DARESBURY LABORATORY LENDING COPY

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 26 SEPT 1987

Contents

Editor: Dr. William Smith
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Science & Engineering Research Council,
Daresbury Laboratory, Daresbury,
Warrington WA4 4AD, England.

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only recently been added to the list, but the mailing list is now over six years old and is inevitably significantly out-of-date.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.

CCP5 REGISTRATION FORM

Please use block capitals. Thank you for your cooperation.

NAME : ______________________________________ TITLE: __________

ADDRESS: ____

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JANET/EARN/ARPANET/BITNET ADDRESS:

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Editorial

Time moves quickly in the life of a project such as CCP5. It is not too soon to be thinking about the case that must be prepared for a fresh renewal proposal. No doubt many of the participants in the activities of CCP5 have sound ideas about the directions the Project should take over the next few years. Their opinions will be welcomed by the CCP5 Steering Committee. One area in which CCP5 might make some firm commitments is in the development of the industrial applications of simulation. There can be few simulators that have not realised the suitability of simulation methods for industrial research. The pharmceutical applications of large molecule simulations, the simulation of rheological properties of lubricants, heterogeneous catalysis, the physical properties of polymers, electrolytic processes and even simulations of quantum devices, all fall within the 'brief' of CCP5. No doubt every reader could add substantially to the list.

It is true, of course, that CCP5 has already shown a commitment in this area, as is shown by the forthcoming CCP5 conference on this subject in January 1988. However, this could be regarded as merely a begining. At present there is no official overlap between CCP5 and industry; no structured mechanism for initiating collaboration between the universities and scientific industries. CCP5 is presently in a good position to take on such activities. It could provide a forum for discussion of common interests; a kind of 'club' where academics could meet industrial collegues and advocate the techniques of simulation for specific industrial problems and where academic research could be married to appropriate industrial sponsorship. As an example of this; could not CCP5 organise regular workshops on (say) simulations of the rheological properties of powders, or polymeric liquids, or on the simulation of ceramics - to inform industrialists of the power of simulation methods and offer them as *realistic* tools of industrial research. Equally, could not industrialists come along to such workshops with specific problems in mind to discuss appropriate solutions? The possibilities are worth thinking about!

Contributors to the current issue.
Our thanks go to:

C.R.A. Catlow R.A. Jackson	Department of Chemistry, University of Keele, Keele, Staffs ST5 5BG.
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Royal Holloway and Bedford New College,
Egham, Surrey TW20 OEX.

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General News.

1) CCP5 is organising a number of interesting events for the next few months. Of immediate interest are the sponsored visits to the U.K. by Professor M. Parrinello and Professor H.J.C. Berendsen, both of whom will visit Cambridge, Oxford and Daresbury to give seminars and to discuss aspects of their work in workshops. The details pertaining to these visits, *as they are currently known,* are given in announcements at the end of this section of the newsletter. Readers should contact the local organisers mentioned for more up-to-date information. It is hoped that as many people as possible will take advantage of these visits by our illustrious colleagues.

2) The CCP5 conference on "The Industrial Applications of Computer Simulation" is going ahead as scheduled in January. Readers will find details of this meeting in the appropriate pages after this section. The meeting is something of a departure from previous CCP5 meetings and it is hoped that CCP5 members and visiting industrial scientists will find the meeting stimulating.

3) 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.

4) The Institute of Physics is organising a conference on "High Temperature Superconductivity" at Bristol in December (14th.-15th.) 1987. For those members of CCP5 who are interested in this conference we enclose a copy of the programme.

5) The University of Manchester Regional Computer Centre has announced some changes in the CYBER 205 service. Firstly, from the start of August, the allocation of 205 resources came under peer review, under the national scheme covering all major computing centres. Thus changes have been made to job classes, disc configuration (a new 819 disc is available for scratch space) and resource control. Similarly MVS filestore allocations have been changed. Users should be sure of the impact of these changes. Secondly, a new release of the FTN200 compiler (L678A) offers some enhancements (and bug fixes) over the previous version. This will require recompiling of existing binary datasets when released. The task name FORTRAN, which called the older compiler was withdrawn at the start of August. Users of the 205 may also be interested in the availability of a manual (NAT 654) entitled 'Vector Programming on the CYBER 205' and an associated algorithms library; ACVLIB.

Users automatically registered to use the VM/CMS service when it began, but have not actually used the service, are to have their IDs deleted to reduce overheads. Reregistration is required. This is thought preferable to carrying several thousand unused IDs. Equally sensible is the final removal of the 1000 unused ICL tapes hanging on from the old ICL 1900 days, none of which has been accessed for six months!

