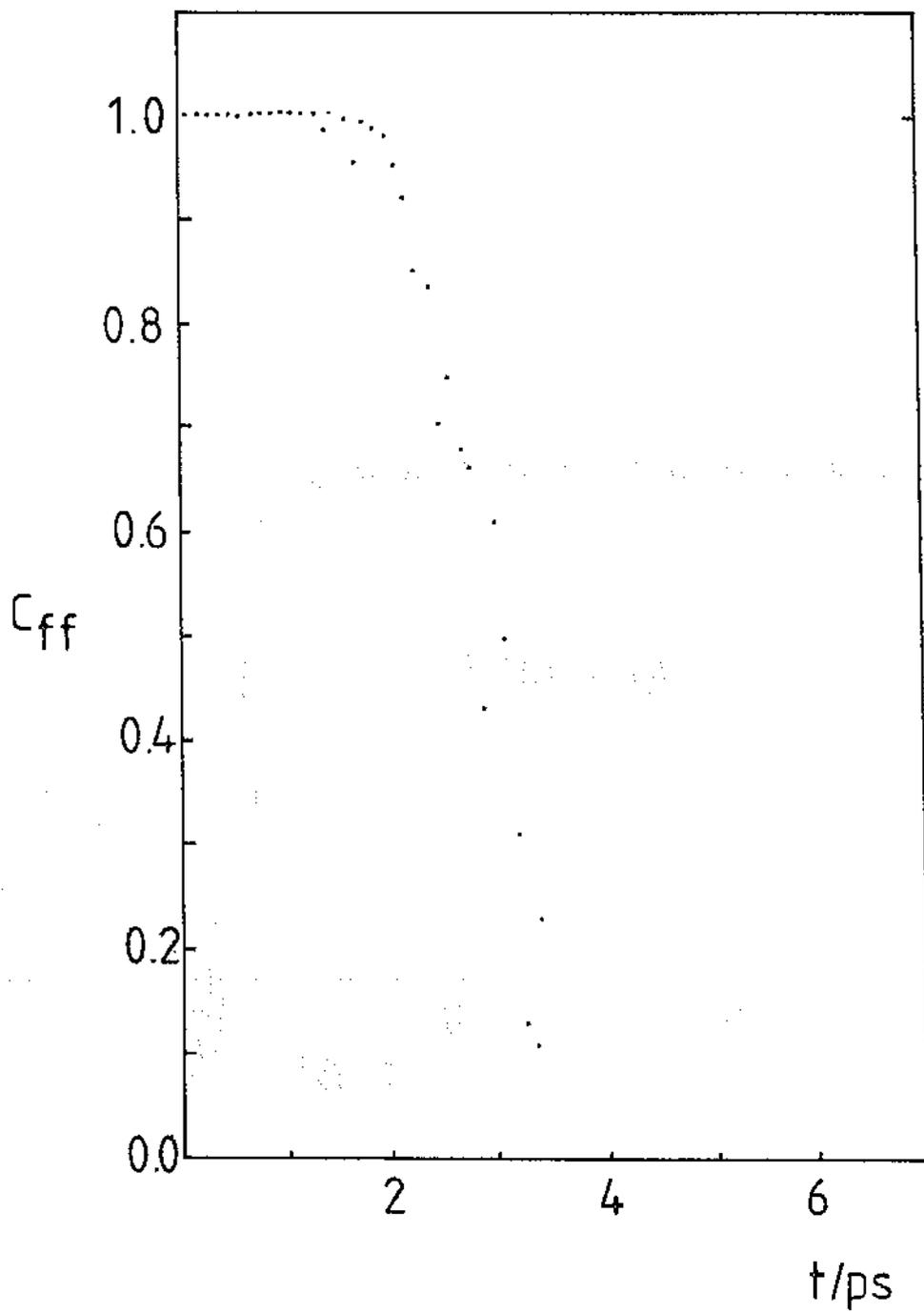
FIGURE 1
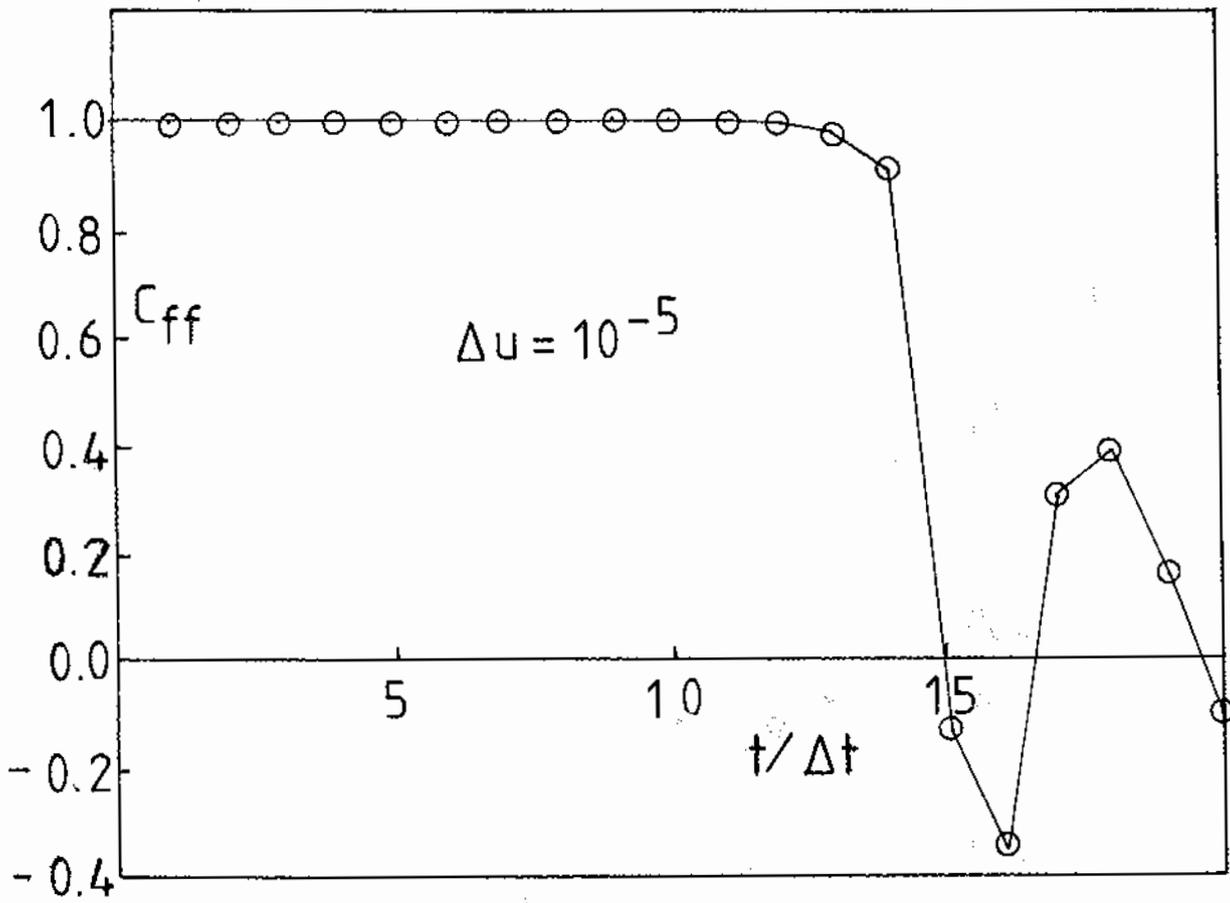
FIGURE 2
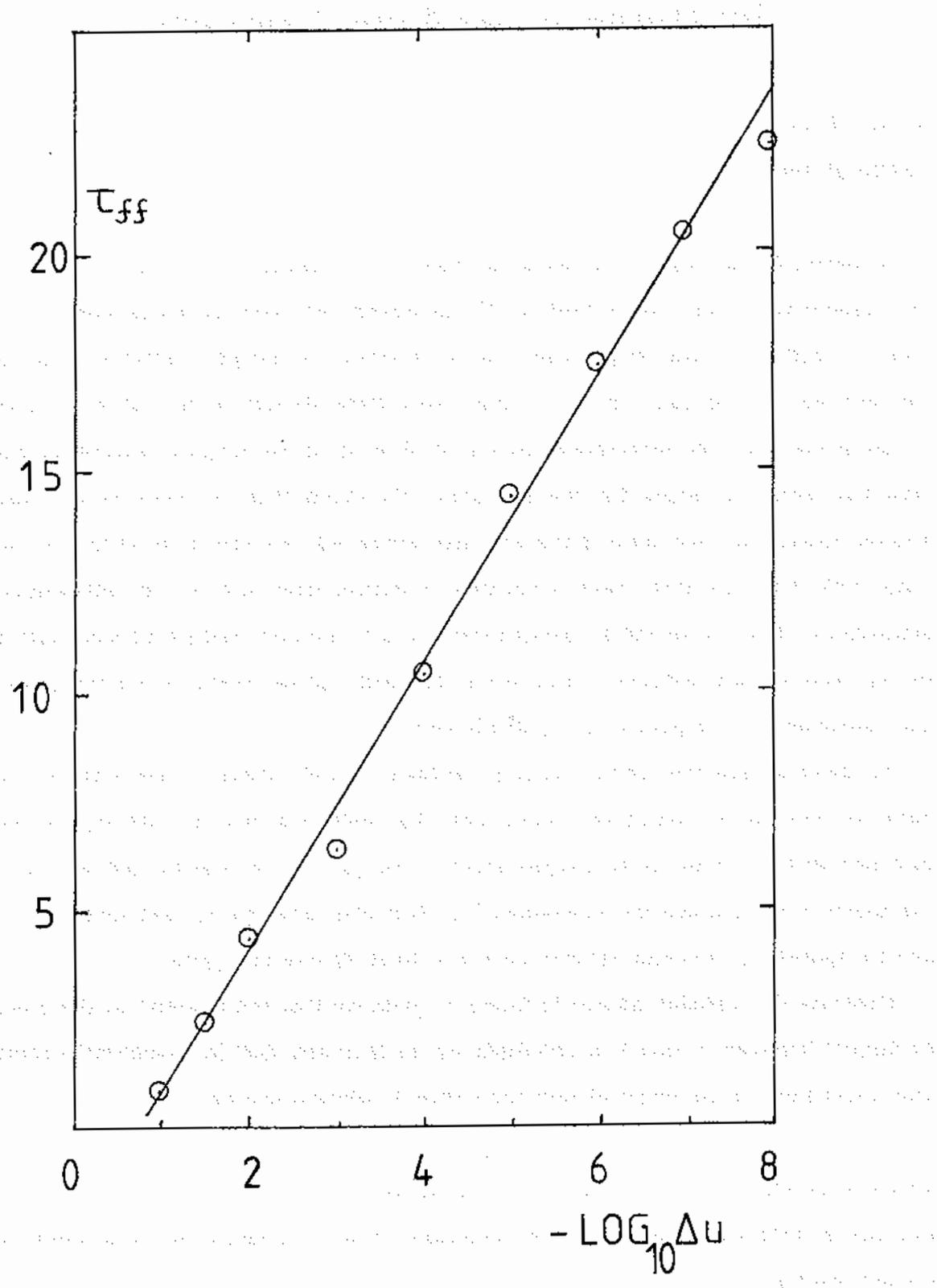
FIGURE 3

