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DARESBUURY LABORATORY

INFORMATION QUARTERLY for COMPUTER SIMULATION OF CONDENSED PHASES

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

Number 25

June 1987

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IMPORTANT NOTICE

(RE)REGISTRATION OF CCP5 MEMBERS

CCP5 is to reorganise the mailing list by means of which the CCP5 newsletter and documents relating to CCP5 are distributed. The main purpose of this is to remove redundant and erroneous addresses from the list, thereby reducing costs and improving the reliability of our mailing service.

Also, under the terms of the UK's DATA PROTECTION ACT 1984, we are obliged to notify you that your name and address are held on our computer and we require your consent to keep this information.

There is no way to do this other than to request all recipients of the newsletter to re-register their names and addresses with CCP5. We apologise to all our readers for the inconvenience of this request, particularly to those who have only recently been added to the list, but the mailing list is now over six years old and is inevitably significantly out-of-date.

PLEASE COMPLETE AND RETURN THE REGISTRATION SLIP BEFORE DECEMBER 30 1987. FAILURE TO DO SO WILL RESULT IN THE REMOVAL OF YOUR NAME FROM THE CCP5 MAILING LIST.

The completed registration slips should be returned to:

Dr. W. Smith,
T.C.S. Division,
SERC Daresbury Laboratory,
Daresbury,
Warrington WA4 4AD,
United Kingdom.

REPORT ON THE PROGRESS

OF THE WORK OF THE COMMITTEE

The Committee has the honor to acknowledge the receipt of the report of the Commission on the subject of the proposed amendments to the Constitution of the United States, and to express its appreciation for the valuable information contained therein.

The Commission's report is a most interesting and valuable contribution to the study of the subject, and the Committee has the honor to express its appreciation for the same.

The Committee has the honor to express its appreciation for the valuable information contained in the report of the Commission, and to express its appreciation for the valuable information contained therein.

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Very respectfully,
Your obedient servant,
[Signature]

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NAME : _____ TITLE: _____

ADDRESS: _____

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10/10/2019 10:10:10 AM

Editorial.

CCP5 continues to be an active and exciting project. The current issue of the newsletter shows that there are several interesting events in the offing in the form of conferences and workshops. We hope that many of our readers will be able to participate in them.

Also of great interest to those of us actively involved in producing new simulation methods are the current exciting developments in parallel processing. Daresbury Laboratory intends to be in the forefront of these developments with the formation of the 'Advanced Research Computing Group' under Dr. M.F. Guest. This group will include several CCP5 stalwarts and will endeavour to produce new programming algorithms for parallel processors, which, it is anticipated, will provide a radical new springboard for computational science in the UK and for the CCP's in particular. The group currently has access to several powerful computers with new architectures; namely the Cray XMP/48 at RAL, the FPS T/20 and Meiko computing surface at Daresbury. We shall watch developments on this front with enthusiasm.

Contributors to the current issue.

Our thanks go to:

C.R.A. Catlow	Department of Chemistry,
R.W. Grimes	University of Keele, Keele, Staffs ST5 5BG.
P. Clancy	School of Chemical Engineering, Olin Hall, Cornell University, Ithaca, New York 14853, USA.
S.L. Fornili	Istituto di Fisica,
V. Martorana	Via Archirafi 36,
M. Miliore	I-90146 Palermo, Italy.
S. Gupta	Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, USA.
M. Heggie	Department of Physics, University of Exeter, Exeter EX4 4QL, Devon.
D.M. Heyes	Department of Chemistry,
K. Singer	Royal Holloway and Bedford

New College, Egham TW20 0EX,
Surrey.

W. Smith

Theory and Computational Science
Division, S.E.R.C. Daresbury
Laboratory, Daresbury, Warrington
WA4 4AD, Cheshire.

[Faint, mostly illegible text, likely bleed-through from the reverse side of the page]

General News.

a) Aneesur Rahman.

Aneesur Rahman died on June 6th after a long illness which left his intellect unimpaired to the last. It is hard to realise the magnitude of this loss to those interested in computer simulation. He was the first to show that a realistic simulation of a real liquid by molecular dynamics was possible and to describe the mechanism of diffusion (1964,66). He continued - in collaboration with others - to apply MD simulation to problems which at the time appeared hopelessly difficult; e.g. the calculation of collective modes in LJ and metallic liquids, the simulation of water, the onset of superionic conductivity above a certain temperature in CuI and phase changes in solids produced by imposed stresses. Other papers, if not the first in the field, were always original and brought new insights (e.g. the structure of ionic melts, epitaxial growth, the solvation of an electron in liquid KCl, etc.) If scientists stand on the shoulders of others, most of those who use MD methods stand on the shoulders of Aneesur Rahman. His death will be felt as a personal loss by everyone who knew him.

We hope to present an appreciation of Dr. Rahman's work in a later issue of this newsletter.

b) CCP5 is to organise a meeting on the subject of bio-organic applications of computer simulation, which provisionally, is scheduled for Easter 1988. More details of this will be revealed as the organisation develops.

c) The CCP5 Executive Committee wish to remind all U.K. participants in CCP5 that it has set aside a part of the CCP5 budget for the purpose of assisting collaborative work in the U.K. simulation community. These funds are to assist with expenses for travel between collaborating centres. So far, CCP5 has agreed to assist the following collaborating groups:

J. Clarke and D. Tildesley (Transport Properties),
S. Parker and G. Price (Lattice Simulations),
M. Allen and G. Evans (Hard Ellipsoids), K. Singer and W. Smith (Quantum Simulations).

Other groups who wish to be considered for this assistance should write to the CCP5 Chairman, Prof. C.R.A. Catlow, Department of Chemistry, University of Keele, Keele, Staffs. ST5 5BG.

d) CCP5 participants are reminded that CCP5 has an annual allocation of Cray time at each of the centres: London (Cray 1s) and Rutherford (Cray XMP-48), which is available for the development of simulation programs prior to a grant allocation. At present CCP5 is allocated 15 hours a year at London and 5 hours quarterly at Rutherford. Readers who wish to use some of this allocation should write to the CCP5 Secretary, Dr. M. Leslie, TCS Division, SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD.

e) The University of Manchester Regional Computer Centre is currently negotiating yet another extension of the lives of the departing CDC 7600 mainframes. (So great is their popularity.) The current plan is that one 7600 (MFZ) will depart as scheduled 31 July 1987. The second 7600 (MFY) will survive for five months longer and depart 31 December. The CYBER 176 (MFX) will be retained until 31 July 1988. Altogether the proposals mean a continuation of the 7600 service for one extra year. A further extension of the CYBER 176 until December 1988 is also possible.

Early June saw the commencement of the VM/CMS service on the Amdahl 5890/300. This new service will run concurrently with ROSCOE. In keeping with their policy of providing up-to-date documentation on developments UMRCC have released several 'CMS Notes' and are preparing introductory manuals.

f) At the University of London Computing Centre the planned upgrade of the user discs to 3380 (mentioned in our last newsletter) ran into problems because the new discs proved to be unreliable. Thus the transfer of users' catalogued datasets has been postponed until June, when users may notice the effects of the larger track size on their allocated disc space. ULCC are also planning to upgrade the MVS operating system to MVS (SP 1.3.5) soon and will conduct field trials in late June or July. Users of the Cray-1s computers, with special requirements of the COS operating system are informed that a COS Service Coordinator is available to help. The person to contact is Mr. Christopher Lazou.

g) The Rutherford and Appleton Computer Centre Cray XMP/48 service (now with the proud title 'The Joint Research Council's Supercomputing Unit') has been running successfully for several months. Members of TCS Division at Daresbury have been actively developing programs for the CCPs and other projects during this period and reports of

the quality of the service are uniformly good. Readers should contact the CCP secretaries to learn which packages are available and to recommend other programs for conversion.

A new release of CMS (Release 4) is scheduled and it provides a re-written online HELP system, which will give users better online information about the CMS facilities available.

h) The Institute of Physics is organising the 1987 Solid State Physics Conference for 16-18 December at the H.H. Wills Physics Laboratory, University of Bristol and it will contain a number of symposia that will undoubtedly be of interest to participants in CCP5. Among the intended symposia are: Statistical Mechanics of Disordered and Inhomogeneous Systems; Physics of Sputtering Processes; Polymers and Liquid Crystals; Scattering of Neutrons from Disordered Systems and The Physics of Solids at High Pressures. People interested in attending or contributing a paper should contact Dr. B.L. Gyorfy or Dr. R. Evans at the H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL. We will provide more information in our next newsletter.

i) We are slowly gathering together the electronic mail addresses of our CCP5 colleagues and are thus able to communicate news and information rapidly to many points on the globe! We hope that those readers who have not yet sent us their addresses will do so, and help us to make good use of this facility. In Europe, use of the EARN network is free (for the time being).

j) For the benefit of computational scientists everywhere, we are publishing in this issue a list of the workshops and meetings planned by the CECAM organisation for the remainder of the year. U.K. scientists may be sponsored to attend these meetings if a prior application is made to Dr. J.E. Inglesfield, Theory and Computational Science Division, Daresbury Laboratory, Daresbury, Warrington WA4 4AD. It is requested that applications be given sufficient time to be dealt with (e.g. one month beforehand).

k) Recipients of the CCP5 newsletter are asked to pay particular attention to the notice given at the beginning of this issue and to respond accordingly. CCP5 distributes up

to 500 copies of each newsletter world-wide, a significant number of which, we suspect, go to defunct addresses. To cut costs and to speed the delivery of each issue, we ask our readers to return the registration slip provided. Failure to do this may result in cancellation of future deliveries. Please use this opportunity to correct any addressing errors. If you are reading someone else's copy, we will be glad to provide you with your own!

1) The CCP5 Program Library. Documents and programs are available free of charge to academic centres upon application to Dr. W. Smith, TCS Division, S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K. 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.. Please note that use of inappropriate packing for magnetic tapes (e.g. padded bags) may result in them being considered unusable by Daresbury Computing Division and returned without the required software. Please ensure that these forms of packaging are not used. A list of programs available is presented in the following 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. Smith.

We are pleased to report the addition of another program to the library, supplied by Dr. Sumnesh Gupta (Louisiana State University). It is a Monte Carlo program for simple Lennard Jones systems and has been designed for instructing graduate students in the development and use of Monte Carlo programs. The program will shortly be available to CCP5 participants under the name MCLSU. We thank Dr. Gupta for his support.

THE CCP5 PROGRAM LIBRARY.

ADMIXT [MD,LJA/MIX,LF,TH+MSD+RDF] W. Smith
 CARLOS [MC,VS+AQUO,TH] B. Jonsson/ S. Romano
 CARLAN [DA,CARLOS structure analysis] B. Jonsson/ S. Romano
 CASCADE [LS,DIL,EM,TH+STR] M. Leslie/ W. Smith
 CURDEN [DA,Current Density Correlations] W. Smith
 DENCOR [DA,Density Correlations] W. Smith
 HLJ1 [MD,LJA,LF,TH+MSD+RDF] D.M. Heyes
 HLJ2 [MD,LJA,LF,TH+MSD+RDF+VACF] D.M. Heyes
 HLJ3 [MD,LJA,LF/LC,TH+MSD+RDF] D.M. Heyes
 HLJ4 [MD,LJA,LF/CP+CT,TH+MSD+RDF] D.M. Heyes
 HLJ5 [MD,LJA/SF,LF,TH+MSD+RDF] D.M. Heyes
 HLJ6 [MD,LJA,TA,TH+MSD+RDF] D.M. Heyes
 HMDIAT [MD,LJD,G5+Q4,TH+MSD+QC] S.M. Thompson
 HSTOCH [MD/SD,VS+BA,LF+CA,TH] W.F. van Gunsteren/ D.M. Heyes
 MGN [MC,LJA,TH] N. Corbin
 MCLSU [MC,LJA,TH] C.P. Williams and S. Gupta
 MCRPM [MC,RPE,TH+RDF] D.M. Heyes
 MDATOM [MD,LJA,G5,TH+RDF+MSD+QC] S.M. Thompson
 MDATOM [MD,LJA,LF,TH+MSD+RDF] D. Fincham
 MDDIAT [MD,LJD,LF+CA,TH+MSD] D. Fincham
 MDDIATQ [MD,LJD+PQ,LF+CA,TH+MSD] D. Fincham
 MDIONS [MD,BHM,LF,TH+MSD+RDF+STF] D. Fincham/ N. Anastasiou
 MDLIN [MD,LJL,G5+Q4,TH+MSD+QC] S.M. Thompson.
 MDLINQ [MD,LJL+PQ,G5+Q4,TH+MSD+QC] S.M. Thompson
 MDMANY [MD,LJS+FC,LF+QF,TH] D. Fincham/ W. Smith
 MDMIXT [MD,LJS/MIX,LF+QF,TH] W. Smith
 MDMPOL [MD,LJS+FC/MIX,LF+QF,TH] W. Smith and D. Fincham
 MDPOLY [MD,LJS,G5+Q4,TH+MSD+QC] S.M. Thompson
 MDMULP [MD,LJS+PD+PQ/MIX,LF+QF,TH] W. Smith
 MDTETRA [MD,LJT,G5+Q4,TH+MSD+QC] S.M. Thompson
 MDZOID [MD,GAU,LF+QF,TH+MSD+RDF+VACF] W. Smith
 SCN [MC,LJA,RFD,TH] N. Corbin
 SURF [MD,BHM/TF/2D,LF,TH+RDF] D.M. Heyes
 SYMLAT [LS,PIL,EM+SYM,TH+STR] Harwell
 THBFIT [LS,PIL,EM,Potential fitting] Harwell
 THBPHON [LS,PIL/3B,EM,Phonon dispersion] Harwell
 THBREL [LS,PIL,EM,TH+STR] Harwell

Key:

Program types : MD - Molecular dynamics
 MC - Monte Carlo
 LS - Lattice simulations
 SD - Stochastic dynamics
 DA - Data analysis

System models : LJA - Lennard-Jones atoms
 LJD - Lennard-Jones diatomic molecules

LJJ - Lennard-Jones linear molecules
 LJT - Lennard-Jones tetrahedral molecules
 LJS - Lennard-Jones site molecules
 RPE - Restricted primitive electrolyte
 BHM - Born-Huggins-Meyer ionics
 TF - Tosi-Fumi ionics
 VS - Variable site-site model
 BA - Bond angle model
 PD - Point dipole model
 PQ - Point quadrupole model
 MIX - Mixtures of molecules
 GAU - Gaussian molecule model
 FC - Fractional charge model
 PIL - Perfect ionic lattice model
 DIL - Defective ionic lattice model
 3B - 3-body force model
 2D - Two dimensional simulation
 SF - Shifted force potential
 FC - Fractional charge model

Algorithm used : G5 - Gear 5th order predictor-corrector
 Q4 - Quaternion plus 4th. order Gear P-C.
 LF - Leapfrog (Verlet)
 QF - Quaternion plus Fincham algorithm
 LC - Link-cells MD algorithm
 CP - Constant pressure
 CT - Constant temperature
 TA - Toxvaerd MD algorithm
 CA - Constraint algorithm
 EM - Energy minimisation
 SYM - Symmetry adapted algorithm
 RFD - Rosky-Friedman-Doll algorithm

Properties : TH - Thermodynamic properties.
 MSD - Mean-square-displacement
 RDF - Radial distribution function
 STF - Structure factor
 VACF - Velocity autocorrelation function
 QC - Quantum corrections
 STR - Lattice stresses

CONFERENCES, WORKSHOPS ETC.

