

DARESBUY LABORATORY

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# INFORMATION QUARTERLY

## for

# COMPUTER SIMULATION OF CONDENSED PHASES

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

Number 22

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### Contents

Editorial	1
General News	2
Report on the CECAM Workshop on "Wave Packet Dynamics", Orsay 15-25 July 1986. W. Smith	14
Report of Meeting on Advanced Research Computing held at Imperial College on 8 July 1986. D. Fincham	21
The Molar Free Energy of Solids K. Singer	24
Simulated Annealing of Atomic Clusters. L. Wille	29
Ewald Sum Made Easy. D. Adams and G. Dubey	39
Calculating Orientational Order in MD Simulations. W. Smith	44
The Transputer D. Fincham	51
The CCP5 Program MDZOID W. Smith	53

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## Editorial.

The most gratifying piece of news we can report in this issue is that CCP5 has successfully been renewed for a few more years! It is appropriate then to thank the CCP5 Chairman Julian Clarke and the authors of the Renewal Proposal, Richard Catlow, Dominic Tildesley, M. Leslie and W. Smith for their efforts. Thanks are also due to several members of the CCP5 Steering Committee, who provided useful advice and information.

It has to be said however that not all the requests made to SERC in the CCP5 Renewal Proposal have been granted and the renewed project will not have quite the diversity we had anticipated. The reasons for this are probably more to do with administrative necessity than with any weakness in the scientific case. An example of this is the radical change in the way in which all the CCPs are to be funded in future. This has introduced a more competitive aspect into the funding of the CCPs than existed previously. Nevertheless we can be glad that CCP5 has come through with most of its requests having been met and we can look forward to a programme that is still exciting. Further details of the renewal of CCP5 are given within.

Our thanks go to this month's contributors to our newsletter.

### Contributors:

- D. Adams            The Department of Chemistry,  
University of Southampton,  
Southampton SO9 5NH.
- D. Fincham        Department of Chemistry, The  
University of York, Heslington,  
York YO1 5DD.
- K. Singer         Department of Chemistry, Royal  
Holloway and Bedford New College,  
Egham, Surrey TW20 0EX.
- W. Smith         Theory and Computational Science  
Division, S.E.R.C. Daresbury  
Laboratory, Daresbury, Warrington  
WA4 4AD.
- L. Wille         Division, S.E.R.C. Daresbury  
Laboratory, Daresbury, Warrington  
WA4 4AD.

## General News.

a) The renewal of CCP5 was confirmed by SERC during the summer months. The finally approved project however was reduced from that contained in the Renewal Proposal. The Proposal contained collaborative projects in four distinct areas: simulations of molecular and macromolecular systems; simulations of polar solids; simulations of fluid transport properties and simulations of quantum systems. The last of these projects carried a requirement for a postdoctoral research assistant. Each project was to be supported by a programme of workshops and invitations to overseas scientists.

In the approved Project, funding of the quantum mechanical simulations was not recommended. In addition the renewable life of the Project was reduced from three to two years. The support of the scientists at Daresbury Laboratory (in the persons of M. Leslie and W. Smith) was reduced by half (this is not likely to take immediate effect).

These reductions in the scope of the Project, while disappointing, still leave a substantially viable Project. The surviving projects will be able to proceed in much the same way as was planned (albeit for two instead of three years) and we can be confident that some very useful work will be done.

In order that the terms of the renewal can be discussed more fully by the participants in CCP5, a CCP5 Steering Committee Meeting is being arranged during the CCP5 meeting in Manchester in January 1987, the details of which are given below.

b) CCP5 is organising a meeting entitled "New Horizons in the Computer Simulation of Condensed Phases". The meeting will take place in Manchester 8-9 January. The purpose of the meeting is to discuss recent developments and future possibilities in the following fields:

- Molecular and macromolecular systems
- Polar solids
- Fluid Transport Properties
- Quantum Mechanical Simulations (not specifically funded)

It is hoped to include substantial time in the programme for discussion. The invited speakers include Jorgensen (Purdue) and Price (U.C.L.). A poster session will also be organised. A CCP5 Steering Committee meeting will take place on the Thursday, before dinner.

Those interested in participating should contact Dr. J.H.R. Clarke, Department of Chemistry, U.M.I.S.T., Sackville Street, Manchester M60 1QD. Those wishing to contribute a talk are requested to send a short abstract for consideration.

c) CCP5 is also organising a workshop on sorption in porous solids sometime in January 1987. The discussions will cover both molecular dynamics and static simulations and will include experimental input. Readers interested in attending this workshop should contact Dr. M. Leslie, SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD.

d) The Rutherford and Appleton Computer Centre recently organised an Open Meeting Imperial College London to provide prospective users of the new Cray XMP/48 supercomputer with some details of the service RAL will offer. We are fortunate that D. Fincham attended the meeting and has reported the meeting for CCP5 (see within). UK readers will probably have seen press reports regarding the negotiations with the American authorities over the 'transfer of technology' restrictions operating for machines such as the Cray computer. It is to be hoped that no serious delay in establishing the service will result. With a little goodwill and patience all should be well!

e) The University of London Computing Centre has announced the new Cray service for the end of October, when the second Cray 1s computer with 2 Mwords of memory, becomes available to users. The two Cray computers will operate as if in separate environments and users will need separate accounts if they are to use both machines. Users should contact Allocation and Control for advice on this.

With regard to the current Cray service, ULCC have announced their intention to enable COS Permanent Dataset Privacy at the end of 1986. The tools provided by this will allow users to protect datasets from unauthorised use. This implementation will affect everyone and users are recommended to consult the ULCC newsletter for July 1986 for details.

Also via ULCC we learn that the long awaited Mini-DAP has emerged and has been installed at the DAP Support Unit at Queen Mary College. This small version of the now-famous DAP has about one third of the processing power and is to be combined with an ICL Perq to produce a graphics workstation. The potential of this combination for molecular graphics is considerable and it will be interesting to hear of future developments.

f) The University of Manchester Regional Computing Centre has announced the imminent withdrawal of the CYBER 7600 service known locally as MFZ. The improvements in the SCOPE 2 RHF software since its initial implementation have meant that the presence of an additional number-cruncher cannot be justified. The withdrawal of MFZ means that UMRCC is left with one CYBER 7600, a CYBER 176, a CYBER 205 and the AMDAHL 470/V8 as the main facilities.

Meanwhile, August saw upgrades to several software packages including the FTN5 compilers and GHOST-80 on both the 176 and 7600 machines and also the 205. August/September was also scheduled as

the time of the introduction of Version R54A of ROSCOE on the AMDAHL 470/V8. 'AMDAHL NOTES' 59 and 60, published by UMRCC give details of the new facilities available.

g) 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.

It is pleasing to report that some members of the CCP5 community are already making use of this facility.

h) The CCP5 Editor continues to hear reports that our readers are citing the CCP5 Newsletter in the established scientific journals. Some concern has been expressed to us that the function of the newsletter is being exceeded by this practice, since the newsletter is an informal journal and is meant only to stimulate discussion and provide information. It does not therefore carry the same weight as a fully fledged journal. If our readers wish to cite the newsletter in the wider literature we ask that they declare its informality. Its availability from Daresbury Laboratory should also be mentioned, so that interested parties can obtain the relevant information.

i) We have received from colleagues in the Netherlands information on the simulation package known as GROMOS86. The package has been developed by the simulation group at Groningen and it appears to be an extremely versatile and powerful package for simulation work. Many different kinds of molecules may be simulated, using different kinds of interaction models and boundary conditions. (A full description of the package would require more space than can be afforded here). Readers interested in the package should write to Dr. W.F. Gunsteren or Prof. H.J.C. Berendsen at the Laboratory of Physical Chemistry, The University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands. The program package is available via a small company set up by the Groningen group to distribute the program. A handling fee only (\$200) is charged to academic centres, but commercial companies will be required to pay substantially more.

j) 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. Clementi 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).

k) Anyone wishing to make use of the CCP5 Program Library is invited to do so. Documents and programs are available free of charge to academic centres upon application to Dr. M. Leslie (\*) at Daresbury Laboratory. Listings of programs are available if required but it is recommended that magnetic tapes (to be supplied by the applicant) be used. 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.

MDZOID by W. Smith & K. Singer.

M.D. simulation of ellipsoidal gaussian molecules. Uses ellipsoidal gaussian probability distribution to represent molecules and a sum of gaussian functions to represent the potential, giving a model of great flexibility. Uses the 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, virial and associated R.M.S. deviations and pressure and temperature. Also calculates centre-centre RDF, orientational order parameters and translational and rotational velocity autocorrelation functions.

DENCOR by W. Smith.

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

CURDEN by W. Smith.

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

HLJ1 by D. M. Heyes.

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

HLJ2 by D. M. Heyes.

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

HLJ3 by D. M. Heyes.

M.D. simulation of atomic fluids. Uses 12/6 Lennard - Jones site - site potential function and a Verlet leapfrog algorithm for centre

- of - mass motion. The link - cell method is employed to enable large simulations. Calculates system average configuration energy and kinetic energy and associated R.M.S. deviations and also pressure, temperature, mean square displacements and radial distribution function.

HLJ4 by D. M. Heyes.

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

HLJ5 by D. M. Heyes.

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

HLJ6 by D. M. Heyes.

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

MCRPM by D. M. Heyes.

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

SURF by D. M. Heyes.

M.D. simulation of model alkali halide lamina. Molecular dynamics simulation for ionic laminae using the Tosi-Fumi / Born-Mayer-Huggins potential and the Evjen method for evaluating

the lattice sums. The integration algorithm used is the Verlet method. The program calculates the system potential and kinetic energies, the pressure and the final averages and R.M.S. fluctuations. The program also calculates density profiles such as number density, temperature, energy and pressure.

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

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

MDATOM by D. Fincham.

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

MDDIAT by D. Fincham.

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

MDDIATQ by D. Fincham.

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

MDIONS by D. Fincham & N. Anastasiou.

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

displacements. ...  
 ...  
 MDMANY by D. Fincham & W. Smith. ...

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

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

MCN by N. Corbin.

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

SCN by N. Corbin.

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

SMF by N. Corbin.

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

#### 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.

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For further information about submission of manuscripts please contact any of the editors. For a free sample copy or subscription details when available please contact the publishers marketing department.

Report on the CECAM Workshop on 'Wavepacket Dynamics', Orsay  
15-25 July 1986.

W. Smith

Most chemical physicists are familiar with the concept of a wavepacket. The utility of wavepackets in demonstrating the Heisenberg Uncertainty Principle is basic to most introductory treatments of quantum mechanics. In the past however, wavepackets were confined to rather esoteric aspects of quantum mechanics and were not commonly encountered in the subject at large. The story is somewhat different today. It is now becoming apparent that wavepackets offer a useful approach to the solution of the Time Dependent Schroedinger Equation (TDSE) in a wide variety of applications. The CECAM workshop on wavepacket propagation is a sign of the growing importance of wavepacket methods in chemical physics and followed from an introductory conference on 'Dynamics of Wavepackets in Molecular and Nuclear Physics' [1] which took place in Belgium in 1985. Unlike that particular conference however, the workshop concentrated on the molecular aspects.

The workshop was organised by P. van Leuven, L. Lathouwers and J. Broeckhove of the University of Antwerp. Together they guided the developments of the workshop and maintained the momentum. Theirs was not an easy task given the diversity of interests and potential applications of wavepacket methods and some difficult decisions were undoubtedly called for to produce a successful blend of the expertise available. They were successful to the extent that most participants found useful work to keep them occupied for the two weeks of the workshop, the fruits of their endeavours however, cannot yet be displayed, as most of the work initiated longer term projects. The results of these projects will no doubt emerge in due course. In the description of the workshop that follows, I must give a somewhat selective account of the proceedings. The full account of the different areas covered must await a more comprehensive (and expert) description.