The Stability of Hard Sphere Trajectories

Andrew Brass

Edinburgh University

In recent CCP5 newsletters there has been much discussion on the accuracy of MD trajectories [1,2]. Nigel Corbin [1] calculated the velocity cross-correlation funtion (ccf) for two trajectories in a system of single particles with a Lennard-Jones potential. The two trajectories were started at the same point in phase space and then integrated forward in time using the leapfrog algorithm but with two different values for the timestep. He found that the velocity ccf was approximately unity for about 2.5ps and then dropp ed very rapidly to zero. In this note I will show that this effect is not due to inadequacies in either the integration algorithm or the size of the timestep used but is an intrinsic feature of any system of interacting 'hard' spheres. Trajectories in 'hard' sphere systems are inherently very unstable with respect to any perturbation.

To demonstrate this effect consider oxygen at NTP. Place an electron at the edge of the known universe. After only 56 collisions the uncertainty in the direction of the motion of an oxygen atom in the gas due to gravitational effect of the electron is as much as one radian [3]. A similar analysis to that given in [3] can be applied to calculate velocity ccfs in a 'hard' sphere simulation.

Consider the collision shown in figure 1. Assume that the position of the point of impact between 1 and 2 is uncertain by Δs (perhaps due to round-off errors). The uncertainty in the angle of reflection after 1 collision will be :-

$$\Delta \theta_1 = \Delta s/r$$

where r is the interaction radius of the atom. Molecule 1 will now travel on average a distance l before its next collision. The uncertainty in its position of impact will be :-

$$\Delta s_2 = l\Delta \theta_1 = l\Delta s/r$$

So the uncertainty in the angle of reflection will be :-

$$\Delta \theta_2 = (l/r)(\Delta s/r).$$

1

After n collisions the uncertainty in the angle of reflection will be :-

$$\Delta\theta_n = (1/r)^{(n-1)}\Delta s/r.$$

Consider the effect of this uncertainty on the velocity ccf defined in [1].

$$C(t) = \left\langle v^1(t).v^2(t)/v^1(t)v^2(t) \right\rangle$$

where $v^1(t)$ and $v^2(t)$ are the velocities of one atom at time t in the two trajectories. The angular brackets denote an average over all atoms in the system. $C(t)$ measures the average value of $\cos(\theta)$ where θ is the difference in angle between the directions of the velocities in the two trajectories. Assume that after time t each atom has undergone, on average, n collisions. The uncertainty in the angle of both the velocities will be :-

$$\epsilon = \Delta\theta_n.$$

If we assume that the uncertainty in the angle is uniformly distributed over the range 0–ϵ and that the number of particles N $\rightarrow \infty$ then :-

$$C(t) = 1/N \sum_{\text{All particles}} \cos(\theta)$$

$$= \int_{-\epsilon}^{\epsilon} \cos(\theta)d\theta/2\epsilon$$

$$= \sin(\epsilon)/\epsilon$$

It was stated in [1] that the velocity ccf, $C(t)$, is insensitive to the potential used in the simulation. As a first approximation to calculating the velocity ccf for a Lennard-Jonesium system it therefore seems reasonable to treat the system as a collection of 'hard' spheres with some effective radius a.

Take a 2-d L-J system with $\rho^* = 0.92$ and $T^* = 0.43$ (for a description of reduced units see reference [4]). Define r to be the separation between two particles at which the PE of the particles is equal to the average KE of a particle. If a is the average interparticle spacing (defined by the minimum in the PE) then approximate the mean free path by a. Set Δs to be the round-off error (= 1×10^{-6}). Figure 2 shows how the velocity ccf varies with the number of collisions. Compare this with fig. 3 which shows a velocity ccf calculated via an MD simulation for a system of Lennard-Jonesium at the same state point. The form of the velocity ccf calculated via the above analysis shows many of the features

2

found in the experimental velocity ccf. If the value of the round-off error is decreased by 6 orders of magnitude to 1×10^{-12} then the number of collisions needed before the ccf falls to zero about doubles. The form of C(t) only depends weakly on the initial perturbation (as found in [1]). Approximating the average time between collisions by l/v_{av}, C(t) drops to zero after 20ps. This is within an order of magnitude of the time taken for C(t) to drop to zero experimentally, reasonable agreement for such a simple analysis.