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*          CCP5 ANNUAL CONFERENCE 1988
*  INDUSTRIAL APPLICATIONS OF MOLECULAR SIMULATION
*  BIRKBECK COLLEGE 6-8TH JANUARY 1988
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Molecular simulation methods are increasingly being used as an aid in understanding and predicting the behaviour of real substances. It is appropriate therefore to bring together both industrial and academic experts to consider what progress has been made and how best to further exploit these new tools. The conference will be concerned with the application of molecular simulation methods (molecular dynamics, Monte Carlo etc.) to problems of industrial (and academic) interest. In addition to providing a forum for discussion, the meeting will be a showcase for simulation methods and an opportunity for the academic simulation community to interact with industrial researchers and sponsors.

The conference will be held at **Birkbeck College, London** from 6th to 8th January 1988. Accommodation will be in the Hughes-Parry Hall. The subject matter of the conference will be in the general area of molecular simulation but particular attention will be given to applications in:

- .Prediction of bulk phase behaviour (e.g. phase equilibria, rheological properties)
- .Macromolecules (e.g. polymers and related molecules)
- .Porous media (phase behaviour in pores, diffusion in pores, fractals)
- .Solid state chemistry
- .Materials science
- .Pharmaceuticals (molecular modelling).

The proceedings will be published in the journal "Molecular Simulation".

Among the speakers who have agreed to take part in the conference are:

J. Bendler (General Electric Research),
 C.R.A. Catlow (Keele and Daresbury),
 A. Cheetham (Oxford),
 M. Gillan (Harwell),
 K. Gubbins (Cornell),
 W.C. Mackrodt (Imperial Chemical Industries),
 N. Quirke (British Petroleum),
 L. Woodcock (Bradford),
 D. White (Glasgow).