The first day of the workshop was taken up by an informal session in which the participants gave descriptions of their interests in wavepacket dynamics. Most of these interests seemed to fall into three distinct (but not unrelated) categories. Firstly, the theoreticians were concerned with the properties of wavepackets as revealed by their algebra or with the derivation of their equations of motion through Lie algebras or variational principles and the propagation of wavepackets in idealised systems. The group from Antwerp

were very concerned with this area, that is; F. Arickx, J. Broeckhove, H. Hensberg, L. Lathouwers and P. van Leuven and also M. Berman (Jerusalem). Secondly, the chemical physicists used wavepackets as a tool in studies of excited states in spectroscopy and photodissociation and also in chemical reaction dynamics and small molecule scattering. Those with the strongest interest in this category were R. Coalson (Los Alamos), B. Jackson (Massachusetts), C. Leforestier (Paris), C. Nessmann (Pennsylvania) and O. Rojas. In the third group were the simulators, who were primarily concerned with the use of wavepackets in solving specific problems in computer simulations. In this category R. Kosloff (Jerusalem), K. Singer (London) and W. Smith (Daresbury) were most evident. As I have indicated these categories were by no means unrelated and many participants had interests in all three. There were many fundamental questions to be asked which had bearing on all three areas and only through a combined effort could they be addressed. In this context, the participation of R. Kosloff had particular significance since the essentially exact discrete methods he employed offered a means of tackling many of these questions.

The wavepackets employed in the various methods are of two kinds; analytical and discrete. The analytical forms were exclusively based on the gaussian representation of a wavepacket, which in one dimension takes the form (written in atomic units with  $\hbar/2\pi = 1$ ):

$$\phi(x,t) = \exp(iA(t) \cdot (x-X)^2 + iP(t) \cdot (x-X) + iD(t))$$

in which A is a complex parameter defining the width of the gaussian, X is the position of the wavepacket centre, P is the momentum of the wavepacket centre (its so-called classical momentum) and D is a complex combined phase and normalisation factor. The gaussian form appears in a number of guises in wavepacket technology; in the three dimensional form (either in a spherical or aspherical form), as Hartree products for many-particle systems and as linear combinations for more sophisticated wavepacket representations. The form is favoured because of its convenient analytical properties and because the parameters used in the definition retain useful physical interpretations. The dynamics of the wavepackets are derived from approximate solutions to the TDSE, usually following from the methods of Heller [2] which are based on the time dependent variational principle known as the Dirac-Frenkel-McLachlan (DFM) principle [3]. Other routes to the equations are possible such as the Minimum Error Method (which may be formally equivalent to the DFM method) [4] and

Lie algebra combined with the maximum entropy method [5]. In the dynamics of the wavepackets the  $A$  parameter may be either fixed (the 'frozen' gaussian method) or allowed vary in a manner determined by the dynamical equations.

In the discrete methods the convenience of an analytical form is relinquished in favour of a representation of the wavepacket on a one-, two- or three-dimensional grid. This representation affords a very accurate description of quantum behaviour and phenomena such as tunneling are observable without any special treatments. In the basic method of Kosloff and Kosloff [6] the TDSE is propagated in time by a simple finite differencing scheme:

$$\Psi(t_{n+1}) = \Psi(t_{n-1}) - 2i\Delta t H \Psi(t_n)$$

where  $H$  represents the Hamiltonian operator written in a discretized form. Crucial to the method is the accurate evaluation of the effect of the kinetic energy operator on the discrete wavefunction. This requires the evaluation of the second derivative of the wavefunction. In the Kosloff scheme this is done by Fourier transforming the wavefunction to  $k$ -space, multiplying the result by  $k^2$  and inverse Fourier transforming the product back to real space. The use of the Fast Fourier Transform in this procedure gives a quick and extremely accurate method. The choice of mesh is determined via the 'uncertainty relation', whereby the maximum momentum anticipated in the physical system is translated into the required mesh spacing. A similar relationship exists between the energy and the required simulation timestep. A method similar to this is described by Feit, Fleck and Steiger [7] and a very accurate scheme for fixed potential fields has been given by Tal-Ezer and Kosloff [8]. Some idea of the usefulness of these methods can be seen in the treatment of helium desorption from a tungsten surface by Kosloff and Cerjan [9] and the dynamics of a quantal electron in classical liquid KCl by Selloni et al. [10].

On the second day of the workshop the participants split into groups to investigate some nominated problems. This was to be the pattern for the remainder of the meeting, with morning sessions to report on progress and discuss new ideas. It was in one such group that Konrad Singer and I combined with Luc Lathouwers to derive the equations of motion for a system consisting of two diatomic molecules interacting via a Lennard-Jones type of potential. The reasons for considering this apparently simple model were twofold; firstly we were very keen to get a deeper understanding of the many-particle aspects of wavepackets and secondly, we wanted to investigate the effects of

correlation and the proposed model offered the best chance of being tractable. In fact we considered three variations of the model. In the first of these the wavefunction of the diatomic system was represented by a single correlated gaussian wavepacket of the form:

$$\Psi(\xi, t) = \exp(i\xi \cdot A(t) \cdot \xi + iP(t) \cdot \xi + iD(t))$$

in which  $\xi = (r-R(t))$  and  $r$ ,  $R$  are 12 component spatial vectors and  $A$  is a 12x12 matrix describing the shape and size of the component gaussian wavepackets and also the correlation between the four centres.  $P$  is a 12 component momentum vector and  $D$  a phase and normalisation parameter. In the second model the  $A$  matrix was simplified by insisting that the gaussian wavepacket on each centre be spherical, this reduced  $A$  to a 4x4 matrix. In the third model it was assumed that intermolecular correlation was negligible, this allowed a reduction of  $A$  to two 6x6 matrices, which could, if need be, be reduced to two 2x2 matrices if spherical gaussians were once again assumed. In all cases the correlation was handled by a Jastrow type of wavefunction; that is a term  $\lambda(t)[r_1-r_2]^2$  was included in the wavefunction exponent to reduce the probability of close encounters between particles. (This term is embedded in the definition of the matrix  $A$  above.) After some lengthy algebra and using the DFM principle mentioned above, the equations of motion of these systems were obtained. It is fair to say that they represent a large increase in complexity over previous applications of gaussian wavepackets to many-particle systems [11] and this suggests that correlated wavepackets may be too expensive to use in large systems. (We estimated the computational cost for the two simpler model above and compared it with a 108 particle simulation using spherical gaussian wavepackets. The estimates showed that the two diatomic molecule case was already the more expensive.) A more detailed analysis may yet show us that reductions in computation are possible, but the results so far obtained are not wholly encouraging. Nevertheless, we hope to continue this investigation in the near future.

While we were deriving the equations for the diatomic molecule dimer system, other groups were conducting investigations of their own into other aspects of wavepacket dynamics. One group, consisting of F. Arickx, M. Berman, H. Hensberg R. Kosloff, C. LeForestier and P. van Leuven studied the properties of a wavepacket represented by a combination of two gaussians:

$$\Psi(x, t) = N(t) \{ G_1(x, t) + [\alpha(t) + i\beta(t)] G_2(x, t) \}$$

where  $G_1$  and  $G_2$  are the gaussians,  $N(t)$  is the overall normalisation and phase factor and  $\alpha(t)$  and  $\beta(t)$  describe the relative phase and amplitude of the component gaussians. The equations of motion were derived using the DFM Principle. The application they considered was the collision of the wavepacket with a gaussian potential barrier, with the idea of investigating the splitting of the wavepacket for a range of starting conditions and barriers. This study was backed by an exact investigation of the phenomena using Kosloff's discrete method. In a limited study, the Kosloff method showed that the gaussians could represent the transmitted and reflected waves quite well, the difficulty was then to define suitable starting conditions for the double gaussian model. The obvious choices for the initial state led to mathematical instabilities. They settled upon a representation containing an incoming gaussian and its mirror image with respect to the potential.

An extension of this study to incorporate the Pauli exclusion principle (i.e. include the effects of (anti)symmetrisation) was also undertaken. The case of two identical particles interacting via a quadratic potential was considered. (In this system the centre-of-mass motion is separable from the relative motion.) Once again, the equations of motion were derived using the DFM Principle. It was hoped that a comparative study of the non-symmetrised model and the (anti)symmetrised model would provide insight into the physical effects of (anti)symmetrisation. So far they have found that exact solutions are possible for the (anti)symmetrised model (using the DFM procedure), just as they are for the corresponding non-symmetrised model. The study is continuing.

The second project Konrad Singer and I were involved with was an investigation of the collision between two wavepackets experiencing a mutual (gaussian) repulsion. Our collaborators in this were Ronnie Kosloff and Claude LeForestier. Several ways of modelling this system were available to us and we decided upon a scheme that would explore the accuracy of the different models, with the principal objective of discovering the regimes (quantum / semiclassical / classical) under which the different models became most appropriate. The models we considered were:

- discrete wavepackets with exchange
- discrete wavepackets without exchange (Hartree product)
- correlated gaussian (Jastrow type wavefunction)
- discrete wavepacket and gaussian wavepacket (Hartree product)
- two gaussian wavepackets (Hartree product)

In the time available to us we could not take the project beyond discussion, formulation and some inevitable algebra.

However we were able to begin to use the programs provided by Ronnie Kosloff for the models involving the discrete wavepackets. We are currently working on this programme and hope to provide some interesting results in the near future.

Another project that was being studied in the workshop involved R. Coalson, Bret Jackson and Luc Lathouwers. Theirs was a study of wavepacket propagation in a two-state model. In one model the dynamics of a wavepacket in a double well potential was considered. The existence of any possible state above this was ignored (the adiabatic model). In the second model the double well consisted of overlapping harmonic potentials with a coupling term between. In this case the existence of an excited state was built into the model (diabatic model). Using the Kosloff method the propagation of wavepackets at different energies, in both these models, could be determined. It was hoped that the study would reveal the nature of the breakdown of the adiabatic approximation.

A small group consisting of Michael Berman and Jan Broeckhove studied the use of Lie algebra and group theory in wavepacket problems. Their objective was to determine the correct algebra to describe the physics of wavepacket problems and gain insight into the nature of the approximations inherent in the time dependent variational (DFM) principle. (The method appears to be based on the quantum analogue of the Poisson Bracket formulation of classical mechanics [12].)

This summary cannot provide full description of the intellectual content of a meeting such as this. A great deal of activity occurred which has not been reported. This is due in part to the parallel sessions that occurred in the workshop, but also to the breadth of the applications discussed, which included material beyond the ken of at least one participant! However it is to be hoped that the flavour of the workshop has been conveyed. One of the virtues of a workshop such as this is that it brings together scientists from other disciplines and allows them to learn from each other. It was particularly helpful to me to talk and listen to Herman Hensberg, Luc Lathouwers, Piet van Leuven and Ronnie Kosloff and I am pleased to have this opportunity to thank them. It is also appropriate that I thank C. Moser and the CECAM organisation for creating the possibility of my participation in this workshop and also my first visit to the city of Paris!