As the decay in the velocity ccf is an inherent feature of hard sphere systems (and presumably many other systems as well) it is presumably impossible to find long time correlations in a physical experiment on these systems. For systems that exhibit long time correlation effects, e.g. phonons in solids, then the velocity ccf does seem to decay much more slowly. For the above system at $\rho^* = 0.92$, $T^* = 0.12$ (well into the solid phase), the velocity ccf stayed at unity for at least 20ps. This would suggest that in measuring the rapid fall in the velocity ccf we are measuring a real physical effect (consider oxygen at NTP). For systems that do exhibit long time correlations, e.g. phonons in LJ at $\rho^* = 0.92$, $T^* = 0.12$, the velocity ccf can stay at unity for a lot longer.

References

[1] N. Corbin, CCP5 Quarterly, No. 16 p86 (1985)

[2] D. M. Heyes, CCP5 Quarterly, No. 19 p43 (1985)

[3] M. V. Berry in 'Topics in Non-Linear Dynamics'.
    ed. S. Jorna, A.I.P. Conference Procedings (No. 46)

[4] D. M. Heyes J.C.S. Faraday Trans. 79 1741 (1983)

3

$\Delta\theta$

Δs

r

l

V_{av}

Figure 1.

4
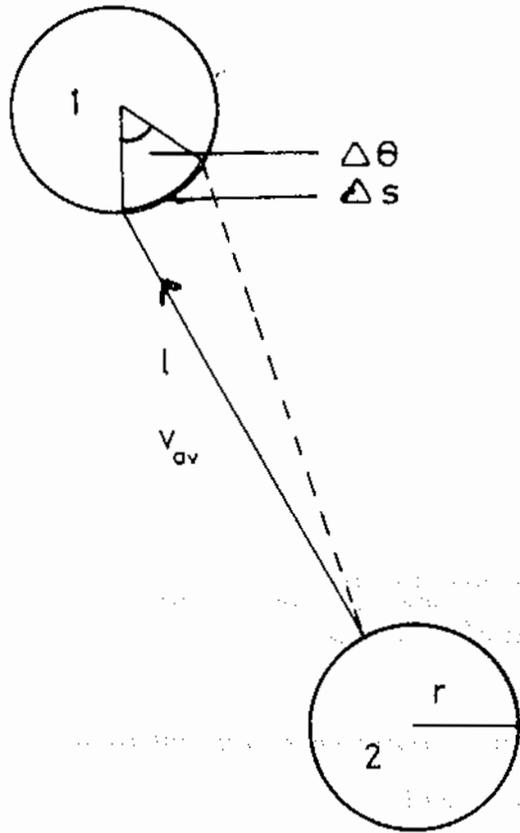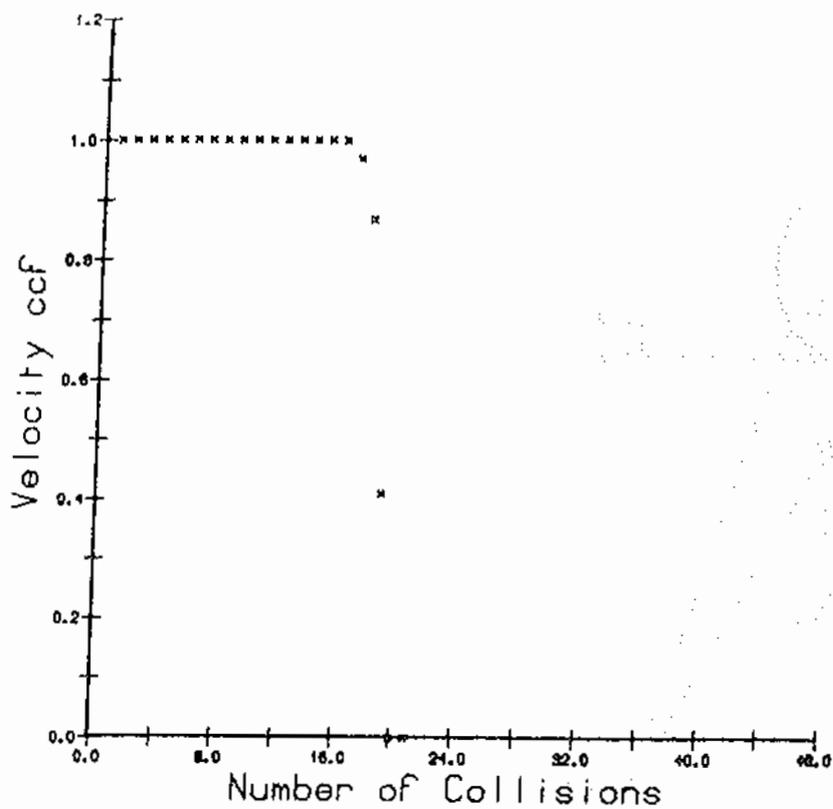
Figure 2. Velocity ccf vs number of collisions calculated for an LJ
system at $\rho^* = 0.92$ and $T^* = 0.43$.
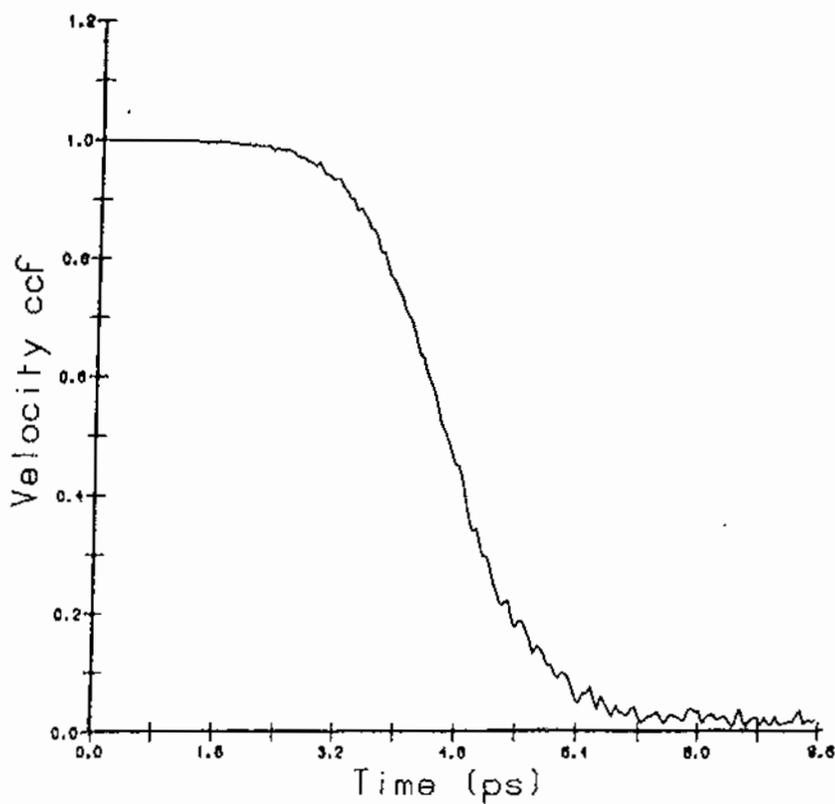
Figure 3. Velocity ccf vs. time given by an MD simulation of a 2-d LJ
system at the same state point as figure 2.

FORTRAN Code for the EWALD SUMMATION Method

W. Smith

Introduction

The object of this note is to describe how one may go about coding the Ewald summation method in a simple molecular dynamics application. The application considered is the simulation of an alkali-halide system, but the method is easily extended to other examples. It is not proposed to go into the details of the derivation of the method [1] nor to discuss its convergence properties [2]. The reader is recommended to study the relevant details in more august journals.