Further contributions in the general area of industrial applications of molecular simulation (but especially in the above outlined areas) will be welcome. Potential contributors and applicants should contact Dr. N. Quirke (address below) for further details.

```

*****
*           Dr. N. Quirke           *
*           B.P. Research Centre     *
*           Chertsey Road           *
*           Sunbury-on-Thames,      *
*           Middlesex TW16 7LN,     *
*           England                 *
*****

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 *
 * **THERMODYNAMICS & STATISTICAL MECHANICS OF SMALL SYSTEMS** *
 *

A meeting is being organised by the Royal Society of
 Chemistry Statistical Mechanics and Thermodynamics Group at:

 * THE UNIVERSITY OF YORK *
 * 24-25th September 1987 *

The topics for discussion include small system behaviour in
 porous media and as crystallites, clusters and micelles.
 Both theoretical and experimental aspects will be discussed
 and contributions are invited.

The speakers include Dr. R.J. Evans (Bristol), Prof. D.H.
 Everett (Bristol) and Prof. J.S. Rowlinson (Oxford).

Please contact:

 * Dr. J.H.R. Clarke *
 * Department of Chemistry, *
 * U.M.I.S.T. *
 * Sackville Street, *
 * Manchester M60 1QD *

P.G. Francis

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*****
*
*   COMPUTER      SIMULATION    OF    TRANSPORT    PROCESSES   *
*
*****

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A workshop is being organised by CCP5 on computer simulation of transport processes at

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*****
*   THE UNIVERSITY OF YORK   *
*   23-24th September 1987  *
*****

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This workshop precedes the Royal Society of Chemistry, Statistical Mechanics and Thermodynamics Group meeting on Thermodynamics and Statistical Mechanics of Small Systems [1]. The CCP5 workshop is organised so that the RSC meeting will follow on from the CCP5 workshop.

It will have a round-table format with a loosely structured timetable to encourage discussion in areas of interest that arise.

Topics for discussion are **likely** to include:

- Methods for computing transport coefficients (e.g., self-diffusion coefficients, viscosity and thermal conductivity) by Green-Kubo and NEMD techniques. Results.
- Methods for simulating dynamics and transport coefficients of long chain molecules, micelles, lipid bilayers. Results.
- Brownian and Stokesian Dynamics, rheology, inclusion of hydrodynamic effects in the simulations. Results.
- Special problems of transport in solids (Static lattice and MD) and glasses. Techniques. Results.

If you are interested in attending the CCP5 Workshop then write before September 7th to:

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*****
*   Dr. D.M. Heyes,           *
*   Department of Chemistry,  *
*   Royal Holloway and Bedford New College, *
*   University of London,     *
*   Egham, Surrey TW20 OEX.  *
*****

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It may be necessary to introduce a small charge to support the workshop.

([1] Please contact Dr. J.H.R. Clarke, Department of Chemistry, U.M.I.S.T., Sackville St., Manchester M60 1QD if you are interested in attending the RSC Meeting mentioned above.)

 *
 * VISIT OF PROF. H. J. C. BERENDSEN, 23-26 NOVEMBER 1987 *
 *

As part of the CCP5 Visitor Programme, we have invited Prof. Herman Berendsen (University of Groningen) to spend a few days in the UK. The visit is provisionally scheduled for November, with a tentative itinerary as follows:

Monday 23 November Department of Crystallography,
 Birkbeck College, London
 Tuesday 24 November Department of Physical Chemistry,
 Cambridge
 Wednesday 25 November SERC Daresbury Laboratory

A short workshop will be held at Birkbeck on the Monday, in the general area of Macromolecules. More details will be issued closer to the date of the visit.

 Contact for the visit: Dr. Mike Allen,
 H.H. Wills Physics Laboratory,
 Royal Fort,
 Tyndall Avenue,
 BRISTOL BS8 1TL.
 or MPA UK.AC.BRISTOL.PVA.

Contact for the workshop: Prof. John Finney,
 Liquids and Disordered Systems
 Laboratory,
 Department of Crystallography,
 Birkbeck College,
 Malet Street,
 LONDON WC1E 7HX.

CECAM

Bâtiment 506, Université de Paris-Sud, Orsay (France)

Tél. : (1) 69.41.82.50, Poste 33-37

Workshops, Preparatory and Discussion Meetings 1987

Ateliers de travail et Réunions Préparatoires 1987

Titre/Title	Organisateurs/Organizers	Dates
Interaction, Transport and Hydrodynamics in Laser Plasmas	M.G. Haines, London B. Sitt, Centre d'Etudes de Limeil	11-13 May
Dynamics Processes at Surfaces	D. News, IBM-Yorktown Heights D. Spanjaard M.C. Desjonquères } Orsay A. Nourtier	1-12 June
Vibrational Predissociation	C. Leforestier, Orsay	15-26 June
Quantum Monte Carlo Methods for Fermion Problems : From Field Theory to Atomic and Molecular Physics	P. Claverie, Paris	22-23 June
Quantum Simulation of Condensed Matter	M.J. Gillan, Harwell P. Madden, Oxford	6-17 July
Forces Fields for Computer Simulations on Molecules	S. Wodak, Brussels	20-24 July
Computational Methods in Electron Molecule Collisions	C.J. Noble, Daresbury	20-21 July
Computer Simulation of System with Long Range Forces	M. Neumann, Vienna S. de Leeuw, Amsterdam	27 July - 7 August
Interatomic Forces in Semiconductors and Metals	A. Sutton, Oxford	17-28 August
Computer Simulation and Theory of Solution Phase Chemical Reactions	J.T. Hynes, Boulder M. Mareschal, Brussels P. Turq, Paris	24 August - 4 September
Free Energy Computations in Complex Systems	D. Frenkel, FOM Amsterdam	7-18 September
Nonlinear Magneto-Hydrodynamic Phenomena in Stellar Atmospheres	A.G. Hearn, Utrecht	9-11 September
Brownian Dynamics and Cellular Automata	D. Frenkel, FOM Amsterdam	21-23 September
Complex Optimization and Stochastic Computing	D. Sherrington, Imperial College, London	21 September - 2 October
Electrostatics in Recognition Processes between Biological Macromolecules	E. Westhof, Strasbourg	19-23 October
Galaxy Formation and Matter Distribution	M. Lachièze-Rey, CEN Saclay R. Schaeffer, CEN Saclay	9-20 November
Problem Oriented Architecture for Computational Physics in particular for many particle Interactions	B.P.Th. Veltman, Delft A.F. Bakker, Delft	7-8 December

M A S P

The world's most important information (the world's
 most important information) is not in the
 world's most important information, but in the
 world's most important information.

Year	Country/Region	Value
1990	United States	100
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2050	United States	100

AN INTRODUCTION TO PATH INTEGRAL MONTE CARLO FOR CONDENSED PHASES

W. Smith and K. Singer

Path Integral Monte Carlo (PIMC) is one of the methods currently being used to simulate quantum mechanical systems. As its name suggests, it is the combination of the path integral formulation of quantum mechanics, devised by Feynmann¹, and the familiar Metropolis Monte Carlo method² more commonly used in simulations of classical systems. Such a combination of approaches might be regarded as conceptually or practically difficult, but fortunately this is not the case. In practice it proves to be no more difficult to implement than an ordinary Monte Carlo simulation. Conceptually, the difficulties arise more from unfamiliarity with the approach than with physical principles. Our purpose in presenting this article is to provide a pedagogic introduction to PIMC in the spirit of M. Gillan's description at the CCP5 meeting in Manchester. Secondly, we wish to show that the PIMC method is simple to use. Thirdly we wish to say something about our own experiences in simulating bulk Neon and Argon.

The PIMC method does not provide information on the dynamical aspects of the system being simulated, but it is extremely useful when it comes to providing structural and thermodynamic information. With respect to time dependence it is inferior to the gaussian wavepacket methods³ and the discrete wavepacket methods⁴. However it has some advantages of its own. The method is rigorous, and we have found it to be easily adaptable to many-particle systems (without exchange). Gaussian wavepackets are not yet sufficiently accurate³, while discrete wavepackets presently appear to require too much computer memory for practical simulations. The interpretation of the physical properties of the system is another advantage. It is difficult, for example, to define the temperature in a system of gaussian wavepackets⁵, (presumably the problem is worse in systems of discrete wavepackets), whereas it is an explicit parameter in PIMC. Also, the delocalisation of the quantum particles is easily dealt with in PIMC, but in wavepacket methods, the break-up of the scattered wavepackets is problematical.

The Propagator

We begin with the simple case of a single particle moving in one dimension and consider the concept of a propagator. Suppose we wish to solve the time dependent

Schroedinger equation (in which the Hamiltonian operator \mathbf{H} is **not** an explicit function of time and \mathbf{h} is Planck's constant; $\mathbf{h}/2\pi$.)

$$\mathbf{H} \Psi = i\mathbf{h} \partial \Psi / \partial t$$

given that the solution $\Psi = \Psi(x,0)$ is known at time $t=0$. A possible solution is provided by the following integral:

$$\Psi(x,t) = \int G(\xi,x;t) \Psi(\xi,0) d\xi$$

In which the function G (the Green's function) is known as a propagator, since a knowledge of the initial state of the wavefunction $\Psi(\xi,0)$, and the function G , allows us to propagate the wavefunction through time, thus providing a solution of the Schroedinger equation at a later time t . Obtaining the form of the function G , is therefore formally equivalent to solving the time dependent Schroedinger equation. Clearly, this is not the only way the equation could be solved, but the concept of a propagator is central to the Feynmann interpretation of quantum mechanics, and it is to that interpretation that we look to guide us to the correct form of the function G in difficult cases. For the simple case being considered here however, we write the function G directly as (see Appendix):

$$G(\xi,x;t) = \sum_n \psi_n^*(\xi) \psi_n(x) \exp(-i\mathbf{h}^{-1} E_n t)$$

in which the functions ψ_n are the eigenfunctions of the operator \mathbf{H} and E_n are the corresponding eigenvalues. Thus, provided we can solve the time independent Schroedinger equation for the operator \mathbf{H} we have, through G , the solution to the more difficult problem of the propagation of a wavefunction Ψ through time.

A simple example of the use of a Green's function, and one which is of particular relevance to PIMC (see below), is the propagation of a free-particle wavefunction (i.e one moving in a constant potential V_0). The eigenfunctions for the Hamiltonian appropriate to this case have the form:

$$\psi_p(x) = (2\pi\mathbf{h})^{-1/2} \exp(i\mathbf{h}^{-1} px)$$

In which $p^2 = 2m(E_p - V_0)$, p is the momentum and E_p the energy. Using this form of eigenfunction, the Green's function may be written as:

$$G(\xi, x; t) = (2\pi\hbar)^{-1} \int \exp(-i\hbar^{-1} \{ (p^2/2m)t + p(\xi-x) + tV_0 \}) dp$$

In which the sum has been replaced by an integral to exploit the infinitesimal differences between the possible eigenvalues. Performing this integration leads to:

$$G(\xi, x; t) = (m/i2\pi\hbar t)^{1/2} \exp(-i(m/2\hbar t) \{ (\xi-x)^2 + 2t^2V_0/m \})$$

From which it is important to note that the Green's function is a Gaussian in terms of the spatial coordinates. In practice one may now use this function to propagate a given starting wavefunction, and derive the time evolution. However it is not the purpose of this note solve problems of this nature. What is of interest however is the case where the potential is a function rather than a simple constant. In this circumstance the Green's function cannot, in general, be obtained in closed form, but we can use Feynman's path integral approach to derive an acceptable approximation to the correct solution, which can be made as accurate as desired.

Consider the space-time diagram for the propagation of a particle in a one-dimensional space (Figure 1). The particle moves from point A at time zero to point B at time t. According to the tenets of quantum theory we cannot know what path the particle follows with certainty; we can only make probabilistic statements about where the particle is likely to be at a given time. Neither can we perform any experiment to reveal its position, since this will disrupt the process of propagation. However, the path integral theory provides a way of analysing the propagation from point (A;0) to point (B;t) through consideration of the intermediate points of the trajectory. Basically the theory postulates that all possible trajectories starting at (A;0) and ending at (B;t) are equally admissible. The probability amplitude of arrival at B arises from a sum (or integral) over all the possible paths. Most of the possible paths cancel each other through their different phase factors (destructive interference); only those paths close to the classical trajectory will effectively contribute to the propagation process. In the classical limit there is no significant contribution from any but the classical trajectory. On the atomic scale however one cannot specify the path followed with such certainty.

If we consider a point in time t_c between 0 and t (Figure 1) then we understand that the moving particle has a finite probability of crossing the line t_c at **any** position (e.g. x_{c1} , x_{c2} etc.). If we choose a point along this line

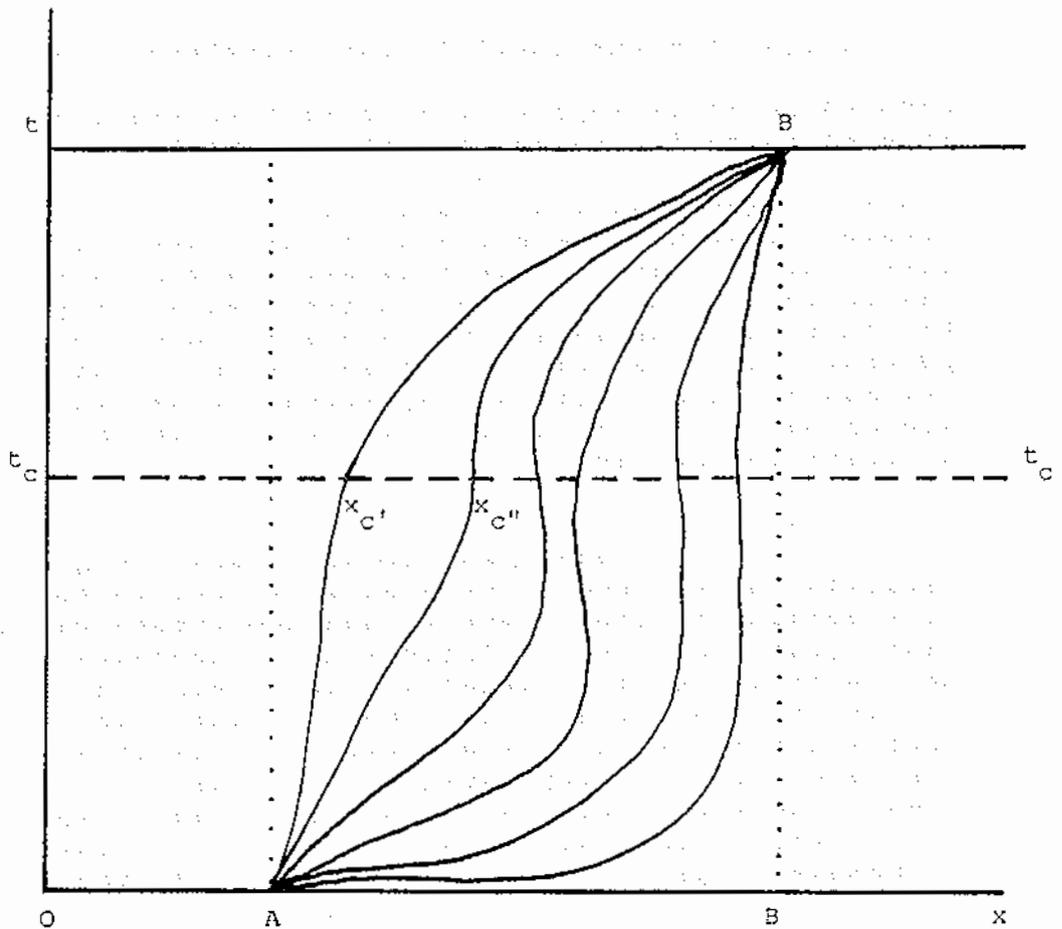


FIGURE 1