### References

- [1] J. Broeckhove, L. Lathouwers and P. van Leuven (Editors), 'Dynamics of Wave Packets in Molecular and Nuclear Physics', Lecture Notes in Physics (256), Springer-Verlag, Berlin Heidelberg 1986.
- [2] E.J. Heller, J. Chem. Phys. v62 p1544 (1975) and v64 p63 (1976).
- [3] A.D. McLachlan, Molec. Phys. v8 p39 (1964).
- [4] S. Sawada, R. Heather, B. Jackson and H. Metiu, J. Chem. Phys. v83 p3009 (1985).
- [5] M. Berman, R.D. Levine, method described by M. Berman at workshop.
- [6] D. Kosloff and R. Kosloff, J. Comput. Phys. v52 p35 (1983).
- [7] M.D. Feit, J.A. Fleck and A. Steiger, J. Comput. Phys. v47 p412 (1982).
- [8] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. v81 p3967 (1984).
- [9] R. Kosloff and C. Cerjan, J. Chem. Phys. v81 p3722 (1984).
- [10] A. Selloni, P. Carnevali, R. Car, M. Parrinello, Report of the CECAM Meeting on "Quantum Simulation for Condensed Matter Systems" 12-15 May 1986.
- [11] K. Singer and W. Smith, Molec. Phys v57 p761 (1986).
- [12] H. Goldstein, "Classical Mechanics" Second edition, Addison Wesley 1980, p397.

# REPORT OF MEETING ON ADVANCED RESEARCH COMPUTING

HELD AT IMPERIAL COLLEGE ON 8 JULY 1986

D. Fincham

## 1. The Forty Report

Professor Forty described the recommendations of the Forty report, and subsequent developments. There ought to be

- more central super-computers
- enhancement of JANET
- specialised facilities distributed at key locations.

In the short term money has been found for

- improved front end at London, plus a second (second-hand) Cray 1S
- improved front end at Manchester, and compatibility with London
- enhancement of JANET
- a Cray XMP-48 at Atlas Centre, RAL.

A national Board for Advanced Research Computing will be set up, and will consider initially the development of the distributed computing initiative recommended by Forty, and a next generation super-computer at one of the four centres (London/Manchester/RAL/Daresbury) in 1990+.

The report also proposed the establishment of a Fellowship Scheme, and emphasised that Advanced Research Computing is a good vehicle for collaboration between industry and academia.

## 2. The Cray XMP-48

Dr. Robb (Cray Research) described the Cray XMP-48. It has 4 processors and 8 Megawords of memory. There will also be a 32 Megaword solid-state storage device (silicon disk) with a 1 Gigabyte/s channel. The four processors plus various other improvements will give an average performance of 6-10 times the Cray 1S.

It is possible to have separate processes running in the 4 processors, or one process distributed between them. Communication between processors is by registers and can be accessed via library routines callable from Fortran. Alternatively, in microtasking, successive iterations of a DO loop are distributed to the processors. This feature is controlled by compiler directives.

### 3. The Atlas Centre

Brian Davies (Head of Computing, SERC) described the plans for installation of the machine at the Atlas Centre. It is thought that the political problems will be overcome. The machine will be used by all research councils, but run by SERC. There will be 14.4 Gigabytes of disc, and the operating system will be COS. The front end will be the IBM 3081 K with VM/CMS. Formal acceptance will be during April 1987. JTMP will be available by delivery time. Thought will be given to VAX/VMS (enthusiastically supported by the audience) and Unix front ends, and to Cray Unix.

Current ideas on data set management are to provide each user with 6.4 Megawords of permanent space on Cray disc, and 32 Megawords (= 1 silicon disc) of scratch space. Magnetic tapes and Masstore communication will be via CMS minidisks. Current ideas on libraries include NAG (+ graphics) and GKS, and possibly Gino and Ghost.

Hardcopy local graphics are available now on the IBM. Local viewable graphics would be possible with an ES300 on the IBM. A VAX front end would provide further possibilities, and graphics workstations might be attached to the existing hyperchannel. Distributed viewable graphics might be possible between a VAX front end and remote VAX if Decnet could be "janetised". Suggestions would be welcome for 3D graphics packages.

There seems to have been little thought given yet to the scheduling of the Cray XMP48. The support staff of the Atlas Centre will be increased by four to support the Cray (two systems, two administration).

### 4. JANET

Dr. Linington described the JANET enhancements. £5 M will be spent over 3 years; 70% on LAN S and 30% on the wide area network. Objectives for the latter are

- reduce transit delay
- give predictable response
- allow bulk transfers at 50 kbits/s.

Most trunks will be upgraded from 48 kbits/s to 256 kbits/s, and switches will be upgraded as traffic growth demands. (Note: at 64 kbits/s one A4 page of characters takes 0.5 s; one frame of monochrome video takes 35 s.) Protocols available will be FTP, JTMP, Mail, SSMP (screen system protocol).

It is a goal to give common solutions at all National centres for

- the user interface
- the operating system
- graphics

## 5. Scientific Support

Professor Burke discussed the scientific support of advanced research computing. There is no extra money for this. Support for existing CCPs will continue to be based at Daresbury. Support for new application areas will be provided at the Atlas centre by means of secondments and fellowships. Possible new areas are

- Plasma and laser physics
- Nuclear and particle physics
- Earth Sciences
- Engineering
- Molecular biology, other than crystallography.

There will be attempts at promoting international collaboration.

The initiative on distributed computing is unfunded so far. However there are committees looking at the technical options (Spratt, Kent) and scientific possibilities (Wallace, Edinburgh).

## 6. Peer Review

Brian Davies described the procedures for peer review which will apply at all the national supercomputer centres from Sept. 86. (The present method of charging for time at ULCC will be dropped). The peer review will examine applications for scientific merit and computational soundness. There will be four types of application.

1. Two-three year programme subject to full Peer Review. Apply to Research Council in normal way BUT via the selected computer centre. (In SERC case this means fill in RG2 and AL54 forms).
2. Pump priming for potential applicants. Limited to 0.1 % of resources per applicant over 3 months. Apply direct to Director of selected computer centre.
3. Beginners (UMRCC and ULCC only). Up to 0.1 % of resources per applicant over 12 months. Apply to Director of selected centre via Director of local computer centre.
4. Industrial users on full repayment basis. Apply to Director.

There is no fixed allocation to particular research councils or subject areas. Each centre will have a Management Committee (and there will be an ad hoc national allocations committee) to resolve allocation problems and grievances. Technical information on the Cray XMP/48 can be obtained from P. Thomson, Atlas Centre.

D. Fincham.

The Molar Free Energy of Solids

K. Singer

The most general and oldest method for the calculation of the molar free energy (= the chemical potential) of liquids and solids by computer simulation is based on thermodynamic integration which relates the free energy of the target system to that of a reference system of known free energy

$$A_{ta} - A_{ref} = \int_0^1 V(\lambda) d\lambda \quad (1)$$

where V is the potential energy and

$$V(\lambda) = \lambda V_{ta} + (1 - \lambda) V_{ref} \quad (2)$$

In practice the integration is performed numerically by calculation of the mean potential energy at a sufficient number of  $\lambda$ -values between 0 and 1. If the reference and target potentials are very similar the integration may be replaced by first order thermodynamic perturbation theory:

$$A_{ta} - A_{ref} = \langle V_{ta} - V_{ref} \rangle_{ref} = \langle V(\lambda=1) - V(\lambda=0) \rangle_{\lambda=0} \quad (3)$$

where it is only necessary to evaluate the target potential energy at each step in a simulation of the reference system.

Frenkel and Ladd have recently proposed a useful method for the computation of the chemical potential of crystalline solids in which the reference system is the classical Einstein model, that is, a system of  $3N$  independent linear harmonic oscillators with equal frequency<sup>1</sup>.

The purpose of this note is to suggest a modification of this method which is suitable for continuous target potentials: the Einstein model is replaced by the potential commonly used in lattice dynamical calculations, i.e. by the Taylor expansion of the target potential up to second order

$$V(\underline{r}^N) = V(\underline{r}_0^N) + \sum_i^N (\underline{r}_i - \underline{r}_{0i}) \cdot \nabla_i V(\underline{r}^N = \underline{r}_0^N) + \frac{1}{2} \sum_{i \neq j}^N \sum_j^N \langle (\underline{r}_i - \underline{r}_{0i}) \cdot \nabla_i (\underline{r}_j - \underline{r}_{0j}) \cdot \nabla_j V(\underline{r}^N = \underline{r}_0^N) \rangle \quad (4)$$

where the first term on r.h.s. is the lattice energy ( $E_{latt}$ ); the second represents forces which vanish if  $\underline{r}_0^N$  represents particles situated at potential energy minima, and the third determines the matrix of force-constants

$\nabla \nabla V/m$ . The advantage of this reference potential is twofold:

1. It is much closer to the target system than a system of uncoupled oscillators; it is in fact an excellent approximation at low temperature.
2. The frequency spectrum obtained from the eigenvalues of the force-constant matrix yields the classical and quantum mechanical free energies and other thermodynamic properties in the harmonic approximation (ha) without computer simulation.

The similarity of the reference to the target potential makes the thermodynamic integration (1) 'short' and for a given computing effort much more accurate. The frequency spectrum obtained as square roots of the eigenvalues of the force-constant matrix determines the classical and quantum mechanical 'harmonic' free energies through the expressions

$$A_{cha} = E_{latt} - k_B T \sum_j 3N \log(\pi \omega_j / k_B T) \quad (*) \quad (5)$$

$$A_{qha} = E_{latt} + \sum_j \left( \frac{1}{2} \pi \omega_j + k_B T \log(1 - \exp(\pi \omega_j / k_B T)) \right) \quad (6)$$

[(\*) strictly speaking 3 degrees of freedom are translational, i.e.  $\omega_j = 0$  ( $j \leq 3$ )]

The corresponding formulae for the Einstein solid are

$$A_{cE} = E_{latt} - 3 N k_B T \log(\pi \omega_E / k_B T) \quad (7)$$

$$A_{qE} = E_{latt} + 1.5 N \pi \omega_E + 3 N k_B T \log(1 - \exp(\pi \omega_E / k_B T)) \quad (8)$$

All of this is well known, particularly to spectroscopists and practitioners of lattice dynamics. It may nevertheless surprise some readers that the calculation of all eigenvalues of the  $324 \times 324$  matrix which is required for 108 particles by 'brute force', i.e. without any factorisation on account of symmetry, is performed in only 1.5 seconds on the ULCC Cray 1 computer (by means of NAG routine F02AAF). Another point in favour of the reference potential (4) is that equation (6) in contrast to (8) becomes exact at sufficiently low temperature.

Table 1 illustrates the closeness of the LJ(12-6) system for solid (fcc) argon at 0.48 times the triple point temperature and the corresponding reference system (4). Here one MD (or MC) simulation with the potential  $V(\lambda=0.5)$  in (2) was used to determine  $\langle V(\lambda=1) \rangle = \langle V_{LJ} \rangle$  and  $V(\lambda=0) = \langle V_{ref} \rangle$ . The result from (3) was checked against a more accurate numerical integration based on MD runs at  $\lambda = 0, 0.25, 0.5, 0.75$  and 1.0. In these runs the classical Einstein energy was also calculated from

$$V_{cE} = E_{latt} + 1/2 \sum_i |\underline{r}_i - \underline{r}_{oi}|^2 \nabla^2 v.$$

Although this yields only a rough estimate, it is clear that  $\langle V_{LJ} - V_{cE} \rangle$  is by an order of magnitude larger than  $\langle V_{LJ} - V_{cha} \rangle$ .