It should be said that the author learned much about coding the Ewald sum from the CCP5 Program Library, in particular from the program MDIONS [3], written by N. Anastasiou and D. Fincham. This program, so legend has it, benefited from its development within Konrad Singer's group at Royal Holloway College, so a general acknowledgement is given there also. The FORTRAN 77 code presented here, owes much to this source, but any errors that appear are this authors unique contribution.

The Ewald Summation

It is appropriate to begin with the Ewald formula for the Coulombic energy per unit cell of an ionic system:

$$V = \frac{2\pi}{V_0} \sum_{\underline{k}}^{\infty} \frac{\exp(-k^2/4\alpha^2)}{k^2} \left| \sum_{j}^{N} q_j \exp(-i\underline{k}\cdot\underline{r}_j) \right|^2$$
$$+ \sum_{j>n}^{N} \frac{q_j q_n}{|\underline{r}_j - \underline{r}_n|} \mathrm{erfc}(\alpha|\underline{r}_j - \underline{r}_n|) - \sum_{j}^{N} q_j^2 \alpha/\sqrt{\pi}$$

<1>

in which V_0 represents the volume of the unit cell, $\underline{k}$ is a vector in reciprocal space (i.e. for a cubic cell of width L, $\underline{k} = (2\pi/L)(l,m,n)$, with l,m,n integer), $\underline{r}_j$ is a vector locating the j th point charge, α is the Ewald convergence parameter and N is the number of ions in the unit cell. In molecular dynamics, the unit cell is identified with the simulation cell, which is assumed here to be a cube. This

assumes of course, that the pseudo periodic boundary condition normally employed in molecular dynamics is a valid construct in the calculation of the long range forces in liquids, with an effective range exceeding half the width of the MD cell. This is a debatable assumption, but it will not be discussed here.

The formula <1> has three readily identified terms. The first term right of <1> is the so-called 'reciprocal space' or FOURIER term and it is evaluated in the reciprocal space of the cubic lattice representing the pseudo periodic system. The second term is the 'complementary error function' or ERFC term, which is evaluated in real space, usually at the same time as the short-ranged non-Coulombic forces which are also inevitably present. The third term the 'self-interaction correction' (SIC) term, which is trivial to evaluate, but is a significant term nevertheless.

The Ewald method derives its usefulness from the fact that with a suitable choice of the convergence parameter α, the nominally infinite series in both real and reciprocal space can be truncated at some finite limit without loss of accuracy. This is a more satisfactory solution than a direct summation in real space, which may require some rather clever and specific tricks to achieve convergence. Theoretically in the Ewald summation the actual value of α is arbitrary; the same value for the Coulombic potential must (of course) result, whatever value is chosen. However, computationally speaking it is crucial to select a suitable value if the contributing series are to converge rapidly. In practice, a useful working strategy is to choose a value of α which gives the ERFC terms the same effective range as the short range contributions. In other words, the cut-off used in the short range forces calculation determines the value of α. This leads to a working rule that the product of α and the radius of the cut-off should be about 3.5. With this strategy, the ERFC and the short range forces are evaluated concurrently. This is the strategy adopted in the code presented here. One can of course use larger values of α and reduce the range of the real space terms even more, but this will lead to a more expensive FOURIER calculation, since the radius of convergence in reciprocal space will be extended.

Looking more closely at the FOURIER term, some points are worth making. Firstly, it transpires that the magnitude of the contribution it makes to the potential energy, in the application described here, is much smaller than the ERFC or SIC terms. Lest the reader be tempted to

leave it out, it should be said that it is important in the calculation of the forces and in the calculation of the collective response of the system and it is wiser to include it for these reasons. (It is also essential to include it in constant pressure MD of the Parrinello - Rahman type to get the pressure right). Secondly, despite its appearance, the FOURIER term is surprisingly easy to calculate and is highly vectorisable, thus making it particularly suitable for vector processors. (It does not, for example, contain an N-squared dependence on the number of particles, though people sometimes think that it does).

With regard to the ERFC terms, there is little new here for the reader experienced in simulating systems with short ranged forces. The only comment worth making is that the calculation of the complementary error function itself can be very conveniently facilitated through the use of an approximation found in the excellent book by Abramowitz and Stegun [4]:

$$erfc(x) = t*(a_1+t*(a+t*(a_3+t*(a_4+t*a_5))))*exp(-x^2)$$

where $t=1/(1+p*x)$ and:

$p = 0.3275911$	$a_1 = 0.254829592$
$a_2 = -0.284496763$	$a_3 = 1.421413741$
$a_4 = -1.453152027$	$a_5 = 1.061405429$

This approximation is particularly useful, since the exponential term appears also in the force calculation.

The SIC term, as mentioned above, is simple to calculate. It is useful to remember that once the value for α has been chosen, the term is a constant for the simulation and need only be evaluted once.

The Coulombic forces acting on the ions can be obtained from <1> by differentiation to give:

$$\underline{F}_j = -\frac{4\Pi q_j}{V_0} \sum_{k}^{\infty} \frac{exp(-k^2/4\alpha^2)}{k^2} i\underline{k}exp(i\underline{k}\cdot\underline{r}_j) \sum_{n}^{N} q_n exp(-i\underline{k}\cdot\underline{r}_n)$$

$$+ \sum_{n}^{N} \frac{q_j q_n}{r_{jn}^3} r_{jn}[erfc(\alpha r_{jn})+2(\alpha/\Pi)r_{jn}exp(-\alpha^2 r_{jn}^2)]$$

<2>

Which gives is the force acting on the j th point charge

(where $\underline{r}_{jn} = |\underline{r}_j - \underline{r}_n|$ and r_{jn} is the magnitude of $\underline{r}_{jn}$).

The terms in the FOURIER contribution to the force are common to the potential energy calculation. The direction in which the force acts is given by the vector $\underline{k}$. A casual glance suggests that the FOURIER contribution to the force is an complex quantity, but this cannot be the case. The resolution of this lies in the fact that the set of $\underline{k}$ vectors has inversion symmetry about the origin and every term appearing in the FOURIER part appears with its complex conjugate, and thus imaginary parts vanish. The inversion symmetry of the reciprocal lattice can be exploited to reduce the computational labour of the FOURIER calculations, by effectively halving the number of $\underline{k}$ vectors to be included. This possibility is used in the FORTRAN code presented. As for the force contribution arising from the ERFC terms, once again no new terms arise, provided that the approximation for the erfc function above is used. These points represent important economies in the design of an efficient code.

Lastly, there is the calulation of the virial. Happily, for a system of point charges it is easy to show that the virial is equal to the negative of the Coulombic potential energy and this fact may be gratefully exploited. (In the case of the Parrinello – Rahman algorithm however, where the pressure tensor is required, there appears to be no alternative but to calculate the tensor directly via some complicated algebra. Perhaps someone has a better method?)

The FORTRAN 77 Code

The FORTRAN code for the Ewald method is presented in Table 1 (Subroutine EWALD) and Table 2 (Subroutine FORCES). These have been taken from a program called MDNACL, which is available from the author. It is assumed that the interaction between the ions is of the Born-Huggins-Mayer (BHM) type vis:

$$V_{jn} = q_j q_n / r_{jn} + A_{jn} \exp(B_{jn}(\sigma_{jn} - r_{jn})) + C_{jn}/r_{jn}^6 + D_{jn}/r_{jn}^8$$

The subroutine EWALD calculates the FOURIER terms of the potential energy and the associated forces. It is intended that this subroutine be called before the subroutine FORCES, which calculates the ERFC terms and the other short range contributions at each MD time step. The subroutines calculate the electrostatic and short range potential energies, which are stored in the variables QPE and CPE respectively, and the total (electrostatic plus short range) forces, the components of which are stored in the arrays

FRX, FRY and FRZ respectively. The particle positions are stored in the arrays XX,YY and ZZ. The BHM parameters are stored in arrays AAA, BBB, SIG, CCC and DDD, which correspond with the BHM expression above. The electrostatic charges are stored in arrays CHARGE and CHGE; the former identifying the charge of each ion type, and the latter the charge of each individual ion. It is assumed that in array CHGE, the first N/2 elements refer to the first kind of ion in the system, while the last N/2 refer to the second kind.