6) The University of London Computing Centre have introduced a new version of PHOENIX, with the name PHOENIX 3. This version has improved facilities and is said to be easier to use. Users wishing to try out this new version should consult the July and August/September issues of the ULCC Newsletter. From 27th July, the new allocation year began, with the Peer Review scheme in place. This will affect everyone, not just Cray users. Version 5 of the MVS compiler has been released and new MVS JCL procedures are available. MVS users should note that ULCC intend to tighten up dataset security by setting the ACF2 default to NOREAD. This means that datasets cannot be read by other users without explicit permission by the owner.

An upgrade of the COS operating system to level 1.15 in october will require users to recompile their programs. The CFT compiler will demand a stricter FORTRAN, so users should familiarise themselves with it before the upgrade, using NEWPROD in the Cray JCL.

7) The Rutherford and Appleton Computer Centre have floated the suggestion that the MVS batch service could be phased out and all the batch work done by a SLAC batch service. (A move already adopted by CERN.) They are canvassing users for their opinions on this suggestion. Also, in the interests of good house-keeping, they are proposing to scrap over 5000 tapes associated with defunct projects unless the owners ask for them to be allocated to an *existing* acount. They say this threat is deadly serious! They also intent to phase out the IBM's demountable 3330 disks before the end of the year. If you have data on such a disk, you should move it soon, with the help of program advisory. RAL reports that a meeting was held at London recently to discuss the funding of the European Academic Network (EARN). IBM's financial support of this ends at the close of 1987. A sum of £71,000 is needed by the U.K. to maintain the service. A detailed proposal is being prepared by RAL.

8) 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.

9) We wish to correct a statement regarding funding of scientists attending CECAM meetings made in the last issue of the newsletter. The procedure for U.K. scientists is now the same as for other European

scientists; that is they will receive their expenses in Paris and not via Daresbury as stated. (The procedure was changed earlier this year.) Funding for travel may be available from the appropriate SERC office in Swindon, but it is generally expected that the University of the visiting scientist will meet this cost.

10) Once again we carry an announcement of the re-registration required by *all* CCP5 members. The response so far has been good, but it is clear that many readers have neglected to reply. It cannot be emphasised too strongly that *failure to respond will result in deletion of your name from our mailing list.* Please take this notice seriously. We would, of course, be glad to include newcomers to our list if they have heard or read of the newsletter elsewhere. There is no charge. Readers who have already responded to the first request need not do so again.

11) It has been suggested to CCP5 that a database be set up to store useful simulation potentials. Such a database would be available to all CCP5 participants and include, besides all relevant parameters, such information as published references and known limitations of the potentials concerned. Other requirements may also be demanded for the final version. We would be pleased to hear readers reactions to this proposal. It is likely to be a difficult exercise to follow through (at least initially), so we would like to have readers ideas before beginning. We also need to gauge the interest in the proposal.

12) The CCP5 Program Library.
We are please to report the addition of another program to the library. The program concerned goes by the name MDSGWP, (which is an acronym for Molecular Dynamics of Spherical Gaussian Wavepackets). The program was donated to the CCP5 Program Library by W. Smith and K. Singer, who jointly wrote it. Its purpose is to simulate monatomic solids, liquids and gases using the semi-classical gaussian wavepacket method. The method has been found to be moderately successful in simulations of neon and argon (Ref. K. Singer and W. Smith, Molec. Phys. (1986) **57** 761.)

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.

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
MCN	[MC,LJA,TH]	N. Corbin
MCLSU	[MC,LJA,TH]	C.P. Williams/ 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/ D. Fincham
MDPOLY	[MD,LJS,G5+Q4,TH+MSD+QC]	S.M. Thompson
MDMULP	[MD,LJS+PD+PQ/MIX,LF+QF,TH]	W. Smith
MDSGWP	[MD,LJA/SGWP,LF,TH+VACF+RDF+QC]	W. Smith/ K. Singer
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
	LJL	Lennard-Jones linear molecules
	LJT	Lennard-Jones tetrahedral molecules
	LJS	Lennard-Jones site molecules
	RPE	Restricted primitive electrolyte
	BHM	Born-Huggins-Meyer ionics
	SGWP	Spherical gaussian wavepackets
	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:	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	Rossky-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

SITUATIONS VACANT

1)DARESBURY LABORATORY, RESEARCH ASSOCIATESHIPS IN COMPUTATIONAL SCIENCE

Quantum Chemistry, Molecular Dynamics and Interfacial Science

A major collaboration is starting between Daresbury Laboratory and Imperial Chemical Industries plc to investigate the impact of novel computer architectures and new developments in computational physics and chemistry on problems of scientific and technological interest. We need three scientists to support this collaboration in the study of large molecules using quantum chemical methods, the dynamics of macromolecules, and surface processes and interface physics.