(x_c , say), then we can describe the propagator from point A to x_c , quite simply as $G(A, x_c; t_c)$. Similarly the propagator from x_c to B is $G(x_c, B; t-t_c)$. In Feynman's formulation, the propagator from A to B via x_c is the product $G(A, x_c; t_c)G(x_c, B; t-t_c)$. (This is because the arrival of the particle at x_c from A has a probability amplitude proportional to $G(A, x_c; t_c)$ and the arrival at B from x_c has a probability amplitude proportional to $G(x_c, B; t-t_c)$, thus the probability amplitude of both events occurring in sequence is proportional to the product¹.) To get the correct description of the complete propagator from A to B we must reconstruct all the possible paths in between, that is we must consider all arrivals along the line t_c from A and all the departures from t_c to B. In other words the propagator $G(A, B; t)$ is given by:

$$G(A, B; t) = \int G(A, x_c; t_c)G(x_c, B; t-t_c) dx_c$$

In this decomposition of the propagator we have considered only one partition of the time interval $[0, t]$. Clearly, we may consider any number of partitions, and by a similar process reduce the propagator to:

$$G(A, B; t) = \int \dots \int G(A, x_1; t_1) \left[\prod_{j=1}^{n-2} G(x_j, x_{j+1}; t_{j+1}-t_j) dx_j \right] G(x_{n-1}, B; t-t_{n-1}) dx_{n-1}$$

Which describes the partition of the interval $[0, t]$ into n sub-intervals. (Note the presence of the product of Green's functions within the above expression.)

The purpose of performing such a decomposition of the propagator is to be able to deal with more complicated potential energy functions, because we may now assume that the division of the time interval $[0, t]$ is such that over each sub-interval, the potential energy function hardly varies and we may treat it as a constant (i.e. $V(x) = V(x_i)$ over $[x_i, x_{i+1}]$). Therefore, using these assumptions we can write the propagator for the cases with more complicated potential functions as:

$$G(A, B; t) = (m/2\pi i \hbar (t/n))^{n/2}$$

$$\iint \exp\left(\frac{im}{2\hbar(t/n)} \sum_{j=1}^n [(x_j - x_{j-1})^2 + 2(t/n)^2 V(x_j)/m]\right) dx_1 \dots dx_{n-1}$$

In which the propagator appropriate to the case of a constant potential (i.e. a Gaussian, see p.3) has been used for each sub-interval (Note: $x_0=A$ and $x_n=B$). This description is formally exact in the limit of n tending to infinity. Thus we see how the application of Feynman's path integral method has allowed us sufficient insight into this rather difficult problem to provide an acceptable description of the propagator. Later, we shall make use of this approximation of the trajectory by finite sub-intervals. It is commonly called the short time approximation.

Statistical Mechanics

When a particle is in a quantum state ψ_n , the probability density of the particle at a point x is given by the product $\psi_n^*(x)\psi_n(x)$. However, in a many-particle system, this is merely one of the many states thermally accessible to the particle. Therefore the probability density for the particle in the state ψ_n is given by a Boltzman weighting of the state thus:

$$\psi_n^*(x)\psi_n(x) \exp(-\beta E_n) / Z$$

In which E_n represents the energy (eigenvalue) of the state ψ_n and Z the normalising factor, which is given by

$$Z = \int \sum_n \psi_n^*(x)\psi_n(x) \exp(-\beta E_n) dx$$

This is of course the partition function for the states accessible to the particle. Therefore the average of a physical quantity can be obtained in a way that is analogous to the classical case i.e.

$$\langle A \rangle = \int \sum_n \psi_n^*(x) A \psi_n(x) \exp(-\beta E_n) dx / Z$$

In quantum mechanics, a more general way of expressing the partition function is by means of the density function $\rho(x, x'; \beta)$, which is defined as:

$$\rho(x, x'; \beta) = \sum_n \psi_n^*(x)\psi_n(x') \exp(-\beta E_n)$$

In terms of this function, the partition function may be expressed as:

$$Z = \int \rho(x, x; \beta) dx = \text{Tr}[\rho]$$

and the average of a physical quantity A as:

$$\langle A \rangle = \frac{\text{Tr} \int A \rho(x, x'; \beta) dx}{Z}$$

In which the operation Tr (known as the **trace**) implies that the operator A acts first on functions of the coordinate x' and then x' is set equal to x for the integration. (In the case of the integral for Z the operator is unity.) These equations serve to show the central importance of the density function $\rho(x, x'; \beta)$ in the statistical mechanics of quantum systems.

We are now near to the heart of the PIMC method. We note that the form of the density function, expressed in terms of the wavefunctions ψ_n , is analogous to the Green's function propagator. This suggests at once that any method that we can apply to solving the time dependent Schrodinger equation may also be applied to obtaining the partition function. All that is required is the formal substitution of the quantity $i\hbar^{-1}t$ by β . This is a powerful insight, since it means that we may use the short time approximation described above and other deductions based on the path integral concept to calculate the properties of a quantum mechanical ensemble. Thus the density function $\rho(x, x'; \beta)$ can be written directly as:

$$\rho(x, x', \beta) = (m\hbar/2\pi\hbar^2\beta)^{n/2}$$

$$\iint \exp(-\beta \sum_{j=1}^n [nm/2(\hbar\beta)^2(x_j - x_{j-1})^2 + V(x_j)/n]) dx_1 \dots dx_{n-1}$$

Which is obtained straightforwardly from the expression for the Green's function $G(A, B; t)$ given earlier (and we assume $x=x_0$ and $x'=x_n$).

The extension of this formula to three dimensional problems is trivial; we merely replace the coordinates x_j by the vectors \underline{r}_j and the pre-exponential factor becomes $(m\hbar/2\pi\hbar^2\beta)^{3n/2}$. To evaluate the partition function Z it is necessary to integrate the trace of the density function, which means setting $\underline{r}=r'$ (or equivalently, $\underline{r}_0=\underline{r}_n$) and

integrating over r . We also note that we are still dealing with the partition function of a single particle. We now assume that the partition function for the ensemble of N particles is the product of N single-particle partition functions. These considerations lead to the following form for Z

$$Z = (mn/2\pi\hbar^2\beta)^{3nN/2}$$

$$\iint \exp(-\beta \sum_k^N \sum_j^n (nm/2(\hbar\beta)^2 (r_{k,j} - r_{k,j-1})^2 + V(r_{k,j})/n)) \prod_k^N \prod_j^n dr_{k,j}$$

Where the index k refers to the k th particle (note that $r_{k,0} = r_{k,n}$). In this form the partition function reveals a surprising isomorphism: it is the same as the classical partition function for a system of ring polymers. To be more explicit; the quadratic term within the exponential corresponds to a ring of n 'beads', each of which is coupled to two neighbours via a harmonic spring with force constant $nm/(\hbar\beta)^2$. In addition each bead in the ring experiences the potential $V(r_{k,j})/n$, which arises from the interactions between the different polymer rings. (It is worth pointing out that the reason a ring polymer results from this treatment, is that the application of the Tr or trace operation enforces the closure of the ring).

The most appealing aspect of this isomorphism is the fact that we can use conventional Monte Carlo methods to calculate the properties of the classical polymer system and translate them into the properties of the quantum mechanical system. There is no special difficulty in doing this, though it is important to be aware of the physical interpretation, in the quantum mechanical sense, to avoid some potential pitfalls. Before discussing these aspects we should point out that the Monte Carlo method is not the only option available to us. What is required is some means of sampling the configuration space available to the ring polymers and to that end both molecular dynamics and stochastic dynamics may also be used. However it must not be thought that these methods can be used to give the time dependent properties of the system; the formulation of the method does not support it.

The Properties of the Isomorphic Ring Polymer

The system of isomorphic polymers is one in which the potential energy may be written as:

$$U_{\text{eff}} = \sum_k^N \sum_j^n \{ nm/2(\hbar\beta)^2 \cdot (r_{k,j} - r_{k,j-1})^2 + V(r_{k,j})/n \}$$

We have already remarked on the nature of the quadratic term; classically it is equivalent to the intramolecular interactions of a harmonic ring polymer. What is its physical significance in the quantum mechanical case? Since we have replaced a classical 'point' particle by a more delocalised polymer, we may guess that it reflects the 'Heisenberg uncertainty' in the position of the particle. This intuitively appealing idea is supported by the properties of the spring constant $\kappa = nm/(\hbar\beta)^2$. If the mass of the particle is large, or if the temperature is high (i.e. β is small), κ is large and the ring polymer will tend to be tightly bound into a small volume. These conditions correspond to the classical limit. Conversely, a small mass or a low temperature will weaken the spring constant and the polymer will delocalise to a much greater extent.

Another feature of the ring polymers we should discuss is the number of beads n . In practice this has to be determined by experience. There are however some facts which we need to bear in mind. Firstly, the short time (or high temperature) approximation inherent in the derivation of the partition function requires that the number of beads be sufficiently large to justify the approximation. Thus a rapidly varying potential function implies a need for a large number of beads. Secondly, the presence of the number n in the spring constant κ implies that the appropriate choice of n will be influenced by the mass of the particle and the temperature of the system. Thus we find that simulations of argon below the triple point require about 5 beads⁶ and liquid neon requires 20-40 beads⁷. Simulations of the electron in molten potassium chloride have required about 200 beads⁸ and the electron in liquid ammonia several thousand beads⁹.

The second term of the effective potential U_{eff} is the $V(r_{k,j})/n$ term, which corresponds to the interaction between different polymer rings. We notice the presence of the bead number n in the denominator. The significance of this is that it effectively reduces the interaction between beads on different rings by a factor n . As a result of this, we find that beads on different polymers are allowed to approach

each other more closely than the original classical particles. In other words, the beads have a greater ability to 'tunnel' into classically forbidden regions. This is exactly the kind of behaviour we expect for quantum systems.

As for the potential $V(r_{k,j})$, there are one or two subtleties that must be considered. In principle, it may be treated as the sum of pair interactions between sites (beads) on different polymers, as is normally done in classical simulations. However we should point out an important difference. Namely; each bead on a given polymer ring can only interact with **one** bead on the different polymer ring. It does **not** interact with them all. The reason for this lies in the correspondence between the time dependent Green's function and the temperature dependent density function. The former is constructed from a partition of a time interval into n sub-intervals. The potential energy function is evaluated once for each sub-interval and the contributions all derive from that time interval (i.e. all contributions are evaluated at the same instant in time). Translation of this feature into the calculation of the density function shows that, since each bead corresponds to a time sub-interval in the original Green's function, a bead on a given polymer can only interact with the corresponding bead on another. Another way of saying this is that corresponding beads on different polymers exist at the same moment in imaginary time and can only interact with beads existing at the same moment. Thus we write the potential term as:

$$V(r_{k,j}) = \sum_j \sum_{k=2}^N \sum_{k' < k} U(|r_{k,j} - r_{k',j}|)$$

Where $U(|r_{k,j} - r_{k',j}|)$ is a suitable pair potential, such as the Lennard-Jones potential.

This feature of the inter-polymer potential has two useful consequences. Firstly, the number of bead-bead interactions that must be calculated is considerably less than in a real simulation of a classical polymer. This represents a great reduction in computational cost. Secondly, the straightforward empirical (e.g. Lennard-Jones) potential can be used in the simulation without modification. This aspect only becomes apparent when one tries to simulate quantum systems with wavepackets, since there the basic potential must be modified to take into account the delocalisation of the particle over the wavepacket⁵. In the PIMC case, we are restricted to dealing with corresponding beads on each ring and the delocalisation

of the rest of the ring does not enter into consideration.

Thermodynamic and Structural Calculations

In classical Monte Carlo simulations one of the simplest quantities to calculate is the energy of the system. The expression for this is obtained from the partition function in the form of a derivative:

$$\langle E \rangle = -\partial \ln Z / \partial \beta.$$

Application of this rule to the partition function for the system of isomorphic polymers gives

$$\langle E \rangle = \langle 3nN / (2\beta) - \sum_k \sum_j \left[\frac{1}{2} (r_{k,j} - r_{k,j-1})^2 - V(r_{k,j}) \right] / n \rangle.$$

The first two terms on the right represent the kinetic energy of the system. The last term represents the potential energy. This expression for the energy of the quantum system (which should **not** be confused with the potential energy U_{eff} of the isomorphic polymers that drives the Monte Carlo simulation) has been the subject of much discussion in the literature. Herman et al.¹⁰ have shown that this form for the energy is subject to fluctuations that grow linearly with the number of beads in the polymer rings and consequently leads to poor estimates of the energy. For this reason they have proposed a new form of the energy estimator based on the virial. In the many-particle systems we are concerned with here, the estimator takes the form¹³