The subroutines assume internal units in which the unit of length is half the width of the MD cell. The other units of mass, time, charge and energy are arbitrary. (Readers should however, take care that the electrostatic units are correctly used. In the subroutines the array element CFAC(4) contains a factor which ensures that the correct energy units emerge from the electrostatic calculations. The value of CFAC(4) must be established by the readers themselves according to their own choice of internal units.) There now follows a brief description of each subroutine.

The first statement of note in the subroutine EWALD is the PARAMETER statement (line 250). MSP defines the maximum number of particles the subroutine can handle. KMAX sets an integer limit on the l,m and n values in the $\underline{k}$ vector $\underline{k} = (2\Pi/L)(l,m,n)$. In a similar way KSQMAX effectively defines a spherical cut-off in reciprocal space. (Note that KSQMAX is deliberately set larger than KMAX**2 to include 'boundary' cases.)

The named COMMON area /CMWORK/ (lines 340-360) contains several arrays which are used in the calculation of the $\exp(-i\underline{k}\cdot\underline{r}_j)$ terms. Note that these arrays are NOT COMPLEX; the subroutine is designed to work in real arithmetic. These arrays are calculated between lines 510 and 760. The arrays essentially store the ingredients for a Fourier transform of the particle density, which is calculated in the same way. Between lines 670 and 760 use is made of DeMoivre's theorem to calculate the higher terms.

The subroutine opens with some data initialisation statements, the function of which should be obvious. The width of the MD cell, in internal units, is defined by the variable CL to be 2.0 (line 370).

The so-called Ak coefficients calculated between lines 790 and 860 are in fact the $\exp(-k^2/4\alpha^2)/k^2$ terms apppearing in equations <1> and <2>. They can be calculated and stored in this way only if the MD cell is cubic. In

principle they need only be calculated once in each simulation and not every timestep as is implied here.

The main feature of the subroutine EWALD is the triple DO loop over the components of the $\underline{k}$ vectors. These are the loops DO 230 (line 910), DO 220 (line 940) and DO 210 (line 1100), which terminate at lines 1560, 1540 and 1520 respectively. Notice that the limits of the two inner loops (defined by variables NMIN and MMIN) are updated as the calculation proceeds so that only half of the $\underline{k}$ vectors in reciprocal space are used explicitly. This strategy exploits the inversion symmetry of the reciprocal lattice as outlined above and requires a multiplication of the calculated terms by a factor of 2 at the end. The spherical cut-off in reciprocal space operates at line 1160.

Between lines 990 and 1080 the products of the $\exp(-ik_x \cdot r_{jx})$ and $\exp(-ik_y \cdot r_{jy})$ terms are calculated and stored in arrays CLM and SLM. These are multiplied by the $\exp(-ik_z \cdot r_{jz})$ terms and the particle charges between lines 1190 and 1290 to complete the $q_j \exp(-i\underline{k} \cdot \underline{r}_j)$ construction. The sum of these terms over the particles is calculated in lines 1320 to 1370 and the contribution to the Coulombic potential energy is added in line 1400. Notice that this calculation does not involve a double loop over the particles. The forces are accumulated between lines 1430 and 1480.

The final operations of the subroutine are to add the self interaction correction (lines 1590 to 1600) and to multiply both the potential energy and the forces by the appropriate factors to give the correct internal units.

Subroutine FORCES also begins with some data initialisation statements. The coefficients for the erfc approximation are set in lines 20 to 21. The noncoulombic potential and virial accumulators are initialised in lines 25 and 26. Between lines 27 and 32 the controls for the RDF calculation are set, a discussion of these matters is not relevant to this report.

The main control feature of this subroutine is a quadruple loop, which starts at line 36. The two outer loops DO 160 (line 36) and DO 150 (line 39) range over the particle types (indices L and M). The first loop over the particles; DO 140, begins at line 54 (index I). With this method of control care is required to ensure correct counting of the particle interactions. The conditional adjustments of DO loop limits beween lines 40 and 49, and again between lines 55 and 64 take account of this.

The innermost loop, which is the second loop over
the particles (index J), is in two parts. Between lines 72
and 79 the particle separations are calculated (DO 110), and
the pair forces and potential are calculated between lines
82 and 105 (DO 120). The DO 120 loop shows clearly how the
short range and the ERFC terms are calculated concurrently.
The spherical cut-off in real space is applied in statement
84. This statement will need modification or removal if the
loop is to vectorise (e.g. using the CVMGP function in CRAY
FORTRAN). The workings of this DO loop should be clear,
given that QPE is the Coulombic potential energy, CPE the
short range potential energy and CVR the short range virial.
The RDF is calculated between lines 108 and 115 and the
final forces are summed in lines 117 to 120.

To complete the calculations the reader should
remember that QPE and CPE and the long range corrections to
the short range potential should be added together to get
the final potential. Similarly CVR and -QPE plus the long
range correction of the virial should be added together. (In
the program MDNACL, these additions are made in a separate
subroutine.) A typical run of the program MDNACL
(Optimisation Level 3), with 216 ions in the MD cell, took
1.1 seconds per time step on the FPS 164. This performance
could undoubtedly have been improved if special effort had
been made to 'pipeline' some of the the code more
efficiently. However, this was not the object of this
particular exercise, which was to provide a 'starting point'
for the beginner.

Chosing the Convergence Parameter α.

Earlier on in this report it was suggested that a
working rule for the selection of the convergence parameter
α was that the product of α and the real space cut-off r_c
should be about 3.5. This is by no means a rigid rule and it
will vary according to the dimensions of the simulation
being attempted. In this application a fairly clear picture
of what is required can be given.

In Figure 1 a plot is presented which represents
the calculated molar Coulomb energy, for a system of 216
ions of sodium chloride on a perfect rocksalt lattice with a
molar volume of 2.15×10^{-5} m^3, as a function of the product
αr_c, where $r_c = 0.98781$ nm. Three regions of this plot are
clearly discernible; an initial sharp rise in the energy
followed by a plateau followed by a rapid descent. The
actual Coulomb energy for this system is given by the value
at the plateau, which is -737.36 kJ mole^{-1}. This compares
very well with the value calculated, using the given molar

volume and the Madelung constant of 1.7476, of -737.37 kJ mole^{-1}. Thus the plot suggests that $\alpha = 3.75/r_c$ would be a suitable value for the convergence parameter in this case.

The behaviour of this plot in regions away from the plateau can be simply explained. For small values of αr_c (i.e. small α) the range of the real space contribution to the potential energy is greatest. It therefore follows that the potential cut-off is likely to be too short to account adequately for the potential energy. In regions of high αr_c the real space contribution is very short range and it is the sum in reciprocal space that is now long ranged and inadequately summed.

It should be realised that the precise nature of this plot will depend upon the system being investigated. A large real space cut-off will give a plateau at lower values of αr_c, while a larger number of k vectors in the FOURIER part (i.e. chosing additional k vectors of larger magnitude) will extend the plateau to higher αr_c regions. Qualitatively however it is reasonable expect this kind of behaviour in all applications.