The collaboration with ICI will involve the use of a new FPS T-20 parallel processing computer. Other computing facilities include two FPS-164 attached processors. There will be strong links with the new Advanced Research Computing Group at Daresbury, and scientists from a number of ICI sites.

The successful candidates will be employed at Daresbury.

Applicants should have a Ph.D., probably in Chemistry of Physics, or expect to obtain one before taking up the appointments. The appointments will be for a maximum period of three years in the grade of Junior or Senior Research Associate (depending on age and experience) on a salary scale from £9,321 to £12,488 per annum. There is a non-contributory superannuation scheme. In addition the Research Associate will be expected to act as consultant for ICI, and will be eligable for consultancy fees of up to £1000 during the first and second years of appointment, and £2000 during the third year.

Closing date: 1st. October 1987 (or as soon as possible after).
Further information may be obtained from: Dr. J.E. Inglesfield, (Tel. [0925] 603121) or Dr. M.F. Guest (Tel. [0925] 603247). Application forms are obtainable from: The Personnel Officer, Daresbury Laboratory, Science and Engineering Research Council, Warrington, Cheshire WA4 4AD. (Ref DL/20). (Tel. [0925] 603467).

2)UNIVERSITY OF LONDON, BIRKBECK COLLEGE

A vacancy exists for a postdoctoral research assistant to work on computer simulation of water and specific ionic solutions under elevated conditions of temperature and pressure. This work is part of a recent contract awarded by CEGB, and is ultimately aimed at helping to understand corrosion problems in power station coolants. Calculations will be made in a regime where the fluid begins to become compressible, and raises interesting and not straightforward problems for computer simulation.

Applications are therefore invited from experienced computer simulators for this post. Salary will be on the Research Assistant 1A scale, and it is hoped that a salary significantly above the minimum will be available for a suitable candidate. The appointment will be for three years. Further details can be obtained from Prof. John Finney, Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX (Tel. [01] 631-6138).

3)UNIVERSITY OF MANCHESTER, THEORETICAL CHEMISTRY GROUP

A postdoctoral research assistantship is available from 1st October 1987 for two years, for a chemist or physicist to work with Dr. A.J. Masters on molecular theories and computer simulation of nematic liquid crystals. It is funded by the SERC.

Applicants should preferably have experience of computer simulation of fluids. Salary on the 1A Range for Research and Analogous Staff (£9305-£11,015). Scientific enquiries and applications to Dr. A.J. Masters, (Tel. [061] 273-7121), Department of Chemistry, University of Manchester, Manchester M13 9PL.

4)COMPUTER SIMULATION OF SORPTION IN ALUMINOSILICATE CATALYSTS

Applications are invited for a two year Postdoctoral Research Assistant at the University of Bath in collaboration with Prof. C.R.A. Catlow, University of Keele, from January 1988.

The project, supported by the S.E.R.C. Interfaces and Catalysis initiative, will use static and dynamic simulation methods on the Rutherford and London CRAY supercomputers to study both the stabilities of alumino-silicate catalysts and the properties of sorbed molecules in these materials. Special emphasis will be given to the transport properties of sorbed molecules at temperatures used in real catalyst applications. The work on stability will guide understanding of the synthesis of porous aluminosilicates, while the studies of sorption aim to advance our knowledge of the mode of operation of catalysts.

For further information contact: Dr. S.C. Parker, Department of Chemistry, University of Bath, Claverton Down, BATH BA2 7AY. (Tel. [0225] 826505).

5) U.M.I.S.T. MANCHESTER. POST-DOCTORAL RESEARCH ON DENSE POLYMERS

Applications are invited for a Post-doctoral Research Assistant to work on molecular dynamics computer simulation studies of the glass transition in simple dense polymers.

The position is available for two years at a starting salary of up to £10,440 p.a. plus benefits, dependent on qualifications and experience. The work is directly sponsored by ICI plc. who are likely to have a future direct interest in dynamical modelling of such systems.