Table 2 compares the cha and qha thermodynamic functions for solid LJ-argon at three temperatures. It is clear that even at 60 K the quantum effects in the free energy, energy and pressure are not negligible.

The results presented suggest the following conclusions.

The harmonic approximation (4) to the target potential is an obviously favourable choice as reference system in (1).

The exploration of phase equilibria by means of classical MC and MD methods is only realistic if quantum effects are small. Whether or not this is the case is easily tested by calculation of the cha- and qha- free energies and pressures via the eigenvalues of the force-constant matrix. If quantum effects are significant then the addition of the harmonic quantum correction i.e.  $A_{cta} + A_{qha} - A_{cha}$  is likely to be closer to the true value than the classical  $A_{cta}$ . (A harmonic quantum correction has been applied with success to the thermodynamic properties of even highly anharmonic systems such as liquid water<sup>2</sup>.)

Improvements of the harmonic quantum correction through calculation of anharmonic effects have been described<sup>3</sup>. It seems however preferable to go 'all the way' to the quantum mechanical system by means of path integral MC or quasi-MD simulation. There is some hope that here too the similarity of reference and target potentials will permit economies in the computation of the ratio of the partition functions

$$Q_{qta}/Q_{qha} = \frac{\int \dots \int \exp\{-\beta V_{ta}^{eff}(\underline{r}^{PN})\} \Pi_{i,t}^{N,P} d\underline{r}_{it}}{\int \dots \int \exp\{-\beta V_{ha}^{eff}(\underline{r}^{PN})\} \Pi_{j,s}^{N,P} d\underline{r}_{js}}$$

where the suffices i,j refer to quasi-molecules and t,s to 'beads' in the ring-polymers, and N and P are the corresponding maximum values.

These calculations are now in progress.

References

- 1 Frenkel and Ladd, 1984, J. Chem. Phys. 81 3188
- 2 Berens, Mackay, White and Wilson, 1983, J. Chem. Phys. 79 2375
- 3 Werthamer, 1970, Phys. Rev. B1 572

Table 1

Thermodynamic quantities for the calculation of the classical free energy

Lennard-Jones (12-6) parameters for argon:  $\epsilon/k_B = 119.8$  K,  
 $\sigma = 3.405 \times 10^{-10}$  m

$V_m = 23.0 \times 10^{-6} \text{ m}^3$ ,  $T = 40.0$  K  $E_{\text{latt}} = -8478$  J/mole

$\langle V_{\text{LJ}} \rangle$	$\langle V_{\text{cha}} \rangle$	$\langle \Delta V \rangle$	$A_{\text{cha}}$	$A_{\text{LJ}}$	$\langle V_{\text{cE}} \rangle$	$A_{\text{cE}}$
-8008	-7980	-27	-8177	-8204	-8390	-8590 (J/mol)

$\langle V_{\text{LJ}} \rangle = \langle V(\lambda=1) \rangle$  and  $\langle V_{\text{cha}} \rangle = V(\lambda=0)$  (and  $\langle V_{\text{cE}} \rangle$ ) were evaluated in a MD run with  $V(\lambda=0.5)$ ;  $A_{\text{cLJ}} = A_{\text{cha}}$  (eq. 5) +  $\langle \Delta V \rangle$ ;  $\langle \Delta V \rangle = \langle V(\lambda=1) - V(\lambda=0) \rangle_{\lambda=0.5}$ ;  $A_{\text{cE}} \cong A_{\text{cha}} + (\langle V_{\text{cE}} \rangle - \langle V_{\text{cha}} \rangle)_{\lambda=0.5}$

Table 2

Harmonic approximation to classical and quantum mechanical quantities

Lennard-Jones potential as in Table 1;  $V_m = 23.0 \times 10^{-6} \text{ m}^3$

T/K	$A_{\text{cE}}$	<sup>1)</sup> $A_{\text{cha}}$	<sup>2)</sup> $A_{\text{qha}}$	<sup>3)</sup> $E_{\text{cha}}$	$E_{\text{qha}}$	$P_{\text{cha}}$ Mpa	$P_{\text{qha}}$	$c_{\text{cha}}$ J/k	$c_{\text{qha}}$
20.0	-8940	-7972	-7804	-7979	-7657	-68	-1	24.9	13.8
40.0	-8718	-8177	-7931	-7481	-7151	-1	23	24.9	21.4
60.0	-8588	-8475	-8416	-6982	-6707	59	82	24.9	23.5

$p$  = pressure obtained from  $-\delta A / \delta V_m$  numerically;  $c$  = molar heat capacity.

1) eq. (7) with  $\omega_E = \omega_{\text{max}}$  (clearly not an optimal choice)

2) eq. (5)

3) eq. (6)

## Simulated annealing of atomic clusters.

L. Wille

### 1. Introduction.

The structure and stability of small aggregates of atoms is a very active field of research, both theoretically and experimentally [1]. These objects, intermediate between atoms and solids, have very peculiar properties, such as the predominance of fivefold symmetry, photoyield enhancement, Coulomb explosions, magic numbers, etc. Apart from their intrinsic interest, cluster studies are important in nucleation theory, catalysis, astrophysics, etc. The existence of magic numbers, corresponding to extremely stable sphere packings, was first established for Xe clusters [2]. It was observed that clusters consisting of  $N = 13, 19, 23, 25, \dots$  atoms showed up much more prominently in the mass spectrum than neighbouring cluster sizes.

Computer modelling has usually assumed that the interaction between rare-gas atoms could be described by a two-body Lennard-Jones potential. Three-body interactions have been considered for other systems [3], but are generally believed to be negligible for rare-gas clusters. Before observation in a time-of-flight mass spectrometer the clusters are ionised by a pulsed electron beam and it could therefore be that the magic numbers reflect the stability of positively charged clusters rather than neutral ones. This possibility has been investigated in several studies ([4] and references therein).

Extensive calculations of the morphology and statistical properties of rare-gas clusters have been performed by Hoare and co-workers [5-9]. Originally, this work focused on polyhedral growth sequences [5-7], and reference [5] contains a list of minimum energy configurations within the different growth schemes, which has been the basis for comparison with later work. Later an almost exhaustive search of the potential energy surface was made for the smaller clusters ( $N \leq 13$ ) [8-9]. The possibility of a polyicosahedral growth scheme was first investigated by Farges et al [10-12]. This model of interpenetrating icosahedra led to the prediction of a new structure consisting of 23 atoms [11] with an energy lower than the configuration found by Hoare and Pal [5]. In the course of a quantum Monte Carlo calculation, Freeman and Doll [13],

discovered a new (classical) 17 particle structure, lower in energy than the one reported in reference [5]. The energy difference is marginal and no particularly stable structure results.

In summary, in the size range considered in this note ( $4 \leq N \leq 25$ ), the minimum energy configurations, known so far, are those obtained by Hoare and Pal [5], except for the cases  $N = 23$  [11] and  $N = 17$  [13]. It should also be pointed out that the magic number  $N = 22$ , observed by Echt et al [5], can not be explained in terms of the stability of a neutral cluster. However, calculations for charged clusters predict that the formation of a molecular dimer ion produces a very stable 25 atom structure [4]. In this note a new minimum energy configuration for twenty-four atoms will be discussed; a fuller account is being submitted for publication.

## 2. Method and results.

Originally formulated for discrete optimisation problems, the simulated annealing method [14] is easily extended to deal with continuous ones as well [15-17], and it is this version that will be briefly described here (an overview of the method and its applications has been given in a recent issue of this newsletter [18]). Consider the potential energy to be minimised as  $E(\underline{r}_1, \dots, \underline{r}_N)$  where the  $\underline{r}_i$ , ( $i = 1, \dots, N$ ) are the positions of the particles. The simulated annealing method uses the Metropolis prescription [19] to decide whether or not to accept a random step  $\Delta \underline{r}_i$ ,  $i = 1, \dots, N$ . If the associated energy change

$$\Delta E = E(\underline{r}_1, \dots, \underline{r}_i + \Delta \underline{r}_i, \dots, \underline{r}_N) - E(\underline{r}_1, \dots, \underline{r}_i, \dots, \underline{r}_N) \quad (1)$$

is negative or zero, the step is accepted, otherwise it is accepted with a probability

$$p = \exp(-\Delta E/T) \quad (2)$$

where  $T$  is the temperature (in reduced units). In this way potential energy barriers can be surmounted (at sufficiently high temperatures), i.e. the algorithm is not confined to a single catchment region. In the process of annealing, the system is started in a random initial configuration at a sufficiently high temperature. Several series of steps are attempted and then the temperature is reduced by a certain factor  $\chi_T$  (typically 0.75-0.9). This process is repeated until no further improvements have been made over a number of iterations.

In the present work the initial temperature was taken from a short preliminary simulation and the step length was adjusted so that between 25 % and 50 % of the steps were accepted. The best results were obtained by taking the number of steps proportional to  $(1 - \ln T)$ , i.e. more steps were attempted at lower temperatures. The factor  $\chi_T$  by which the temperature was reduced was 0.9. As soon as the energy dropped below a certain value (also taken from a preliminary simulation) a gradient optimiser was called. Finally the whole process was repeated a number of times for each cluster size  $N$ . This precaution was taken because it was found in previous work [16] that in spite of slow cooling, trapping in low-lying local minima can still occur. In fact, it is important to note that these calculations are not simulations of the freezing of clusters. To this end, the cooling, characterised by  $\chi_T$  and the number of attempted steps, would have to proceed even more slowly. The freezing process could be monitored by looking at the specific heat [14,16], defined as

$$C(T) = T^{-2} ( \langle E^2 \rangle - \langle E \rangle^2 ) \quad (3)$$

where the brackets denote an average over all attempted steps. A large value of  $C$  signals a change in the state of order of the system and can be used as an indication that freezing has begun. In the author's experience, it is computationally more efficient (especially for the larger clusters) to use several runs with a relatively fast cooling as described above (in conjunction with a gradient optimiser) rather than perform a true Monte Carlo simulation of freezing. An additional advantage of using a fairly fast cooling rate is that the algorithm will find low-lying local minima as well. In many physical problems one is not merely interested in the ground state configuration but also in nearby excited states. By determining a certain cooling rate and a threshold value, below which a local minimisation is performed, one selects in fact an energy range in which the algorithm will search for minima. A final feature of the present calculations is that for the smaller cluster sizes ( $4 \leq N \leq 13$ ) one of the atoms was kept in a fixed central position, to eliminate translational degrees of freedom, and for the larger ones ( $14 \leq N \leq 25$ ) thirteen atoms were kept in a central icosahedral environment. The latter calculations were checked against simulations where all atoms (except the central one) were allowed to move and turned out to be in full agreement.

This algorithm has been used to search the potential energy surfaces of atomic clusters held together by two-body forces derived from a Lennard-Jones potential :

$$V(r) = r^{-12} - 2r^{-6} \quad (4)$$

This potential has a minimum energy of -1 at a distance  $r = 1$  which determines the energy and length units that will be used subsequently. In the size range  $4 \leq N \leq 25$  only one new global minimum has been found ( $N = 24$ ) and it turns out that the corresponding structure fits in the polyicosahedral growth scheme developed by Farges et al [11]. This global minimum and a local one very close in energy will be discussed in the remainder of this note.