References

[1] P.P. Ewald, Ann. Physik (1921) v64 p253. Also C. Kittel, "Introduction to Solid State Physics", (Wiley) Second Edition, Appendix A. Also J.C. Slater, "Quantum Theory of Molecules and Solids" (McGraw-Hill) Volume III p.215.

[2] S.W. DeLeeuw, J.W. Perram and E.R. Smith, Proc. R. Soc. Lond. A 373, p27 and Proc. R. Soc. Lond. A 373, p57.

[3] N. Anastasiou and D. Fincham, The Program MDIONS: CCP5 Program Library Documentation 1981.

[4] M. Abramowitz and I.A. Stegun, "Handbook of Mathematical Functions", (Dover) p.299 Ch.7.1.26.
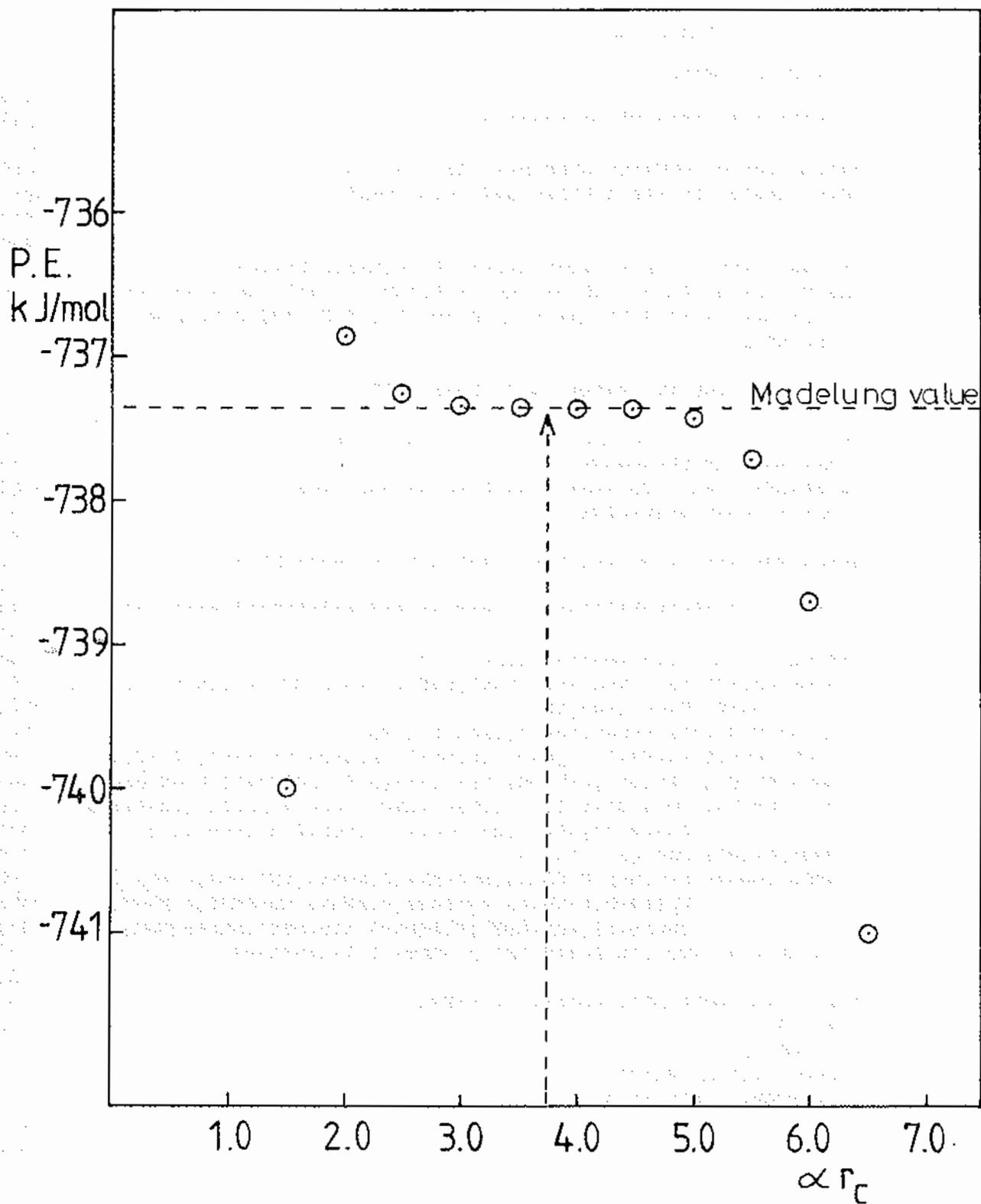
FIGURE 1