Excellent computing facilities are available and you will be joining a lively research group of five people all concerned with applications of molecular dynamics. An example of our recent work on polymers can be found in J. Chem. Phys. 1986, **84**, 2858.

Applications enclosing a curriculum vitae should be sent as soon as possible to:

Dr. J.H.R. Clarke, Chemistry Department, U.M.I.S.T., MANCHESTER M60 1QD.

FORTHCOMING CCP5 EVENTS

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CCP5 ANNUAL CONFERENCE 1988
INDUSTRIAL APPLICATIONS OF COMPUTER SIMULATIONS
BIRKBECK COLLEGE 6-8TH JANUARY 1988

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Molecular simulation methods are increasingly being used as and 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. Accomodation 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 complete the registration form overleaf.

INDUSTRIAL APPLICATIONS OF COMPUTER SIMULATIONS
6-8 JANUARY 1988

REGISTRATION FORM

Conference Fee:	Standard	£50	....
	Academic (employees of Universities)	£10	....
	Student (supervisors letter of support required)	None	....
Accommodation:	Bed and Breakfast at Hughes-Parry Hall for nights of 6th. and 7th. January.	£28	....
	Conference Dinner	£12	....
	TOTAL PAYMENT (Cheque payable to SERC CCP5)		....

Contributed Papers.

I do / do not wish to contribute an oral / poster paper entitled
....

I do / do not wish to contribute a paper to the proceedings.

I enclose an abstract of my paper

NAME ....
ADDRESS ....
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The deadline for abstracts is *November 1st 1987*. Please submit your abstract on A4 paper with a 4 cm. right-hand margin.

Please return with payment to Professor C.R.A. Catlow, Department of Chemistry, University of Keele, Keele, Staffordshire, ST5 5BG.

See overleaf for information on the conference proceedings.

Conference Proceedings

The Proceedings will be published as a special double issue of Molecular Simulation. A personal copy of the proceedings can be obtained for only $ 40 (please check current sterling equivalent) by entering a personal subscription below.

Ordering Information

All orders from individuals must be prepaid. The publisher will pay postage and handling charges. New subscriptions will begin with the current volume. Service begins when the subscription is paid in full. Mailing of journal issues is made world-wide through accelerated surface post. The dollar price applies in North America only; all other countries will be invoiced at current conversion rates.

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VISIT OF PROFESSOR M. PARRINELLO, 2-6 NOVEMBER 1987

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Professor Michele Parrinello is internationally recognised for his original contributions to the science of computer simulation. Among his works are some notable achievements: the Parrinello-Rahman constant pressure MD method for simulating phase transitions in solids; the Car-Parrinello unification of MD and density functional theory to calculate solid state electronic structures and the use of path integral and other methods for simulating quantum systems. We are extremely pleased that he has consented to visit the U.K. under the auspices of CCP5. He will visit three U.K. establishments; Daresbury, Cambridge and Oxford. The details are given below. For general information regarding his visit please contact:

Dr. W. Smith,
T.C.S. Division,
SERC Daresbury Laboratory,
Daresbury,
WARRINGTON WA4 4AD.

(0925) 603257

or WL @ UK.AC.DL.DLGM

The local arrangements (currently known) are as follows.

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Monday 2 November DARESBURY LABORATORY,

Professor Parrinello will visit the Theory and Computational Science Division. He will present a seminar on Monday afternoon at 2 pm, on the subject of the Car-Parrinello method. This will be followed an extended discussion on the simulation of the solid state including classical and quantum methods. Anyone wishing to attend or present material should contact Dr. W. Smith at the above address.

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Wednesday 4 November CAMBRIDGE UNIVERSITY

Professor Parrinello will visit the Cavendish Laboratory on the morning of Wednesday 4th. for disussions with the solid state group. In the afternoon he will visit the Department of Physical Chemistry and give a seminar at 2.15 pm, on the subject of the Car-Parrinello method. This will be followed by an extended discussion in this subject area. Interested readers should contact:

Dr. T. Softley
Department of Physical Chemistry
University of Cambridge
Lensfield Road
CAMBRIDGE CB2 1EP

(0223) 337733

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Friday 6 November OXFORD

Professor Parrinello will be at the Physical Chemistry Laboratory, Oxford on the morning of 6th and take part in informal discussions. A seminar will take place at 2.15 on the Friday afternoon in the Physical Chemistry Lecture Theatre on the subject of "Electrons in Molten Salts - a Quantum Simulation Study". This will be followed by a workshop on quantum simulation, particularly the solution of the time-dependent Schroedinger equation. Anyone who wishes to attend or present material should contact:

Dr. P.A. Madden
Physical Chemistry Laboratory
University of Oxford
South Parks Road
OXFORD OX1 3QZ

(0865) 275400

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VISIT OF PROFESSOR H. J. C. BERENDSEN, 23-25 NOVEMBER 1987

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As part of the CCP5 Visitor Programme, Professor Herman Berendsen will undertake a trip to the UK in November. Details of his itinerary are given below. All are welcome to attend the meetings. For further details of the visit, contact:

Dr. Mike Allen,
H.H. Wills Physics Laboratory,
Royal Fort,
Tyndall Avenue,
BRISTOL BS8 1TL.

(0272) 303030 ext 3669

or MPA UK.AC.BRISTOL.PVA.

or get in touch with one of the local contacts below.

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Monday 23 November BIRKBECK COLLEGE, LONDON

Professor Berendsen will visit the Crystallography Department at Birkbeck College.

At 1pm he will give the Crystallography Lab. Seminar, on the subject of "Calculating Free Energies from MD simulations". The seminar will be in the Large Physics Lecture Theatre.

In the afternoon, there will be an informal workshop in the general area of simulation of Macromolecules. Anyone wishing to attend or present material should contact:

Prof. J. L. Finney
Liquids and Disordered Systems Laboratory
Department of Crystallography
Birkbeck College
Malet Street
LONDON WC1E 7HX

01-631 6138

Tuesday 24 November CAMBRIDGE UNIVERSITY

Professor Berendsen will visit the Department of Physical Chemistry, Cambridge. He will give a seminar at 2.15 pm, the title of which is still to be finalized. Anyone wishing to meet Professor Berendsen at Cambridge should contact:

Dr. I. R. McDonald
Department of Physical Chemistry
University of Cambridge
Lensfield Road
CAMBRIDGE CB2 1EP

(0223) 337733

Wednesday 25 November DARESBURY

Professor Berendsen will visit TCS Division, SERC Daresbury Laboratory. A discussion on the subject of "Parallel Processors and Computer Simulation" will be held, starting at 2pm. This will consist of short presentations and informal round-table discussions. Anyone who wishes to attend or present material should contact:

Dr. W. Smith
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Anees Rahman - An Appreciation

Julian Clarke

September 22,1987

Most of you will have heard the sad news that Anees Rahman died on 6 June 1987 after a brave fight against cancer. He was of a breed of scientists who give real authority and conviction as well as a sense of excitement to a subject. Without his inspiration and example molecular dynamics computer simulation would not hold the prominent position in chemical physics that it does today.

To those who had the honour to meet him and hear him lecture (and I count myself amongst those) he was an eloquent speaker with a marvellous ability to convey the relevance and excitement of research. Those who worked with him will have their own special memories. His warm and generous nature ensured a steady flow of coworkers, although one got the impression that he was never happier than when he was actually doing the work himself! A one-day memorial symposium was held recently at Orsay in France and the lectures, which described some of the major themes of Anees' scientific activity and the ways in which he influenced later work, are to be collected together in a booklet which will be available from C.E.C.A.M. This should provide an extensive documentation of his work.

Broadly there are two views as to the role of computer simulation of condensed phases, standing as it does in the important middle ground between theory and experiment. On the one hand there are those who emphasise its relation with theory and use simulations on highly simplified models as a means to test the predictions of statistical mechanics. On the other hand there are those for whom it is primarily a means of enhancing the interpretation of experimental data on real systems. I believe that Anees belonged firmly in the second school and that this was a direct result of his own early involvement at the Argonne National Laboratory with the interpretation of neutron scattering experiments in the early sixties. His simulation of liquid argon was the first use of molecular dynamics with a realistic potential. His interest in the dynamics of atomic motions in liquids led him to present that classical paper to a Topical Meeting of the American Nuclear Society in which he described how the mechanism of self diffusion could be related to liquid structure.

Perhaps Anees will be most widely remembered for his monumental work in the early seventies with Frank Stillinger on the molecular dynamics of liquid water. At the time this was a giant step forward. Previous simulations had been attempted using the Monte Carlo technique but with only limited success and of course they were limited to the computation of static properties. Aside from the problem of developing a pairwise additive potential that might faithfully reproduce a wide range of properties, the technical difficulties of such a molecular dynamics simulation had seemed unsurmountable. It required someone exceptional skill and dedication to make such a project succeed. With a characteristic thoroughness and attention to detail this series of papers give us a deep insight into the dynamic and structural properties of this ubiquitous liquid. For the first time our understanding was able to rise above the level of the simplistic models which up to then had been used to interpret experimental data. For instance the analysis of pair interaction energy distributions provided a simple but vividly clear method of characterising hydrogen bonding.