$$\langle E \rangle = \langle 3N / (2\beta) + \sum_k \sum_j \left[\frac{1}{2} (r_{k,j} - r_{k,1}) \cdot \partial V(r_{k,j}) / \partial r_{k,j} + V(r_{k,j}) \right] / n \rangle.$$

(Where $r_{k,1}$ refers to the first bead on the k 'th ring.) This estimator is considered to be more accurate than that given above. However we have found that, for the systems we have studied, this is not the case. This may be due to the relatively small numbers of beads in the rings we have used (since our particles; neon and argon atoms, are almost

classical), which do not adequately reflect the differences between the two estimators or to the steepness of the Lennard-Jones potential, which generates large fluctuations in the virial term.

The virial of the quantum system is obtained from the derivative of the inter-polymer potential energy:

$$\langle \Phi \rangle = \langle \sum_j \sum_{k=2}^N \sum_{k'} \langle k | (r_{k,j} - r_{k',j}) \cdot \delta U(|r_{k,j} - r_{k',j}|) / \delta r_{k,j} | \rangle / n$$

which may be used to calculate the pressure p :

$$p = (2\langle KE \rangle - \langle \Phi \rangle) / 3V,$$

where KE is the quantum mechanical kinetic energy:

$$KE = 3nN / (2\beta) - \sum_k \sum_j \langle k | \kappa / 2 (r_{k,j} - r_{k,j-1})^2 | \rangle.$$

A useful quantity to calculate in these quantum systems is the mean-square radius (χ^2) of the polymer rings. This is given quite simply by the formula:

$$\langle \chi^2 \rangle = \langle |r_{k,j} - R_k|^2 \rangle$$

where R_k is the position of the centre of mass of the polymer ring;

$$R_k = \sum_j r_{k,j} / n.$$

The usefulness of this quantity is that it provides a ready measure of the delocalisation of the quantum particle. In this respect it rather resembles the mean-square width parameter [ξ_j^2], encountered in semiclassical simulations of gaussian wavepackets and which roughly corresponds to the mean-squared-width of the wavepackets⁵. It is of the same order of magnitude as the square of the thermal deBroglie wavelength $(h/\sigma)^2 / m\epsilon$ for the Lennard-Jones system.

The calculation of the radial distribution function for a many-particle system presents no special difficulty in

PIMC if we remember to consider only pairs of corresponding beads on different ring polymers. Thus we may write:

$$g(r) = \frac{1}{nN\rho} \sum_{k \neq k'}^N \langle \delta(|\mathbf{r} + \mathbf{r}_{k,j} - \mathbf{r}_{k',j}|) \rangle$$

We now conclude with a short account of our work on neon and argon.

The Simulation of Neon and Argon.

We have carried out PIMC simulations with the 'primitive' high temperature algorithm described above for Lennard-Jones argon (solid)⁶ and neon (liquid and solid)¹⁴.

In the case of argon ($T^* = 0.3$ and 0.33) 4 and 5 beads are sufficient. The main objective was the calculation of the quantum correction to the free energy⁶. The corrections to the Helmholtz free energy and the internal energy are - as expected - small (-2-3%). The effect on the pressure and hence the chemical potential however, is large: 0.35 and 0.5 (=13 and 21 mpa). We also find that at these state points the (quasi-) harmonic approximation is unsatisfactory. Our results indicate that in the study of low temperature phase equilibria in solids the results obtained by classical MC and MD simulations should be treated with caution and that for molecular solids the harmonic approximation is not reliable.

In the PIMC simulations of neon 20-30 beads were required. At the experimental triple point ($\rho^* = 0.808$, $T^* = 0.666$) the quantum correction to the internal energy is ~ 10% and that to the pressure is ~ 20mpa. At $\rho^* = 0.725$, $T^* = 0.95$, where experimental data for $g(r)$ are available, these agree very well with the PIMC results but differ at small r from the classical MC result (as has also been found by Berne et al. for a slightly different state point⁷).

It is pleasing to note that for systems where quantum effects are fairly important but do not predominate (e.g. neon as against helium) many particle PIMC simulations can be carried out by the simple 'primitive' algorithm and that recourse to the much more sophisticated sampling schemes of Pollock and Ceperley¹¹ or that of Sprik et al.¹² - while possibly more economical in computing time - is not necessary.

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Appendix

The Green's Function Propagator

The Green's function propagator represents a formal solution of the time dependent Schroedinger equation;

$$\mathbf{H} \Psi = i\hbar \delta\Psi/\delta t \quad A1$$

in which we assume that the Hamiltonian operator \mathbf{H} is **not** an explicit function of time and that the solution is known at time zero i.e. $\Psi = \Psi(x,0)$ at $t=0$. (We also assume here that the problem is one-dimensional). Since \mathbf{H} does not contain the time explicitly A1 has a solution of the form

$$\psi_n(x,t) = \psi_n(x) \exp(-i\hbar^{-1}E_n t) \quad A2$$

where $\psi_n(x)$ is an eigenfunction of the operator \mathbf{H} and E_n is the corresponding eigenvalue i.e.

$$\mathbf{H}\psi_n(x) = E_n\psi_n(x) \quad A3$$

Since the set of functions $\psi_n(x)$ are orthogonal, the initial wavefunction $\Psi(x,0)$ may be expanded as a linear combination of eigenfunctions;

$$\Psi(x,0) = \sum_n a_n \psi_n(x) \quad A4$$

in which the coefficients a_n are evaluated from the integrals:

$$a_n = \int \Psi(x,0) \psi_n^*(x) dx \quad A5$$

(which is proved by multiplying both sides of A4 by $\psi_n^*(x)dx$ and integrating over x .) Exploiting the relations A2 to A5, it is apparent that an acceptable solution of equation A1 would have the form:

$$\Psi(x,t) = \sum_n a_n \psi_n(x) \exp(-i\hbar^{-1}E_n t) \quad A6$$

Which is easily seen to satisfy both equation A1 and the initial condition $\Psi = \Psi(x,0)$ at $t=0$. Substituting A5 into A6 gives the expression:

$$\Psi(x,t) = \int \sum_n \psi_n^*(\xi) \psi_n(x) \exp(-i\hbar^{-1}E_n t) \Psi(\xi,0) d\xi \quad A7$$

Which may be more succinctly written as

$$\Psi(x,t) = \int G(\xi,x;t) \Psi(\xi,0) d\xi \quad A8$$

with

$$G(\xi,x;t) = \sum_n \psi_n^*(\xi) \psi_n(x) \exp(-i\hbar^{-1}E_n t) \quad A9$$

which is recognisable as the Green's function described in the text of the article. It is apparent from its role in the equation A8 that the Green's function represents a formal solution to A1, since everything that may be deduced about the wavefunctions $\Psi(x,t)$ may be obtained with the aid of it. Extensions to problems of higher dimensionality may also be derived in this way.

NON-EQUILIBRIUM MOLECULAR DYNAMICS

FOR MATERIALS PROCESSING

Paulette Clancy
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Introduction

We are developing new non-equilibrium MD methods to look at technologically important materials processing techniques e.g. laser annealing, rapid solidification, ion implantation and (in the future) molecular beam epitaxy, which also exhibit a wealth of interesting chemical physics. The following article gives a brief description of our first foray into the world of non-equilibrium MD for the study of rapid interfacial kinetics such as those encountered in laser annealing. This work represents one of several PhD projects conducted by Mr. Dhanraj Chokappa who is expected to graduate this summer. Details of the simulation glossed over in this article will be given in an upcoming paper [1].

The Simulation Cell

In our simulation the cell is composed of four regions, as shown in Figure 1. Region A contains a few particles to model the vapour phase, B contains the dynamic portion of the simulation cell initially set up as a regular solid, though of course the configuration of this portion can be modified to model the problem at hand. In our preliminary tests the particles were arranged on fcc lattice sites in a $7\sigma \times 7\sigma \times 16\sigma$ array. Region C represents two planes of particles again on fcc lattice sites which acts as a heat 'bath' for the system. Velocity scaling in this region slowly maintains or restores the temperature of the system to its original preset value. Finally, region D represents a fixed lattice wherein the particles interact with the rest of the dynamic solid but are not allowed to move from their original lattice sites.

The non-equilibrium MD simulation method

The principal interaction of a laser beam with a solid is the heating of the surface. It is believed [2,3] that the coupling of the photons with the surface results in the formation of a plasma which persists for ~ 1 ps before the energy is converted into thermal energy which is then dissipated through the substance. Initially we shall assume that the system is at the post-plasma stage and that all the energy supplied to the system is transferred into thermal energy. A non-equilibrium Molecular Dynamics simulation technique has been developed which is used to follow the time evolution of

such a system. A modified 'leap-frog' algorithm was used to integrate the Newtonian equations of motion. The introduction of a thermal gradient into the system (producing a non-equilibrium system) produced by rapid heating and cooling can be achieved in different ways. Landman [4] simply scales the velocities of the particles according to a simple absorption formula. For LJ systems, Broughton et al. [5] quench a liquid reservoir and allow dissipative forces to cool the 'dynamic' liquid to watch crystal growth.

In our new simulation method, energy transfer is effected through the interaction of a given material with energy carriers ("ghosts") which appear to the solid particles as having no volume and virtually no mass. The velocity of the energy carriers is obtained from a simple energy and momentum balance. In reduced units, this is given by

$$v^* = \left(\frac{2E^*}{N_c (m_c/M)} \right)^{1/2} \quad (2)$$

where $E^* = E/\epsilon$ is the reduced energy input, N_c is the number of energy carriers and m_c/M is the ratio of the mass of the energy carrier to that of the substrate. Initial tests have shown that a reasonable amount of melting occurred in our test system for a mass ratio m_c/M of 10^{-6} , i.e. the energy carriers are one millionth the mass of the substrate ('argon') atoms. If the mass of the ghost particles is increased by an order of magnitude two more atomic planes melted in our test system, but there is excess vaporization which complicates the regrowth of the crystal. The energy (scaled proportionately to the small size of our system) can be chosen freely, e.g. to match an experimental value for the fluence of a laser. This energy is divided equally between a specified number of ghost particles, N_c . The energy given to a single ghost is equally divided between x-, y- and z-directions. The ghosts collide with the solid substrate, transfer their energy, and then disappear. The number of ghost particles is a variable of the simulation whose effect is under investigation.

The ghosts appear less than 1 σ above the original solid/vapor interface. This is in line with the action of a laser which heats only the solid substrate. This also has a practical purpose: allowing collisions with all the vapor particles from the top of the box repeatedly energizes them during the 'irradiation'; these highly energetic atoms then wreck havoc on the surface. The energy pulse is given a Gaussian shape whose peak value can be identified as the power of the laser. The energy is applied to the system every time step for the duration of the pulse (typically, of the order of picoseconds to nanoseconds).

After the chosen amount of energy has been supplied to the system for a specified time, the simulation will be allowed to anneal long enough to achieve its final equilibrium configuration, as determined by the constancy of its thermodynamic and structural properties. The annealing involves a considerable simulation run time, roughly 10-600 times that of the pulse duration, achievable with access to current supercomputers.

Throughout the simulation we monitor the following properties of the system averaged over very small time-intervals (typically 1-5 picoseconds):

Thermodynamic : density profiles as a function of depth; temperature.

Structural : radial distribution function, $g(r)$; structure factor, $S(k)$.

Kinetic : velocity of the solid/liquid interface as a function of depth and temperature; mean-squared displacements and hence diffusion coefficients, velocity autocorrelation functions and memory functions (though these latter properties are computationally very intensive and so are evaluated sparingly in the post-simulation analysis of the stored configurations).

Preliminary Results:

Preliminary studies of the feasibility of the proposed method using the fixed lattice model for the simulation cell are encouraging. A test system of only 1000 Lennard-Jones atoms, initially packed as 20 atomic planes plus a few vapor particles, and acted upon by a 15ps pulse of energy $E = 0.025 \text{ Jcm}^{-2}$ showed that about half the sample melted, producing a broad solid/liquid interface, see Figure 2. Following the cessation of energy input, the solid continues to melt for a short time, before recrystallizing several planes at a time in a roughened manner along its exposed (100) face. These results are in agreement with those obtained for a steady-state moving interface of the same system by Broughton et al. [6]. This seems to suggest that the truly non-equilibrium interface in our method gives the same results for crystal regrowth as that produced by a steady-state interface. The resulting melt thickness versus time plot and interface temperature versus time are shown in Figures 3 and 4; these show all the important qualitative features of experimental results. In these tests, the mass of each of the bulk substrate atoms is chosen to be that of argon and the N atoms initially interact with a Lennard-Jones (12,6) potential with parameters ϵ and σ set to the values of 120K and 0.304 nm commonly used for a Lennard-Jones model of argon. Tests at different energies (25,43,60 mJcm^{-2}) showed the slightly different regrowth characteristics with respect to melt thickness versus time expected experimentally. These results also suggest that the simulation 'clock' is very roughly 10 times faster than real time. But these results will have to be verified by further investigations.