The twenty-three atom structure obtained by the simulated annealing algorithm (Fig. 1) consists of two interpenetrating icosahedra and was first discussed by Farges et al [11]. Its binding energy is 92.844, considerably higher than 90.647 for the dodecahedral model considered by Hoare and Pal [5]. For twenty-four atoms two minima close in energy were found; the binding energies are 97.349 and 97.313 respectively. Both improve on a tetrahedral model with an energy of 96.514, obtained by Hoare and Pal [5]. The corresponding structures are shown in Fig. 2 and turn out to consist of the previously discussed twenty-three atom cluster with an additional surface atom in a fourfold site. The model in Fig. 1 contains only two types of non-equivalent fourfold hollow sites (indicated in heavy outline). The highest binding energy corresponds to an atom in the site labelled A; the local coordination of the two sites (before relaxation) is the same, but an atom in the A-site will be closer to the centre of gravity of the structure, hence the small energy difference. Finally for twenty-five atoms the algorithm found the structure shown in Fig. 3. Its energy is 102.37, and it has previously been obtained by Hoare and Pal [5] within the tetrahedral growth scheme. As can be seen, that model can be derived from the twenty-four atom one by adding an atom in one of the fourfold hollow A-sites.

### 3. Conclusions:

The simulated annealing method has been used to determine low-lying minima on the potential energy surfaces of atomic clusters with up to twenty-five atoms. Two new minima have been found for a twenty-four atom cluster; both structures are an intermediate step between a previously obtained twenty-three atom model (in the polyicosahedral growth scheme) and a twenty-five atom one (in the tetrahedral growth scheme). All other known global minima have been reproduced as well as a number of local ones, some of which appear to be new and will be discussed elsewhere. This illustrates convincingly that simulated annealing is a

powerful method for molecular geometry optimisation. It is important to note that the method is not restricted to two-body forces, but can be extended to deal with fully quantum mechanical Hamiltonians, along the same lines as in Car and Parrinello [20].

#### References.

- [1] K. H. Benneman and J. Koutecky (eds.), Surf. Sci. 156 (1985).
- [2] O. Echt, K. Sattler and E. Recknagel, Phys. Rev. Lett. 47 (1981) 1121.
- [3] I. L. Garzon and E. Blaisten-Barojas, Chem. Phys. Lett. 124 (1986) 84.
- [4] J. J. Saenz, J. M. Soler and N. Garcia, Chem. Phys. Lett. 114 (1985) 15.
- [5] M. R. Hoare and P. Pal, Adv. Phys. 20 (1971) 161.
- [6] M. R. Hoare and P. Pal, J. Cryst. Growth 17 (1972) 77.
- [7] M. R. Hoare and P. Pal, Adv. Phys. 24 (1975) 645.
- [8] M. R. Hoare and J. McInnes, Faraday Discuss. Chem. Soc. 61 (1976) 12.
- [9] M. R. Hoare and J. McInnes, Adv. Phys. 32 (1983) 791.
- [10] J. Farges, M. F. de Feraudy, B. Raoult and G. Torchet, J. Chem. Phys. 78 (1983) 5067.
- [11] J. Farges, M. F. de Feraudy, B. Raoult and G. Torchet, Surf. Sci. 156 (1985) 370.
- [12] J. Farges, M. F. de Feraudy, B. Raoult and G. Torchet, J. Chem. Phys. 84 (1986) 3491.
- [13] D. L. Freeman and J. D. Doll, J. Chem. Phys. 82 (1985) 462.
- [14] S. Kirkpatrick, C. D. Gellat and M. P. Vecchi, Science 220 (1983) 671.
- [15] D. Vanderbilt and S. G. Louie, J. Comp. Phys. 56 (1984) 259.

- [16] L. T. Wille and J. Vennik, J. Phys. A: Math. Gen. 18 (1985) L1113; Corrigendum 19 (1986) 1983.
- [17] L. T. Wille, Nature (accepted for publication).
- [18] L. T. Wille, CCP5 Information Quarterly 20 (1986) 19.
- [19] N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller and E. Teller, J. Chem. Phys. 21 (1953) 1087.
- [20] R. Car and M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471.

#### Figure captions.

Fig. 1. Twenty-three atom cluster consisting of three interpenetrating icosahedra. The structure contains two types of fourfold hollow sites, two of which are shaded and labelled A and B.

Fig. 2. Twenty-four atom clusters found in the present work. They consist of the N=23 model with an additional atom (shaded) in one of the fourfold hollow sites. The two pentagonal caps are also outlined.

(a) additional atom in A-site, binding energy 97.349.

(b) additional atom in B-site, binding energy 97.313.

Fig. 3. Twenty-five atom cluster obtained by adding a further atom to an A-site. The basic structure is the same as in Fig. 1, but it has been rotated slightly to bring the two extra atoms (shaded) to the foreground.

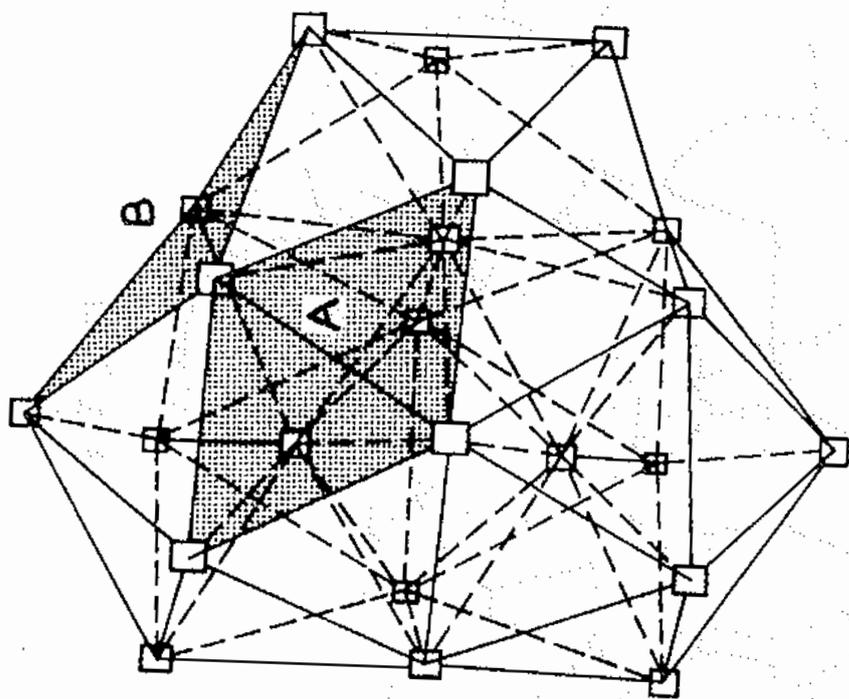


Fig.1

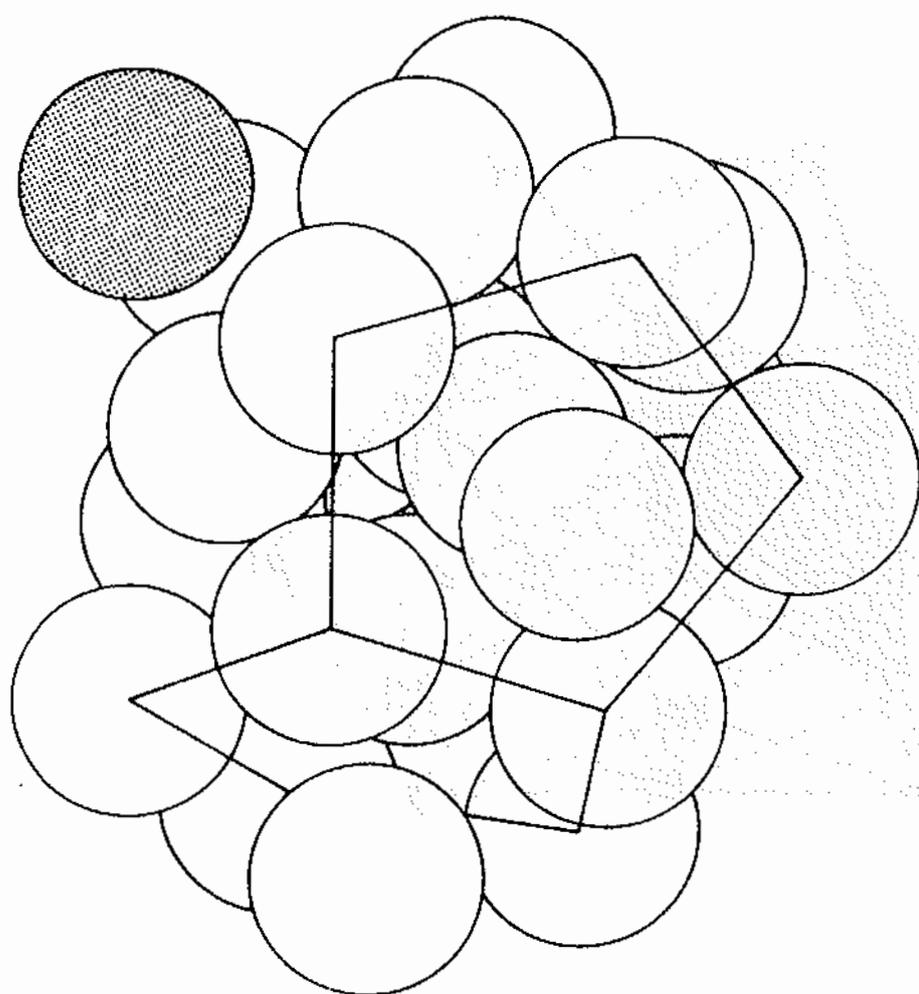


Fig. 2(a)

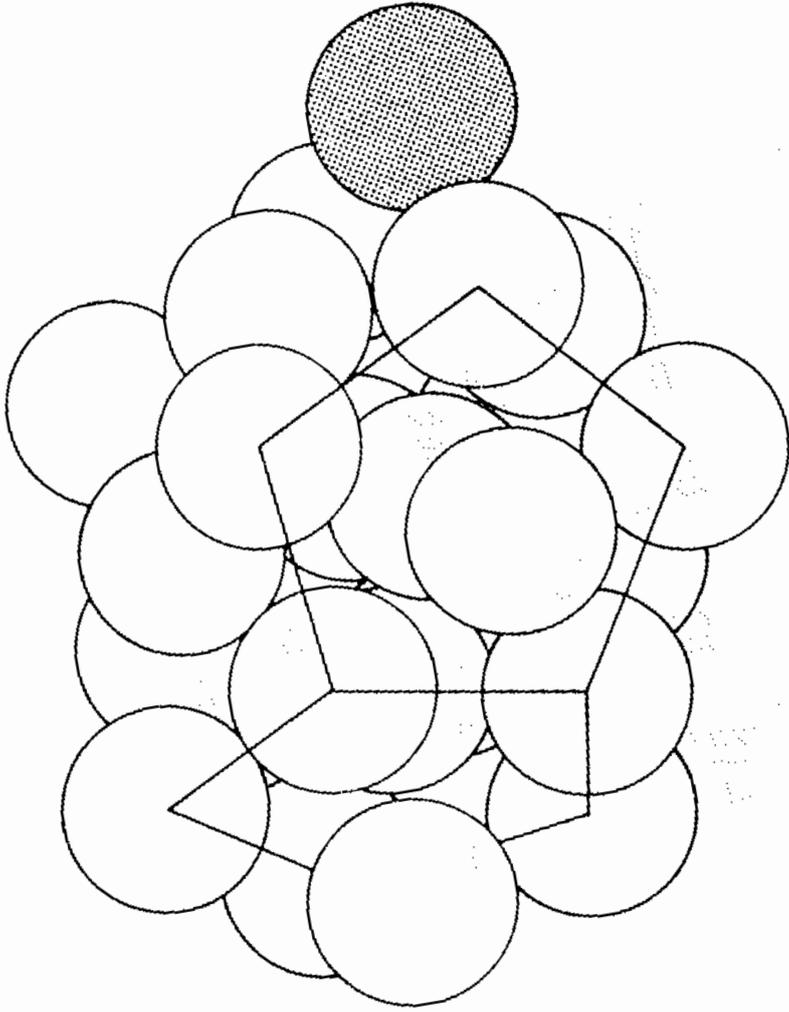


Fig. 2(b)