Another example of his work from the early eighties emphasises the innovative and far-reaching contributions that Anees has made to the applications of molecular dynamics. From his work on crystal nucleation he recognised the growing interest in predicting the stable crystalline phase of a system in terms of the detailed particle interactions but it was also known that direct studies of phase transformations, which often involve a change in size and/or shape of the unit cell, were not in general possible using conventional constant volume molecular dynamics. Previously such questions had been addressed indirectly through calculations of the Helmholtz or Gibbs energies of different phases. Working with Michele Parrinello he invented a novel technique which allowed phase changes to occur spontaneously within a molecular dynamics calculation. They introduced a Lagrangian formulation of molecular dynamics in which a time dependent metric tensor is incorporated in the equations of motion for the system and this allows both the size and shape of the simulation cell to change in response to internally generated stresses. This (S,H,N) ensemble, which is a generalisation of the Andersen constant pressure technique, was quickly adopted by other researchers and a whole new field of study in solid state chemical physics was created.

There are few areas of molecular dynamics computer simulation which have not felt the guiding hand of Anees Rahman. In even a brief outline one would not do justice to his contributions without mentioning his pioneering work on transport mechanisms in superionic conducting crystals, the structural characterisation of non-polar and ionic glasses, the mechanism of crystal nucleation and growth, vapour phase growth of amorphous materials and demonstration of electron localisation in metal-molten salt systems using path integral quantum simulations.

He set high standards which are a challenge and an inspiration to us all.

Report on CCP5 Workshop on Sorption in Porous Media

(23 July, Imperial College London)

R.A.Jackson and C.R.A.Catlow

The aim of the workshop was to review the various techniques used in the calculation of sorption in porous media. The presentations fell into two sections: (i) calculations on specific materials (mainly sorption of hydrocarbons in zeolites) and (ii), model calculations on such phenomena as capillary condensation, and percolation. These presentations were followed by a general discussion of how the various techniques described might be used in future work, and whether other techniques could also be employed.

The first presentation was by A.Nowak (Oxford) who described the use of MNDO techniques to study the isomerisation of n-butene in zeolite Y. A small part of the zeolite, a 4-ring, was treated quantum mechanically, and the calculations were able to suggest the effect of the presence of Al on the isomerisation process. Also, the proton affinity increases with increasing Al content. R.A.Jackson (Keele) then described interatomic potential models that can be used to model effectively framework relaxation in zeolites. Results were presented for Na^+ zeolite A and it was shown that lattice energy minimisation using these potentials gives good agreement with experimentally determined crystal structures. R.Vetrivel (Keele) then described work on the sorption of methanol in silicalite and ZSM-5. This involved both quantum mechanical calculations and calculations using interatomic potentials. The quantum mechanical calculations were carried out using ab initio methods, to SCF level. A cluster of atoms plus the interacting molecule were treated quantum mechanically, and the effect of the remainder of the zeolite lattice modelled by an array of point charges. The calculations enabled the position of a methanol molecule in silicalite and ZSM-5 to be predicted. The final presentation of the first section was by S.C.Parker (Bath) who described some work aimed at obtaining a set of general rules for sorption of molecules in zeolites. A range of zeolites (in siliceous form) were considered, falling into two structural types: those based on sodalite units (zeolites A and Y), and those based on cancranite units (zeolites L and O). The calculations initially held the framework fixed, and looked at the effect of moving the molecule around, but this was followed by relaxation to constant pressure using a supercell for the unit cell. Potentials for the interaction of the molecule with the framework were obtained from compilations (e.g. by Kiselev), and intermolecular potentials were obtained from databases. Results were presented for sorption of methanol and methanoic acid in zeolites A and L.