TABLE 1. THE SUBROUTINE EWALD

```
      SUBROUTINE EWALD                                            0010
C                                                                 0020
C****************************************************************  0030
C                                                                 0040
C     EVALUATION OF FOURIER COMPONENT OF EWALD SUM                0050
C     THIS VERSION IS FOR A CUBIC UNIT CELL ONLY.                 0060
C                                                                 0070
C                                                                 0080
C     IN LOOP OVER ALL K VECTORS K=2PI(LL/CL,MM/CL,NN/CL)         0090
C     THE VALUES OF LL,MM AND NN ARE SELECTED SO THAT THE SYMMETRY OF  0100
C     RECIPROCAL LATTICE IS TAKEN INTO ACCOUNT I.E. THE FOLLOWING 0110
C     RULES APPLY.                                                0120
C                                                                 0130
C     LL RANGES OVER THE VALUES 0 TO KMAX ONLY.                   0140
C                                                                 0150
C     MM RANGES OVER 0 TO KMAX WHEN LL=0 AND OVER                 0160
C     -KMAX TO KMAX OTHERWISE.                                    0170
C     NN RANGES OVER 1 TO KMAX WHEN LL=MM=0 AND OVER              0180
C     -KMAX TO KMAX OTHERWISE.                                    0190
C                                                                 0200
C     HENCE THE RESULT OF THE SUMMATION MUST BE DOUBLED AT THE END. 0210
C                                                                 0220
C****************************************************************  0230
C                                                                 0240
      PARAMETER (MSP=216,KMAX=5,KSQMAX=27)                        0250
      COMMON/CMCNTL/NSP,NRUN,NSTP,KRES,NSEQL,LTSCL,NTSCL,ITSCL,IPRT,NAVG  0260
     X       ,NSTK,LVACF,LRDF,BETA                                0270
      COMMON/CMCNST/PI,AVSNO,BOLTZ,EPSO,ELECHG                    0280
      COMMON/CMVECT/XX(MSP),YY(MSP),ZZ(MSP),PX(MSP),PY(MSP),PZ(MSP)  0290
      COMMON/CMPOTL/CPE,QPE,CVR,FRX(MSP),FRY(MSP),FRZ(MSP),CHGE(MSP)  0300
      COMMON/CMSYST/VOLM,TEMP,TSTEP,PLRC,VLRC,ALPHA,AMASS(2),CHARGE(2),  0310
     X             AAA(2,2),BBB(2,2),SIG(2,2),CCC(2,2),DDD(2,2)   0320
      COMMON/CMUNIT/UNIT(5),CFAC(5)                               0330
      COMMON/CMWORK/ELC(MSP,0:KMAX),EMC(MSP,0:KMAX),ENC(MSP,0:KMAX),  0340
     X             ELS(MSP,0:KMAX),EMS(MSP,0:KMAX),ENS(MSP,0:KMAX),  0350
     X             CKC(MSP),CKS(MSP),CLM(MSP),SLM(MSP),AK(KSQMAX)  0360
      DATA CL/2.0/,TWOPI/6.2831853072/,SQRPI/1.7724538482/        0370
C                                                                 0380
C     INITIALISE COULOMBIC POTENTIAL ENERGY                       0390
      QPE=0.0                                                     0400
      RCL=TWOPI/CL                                                0410
      RALPH=-0.25/ALPHA**2                                        0420
      RVOL=TWOPI/(CL*CL*CL)                                       0430
C                                                                 0440
C     INITIALISE FORCES                                           0450
      DO 100 I=1,NSP                                              0460
      FRX(I)=0.0                                                  0470
      FRY(I)=0.0                                                  0480
      FRZ(I)=0.0                                                  0490
  100 CONTINUE                                                    0500
C                                                                 0510
C     CALCULATE AND STORE EXPONENTIAL FACTORS                     0520
      DO 110 I=1,NSP                                              0530
```

```
      ELC(I,0)=1.0                                                    0540
      EMC(I,0)=1.0                                                    0550
      ENC(I,0)=1.0                                                    0560
      ELS(I,0)=0.0                                                    0570
      EMS(I,0)=0.0                                                    0580
      ENS(I,0)=0.0                                                    0590
      ELC(I,1)=COS(RCL*XX(I))                                         0600
      EMC(I,1)=COS(RCL*YY(I))                                         0610
      ENC(I,1)=COS(RCL*ZZ(I))                                         0620
      ELS(I,1)=SIN(RCL*XX(I))                                         0630
      EMS(I,1)=SIN(RCL*YY(I))                                         0640
      ENS(I,1)=SIN(RCL*ZZ(I))                                         0650
  110 CONTINUE                                                        0660
      DO 130 L=2,KMAX                                                 0670
      DO 120 I=1,NSP                                                  0680
      ELC(I,L)=ELC(I,L-1)*ELC(I,1)-ELS(I,L-1)*ELS(I,1)               0690
      EMC(I,L)=EMC(I,L-1)*EMC(I,1)-EMS(I,L-1)*EMS(I,1)               0700
      ENC(I,L)=ENC(I,L-1)*ENC(I,1)-ENS(I,L-1)*ENS(I,1)               0710
      ELS(I,L)=ELS(I,L-1)*ELC(I,1)+ELC(I,L-1)*ELS(I,1)               0720
      EMS(I,L)=EMS(I,L-1)*EMC(I,1)+EMC(I,L-1)*EMS(I,1)               0730
      ENS(I,L)=ENS(I,L-1)*ENC(I,1)+ENC(I,L-1)*ENS(I,1)               0740
  120 CONTINUE                                                        0750
  130 CONTINUE                                                        0760
C                                                                     0770
C     CALCULATE AND STORE AK COEFFICIENTS                            0780
      EKSQ=1.0                                                        0790
      EXPF=0.0                                                        0800
      IF(RALPH.LT.0.0)EXPF=EXP(RALPH*RCL*RCL)                        0810
      DO 140 I=1,KSQMAX                                               0820
      RKSQ=FLOAT(I)*RCL*RCL                                           0830
      EKSQ=EXPF*EKSQ                                                  0840
      AK(I)=EKSQ/RKSQ                                                 0850
  140 CONTINUE                                                        0860
C                                                                     0870
C     START OF MAIN LOOP OVER K VECTORS                              0880
      MMIN=0                                                          0890
      NMIN=1                                                          0900
      DO 230 LL=0,KMAX                                                0910
      L=LL                                                            0920
      RL=RCL*FLOAT(LL)                                                0930
      DO 220 MM=MMIN,KMAX                                             0940
      M=IABS(MM)                                                      0950
      RM=RCL*FLOAT(MM)                                                0960
C                                                                     0970
C     SET TEMPORARY PRODUCTS OF EXPONENTIAL TERMS                    0980
      IF(MM.GE.0)THEN                                                 0990
      DO 150 I=1,NSP                                                  1000
      CLM(I)=ELC(I,L)*EMC(I,M)-ELS(I,L)*EMS(I,M)                     1010
      SLM(I)=ELS(I,L)*EMC(I,M)+EMS(I,M)*ELC(I,L)                     1020
  150 CONTINUE                                                        1030
      ELSE                                                            1040
      DO 160 I=1,NSP                                                  1050
      CLM(I)=ELC(I,L)*EMC(I,M)+ELS(I,L)*EMS(I,M)                     1060
      SLM(I)=ELS(I,L)*EMC(I,M)-EMS(I,M)*ELC(I,L)                     1070
  160 CONTINUE                                                        1080
```

```
        ENDIF                                                        1090
        DO 210 NN=NMIN,KMAX                                          1100
        N=IABS(NN)                                                   1110
        RN=RCL*FLOAT(NN)                                             1120
C                                                                    1130
C       TEST ON MAGNITUDE OF K VECTOR                               1140
        KK=LL*LL+MM*MM+NN*NN                                         1150
        IF(KK.LE.KSQMAX)THEN                                         1160
C                                                                    1170
C       CALCULATE EXP(IKR) TERMS AND PRODUCT WITH CHARGES           1180
        IF(NN.GE.0)THEN                                              1190
        DO 170 I=1,NSP                                               1200
        CKC(I)=CHGE(I)*(CLM(I)*ENC(I,N)-SLM(I)*ENS(I,N))            1210
        CKS(I)=CHGE(I)*(SLM(I)*ENC(I,N)+CLM(I)*ENS(I,N))            1220
  170 CONTINUE                                                      1230
        ELSE                                                         1240
        DO 180 I=1,NSP                                               1250
        CKC(I)=CHGE(I)*(CLM(I)*ENC(I,N)+SLM(I)*ENS(I,N))            1260
        CKS(I)=CHGE(I)*(SLM(I)*ENC(I,N)-CLM(I)*ENS(I,N))            1270
  180 CONTINUE                                                      1280
        ENDIF                                                        1290
C                                                                    1300
C       CALCULATE VECTOR SUMS                                        1310
        CKCS=0.0                                                     1320
        CKSS=0.0                                                     1330
        DO 190 I=1,NSP                                               1340
        CKCS=CKCS+CKC(I)                                             1350
        CKSS=CKSS+CKS(I)                                             1360
  190 CONTINUE                                                      1370
C                                                                    1380
C       ACCUMULATE POTENTIAL ENERGY                                  1390
        QPE=QPE+AK(KK)*(CKCS*CKCS+CKSS*CKSS)                        1400
C                                                                    1410
C       CALCULATE FORCE ON EACH SITE                                 1420
        DO 200 I=1,NSP                                               1430
        QFORCE=AK(KK)*(CKS(I)*CKCS-CKC(I)*CKSS)                     1440
        FRX(I)=FRX(I)+RL*QFORCE                                     1450
        FRY(I)=FRY(I)+RM*QFORCE                                     1460
        FRZ(I)=FRZ(I)+RN*QFORCE                                     1470
  200 CONTINUE                                                      1480
C                                                                    1490
C       END VECTOR LOOP                                              1500
        ENDIF                                                        1510
  210 CONTINUE                                                      1520
        NMIN=-KMAX                                                   1530
  220 CONTINUE                                                      1540
        MMIN=-KMAX                                                   1550
  230 CONTINUE                                                      1560
C                                                                    1570
C       ADD SELF INTERACTION CORRECTION                             1580
        QPE=CFAC(4)*(2.0*RVOL*QPE-0.5*ALPHA*FLOAT(NSP)*            1590
      X     (CHARGE(1)**2+CHARGE(2)**2)/SQRPI)                      1600
C                                                                    1610
        DO 240 I=1,NSP                                               1620
        FRX(I)=4.0*CFAC(4)*RVOL*FRX(I)                             1630
```

```
      FRY(I)=4.0*CFAC(4)*RVOL*FRY(I)                                    1640
      FRZ(I)=4.0*CFAC(4)*RVOL*FRZ(I)                                    1650
  240 CONTINUE                                                          1660
      RETURN                                                            1670
      END                                                               1680
```