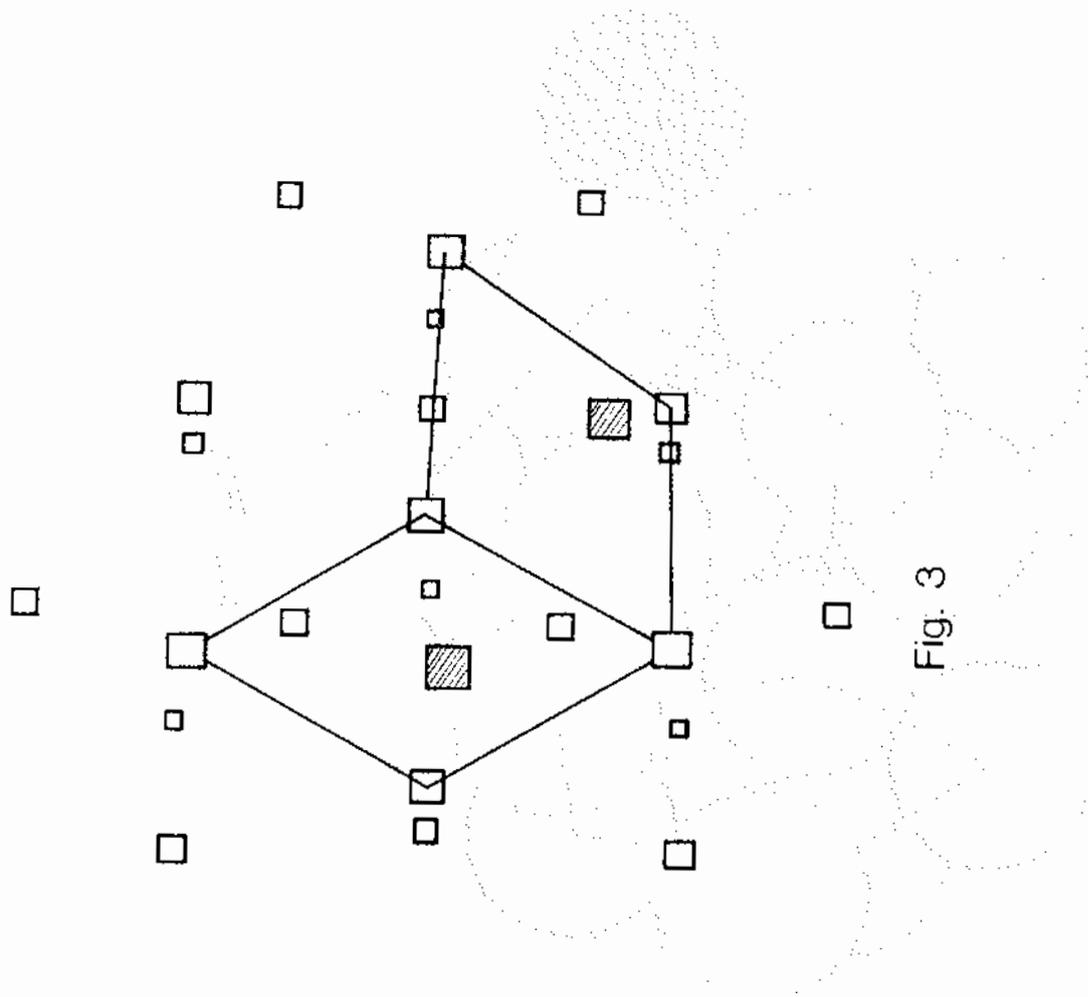


Fig. 3

Periodic boundary conditions are a vital part of simulation technique: they enable a very small volume of material to behave as though it was inside and part of a very large volume of the material. The problem is to calculate the potential of a system of charges in the periodic cell. The best method of calculating the potential is due to Ewald, and so the electrostatic energy of a periodic system has become known as the Ewald potential. The expression derived by Ewald is rather forbidding, requiring as it does two infinite summations, one in real space and the other in reciprocal lattice space. Nonetheless, this is the method now used routinely in molecular dynamics and Monte Carlo programs, as described by many articles in this journal and elsewhere.

There are three alternatives to a direct evaluation. One is to work out the Ewald potential in advance and tabulate it [1,2]. This may well improve the efficiency of the program, but it is more rather than less complicated to program. A second method is Hockney's P<sup>3</sup>M method, which is a very substantial package indeed [3]. The third and simplest approach, long known to those interested in the One Component Plasma [4-6], is to write the Ewald sum in terms of an effective pair potential. There are four terms, though the last is an infinite sum, alas:

$$\psi(r) = 1/r + S + A_2 r^2 + \sum \{ \text{non-singular solutions to Laplace's Eqn.} \} \quad (1)$$

The potential is continuous and differentiable so that expressions for forces, field gradients, etc., are easily obtained. Note that it is essential that the effective pair potential is summed over the nearest image of every charge in the periodic cell, no truncation or cut-off allowed. The total electrostatic energy of a periodic cell containing N point charges is

$$U = \frac{1}{2} \sum_{i=1}^N q_i^2 S + \sum_{i=1}^{N-1} q_i \sum_{j>i}^N q_j \psi(\underline{r}_{ij}) \quad (2)$$

where  $\underline{r}_{ij}$  is the vector between  $q_i$  and the nearest image of  $q_j$ .

The first term in eqn. (1) is the direct Coulombic interaction between the charges,  $1/r$ . Thus the "Nearest Image" or "Minimum Image" summation is the leading term in the full Ewald potential.

The second term in eqn. (1), S, is a constant, the "self term". This term also occurs as the interaction energy of a single charge with its own periodic images, hence the name. If the system of charges in a cell is electrically neutral, which is usually the case, then the terms in S cancel when summed over all interactions, eqn. (2). That is, for most purposes S can be omitted from eqns. (1) and (2).

The third term in eqn. (1),  $A_2 r^2$ , is the only term which is not a solution of Laplace's equation. In order to have an unconditionally convergent sum each charge is considered to be accompanied by a neutralizing charge cloud uniform over the cell containing the charge. The  $r^2$  term is the interaction of one charge with the charge cloud of the other, it is a solution of Poisson's equation.

The simplest acceptable approximation to the Ewald potential is to omit the fourth term altogether. The exact value of  $A_2$  is  $2\pi/3V$  where  $V$  is the cell volume, but this may be altered for a better fit. For simple cubic periodic boundary conditions the value  $A_2 = 1.38306/V$  gives a twofold reduction in the RMS error. With truncated-octahedral PBC the exact value gives a fit close to the optimum. The simple, isotropic approximation

$$\psi_2 = 1/r + S + 1.38306 r^2/V \quad (3)$$

is suitable for systems of low charge density, for example a non-polar molecule modelled with a distribution of point charges. Better isotropic approximations, not of the form of eqn. (1), can be devised which have a much smaller RMS error than eqn. (3) and are suitable for the same sort of application, that is, systems for which one would not consider using a direct evaluation of the Ewald summation. For simple cubic PBC we recommend [7]

$$\psi(r) = 1/r + S + 2.75022r^2 - 2.94414r^4 + 0.86910r^6 \quad (4)$$

where the coefficients are for  $V = 1$ . The truncated octahedral PBC version of this is

$$\psi(r) = 1/r + S + 3.53873r^2 + 8.33958r^4 - 28.51289r^6 \quad (5)$$

these value of coefficients apply for the truncated octahedron which fits into a unit cube, and thus has  $V = \frac{1}{2}$ .

For cases where an Ewald sum is considered necessary, that is, where eqns. (3-5) are not sufficiently accurate, then the expansion of the Ewald potential in solutions of Laplace's equation can be used. The periodic boundary conditions have cubic symmetry, whether they are simple cubic, truncated octahedral [8] or rhombic dodecahedral, and we must use polynomials with the same symmetry. The first few of these polynomials are quite simple. There is one at each even power from four to ten. They are called Kubic Harmonics [9]:

$$\begin{aligned} KH4 &= T_4 - \frac{3}{5} r^4 \\ KH6 &= T_6 - \frac{15}{11} r^2 T_4 + \frac{30}{77} r^6 \\ KH8 &= T_8 - \frac{28}{15} r^2 T_6 + \frac{14}{13} r^4 T_4 - \frac{7}{39} r^8 \\ KH10 &= T_{10} - \frac{49}{19} r^2 T_8 + \frac{630}{323} r^4 T_6 - \frac{210}{323} r^6 T_4 + \frac{252}{3553} r^{10} \end{aligned}$$

where

$$T_n = x^n + y^n + z^n.$$

We have set out a complete list up to power twenty elsewhere [7]. These first few Kubic Harmonics are simple combinations of Legendre Polynomials,

$$KH_n = P_n(x) + P_n(y) + P_n(z),$$

but at power twelve there is a second solution to Laplace's equation which contains the "cross term"  $(xyz)^4$ . However, for  $n < 10$  we have

$$\psi_n = 1/r + S + A_2 r^2 + \sum_{n=4,6,\dots} A_n KH_n(r) \quad (6)$$

Equation (6) is the most economical formula, in terms of length of code versus accuracy, that we have been able to find to approximate the Ewald potential, except that truncation at  $n=4$  is not recommended as the isotropic approximations, eqns. (4,5), are shorter and have comparable accuracy.

Equation (1) is exact and the Ewald potential can be given to any desired accuracy simply by including a sufficient number of terms. In practice it is better to optimise the values of the coefficients  $A_n$  for a given truncation rather than use the correct values. Tables I and II give our optimized coefficients, together with the RMS error resulting, for simple cubic and truncated octahedral PBC respectively. For simple cubic PBC the improvement on optimising the coefficients is considerable. However, optimised coefficients with truncated octahedral PBC give the least error for given length of code and should be used if possible.

Our impetus for using this approach to the Ewald sum is the ease of implementing it on the DAP computer. Clearly, it is easily implemented on vector processors such as the Cyber 205 or the Cray. A nice feature of the Cyber 205 is a fast hardware square root for obtaining the  $1/r$  term. With this approach to the Ewald sum there are no fiddly parameters or number-of-vectors to be adjusted. The only decision is the level of approximation to be used, and as the error decreases rapidly as higher terms are added, it ought to be a simple decision to make. For most purposes  $\psi_{10}$  should be accurate enough, though one study of the OCP used terms up to the twenty second power [6]!

$\psi_n(r)$  is easily differentiated to obtain the necessary expression for the force. A second differentiation gives an expression for the electric field of a system of point dipoles. The terms in this are identical with those in Ladd's summation [10]. The coefficients he gives are the exact values, our optimised coefficients should give more rapid convergence. Note that the  $A_2 r^2$  term in (1) gives the term  $-2A_2 \mu_i \cdot \mu_j$  in the effective pair potential between two point dipoles. This term is important in its effect on dielectric properties [7], it is missing in Ladd's summation.