The second section included three presentations of model calculations. J.Walton (BP) described calculations on molecular simulation of capillary condensation. Pore-fluid systems are important in adsorption, catalysis and separation, and the calculations set out to answer questions such as what is the effect of pores (and pore size) on fluid phase diagrams, and what is the origin of adsorption hysteresis. The system was modelled by a Lennard- Jones fluid between two parallel plates, and a Monte Carlo simulation carried out. The results were interpreted in terms of the behaviour of nitrogen in a graphite slit. D.Nicholson (Imperial College) discussed the relationship between micropores, mesopores and adsorption hysteresis, asking whether there is a boundary between micro- and meso-pore behaviour, and what is the course of hysteresis. Also, does stepwise adsorption occur only on a plane surface, or can it occur in pores? A simulation study of a model pore was reported, with molecules confined to sites, and nearest neighbour interactions only considered. Heat capacity was calculated, and tabulated versus slit width. Hysteresis loops were observed in the calculations - these were compared with experimental results. The final presentation was by N.Parsonage (Imperial College) who described the application of percolation theory to zeolites. This theory can be usefully applied to the behaviour of non-framework cations, which can occupy a number of possible sites in a given zeolite. According to which sites are occupied, the molecular sieve properties of a zeolite may be affected since channels may be blocked. Application of percolation theory via a Monte Carlo simulation suggests that blockage of channels increases with temperature.

The afternoon presentations were followed by a general discussion.

(1) Although it was not the subject of any of the presentations, molecular dynamics clearly has an important role to play in the study of sorption in zeolites, particularly in modelling diffusion.

(2) The Monte Carlo calculations described by Dr. Parsonage could be usefully repeated with energy values from recent calculations.

(3) Recent experimental evidence suggests that sorption of nitrogen in ZSM-5 shows hysteresis effects. It would be worth applying the techniques described by Drs. Walton and Nicholson to this system.

(4) Potentials are, as always, of great importance. For sorbate-framework interactions there is still dependence on potentials such as those of Kiselev. Quantum mechanical methods can be used to calculate potentials, but if they are only carried out to SCF level,

dispersion terms cannot be calculated. In spite of this problem, it is well worth calculating potentials in this way.

(5) In performing quantum mechanical cluster calculations, careful attention must be paid to the size of the cluster, and to the embedding techniques used in representing the effects of the surrounding lattice.

So far, attention has been concentrated on systems containing only one sorbate molecule. If more than one molecule is considered, sorbate-sorbate interactions will need to be included, but potentials are available from other sources, including the molecular crystals literature.

Report on the CCP5 Workshop on "Transport Processes" University of York, September 22/23 1987

D.M. Heyes

September 28, 1987

Another successful CCP5 workshop on transport processes was held recently. This is, in fact, now the third we have held on this topic in the last two years. The idea behind them is to give an opportunity for workers in the area of simulation to discuss at length challenges in the area of dynamical simulation. We held a very enjoyable two days discussing our work.

After establishing a schedule we decided to start with algorithms. I introduced the new algorithm devised by David MacGowan (Research School of Chemistry, Australian National University, now at BP Sunbury-on-Thames) and myself. This is an adaptation of the Verlet Leapfrog algorithm. The trajectory through position space is identical to that of the Verlet algorithm, however the velocities at the time step are calculated by a higher order scheme. It was demonstrated that with increasing time step the temperature of the system can be seriously underestimated using the Verlet time step velocity. As a consequence of this it was shown that one can use a time step several times larger than is usual provided the more accurate estimate of the time step velocity is used. Roger Edberg (UMIST) outlined the method of constraints developed with Denis Evans and Gary Morriss at the Research School of Chemistry, Australian National University. This is used to fix a molecular geometry in multi-atom molecule MD. There was much lively debate through this session from Julian Clarke and David Brown (UMIST) and Professor David Landau (University of Georgia).

Dr. Christer Elvingson (Department of Food Science, University of Leeds) presented some methods and results of Brownian Dynamics simulations of flocculation. He showed the strong effect of hydrodynamic interactions in determining the structure of irreversibly formed aggregates. On a related theme I presented some preliminary results of percolation in LJ fluids (performed with Dr. J.R. Melrose, Royal Holloway and Bedford New College). Dr. B. Vessal (University of Keele) showed the results of recent MD calculations of glass formation of vitreous silica, performed using three-body forces. The agreement with experimental structural data was considerably improved using the three-body forces. There was some discussion about the accuracy of self-diffusion coefficients from MD. It was concluded that the mean square displacement, MSD, route must be employed with time developments of the MSD taken for much longer than the usual 2-4 picoseconds for systems with many degrees of freedom. David Brown (UMIST) showed some MD results of triatomics which demonstrated this point very well. There was a fruitful discussion with Professor C.R.A. Catlow (University of Keele), Professor D. Landau and Dr. J.A. Harrison (Department of Chemistry, University of Newcastle upon Tyne)

CCP5 would like to thank the University of York for their hospitality in providing such a pleasant setting for the discussion. (The seminar room was adjacent to a park with spectacular wild fowl!)