Systematic studies of the effect of system size, lattice strain and the two simulation parameters, the number and mass of the energy carriers, are presently underway. We are fortunate to be able to collaborate with an experimental laser processing group within the Materials Science and Engineering group at Cornell, headed by Professor Michael O. Thompson. They intend to perform studies of the rapid melting and resolidification of inert gases starting this Summer. This will be of enormous value in allowing us to improve our model of the physical system and establish correlations between the simulation and experimental results which will move us closer to our long-term goal of producing a tool capable of quantitatively accurate predictions of the interaction between a given material under rapid melting and resolidification processes.

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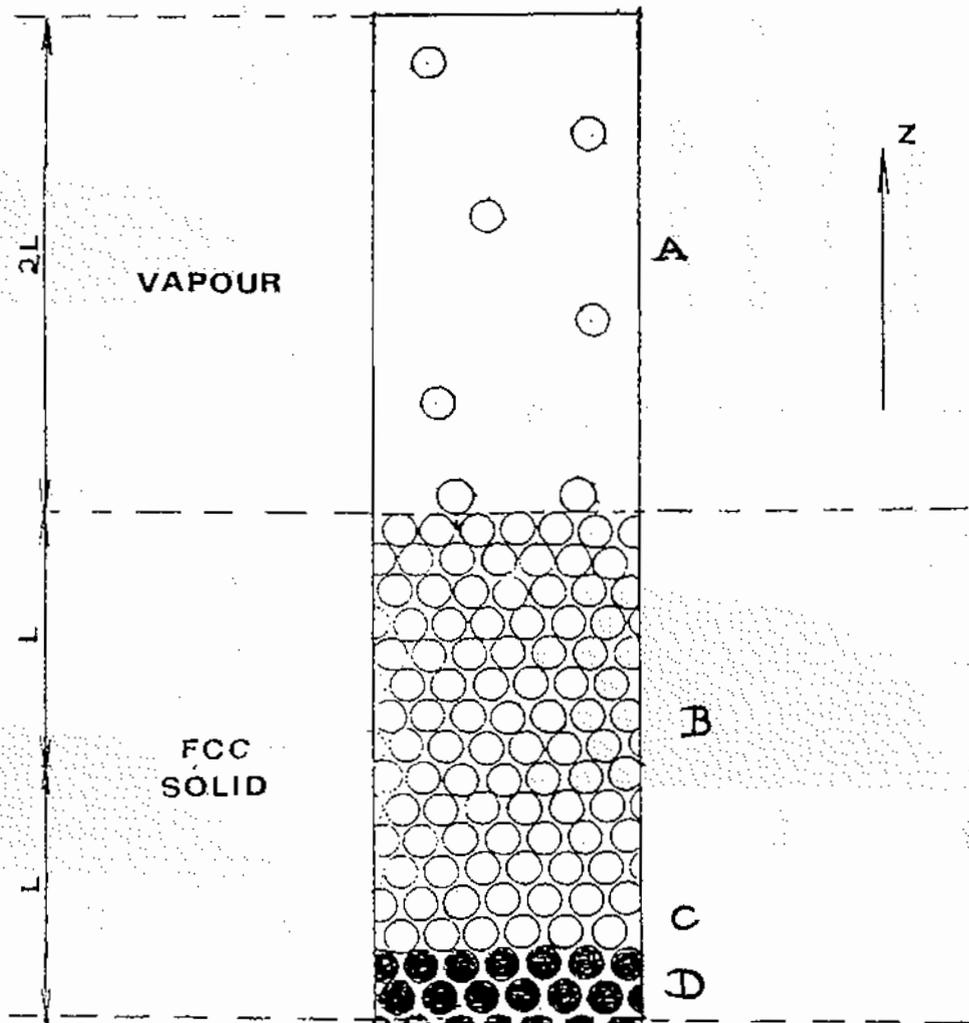
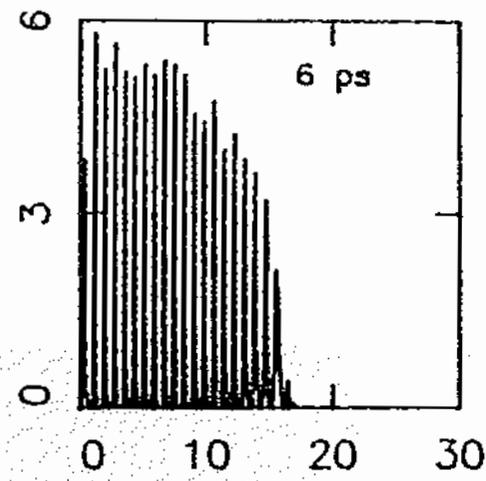
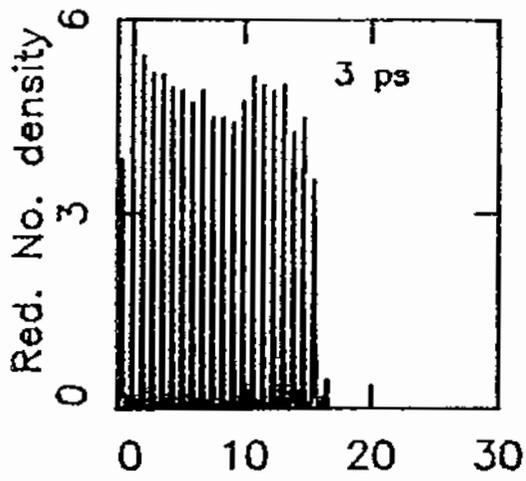


Figure 1

Figure 2(i)



$E = 60 \text{ mJ/cm}^2$

$N_e = 300$

15 ps pulse

Mass ratio = 10^{-4}

7 May 1987

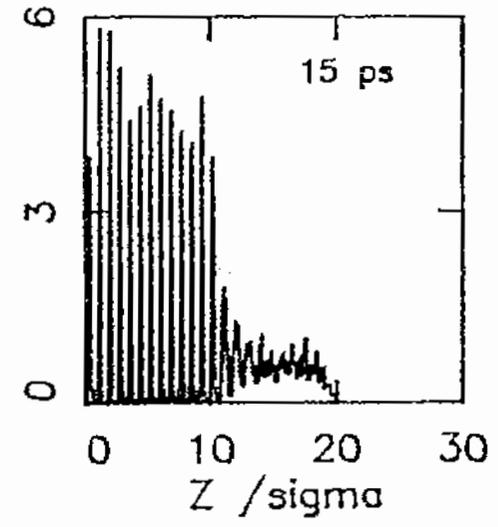
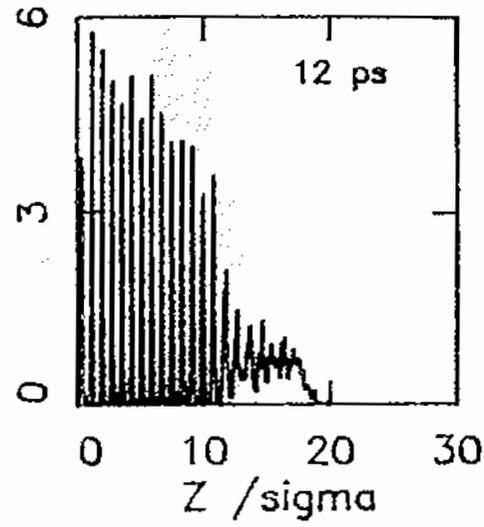
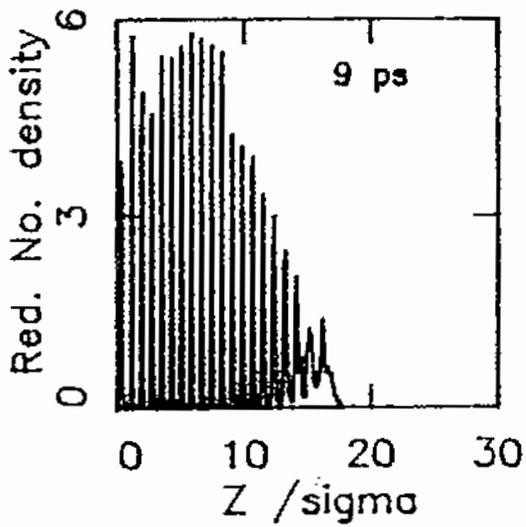
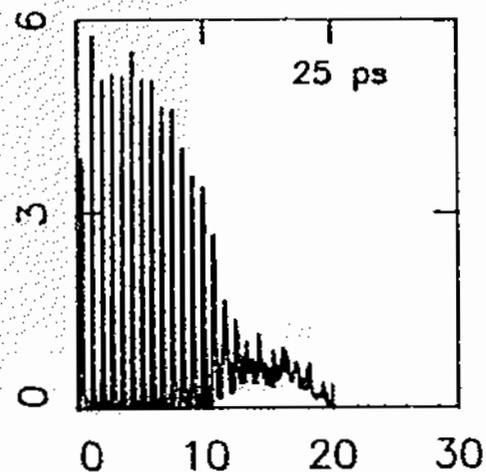
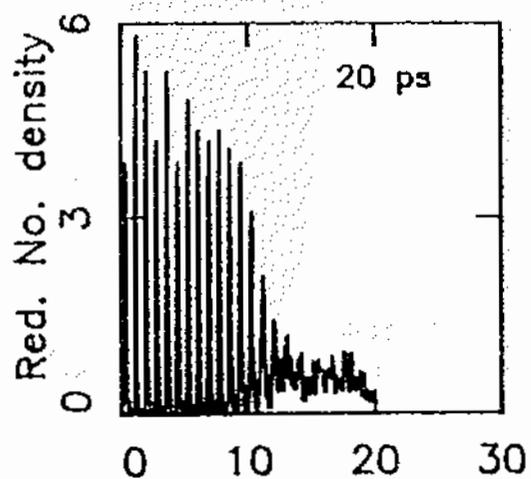


Figure 2(ii)



$E = 60 \text{ mJ/cm}^2$

$N_e = 300$

15 ps pulse

Mass ratio = 10^{-6}

7 May 1987

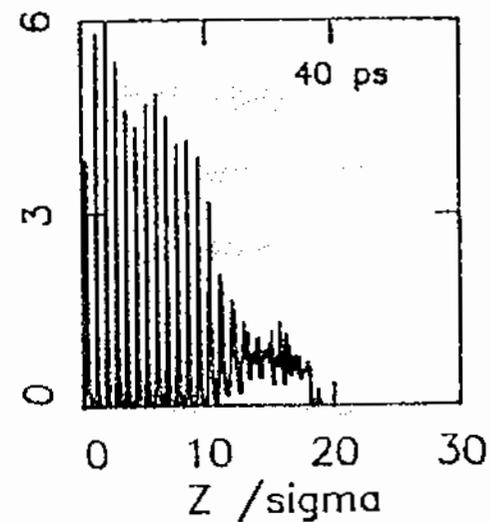
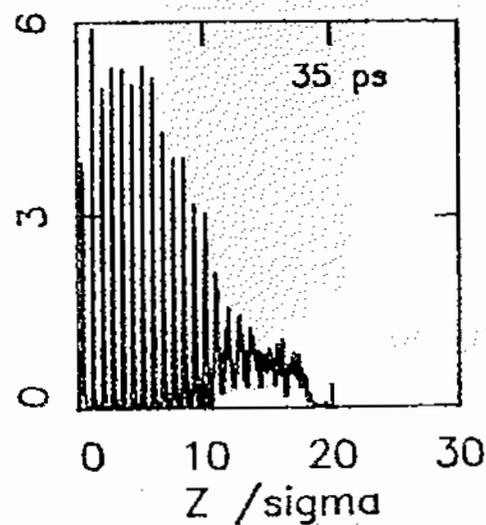
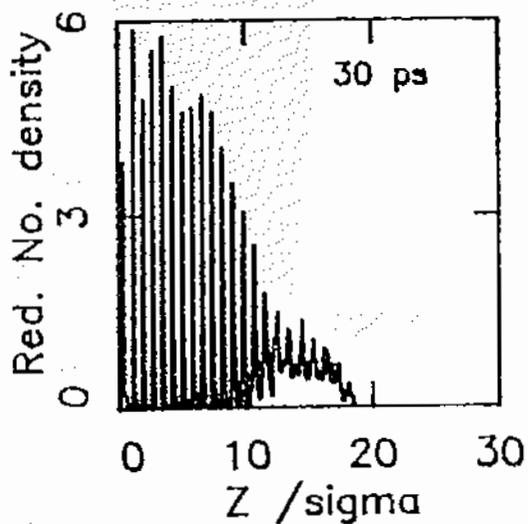
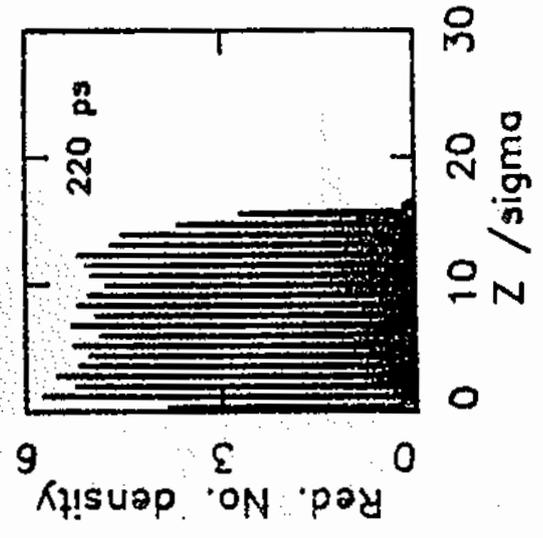
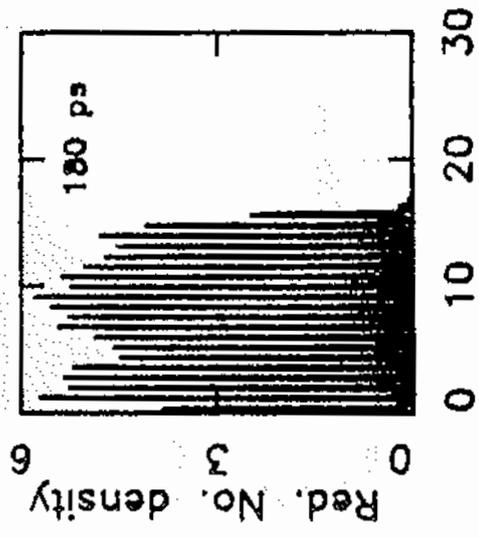
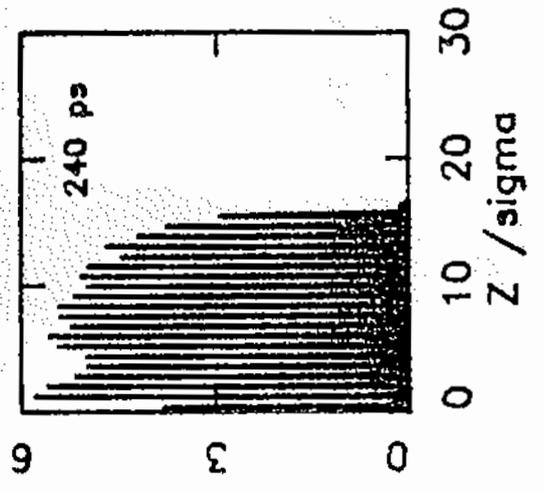
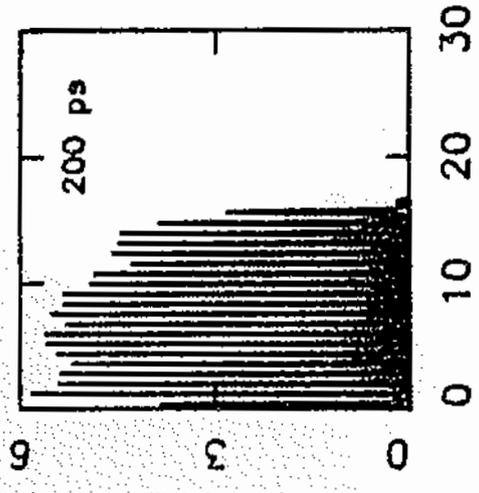


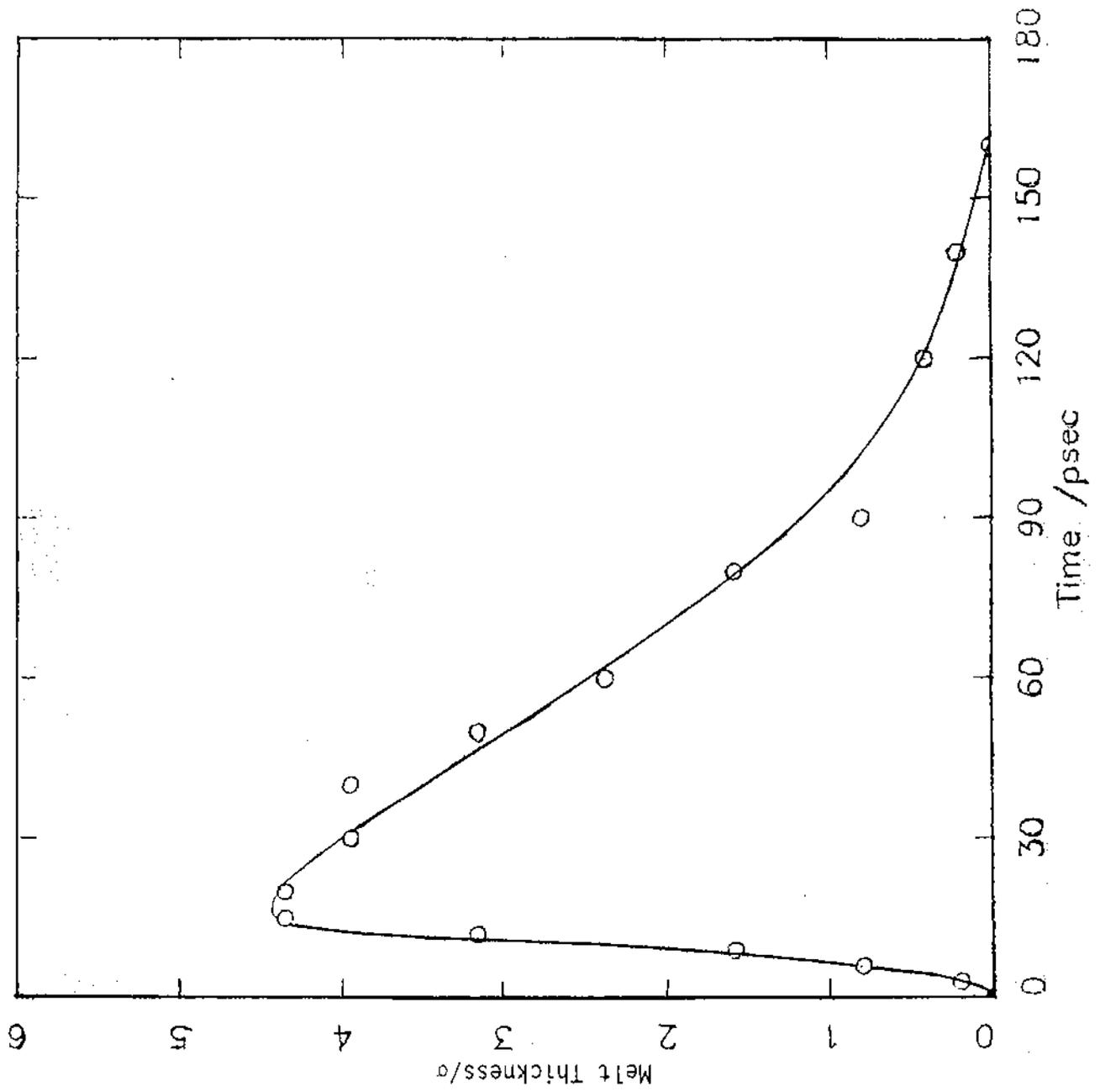
Figure 2(iii)

$E = 60 \text{ mJ/cm}^2$
 $N_e = 300$
15 ps pulse
Mass ratio $\approx 10^{-4}$
9 May 1987



$E = 25 \text{ mJ/cm}^2$
 $N_e = 300$
15 ps pulse
Mass ratio = 10^{-6}

Figure 3



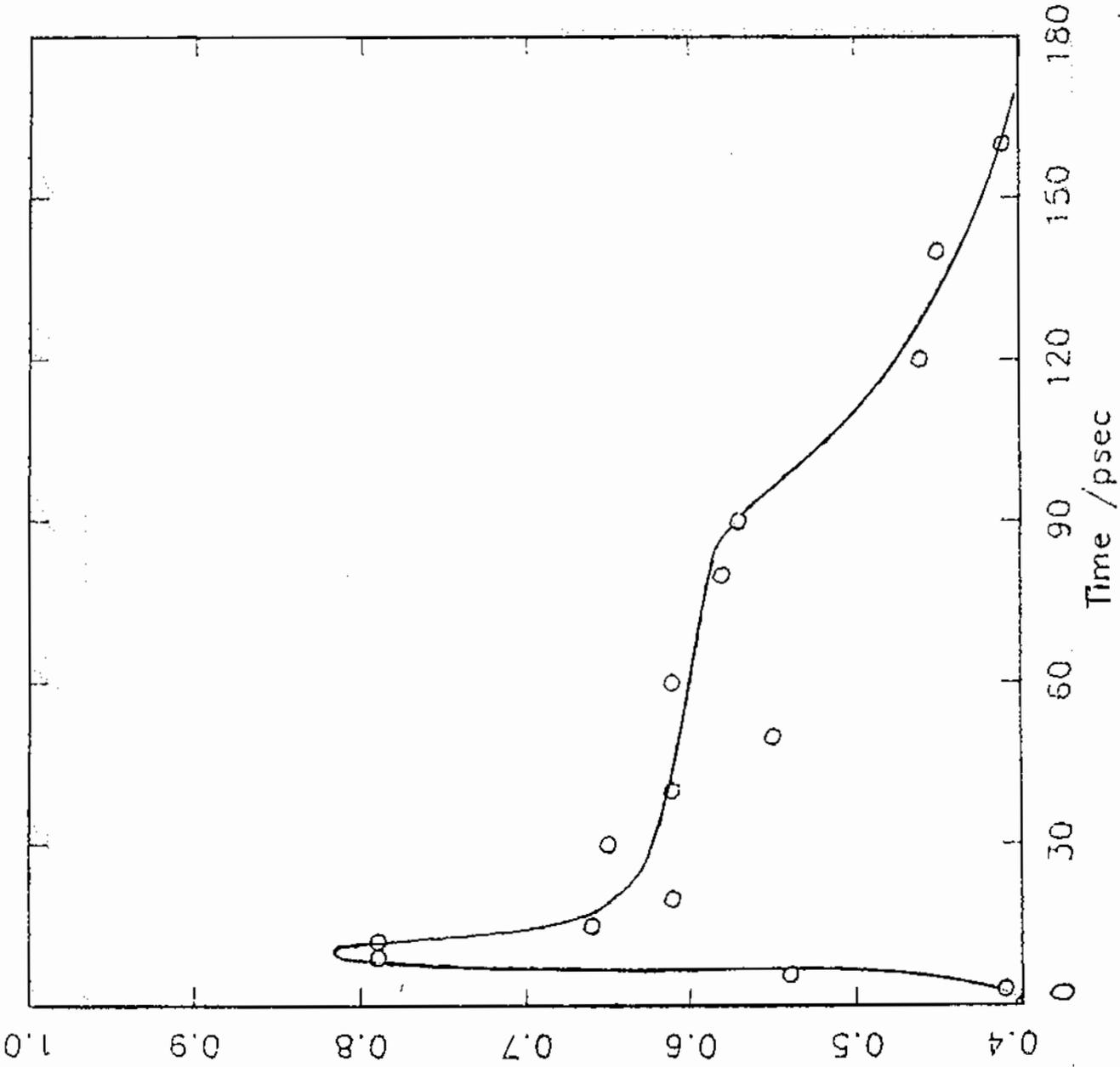
$E = 25 \text{ mJ/cm}^2$

$N_c = 300$

15 ps pulse

Mass ratio $\approx 10^{-6}$

Figure 4



Reduced Temperature at the Interface

Classical and Quantum Mechanical Modelling
of Defect Centres in MgO.

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One of the most intriguing questions confronting contemporary solid state defect studies concerns the limitations of purely classical potential modelling or more precisely, what are the conditions under which quantum mechanical methods become necessary. In the present work, we examine the problem using two different methods applied to simple defect centres in MgO. The first method is based on purely classical potential modelling employing Mott-Littleton procedures, and is embodied in the CASCADE static simulation code. The second (GAMESS) incorporates a high quality quantum mechanical cluster calculation centred at the defect site, surrounded by roughly 100 point charge ions whose purpose is to simulate the rest of the lattice. Thus, it is possible to compare directly the two theoretically distinct modelling methods and understand some of the limitations and strengths of each.

The defect centres chosen for this study are the simple vacancies, $V_O^{\bullet\bullet}$ and $V_{Mg}^{\bullet\bullet}$ and the substitutional ions Li_{Mg}^{\bullet} and F_O^{\bullet} . All these defects assume their formal defect charge states, that is, they remain uncompensated by holes or electrons. This restriction leads to closed shell configurations, a particularly useful restriction for the Quantum mechanical method.

Defect formation energies are calculated in a two step process. First, the defect is introduced into the lattice whilst other lattice ions remain fixed. Second, the lattice ions are allowed to relax in response to the defect and the relaxation energy is obtained. The sum of these two energies yields the total defect formation energy (see table 1).

The most important aspect to take note of in regard to the unrelaxed formation energies is that although the nuclear positions may remain fixed, in the quantum calculation, the self-consistent nature of the method will include relaxation of the electrons in response to the defects incorporation. Thus, in order that the classical simulation can be made comparable, shell relaxation must be allowed on polarizable ions that are included in the quantum cluster. We note that in the present calculations, the only effects the anions as the cations are not polarizable. In fact, because the quantum cluster generally includes only the defect site and the nearest neighbour ions, this effect will only be apparent in the V_{mg}'' and Li_{mg}' defects. We see that for V_{mg}'' and Li_{mg}' the unrelaxed formation energies are significantly lower for CASCADE than for GAMESS calculations, but that for V_o'' and F_o' the energies are very close. This reflects the fact that polarization effects are not accounted for to the same degree in quantum calculations as they are in the classical model. If a more sophisticated quantum mechanical procedure were employed this discrepancy would be expected to decrease.

Due to the lack of short-range repulsion between the point charge ions in the GAMESS cluster, relaxations cannot be explicitly carried out within the GAMESS program. However, relaxed coordinates can be obtained from the CASCADE method and used to define the GAMESS cluster

coordinates. In this manner, relaxation energies are calculated. This means that the GAMESS coordinates are not fully consistent with quantum cluster and hence relaxation energies from GAMESS are expected to be less than those calculated from CASCADE. This is indeed found to be the case. The error found here may be negated by the addition of short range potentials on the point ions and the subsequent self-consistent relaxation of the GAMESS ions with respect to the quantum cluster.

The sum of the component defect formation energies is shown in the table of results. For the reasons given above we expect the CASCADE results to be less than those given by GAMESS but that this discrepancy to be reduced by subsequent improvements in methodology.

Table 1 DEFECT FORMATION ENERGY BREAKDOWN FOR MgO
 (All energies kJ x 10⁻²)

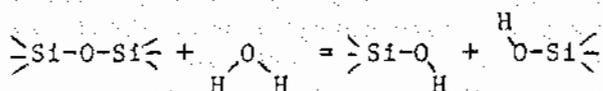
	NUCLEAR POSITION UNRELAXED FORMATION ENERGIES		RELAXATION ENERGY EXCLUDING (100) or (200) POLARIZATION		TOTAL DEFECT FORMATION ENERGY	
	CASCADE	GAMESS	CASCADE	GAMESS	CASCADE	GAMESS
V _O ^{••}	39.675	40.824	-14.745	-12.114	24.930	28.719
V _{Mg} ["]	33.050	35.400	-9.564	-5.703	23.466	29.697
F _O [•]	19.239	19.494	-3.345	-3.165	15.894	16.329
Li _{Mg} [']	15.555	17.050	-2.390	-2.083	13.161	14.967

COMPUTER SIMULATION OF PLASTICITY IN MINERALS

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The aim of this short article is to briefly describe a poster presented at the CCP5 reunion held at UMIST in January last year. The background to the use of computer modelling in plasticity problems has already been described in an earlier article (CCP5 Information Quarterly No. 20 1986 p62). There have been two important developments since then : one involving the use of ab-initio calculations on molecules to check the potentials used for quartz and the other an extension of our modelling to a framework silicate - the potassium feldspar known as sanidine.

The potentials used in the modelling of hydrolytic weakening in quartz [1] were based on the Keating potential for silicon [2] modified to take into account covalently bonded oxygen [3]. The better of the two potentials used also included a repulsive Born-Mayer interaction between oxygen atoms not on the same tetrahedron [4] (in order to cure a soft mode in the phonon spectrum and to prevent oxygen atoms approaching each other closer than 2.2 Å). It is the form of this repulsion that was tested with an ab-initio calculation because the process of Si-O-Si hydrolysis, i.e. the reaction :



which led to release of strain in straight and kinked dislocations in quartz, could not occur if the O-O repulsion were too strong. The calculation [5] was a parameter-free (self-consistent, local density, norm-conserving pseudo-potential) calculation of the system : $\text{H}_3\text{Si-O-SiH}_3 + \text{H}_2\text{O} = \text{H}_3\text{Si-OH HO-SiH}_3$. It was found that this reaction was endothermic, but by only 0.09 eV with infinitely separated products. As the hydroxyl groups in the products approached one another along the common Si-O bond axis the total energy followed the crossed curve of figure 1, from which it can be seen that the empirical O-O potential (uncrossed curve) used in our original calculations was indeed reasonable for separations greater than 2.5 Å. The important common feature of these curves is that the repulsion is almost negligible at separations greater than 2.9 Å, showing that there need be no "steric hindrance" in the hydrolysis reaction at dislocations and kinks where the separations can be greater than 3 Å. Since the strain energy released by hydrolysis of a Si-O-Si linkage in the dislocation core and in the kink was far in excess of 0.09 eV there seems little doubt that hydrolysis should occur, reinforcing the conclusion of ref. 1.

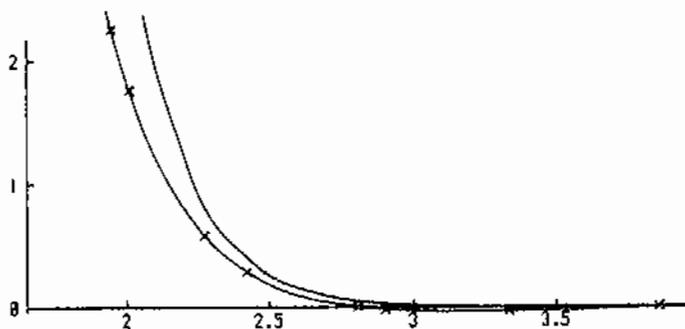


Figure 1 - Total energy (in eV) of two silanol molecules as a function of O-O separation (in Å) along the axis including both Si-O bonds.

It should also be noted that the accuracy of the ab-initio calculation was such as to reproduce even the weak hydrogen bond between the hydroxyl groups causing the total energy curve of figure 1 to have a minimum at a separation of about 3.2 Å.

In the second development the computer modelling was extended to sanidine ($KAlSi_3O_8$) [6] in the spirit of a "computerised ball and stick" model of the aluminosilicate network. It was assumed that this material behaves like an SiO_2 network (replacing Al+K by Si) and that the SiO_2 Keating potential with parameters fitted to quartz, but with the mean bond length for sanidine (1.632 Å), was appropriate. Although the quartz structure was the ground state for this potential, the sanidine structure was only about 2 meV per atom higher in energy and the lattice constants and elastic constants were close enough to the experimental values for our purposes. Since sanidine is likely to be a good model material for the complicated feldspars that form a large part of the earth's crust, geologists studying plate tectonics were very keen to know the answers to these two questions: "Why is deformed sanidine full of $c/2$ partial screw dislocations? And where in the unit cell is the stacking fault between these partials situated? Electron microscopy [7] and non-quantitative modelling [8] partly answered these questions but the quantitative modelling [6] showed that (i) the stacking fault on the bc plane characterised by the lattice vector b shearing between densely-packed planes was relatively low in energy and (ii) the $c/2$ partial dislocations bounding this stacking fault had very low core energies when their axes followed the lattice vector c , i.e. in the screw orientation. It would be interesting to compare the absolute magnitude of the stacking fault energy calculated here (which was much larger than the experimental estimate) with one calculated using an ionic potential.

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THE TRANSPUTER IN STATISTICAL SIMULATION: RESULTS OF A TEST

S.L. Fornili, V. Martorana and M. Migliore

When we read in Information Quarterly for Computer Simulation the enthusiastic paper by David Fincham on the Transputer [1], we were already working with this microcomputer family since a couple of weeks. Our purpose was the same, that is to find out if and to what extent Transputer-based computers are suitable for statistical simulation. In particular, we were interested to test i) how easily simple systems can be assembled by connecting commercially available Transputer-based boards; ii) if their power is really comparable to or even higher than that of superminis like DEC VAX-11, when simulation programs are run rather than benchmarks; iii) how easily can simulation programs be rewritten in Occam language, which is a must, if full advantage has to be taken of the process concurrency features offered by the Transputer architecture. We have then performed a preliminary but rather exhaustive series of tests, whose results we think might help whoever wants to start using Transputer-based systems for statistical simulation calculations.

We chose as a test case the MD simulation of 216 LJ particles, to be run on a two-board system with 5 Transputers and 4-Mbyte memory, which was easily implemented by connecting one B003 board to one B004 board, both available from INMOS. For comparison, a completely equivalent Fortran version of the same program was run on a DEC VAX/11-750 equipped with 5-Mbyte central memory and floating point accelerator. We consider this admittedly simple case significant enough to evaluate the performance of a new computing set-up on the basis of a real program. It is here worth noting that for the presently available Transputer-based systems, both the single and the double precision floating point computations are performed by software, since a floating point unit has been announced by INMOS for the 2nd quarter of 1987.