To summarize: we have described a much simpler representation of the Ewald summation for use in Monte Carlo and molecular dynamics programs. Where an Ewald summation is inappropriate but charges are present, such as a fractional-charge model of a quadrupolar or octopolar molecule, then even simpler isotropic approximations may be used. These should give an improvement over a conventional spherical truncation at very moderate cost. The only important case where these methods cannot be used is the molecular dynamics of charged systems using variable cell shape. An Ewald sum using any method is expensive when the system is very large, this is so in the present case because the effective potential has to be summed over all pairs of particles in the periodic cell. This problem may be amenable to further investigation.

## REFERENCES

- [1] M.J.L. Sangster and M. Dixon, *Adv. Phys.*, 25, 247 (1976).
- [2] H. L. Helfer, R. L. McCrory and H. M. van Horn, *J. Stat. Phys.*, 37, 577 (1984).
- [3] R. W. Hockney and J. W. Eastwood, "Computer simulation using particles", McGraw-Hill (1981).
- [4] S. G. Brush, H. L. Sahlin and E. Teller, *J. Chem. Phys.*, 45, 2102 (1966).
- [5] J. - P. Hansen, *Phys. Rev.*, A8, 3096 (1973).
- [6] W. L. Slattery, G. D. Doolen and H. E. DeWitt, *Phys. Rev.*, A21, 2087 (1980).
- [7] D. J. Adams and G. S. Dubey, submitted to *J. Comput. Phys.*
- [8] D. J. Adams, *CCP5 Newsletter* 10, 30 (1983).
- [9] F. C. von der Lage and H.A. Bethe, *Phys. Rev.* 71, 612 (1947).
- [10] A.J.C. Ladd, *Molec. Phys.*, 33, 1039 (1977), *Ibid* 36, 461 (1978).

TABLE I Optimised coefficients for eqn.(6) using simple cubic PBC.

Coefficient	n = 8	n = 10
S	-2.8373	-2.8373
A <sub>2</sub>	2.0944	2.0944
A <sub>4</sub>	7.5113	7.7045
A <sub>6</sub>	17.0716	20.5633
A <sub>8</sub>	60.5399	86.4240
A <sub>10</sub>		181.0800
RMS Error	$2.4 \times 10^{-3}$	$6.2 \times 10^{-4}$

TABLE II Optimised coefficients for eqn.(6) using truncated octahedral PBC

Coefficient	n = 6	n = 8	n = 10
S	-3.6392	-3.6392	-3.6392
A <sub>2</sub>	4.1888	4.1888	4.1888
A <sub>4</sub>	-7.7620	-7.5960	-7.7762
A <sub>6</sub>	194.329	199.285	207.362
A <sub>8</sub>		208.641	251.058
A <sub>10</sub>			-2680.16
RMS Error	$4 \times 10^{-3}$	$1.3 \times 10^{-3}$	$3.3 \times 10^{-4}$

## CALCULATING ORIENTATIONAL ORDER IN MD SIMULATIONS

W. Smith

### Introduction

One of the interesting properties of molecular materials which one may wish to investigate by MD is the orientational order. Two examples which spring quickly to mind are the structures of liquid crystals and the orientations of molecular ions in ionic crystals. My intention here is to describe a simple way of determining the order parameters that characterise the orientational order. I cannot say if this is the best way of doing things but I hope that readers more familiar with the calculation of order parameters will be encouraged to submit accounts of their own methods.

### Theory

The first step in describing the orientational order is to define a convenient set of vectors that characterise the orientation of each molecule. The simplest set of vectors one can envisage are unit vectors along the principal axes of the molecule. Another convenient set, especially for simple molecules with a high degree of symmetry, are the unit vectors aligned along the atom-atom bonds. (Initially however, I assume that the molecules possess no symmetry; any symmetry present can be exploited later.) They are, of course, regarded as fixed in the frame of the molecule associated with them. In the laboratory frame these vectors rotate or oscillate with the motion of the molecule.

Taking each vector in turn, it is possible to define a probability density function  $P(\theta, \phi)$ , which determines the probability of finding the vector in the angular direction given by the angle pair  $(\theta, \phi)$ . The orientational order parameters arise from an expansion of the orientational probability density function in terms of standard spherical harmonics:

$$P(\theta, \phi) = \sum_L \sum_m \langle Y_{Lm} \rangle Y_{Lm}(\theta, \phi) \quad \langle 1 \rangle$$

where the  $\langle Y_{Lm} \rangle$  functions represent the orientational order parameters and  $Y_{Lm}(\theta, \phi)$  the spherical harmonics. As is well known from the properties of spherical harmonics the index  $L$  ranges from 0 to infinity (or some arbitrary large value) and the absolute value of  $m$  is always less than or equal to index  $L$  [1]. It is important to realise that the expansion is in the laboratory reference frame. Two points are worth making about this expansion.

Firstly, the expansion is most conveniently handled mathematically using the COMPLEX representation of the spherical harmonics, but I suspect that most chemists prefer to use a representation in which each spherical harmonic is combined with its complex conjugate to produce two REAL harmonics (c.f. the familiar s, p, d, ...etc. -type orbitals arising in the Schroedinger solution for the hydrogen atom). This REAL representation shows the orientational properties of the functions more clearly and for this reason I assume henceforth that the expansion refers to the REAL form.

Secondly, this expansion, while being generally applicable, may not always be the most convenient. In cases where one is dealing with molecules of (say) cubic symmetry and these are located in crystals with cubic symmetry, then as an alternative, special combinations of spherical harmonics, known as KUBIC harmonics [2] are more appropriate. The principles of calculating the order parameters are the same as those given here, but the details of the analysis are different.

The calculation of the order parameters  $\langle Y_{Lm} \rangle$  is simple enough in principle. At regular intervals in the MD simulation the value of each function  $Y_{Lm}(\theta, \phi)$  is calculated for each unit vector and added to an accumulator. At the end of the simulation the average over timesteps (i.e. configurations) and over all the molecules is calculated; this gives the order parameter  $\langle Y_{Lm} \rangle$  for each unit vector. If the molecule possesses symmetry, then some of the unit vectors may be equivalent. In this case the order parameters may be obtained by averaging over these equivalent vectors as well.

The reasoning behind this method is easy to see if one considers a simple case. If we imagine a unit vector constrained always to point along the positive z-axis (in the laboratory reference frame) the spherical harmonics which have nonzero projections along the z-axis will obviously give rise to nonzero order parameters. Spherical harmonics which have a zero projection along the z-axis must necessarily have zero order parameters. Thus if we looked at the complete set of order parameters, we would find that the parameters  $\langle s \rangle$ ,  $\langle p_z \rangle$ ,  $\langle d_{z^2} \rangle$ ,  $\langle f_{z^3} \rangle$ ...etc. would have significant values, while the  $\langle p_x \rangle$ ,  $\langle p_y \rangle$ ,  $\langle d_{xy} \rangle$ ,  $\langle d_{x^2-y^2} \rangle$ ...etc. parameters would have negligible values. If on the other hand for half of the molecules the vector always pointed along the positive z-axis and half always pointed along the negative z-axis, the  $\langle p_z \rangle$  and  $\langle f_{z^3} \rangle$  parameters would now average out to zero, since their projections along the positive and negative z-axis have opposite signs. In

this way, the order parameters betray the preferred orientations of the vector. In real systems, the orientational ordering is more dynamic in nature and this kind of analysis is much more difficult, but in these cases a two dimensional plot, or contour map, of the function  $P(\theta, \phi)$  using the calculated order parameters and the spherical harmonic expansion, can be very revealing [3].

The main difficulty with calculating the orientational order parameters lies in the calculation of the spherical harmonics. The explicit expressions for the spherical harmonics are, to say the least, cumbersome and one would not wish to use them for values of  $L$  beyond 2 or 3. (In practice values beyond 12 may be needed to get reasonable representations of the function  $P(\theta, \phi)$  [3].) The rest of this note describes a method of calculating the spherical harmonics efficiently with what is hopefully reasonable accuracy and minimum fuss.

#### Calculation of the Spherical Harmonics

The spherical harmonics (in the COMPLEX representation) may be written as:

$$Y_{Lm}(\theta, \phi) = N_{Lm} \cdot J_{Lm}(\cos\theta) \cdot K_m(\theta, \phi) \quad \langle 2 \rangle$$

The three terms appearing have the following forms:

$$N_{Lm} = ((2L+1)(L-M)! / (2(L+M)!))^{1/2}$$

$$J_{Lm}(\cos\theta) = \frac{1}{2^L L!} \frac{d^{L+M}}{(d \cos\theta)^{L+M}} (\cos^2\theta - 1)^L$$

$$K_m(\theta, \phi) = (2\pi)^{1/2} \sin^M\theta \cdot \exp(im\phi)$$

where  $M = \text{ABS}(m)$ .

The terms  $N_{Lm}$  represent the normalisation constants of the spherical harmonics. They need only be calculate once in the course of a given simulation. The functions  $J_{Lm}(\cos\theta)$  resemble the associated Legendre polynomials, except that the  $\sin^M\theta$  part is split off. The functions  $K_m(\theta, \phi)$  carry the  $\phi$  dependence of the spherical harmonic. This is not the usual representation as it contains the  $\sin^M\theta$  part from the associated Legendre polynomial. This shift of the sine function is needed to facilitate a convenient REAL representation of the spherical harmonics.

The  $J_{Lm}(\cos\theta)$  terms may be efficiently evaluated using recurrence relations. The first recurrence relation applies

when  $m=0$ . In this case the  $J_{L0}$  functions are Legendre polynomials, which have the well-known recurrence relation [4]:

$$J_{(L+1)0}(z) = ((2L+1) \cdot z \cdot J_{L0}(z) - L \cdot J_{(L-1)0}(z)) / (L+1)$$

or:

$$J_{L0}(z) = ((2L-1) \cdot z \cdot J_{(L-1)0}(z) - (L-1) \cdot J_{(L-2)0}(z)) / L \quad \langle R1 \rangle$$

in which the substitution  $z = \cos \theta$  has been used. A second recurrence relation may be obtained as follows.

Writing  $z = \cos \theta$ ,  $d^{L+M}/dz^{L+M} = D^{L+M}$  and  $M = \text{ABS}(m)$  then:

$$\begin{aligned} J_{Lm}(z) &= D^{L+M} (z^2-1)^L / (2^L L!) \\ &= D^{L+M-1} \cdot D^1 (z^2-1)^L / (2^L L!) \\ &= D^{L+M-1} \cdot (2Lz(z^2-1)^{L-1}) / (2^L L!) \\ &= (z D^{L+M-1} (z^2-1)^{L-1} + (L+M-1) D^{L+M-2} (z^2-1)^{L-1}) \\ &\quad / (2^{L-1} (L-1)!) \end{aligned}$$

(using Leibnitz' theorem.) Hence

$$J_{Lm}(z) = z J_{(L-1)m}(z) + (L+M-1) J_{(L-1)(m-1)}(z) \quad \langle R2 \rangle$$

Using  $\langle R1 \rangle$  with  $J_{00}=1$  and  $J_{10}=z$  all the  $J_{L0}$  terms may be generated. Using  $\langle R2 \rangle$  with  $J_{Lm}=0$  for the fictitious cases  $M>L$ , all the remaining  $J_{Lm}$  terms may be generated. It should be noted that the parameter  $z$  is identical to the  $z$  component of the unit vector in the laboratory frame.