TABLE 2. THE SUBROUTINE FORCES

```
      SUBROUTINE FORCES                                              001
C                                                                    002
C*********************************************************************003
C                                                                    004
C     CALCULATE REAL SPACE POTENTIAL ENERGY AND FORCES               005
C                                                                    006
C*********************************************************************007
C                                                                    008
      PARAMETER (MSP=216)                                            009
      LOGICAL LTSCL,LVACF,LRDF,LGORDF                                010
      COMMON/CMCNTL/NSP,NRUN,NSTP,KRES,NSEQL,LTSCL,NTSCL,ITSCL,IPRT,NAVG011
     X           ,NSTK,LVACF,LRDF,BETA                              012
      COMMON/CMSYST/VOLM,TEMP,TSTEP,PLRC,VLRC,ALPHA,AMASS(2),CHARGE(2),013
     X               AAA(2,2),BBB(2,2),SIG(2,2),CCC(2,2),DDD(2,2)   014
      COMMON/CMUNIT/UNIT(5),CFAC(5)                                  015
      COMMON/CMVECT/XX(MSP),YY(MSP),ZZ(MSP),PX(MSP),PY(MSP),PZ(MSP)  016
      COMMON/CMPOTL/CPE,QPE,CVR,FRX(MSP),FRY(MSP),FRZ(MSP),CHGE(MSP) 017
      COMMON/CMCRDF/IRDF,IPRDF,MAXRDF,RDF(1024,3)                    018
      DIMENSION RSQ(MSP),RX(MSP),RY(MSP),RZ(MSP),RRR(MSP)            019
      DATA A1,A2,A3/0.254829592,-0.284496736,1.421413741/           020
      DATA A4,A5,PP/-1.453152027,1.061405429,0.3275911/             021
      DATA SQRPI/1.7724538482/                                      022
C                                                                    023
C     INITIALISE NONCOULOMBIC POTENTIAL AND VIRIAL                   024
      CPE=0.0                                                        025
      CVR=0.0                                                        026
C                                                                    027
C     SET RDF CONTROLS                                               028
      LGORDF=.FALSE.                                                 029
      IF(MOD(NSTP-NSEQL,IRDF).EQ.0)LGORDF=.TRUE.                     030
      IF(.NOT.LRDF.OR.NSTP.LE.NSEQL)LGORDF=.FALSE.                   031
      DELRDF=1.0/FLOAT(MAXRDF)                                       032
C                                                                    033
C     PRIMARY LOOP OVER PARTICLE TYPES                               034
      NS2=NSP/2                                                      035
      DO 160 L=1,2                                                   036
C                                                                    037
C     SECONDARY LOOP OVER PARTICLE TYPES                             038
      DO 150 M=1,L                                                   039
      IF(L.EQ.1)THEN                                                 040
      IA=2                                                           041
      IB=NS2                                                         042
      ELSE IF(M.EQ.1)THEN                                            043
      IA=NS2+1                                                       044
      IB=NSP                                                         045
      ELSE IF(M.EQ.2)THEN                                            046
      IA=NS2+2                                                       047
      IB=NSP                                                         048
      ENDIF                                                          049
      K=(L*(L-1))/2+M                                                050
      CHGP=CFAC(4)*CHARGE(L)*CHARGE(M)                               051
C                                                                    052
C     PRIMARY LOOP OVER PARTICLES                                    053
```

```
      DO 140 I=IA,IB                                                       054
      IF(L.EQ.1)THEN                                                      055
      JA=1                                                                056
      JB=I-1                                                              057
      ELSE IF(M.EQ.1)THEN                                                 058
      JA=1                                                                059
      JB=NS2                                                              060
      ELSE IF(M.EQ.2)THEN                                                 061
      JA=NS2+1                                                            062
      JB=I-1                                                              063
      ENDIF                                                               064
C                                                                         065
C     SET TEMPORARY ACCUMULATORS                                         066
      FTX=0.0                                                             067
      FTY=0.0                                                             068
      FTZ=0.0                                                             069
C                                                                         070
C     SECONDARY LOOP OVER PARTICLES                                      071
      DO 110 J=JA,JB                                                      072
C                                                                         073
C     APPLY MINIMUM IMAGE CONVENTION                                     074
      RX(J)=XX(I)-XX(J)-AINT(XX(I)-XX(J))-AINT(XX(I)-XX(J))               075
      RY(J)=YY(I)-YY(J)-AINT(YY(I)-YY(J))-AINT(YY(I)-YY(J))               076
      RZ(J)=ZZ(I)-ZZ(J)-AINT(ZZ(I)-ZZ(J))-AINT(ZZ(I)-ZZ(J))               077
      RSQ(J)=RX(J)**2+RY(J)**2+RZ(J)**2                                   078
  110 CONTINUE                                                            079
C                                                                         080
C     CALCULATE POTENTIAL,VIRIAL AND FORCES                              081
      DO 120 J=JA,JB                                                      082
      RRR(J)=RSQ(J)                                                       083
      IF(RSQ(J).LE.1.0)THEN                                              084
      RRR(J)=SQRT(RSQ(J))                                                085
      TT=1.0/(1.0+PP*ALPHA*RRR(J))                                       086
      EXP1=EXP(-(ALPHA*RRR(J))**2)                                       087
      EXP2=AAA(L,M)*EXP(BBB(L,M)*(SIG(L,M)-RRR(J)))                      088
      ERFCR=TT*(A1+TT*(A2+TT*(A3+TT*(A4+TT*A5))))*EXP1*CHGP/RRR(J)       089
      EGAMMA=(ERFCR+2.0*CHGP*(ALPHA/SQRPI)*EXP1)/RSQ(J)                  090
      SGAMMA=(EXP2*BBB(L,M)*RRR(J)+(6.0*CCC(L,M)+8.0*DDD(L,M)/RSQ(J))    091
     X        /RSQ(J)**3)/RSQ(J)                                         092
      QPE=QPE+ERFCR                                                       093
      CPE=CPE+EXP2+(CCC(L,M)+DDD(L,M)/RSQ(J))/RSQ(J)**3                  094
      CVR=CVR-SGAMMA*RSQ(J)                                              095
C                                                                         096
C     CALCULATE FORCES                                                   097
      FTX=FTX+(SGAMMA+EGAMMA)*RX(J)                                      098
      FTY=FTY+(SGAMMA+EGAMMA)*RY(J)                                      099
      FTZ=FTZ+(SGAMMA+EGAMMA)*RZ(J)                                      100
      FRX(J)=FRX(J)-(SGAMMA+EGAMMA)*RX(J)                                101
      FRY(J)=FRY(J)-(SGAMMA+EGAMMA)*RY(J)                                102
      FRZ(J)=FRZ(J)-(SGAMMA+EGAMMA)*RZ(J)                                103
      ENDIF                                                              104
  120 CONTINUE                                                           105
C                                                                         106
C     CALCULATE CLASSICAL RDF                                            107
      IF(LGORDF)THEN                                                     108
```

```
      DO 130 J=JA,JB                                     109
      IF(RRR(J).LT.1.0)THEN                              110
      N=1+INT(RRR(J)/DELRDF)                             111
      RDF(N,K)=RDF(N,K)+1.0                              112
      ENDIF                                              113
  130 CONTINUE                                           114
      ENDIF                                              115
C                                                        116
C     COMPLETE SUMMATION OF FORCES ON PARTICLE I         117
      FRX(I)=FRX(I)+FTX                                  118
      FRY(I)=FRY(I)+FTY                                  119
      FRZ(I)=FRZ(I)+FTZ                                  120
  140 CONTINUE                                           121
  150 CONTINUE                                           122
  160 CONTINUE                                           123
      RETURN                                             124
      END                                                125
```

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