The parallel version of the MD program was written in Occam2, debugged and run using the TDS700 Development System, that INMOS has developed for IBM-PC/AT or /XT with fixed disk and 640-kbytes memory. It consists of a B004 board with a 32-bits T414 Transputer working at a 12.5-Mc/s clock rate, 2 Mbytes memory and interface circuitry, and a software package including folding editor, compiler and configurator. Although the Occam2 version of this package is still in beta-release, we found it not too difficult to use and free of relevant undeclared bugs. A major advantage of this development system is that it is possible to emulate on the single Transputer of the B004 board concurrent processes which will actually run on a number of Transputers of the target multiprocessor computer. In our case, the MD program was developed on the B004 board and then loaded on the two-board system consisting of the same B004 and one B003 board with four 15-Mc/s T414 Transputers and 4 Mbytes memory.

Parallelism was achieved using a number of different schemes. Among them, we found particularly efficient the "uniform subtask allocation" ("usa") approach that has been proposed by Clementi's group [2] for lCAP parallel machines. In Tab.1 we report the value of the execution time per time-step for our Occam2-coded MD program running on the two-board Transputer-based system, whose processors were connected according to the ring topology. The most time consuming part of the program was paralleled using the "usa" scheme. In the same Table is shown the value obtained with the parallelism approach of mapping an equal number of particles per Transputer ("pm") [3]. For comparison, analogous results are also reported, which refer to sequential implementations

of the same MD program running on one of the four Transputers of the 3003 board, and on the above mentioned VAX-11/750 computer, respectively.

Table 1 - Execution time (in sec) per MD time-step and memory occupation (in Kbytes) for different schemes of parallelism and computer systems.

Type	Computer	Algorithm	time (sec)	memory (kbytes)
parallel	5-Trans.	"usa"	9.1	35/Trans.
	5-Trans.	"pm"	14.2	35/Trans.
sequential	1-Trans.		33	47
	VAX		6.5	

Our code cannot be easily optimised by selectively using the relatively small internal memory of the Transputers. Then, their performance is worse than that one might expect on the basis of INMOS specifications. Nevertheless, the results of our test suggest an optimistic view about the potential of the Transputer for statistical simulations and similar applications. Furthermore, Transputer improvements have been already announced by INMOS, such as higher clock rates (20 and 30 Mc/s rather than 12.5 and 15 Mc/s, as in the present test) and floating point unit.

The only serious problem that now may restrain the use of Transputer-based computers for the production phase of statistical simulations is the lack of an efficient way of directly interfacing Transputer with high-capacity storage devices. In fact, the INMOS B005 disk controller, based on T212 16-bit Transputer, interfaces one 640 kbyte floppy drive and one 20 Mbyte winchester drive, and the performance of other approaches depends on the limited addressing capability of MS-DOS of IBM-PC or compatible computers and on the characteristics of their hardware communication channels. A preferable solution would be an Ethernet interface that could provide a direct connection of Transputer-based systems to suitable high-capacity winchesters already commercially available. This would really allow the profitable use of several Transputers that could be configured, according to the organization type best suited to the application, either as high-connectivity "personal supercomputers" or as smaller VAX-like systems.

In conclusion, since we feel that the above problem will soon be solved, we share Fincham's enthusiastic view about the Transputer potential for simulation calculations.

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Vectorization on Supercomputers

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We have read with interest "The FPS-164: A User's Tale" written by Dr. W. Smith in a recent issue of this magazine and have some thoughts to share. With the availability to many researchers, of scientific computers/supercomputers, for molecular dynamics and Monte Carlo simulations, it is natural that we start thinking about vectorization or pipelining to make the best use of these computers. The possibility of parallel processing seems not too distant in the future either.

Last year computing time became available to us, through National Science Foundation, on the Cornell National Supercomputing Facility for performing molecular dynamics and Monte Carlo simulations. At that time several FPS-264 and FPS-164 array processors were available. We started investigating the possibility of pipelining our molecular dynamics simulation code for Lennard-Jones spheres. We modified our code in a way quite similar to that outlined by Fincham² for CRAY-1 computers. The program did not run any faster on FPS-264 in comparison to the earlier scalar code. We also realized that in order to make this particular code run significantly faster than the original code, assembler instructions would be needed.

Soon afterwards an IBM-3090/400 VF supercomputer was delivered to Cornell. This particular model contains four scalar processing units (of course we use only one) with 64K CACHE memory and one tightly-coupled Vector Facility per processor. The optimum vector length is 128 elements and peak speed-ups of 3 to 5 are possible over the scalar mode. Scalar processors can run about 2.75 times faster than an IBM-3084 and have S/370 architecture. A VS FORTRAN 2 compiler is available with automatic vectorization obtained by using the vector option level(2). At the vector option level(0), computations are performed in the scalar mode

only. Due to the availability of Vector Masking hardware, simple IF statements etc. can also be vectorized. Also available is the indirect addressing in the Vector Facilities.

We made some runs using this computer to study the vectorization of the code for molecular dynamic's simulation of Lennard-Jones fluid. This was modified, again, in a manner similar to that of Fincham with the only difference being that GATHER and SCATTER loops are not needed here. This program ran 22 % faster than the original program for a system of 256 spheres at a high density state point. A Verlet neighbor list with a 2.8σ cut-off and potential truncated at 2.5σ was used.

We then modified our code in a slightly different manner. We used a neighbor list building subroutine which essentially consists of an outer loop (DO I=1,N-1) and an inner loop (DO J=I+1,N). After applying the minimum image criteria, for the pairs for which the scalar distance was within the list cut-off, both I and J numbers were stored. The neighbor list was updated every ten times or so. A separate subroutine was then used to evaluate the intermolecular forces. This subroutine basically consisted of a single loop over element pairs in the neighbor list. We considered this to be our new scalar program. This program was easily vectorized and we only had to ensure that computations were performed in vector sections of 128 or close. The vectorized program ran about 25 % faster than the new optimized scalar code for a system of 256 spheres. We point out that speed-up obtained this way is relatively independent of the system density and potential cut-off. Also, time savings due to the use of neighbor list are kept and simplicity and also the portability of the scalar code is retained.

Our numbers are not as impressive as those reported by Dr. Smith which are closer to 40 % (after the use of assembler level instructions for vectorization). Detailed tests show that in our case, the minimum image condition part of the pair interaction evaluation has only a

small speed-up in spite of full vectorization. Of course, the whole code can be further tuned with the use of assembler instructions.

We then looked at vectorization of the code for molecular dynamics simulation of the Gaussian overlap fluid³. Here we use the method of Cheung⁴ for the torque evaluation and quaternions for solving the rotational equations of motion. We modified our code for vectorization using the latter procedure discussed above and show the run timings in the following table:

Comparison of run timings for molecular dynamics simulation of the Gaussian overlap fluid. Time is in seconds.

	IBM-3084 QX VS FORTRAN 1.4	IBM-3090/VF VS FORTRAN 2 level(0) level(2)	CRAY-XMP CFT-1.14
Original scalar code	1100	420	420
Vectorized version	1182	425	189

On IBM computers calculations were performed using 64-bit precision. The program was also run on a CRAY-XMP computer at NMFE computer center, Livermore, without making many changes. The overhead in converting from scalar to vector, as shown by IBM-3084 timings, comes from the use of the minimum image method suggested by Fincham and Heyes⁵ for vectorization.

Our experience with these simulations indicates that molecular dynamics simulation of fluids of spheres may not be a very good example problem for vectorization studies using FORTRAN, unless computations of pair interactions are far more complicated than those

involving the Lennard-Jones (12:6) potential or significant attention is focused on the architecture of a particular machine and system specific subroutines are used. The latter, however, can reduce the portability of the FORTRAN code. Vectorization seems to work better for nonspherical molecules. Recently, Brode and Ahlrichs⁶ have also reported good speed-ups for polyatomic molecules on a CYBER-205 computer. In that case, however, the scalar program seems to have been well tuned for a SIEMENS-7880 computer. While we have not performed pipelining studies for the case of nonspherical molecules using the FPS-X64 array processors, we suspect good speed-ups may be possible and perhaps without the use of assembler level instructions. Also suitable for vectorization, or pipelining, are computations involving transport coefficients, such as the self diffusion coefficient through Green-Kubo or Einstein relations. Here large central storage or the extended storage architecture, available with many computers, can also be useful, in addition to substantial vectorization of the FORTRAN code.

We have also studied the vectorization of a Monte Carlo simulation code for the Lennard-Jones quadrupolar fluid. A comparison of the run timings on different computers for the case of $Q^* = 1.0$, at a high density state point ($\rho^* = 0.85$) is shown in the following table.

Comparison of run timings for Monte Carlo simulation of the Lennard-Jones quadrupolar fluid. Time is in seconds.

	IBM-3084 QX VS FORTRAN 1.4	IBM-3090/VF VS FORTRAN 2 level(0)	CRAY-XMP CFT-1.14 level(2)	
Original scalar code	2489	950	940	588
Vectorized version	2684	1068	362	345

The increase in overhead in converting from scalar to vector code in this case comes from the use of the minimum image technique suggested by Fincham and Heyes : This can be avoided at only a small cost to the speed-up. The Monte Carlo code was vectorized and run on IBM-3090 by C. P. Williams who has now joined the Royal Dutch Shell at KSLA, Amsterdam.

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LARGE NUMBERS OF PARTICLES ON THE CRAY-1

by David Heyes

MD simulations sometimes have to be performed on large numbers of particles, N , say, over 1000 in order to test for N -dependencies in properties where long range correlations are suspected, e.g., in the solid and glassy states. The normal method for smaller systems is to consider all pairs of particles and then reject interactions from pairs separated by some arbitrary distance, called the cut-off. The number of interactions is $N(N-1)/2$. CPU computational time increases in proportion to this. Therefore the CPU time increases approximately in proportion to N to the power 2. It is essential to lower this power if large N is to be considered in practice. This can be achieved by performing some form of sorting of the particles before the forces loop is entered so that those pairs which have no hope of interacting are not considered in specific pair searches. One way of achieving this is embodied in the Link Cell algorithm. The Link Cell method breaks the MD cell into sub-boxes. Only the particles within adjacent boxes need be considered, as each sub-box has a minimum sidelength equal to the interaction cut-off. Another method is called the Neighbourhood Table scheme. The Neighbourhood Table approach is quite different, in periodically creating lists of likely interaction partners for each particle. This is not the place to go into the details of these techniques, as they have already been considered elsewhere [1-3]. These techniques were developed in the days of serial mainframe computers. It occurred to me that there might be other ways of presorting the particles that make use of the vector architecture and scientific subroutines of supercomputers such as the CRAY-1. My objective is to devise a scheme which is,

- (i) Fast,
- (ii) Compact, i.e., easy to understand. Neighbourhood tables and especially the Link Cell scheme are definitely not these.
- (iii) 'Failure free', even at the expense of extra memory, but not too much extra memory!

Although I am still working on these methods I feel that a preliminary report is warranted because readers of the CCP5 Newsletter may be able to suggest improvements on

the proposed method, alternative schemes or simply be able to use the scheme proposed below.

First I give a typical forces loop for the CRAY-1, suitable for N less than about 256. The code is constructed so that each element of the inner (J) loop does not depend on any other, so then they can be gone through essentially independently or in a 'pipeline' fashion.