The  $K_m(\theta, \phi)$  terms may be calculated as follows. Firstly we use DeMoivre's theorem to write:

$$\begin{aligned} K_m(\theta, \phi) &= (2\pi)^{1/2} \cdot \sin^M \theta \cdot (\cos m\phi + i \sin m\phi) \\ &= (2\pi)^{1/2} \cdot \sin^M \theta \cdot (\cos \phi + i(m/M) \sin \phi)^M \\ &= (2\pi)^{1/2} \cdot (x + i(m/M)y)^M \end{aligned}$$

where  $x = \sin \theta \cdot \cos \phi$  and  $y = \sin \theta \cdot \sin \phi$  are the  $x$  and  $y$  components of the unit vector.

Thus the higher orders of  $K_m(\theta, \phi)$  can be generated by repeated multiplication of the COMPLEX expression  $(x + i(m/M)y)$ . In practice we need not be concerned about the sign factor  $(m/M)$ , since we have elected to use REAL spherical harmonics in the expansion  $\langle 1 \rangle$ . The spherical harmonics for this case require the definition of two new functions:

$$\begin{aligned} K_m^+(\theta, \phi) &= (K_{+M}(\theta, \phi) + K_{-M}(\theta, \phi)) / 2^{1/2} \\ &= \text{REAL}((x + iy)^M) / \pi^{1/2} \end{aligned}$$

and

$$K_m^-(\theta, \phi) = -i(K_{+M}(\theta, \phi) - K_{-M}(\theta, \phi)) / 2^{1/2} \\ = \text{IMAG}((x+iy)^M) / \pi^{1/2}$$

These functions are used in place of the  $K_m(\theta, \phi)$  functions in the spherical harmonic expression <2>. They also may be calculated using repeated COMPLEX multiplication.

#### Example FORTRAN Code

Armed with the above algebra, a simple FORTRAN code may be written. In the Listing the essential ingredients of such a code are presented. The workings of this code should be reasonably comprehensible, but a few comments are in order.

In the code presented it is assumed that the system to be simulated contains 108 identical molecules, each of which has 3 unit vectors characterising the orientations. The order parameters are accumulated in the array YLM, which must be initialised with zeros at the start of the simulation. It is assumed that the spherical harmonics are required to the order  $L=12$ . The array YLM, in this example, may be regarded as a set of three  $13*13$  matrices; one for each unit vector. Each matrix is designed so that the  $Y_{L0}$  parameters are stored along the diagonal, the  $Y_{Lm}$  parameters derived from the  $\cos M\phi$  dependence are stored in the lower triangle of the matrix and those derived from the  $\sin M\phi$  dependence in the upper triangle. The normalisation factors are stored in the matrix YLMNRM. These values should only be calculated once, either at the start or the end of the simulation. The rest of the code is called at regular intervals throughout the simulation. The final order parameters are obtained by multiplying each YLM element by the corresponding YLMNRM element and dividing the product by the number of molecules times the number of timesteps in which the data were accumulated.

#### References

- [1] H. Eyring, J. Walter and G.E. Kimball, 'Quantum Chemistry' Wiley (1944), Chapter 4.
- [2] F.C. van der Laage and H. Bethe, Phys. Rev. v71, 6171 (1947).
- [3] M. Meyer, Proceedings of the 'Enrico Fermi' Summer School on 'Molecular Dynamics Simulation of Quantum Mechanical Systems', Varenna, Italy 22 July - 2 August 1985.
- [4] e.g. see reference [1], equation 4.81, (setting  $m=0$ ).

LISTING

```

DIMENSION YLM(0:12,0:12,3),RLO(108,0:12),RLI(108,0:12),
X CCN(108),SSN(108),CCI(108),SSI(108),ZTM(108),
X YLMNRM(0:12,0:12)

C
C   LOOP OVER UNIT VECTORS
DO 500 K=1,3

C
C   SET STARTING VALUES OF ARRAYS
DO 100 I=1,108
RLO(I,0)=1.0
RLI(I,0)=0.0
CCN(I)=X Component of unit vector K on molecule I
CCI(I)=CCN(I)
SSN(I)=Y Component of unit vector K on molecule I
SSI(I)=SSN(I)
ZTM(I)=Z Component of unit vector K on molecule I
RLO(I,1)=ZTM(I)
100 CONTINUE C
C   CONSTRUCT Y(L,M) FOR L=2 TO 12 AND M=0
DO 120 L=2,12
DO 110 I=1,108
RLO(I,L)=(ZTM(I)*RLO(I,L-1)*(2*L-1)-RLO(I,L-2)*(L-1))/L
110 CONTINUE
120 CONTINUE

C
C   ACCUMULATE THE Y(L,0) TERMS
DO 140 L=0,12
DO 130 I=1,108
130 YLM(L,L,K)=YLM(L,L,K)+RLO(I,L)
140 CONTINUE

C
C   ACCUMULATE Y(L,M) FOR L=M TO 12 AND M>0
DO 400 M=1,12
DO 160 L=M,12
DO 150 I=1,108
RLI(I,L)=ZTM(I)*RLI(I,L-1)+RLO(I,L-1)*(L+M-1)
YLM(L,L-M,K)=YLM(L,L-M,K)+RLI(I,L)*CCN(I)
YLM(L-M,L,K)=YLM(L-M,L,K)+RLI(I,L)*SSN(I)
150 CONTINUE
160 CONTINUE

C
C   UPDATE THE WORKING ARRAYS
IF(M.LT.12)THEN

```

```

DO 180 L=M,12
DO 170 I=1,108
170 RLO(I,L)=RLI(I,L)
180 CONTINUE
DO 190 I=1,108
RLI(I,M)=0.0
STORE =CCN(I)*CCI(I)-SSN(I)*SSI(I)
SSN(I)=SSN(I)*CCI(I)+CCN(I)*SSI(I)
CCN(I)=STORE
190 CONTINUE
ENDIF
400 CONTINUE
500 CONTINUE

```

C  
C

```

NORMALISATION CONSTANTS
YLMNRM(0,0)=1.0/SQRT(4.0*PI)
DO 200 L=1,12
FACTRL=(2*L+1)/(2.0*PI)
YLMNRM(L,L)=SQRT((2*L+1)/(4.0*PI))
DO 190 M=1,L
FACTRL=FACTRL/(L*L-M*M+L+M)
YLMNRM(L,L-M)=SQRT(FACTRL)
YLMNRM(L-M,L)=SQRT(FACTRL)
190 CONTINUE
200 CONTINUE

```

## THE TRANSPUTER

David Fincham

Many readers of this Newsletter will have seen press references to Transputers, and wondered what they are and whether they have any relevance to molecular simulation. This article, though written by a beginner, attempts to give brief answers to these questions.

The Transputer is a very powerful 32 bit microprocessor, designed and produced by the British company INMOS. It is an example of an increasingly popular category of processor known as the reduced instruction set computer (RISC). Conventional microprocessors have a large repertory of fundamental instructions in their machine or assembly languages. However, analysis of typical applications shows that some instructions are rarely used. The RISC computer gains design simplicity, and hence speed, by implementing only the most frequently used instructions. The basic processing speed of the Transputer is 10 Mips (million instructions per second). A single Transputer has been benchmarked at six times a VAX 11/780 (with floating point arithmetic in software in each case). For the technical, the device uses advanced CMOS 1.5 micron technology. There is an on-chip memory of 2 kbytes, and an interface to external memory chips (static or dynamic). The speed of this interface is 25 Mbytes/s. With its links (see below) the Transputer is a complete computer on a chip.

The most distinctive and important feature of the Transputer is the set of links or communication channels. Each Transputer has four links. A link can communicate with the outside world, by means of a link adaptor chip which converts it to a standard serial or parallel interface. Alternatively, Transputers can be connected together by means of their links. The four links work simultaneously, each at 10 Mbits/s. By connecting Transputers together it is possible to create multi-processor computers of almost arbitrary speed, memory and peripheral bandwidth at modest cost. Although such parallel computers can be built using conventional microprocessors (e.g. the INTEL hypercube) problems arise because their communication is via a bus or highway which is limited in the amount of traffic it can handle.

What about programming: can we use multi-Transputer arrays effectively? The Transputer is designed to be programmed in Occam, the parallel processing language originating with Professor Hoare's group in Oxford. The basic concepts in the language are the process and the channel. A program consists of a hierarchy of processes, from the individual assignment statements up to the complete program itself. At each level processes are explicitly executed sequentially or in parallel. Thus Occam is a much more flexible language than, say, DAP

Fortran, which only allows parallelism at the statement level. Processes communicate by means of channels, one process sending data over the channel and the other receiving it: the data are only sent when both processes are ready, so that synchronisation is automatic. In the case of processes running on different Transputers the channels are, of course, implemented over the links. However, parallel processes and channels execute in a logically identical manner on a single Transputer, and algorithms can thus be developed on a single Transputer before being transferred to an array.

At present, Transputers perform fixed point arithmetic in hardware, and floating point arithmetic in software. This means that their floating point performance is not quite as sparkling as my second paragraph might have lead you to expect. There are three solutions to this problem: a) use fixed point arithmetic for simulation, together with energy and force look-up tables: this is the method used in the Delft special purpose molecular dynamics computer; b) attach external additional floating-point chips to the Transputer; and c) wait for the promised floating-point Transputer.

I am enthusiastic about the potential of Transputer arrays for molecular simulation. To use such an array effectively we need suitable parallel algorithms, and of course our DAP experience is a help here. My current research is examining a range of molecular simulation problems, from the Ising model to protein dynamics, to understand how they may best be implemented. I then plan to program a complete demonstrator system for polymer dynamics. This application is chosen because its heterogeneous interactions make it unsuitable for machines like the DAP; it should effectively test the ability of a Transputer array to do many different things at once.

The CCP5 Program MDZOID.

W. Smith

The program MDZOID is a molecular dynamics program for the simulation of small-molecule systems. The molecules are represented as ellipsoidal gaussian distributions interacting via a primitive potential described by a series of gaussian terms (which may be fitted to a wide range of common pair potentials). The shape of the ellipsoidal gaussians is defined by the user at the start of the simulation. Through this facility the user may approximate many small molecule shapes. The program should be of value in the study of orientational order in, for example, liquid crystals and may also be useful as a model for complex rigid molecules with an overall ellipsoidal shape.

The program uses a cubic simulation cell with a periodic boundary to remove surface effects. A spherical cut-off, set to half the cell width, is employed. The program calculates the configuration energy, translational and rotational kinetic energies, total energy, pressure, virial and temperature, together with the RMS fluctuations. The structural functions calculated are the centre-centre radial distribution function and the bulk orientational order parameters derived from the spherical harmonic expansion of the orientational probability density function. The time correlation functions calculated are the translational and rotational velocity autocorrelation functions.

The program was devised by W. Smith and K. Singer [1] and is now available through the CCP5 Program Library.

Reference

[1] W. Smith and K. Singer, CCP5 Info. Quart. v17 p53 (1985).

1/1/2025

The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that proper record-keeping is essential for financial transparency and accountability. The document outlines the various methods used to collect and analyze data, ensuring that the information is reliable and up-to-date. It also mentions the role of technology in streamlining these processes and reducing the risk of human error.

The second part of the document focuses on the implementation of these practices across different departments. It provides a detailed overview of the current state of affairs and identifies key areas for improvement. The document highlights the need for cross-departmental collaboration and communication to ensure that everyone is working towards the same goals. It also discusses the importance of training and development to equip staff with the necessary skills and knowledge to perform their roles effectively.

The final part of the document concludes with a summary of the key findings and recommendations. It reiterates the importance of ongoing monitoring and evaluation to ensure that the implemented changes are having the desired impact. The document also provides a clear timeline for the next steps and assigns responsibilities to the relevant stakeholders.

Prepared by: [Name] | Date: 1/1/2025