```

*****
*   OLD CODE   *
*****

DO 1654 I=1,N ! N PARTICLES
FX(I)=0.0 ! X FORCE ARRAY
FY(I)=0.0
FZ(I)=0.0
PRXX(I)=0.0 ! SINGLE PARTICLE XX COMPONENT OF THE
PRYY(I)=0.0 ! PRESSURE TENSOR
PRZZ(I)=0.0
PRXY(I)=0.0
PRXZ(I)=0.0
PRYZ(I)=0.0
POTR(I)=0.0 ! REPULSIVE PART OF THE SINGLE PARTICLE
! ENERGY
POTA(I)=0.0 ! ATTRACTIVE PART OF THE SINGLE PARTICLE
! ENERGY
1654 CONTINUE
DO 1062 I=1,N1
RXI=RX(I)
RYI=RY(I)
RZI=RZ(I)
I1=I+1
M=0
DO 1063 J=I1,N
X=RXI-RX(J)-S*INT(S2I*(RXI-RX(J))) ! S IS THE
Y=RYI-RY(J)-S*INT(S2I*(RYI-RY(J))) ! SIDELNGTH. S2I
Z=RZI-RZ(J)-S*INT(S2I*(RZI-RZ(J))) ! IS 1./(.5*S)
RR=X*X+Y*Y+Z*Z
RRI=1.0/RR
RRI=CVMGP(RRI,0.0,CU2-RR) ! RETURNS RRI IF CU2-RR > 0;
M=M+1 ! OTHERWISE RRI SET TO 0.0
R6I=RRI*RRI*RRI ! LENNARD-JONES, LJ, POTENTIAL.
R12I=R6I*R6I ! ALL UNITS ARE LJ UNITS
POTR(J)=POTR(J)+R12I
POTRI(M)=R12I
POTAI(M)=-R6I
POTA(J)=POTA(J)-R6I

```

```

FF=(R12I+R12I-R6I)*RRI
FXI(M)=X*FF      ! X FORCE COMPONENT (/24.0)
FYI(M)=Y*FF
FZI(M)=Z*FF
FX(J)=FX(J)-X*FF
FY(J)=FY(J)-Y*FF
FZ(J)=FZ(J)-Z*FF
XX=X*X
YY=Y*Y
ZZ=Z*Z
PRXXI(M)=XX*FF
PRYYI(M)=YY*FF
PRZZI(M)=ZZ*FF
PRXYI(M)=X*Y*FF
PRXZI(M)=X*Z*FF
PRYZI(M)=Y*Z*FF
PRXX(J)=PRXX(J)+XX*FF
PRYY(J)=PRYY(J)+YY*FF
PRZZ(J)=PRZZ(J)+ZZ*FF
PRXY(J)=PRXY(J)+X*Y*FF
PRXZ(J)=PRXZ(J)+X*Z*FF
PRYZ(J)=PRYZ(J)+Y*Z*FF
1063 CONTINUE
MAX=M
FX(I)=FX(I)+SSUM(MAX,FXI,1) ! SUMS FIRST MAX ELEMENTS
FY(I)=FY(I)+SSUM(MAX,FYI,1) ! OF FXI ETC.
FZ(I)=FZ(I)+SSUM(MAX,FZI,1)
PRXX(I)=PRXX(I)+SSUM(MAX,PRXXI,1)
PRYY(I)=PRYY(I)+SSUM(MAX,PRYYI,1)
PRZZ(I)=PRZZ(I)+SSUM(MAX,PRZZI,1)
PRXY(I)=PRXY(I)+SSUM(MAX,PRXYI,1)
PRXZ(I)=PRXZ(I)+SSUM(MAX,PRXZI,1)
PRYZ(I)=PRYZ(I)+SSUM(MAX,PRYZI,1)
POTR(I)=POTR(I)+SSUM(MAX,POTRI,1)
POTA(I)=POTA(I)+SSUM(MAX,POTAI,1)
1063 CONTINUE

```

The proposed method uses a vectorised scientific subroutine to find the index of all those pairs within the cut-off. It does this each time it goes through the outer I loop. I have not been able to vectorise the inner loop using GATHER and SCATTER routines and improve the speed over the unvectorised code. Perhaps because this is usually a short vector loop of about 50 elements. The underlying philosophy of this algorithm is different to the Link Cell or Neighbourhood Table techniques. Here we go through $N*(N-1)/2$ interactions in the forces loop but make the searching for neighbours an 'insignificant' part of the CPU time, using vectorised subroutines.

* NEW CODE *

```

N1=N-1
DO 1654 I=1,N
FX(I)=0.0
FY(I)=0.0
FZ(I)=0.0
PRXX(I)=0.0
PRYY(I)=0.0
PRZZ(I)=0.0
PRXY(I)=0.0
PRXZ(I)=0.0
PRYZ(I)=0.0
POTR(I)=0.0
POTA(I)=0.0

```

1654

```

CONTINUE
DO 1062 I=1,N1
RXI=RX(I)
RYI=RY(I)
RZI=RZ(I)
M=0

```

```

I1=I+1
DO 1063 J=I1,N ! FIRST FIND THE SQUARE OF THE
M=M+1 ! SEPARATIONS
X=RXI-RX(J)-S*INT(S2I*(RXI-RX(J)))
Y=RYI-RY(J)-S*INT(S2I*(RYI-RY(J)))
Z=RZI-RZ(J)-S*INT(S2I*(RZI-RZ(J)))
ARR(M)=X*X+Y*Y+Z*Z ! PUT THEM IN THIS ARRAY

```

1063

```

CONTINUE
CALL WHENFLE(M,ARR(1),1,CU2,INDEX,MAX)
C THIS CRAY ROUTINE FINDS THE FIRST M ELEMENTS OF
C ARR WHICH ARE LESS THAN CU2 ( THE CUT-OFF SQUARED)
C AND PUTS THEIR INDICES IN ARRAY INDEX.
C THERE ARE MAX ELEMENTS FOUND IN THIS WAY.
DO 5063 M=1,MAX
MM=INDEX(M)
J=I+MM
X=RXI-RX(J)-S*INT(S2I*(RXI-RX(J)))
Y=RYI-RY(J)-S*INT(S2I*(RYI-RY(J)))
Z=RZI-RZ(J)-S*INT(S2I*(RZI-RZ(J)))
RRI=1.0/(X*X+Y*Y+Z*Z)
R6I=RRI*RRI*RRI
R12I=R6I*R6I ! NOW FIND PAIR PROPERTIES AS YET
POTR(I)=POTR(I)+R12I ! UNVECTORISED (UNFORTUNATELY)
POTA(I)=POTA(I)-R6I
POTR(J)=POTR(J)+R12I
POTA(J)=POTA(J)-R6I

```

```

FF=(R12I+R12I-R6I)*RRI
FX(I)=FX(I)+X*FF
FY(I)=FY(I)+Y*FF
FZ(I)=FZ(I)+Z*FF
FX(J)=FX(J)-X*FF
FY(J)=FY(J)-Y*FF
FZ(J)=FZ(J)-Z*FF
PRXX(I)=PRXX(I)+X*X*FF
PRYY(I)=PRYY(I)+Y*Y*FF
PRZZ(I)=PRZZ(I)+Z*Z*FF
PRXY(I)=PRXY(I)+X*Y*FF
PRXZ(I)=PRXZ(I)+X*Z*FF
PRYZ(I)=PRYZ(I)+Y*Z*FF
PRXX(J)=PRXX(J)+X*X*FF
PRYY(J)=PRYY(J)+Y*Y*FF
PRZZ(J)=PRZZ(J)+Z*Z*FF
PRXY(J)=PRXY(J)+X*Y*FF
PRXZ(J)=PRXZ(J)+X*Z*FF
PRYZ(J)=PRYZ(J)+Y*Z*FF
5063 CONTINUE
1062 CONTINUE

```

I find this method convenient for moderately large N . For example for $N = 1372$ the times per step on the COSIM CRAY-1S at ULCC are 1.23 and 0.50 s, respectively. This includes the same code in both programs for flux autocorrelation function determination, and particle and property updates. Therefore the time spent in the forces loop is somewhat less than these numbers. I hope in the future to be able to report any improvements I make to this scheme.

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