Research on the Condensed Phase in the USSR.

Keith E. Gubbins
Cornell University

July 14,1987

1 Introduction

During the period June 2-17, 1987 I visited Leningrad State University (Chemistry Department), the Institute for Low Temperature Physics and Engineering, Academy of Sciences of the Ukr SSR, Kharkov, and the Institute for Physical Chemistry, Academy of Sciences of the USSR, Moscow, to give research seminars and to discuss research. I also met with scientists from Odessa, Kiev, and Lvov who worked in similar areas to us and who came to meet with me. The notes below were compiled on my visit, mainly as an aid to my poor memory; they summarize some of the research going on in areas of interest to me in the USSR, and I enclose them here in case they may be of interest to some CCP5 members. At Kharkov the discussion was more general, and included a wide range of research going on at the institute, since they were interested in establishing some sort of joint agreement with Cornell for the exchange of researchers. Such a formal agreement would make it much easier for their scientists to visit us and vice-versa. A specific feature of glasnost is the encouragement of such joint ventures between institutes and universites in the USSR and corresponding institutions in the West. Leningrad State University was just concluding such an agreement with the University of California when I visited, and this will include Chemistry and specifically phase equilibria as a topic.

Only a few of the people I spoke with knew about CCP5, but many of them were very interested in the possibility of receiving the newsletter. Most of their computer simulation work seems to be done on machines that are rather out-of-date by Western standards, with speeds in the 0.1 to 1 MFlop range.

2 Leningrad

My hosts were Professors N.A. Smirnova, A.G. Morachevsky, and A. Rusanov, who were the senior people in my area. I also met with quite a number of more junior faculty, and had lengthy discussions with Dr. E.M. Piotroskaya, who is doing simulations of fluids in pores which are similar to our own studies.

2.1 Fluids in Pores

N.A. Smirnova and E.M. Piotrovskaya have been studying Lennard-Jones fluids between parallel plates using MD. They have done pure fluids and Ar/Kr mixtures with both continuum and structured walls. The only writeup in English is a paper they sent me last July (1986), but they hope to publish some of their work in either Molecular Physics or Molecular Simulation. There is a review of their work on this and related surface problems (drops, fluids near a single wall) in an internal report put out by Leningrad State University by E.N. Brodskaya and E.M. Piotrovskaya. However it does not have an English summary. Their future plans in this area are to study pure krypton and argon-krypton mixtures between two parallel structured graphite walls, and later to study molecular fluids.

2.2 Water clusters, drops

E.I. Brodskaya and A.I. Rusanov are studying small water droplets by MD using the ST2 model; they have studied N=15, 27, 64 at T=222, 263, 314 K. They calculate the density profiles $\rho(r)$ for the H and O sites, $\rho(r,\theta)$ where θ is the orientation of the dipole relative to the normal to the surface, the average Coulomb potential ϕ, the energy density, and the normal pressure. They find that the dipole prefers an orientation parallel to the surface, in agreement with the work of ourselves and others.

2.3 Liquid crystals

K. Skolowa and A.Yu. Vlasov do model calculations for liquid crystals, nematics and smectic-A. They use lattice models, a generalization of Flory, and treat attractions by mean field theory. They have done mixtures of hard rods and also of flexible molecules. More recently they have done hard molecules with attractions. Recently they have worked on the Smectic-A transition and also a slab model of p-azoxyanisole. Andrew Vlasov (a postdoctoral worker with Skolowa) is studying mixtures of MBPNA + solvent (CCl_4, n-C_7H_{16}, C_6H_6), particularly heat of mixing and heat capacity. They measure heat capacity C_p vs. T experimentally. They are presently studying lyotropic liquid crystals.

2.4 Polymer solutions

J.M. Bolaskova's group is studying polymer-monomer solutions - VLE, vapor-solid equilibria by head space analysis, using gas chromatography.

2.5 Ionic solutions, clusters

P.N. Vorontsov-Velyaminov, S.V. Shevkunov and A.P. Lubartsev (Institute of Physics) do 'mean field Monte Carlo' for ionic solutions. That is they include the nearby interactions explicitly as usual, but more distant particles are included as a mean field. They use this method to study polyelectrolytes. I have 3 preprints of their work, but without English summaries. They are also doing quantum MC. Shevkunov has a method for getting phase equilibria by a new, more direct method, which he says is similar to the method of Thanasis Panagiotopoulos. He uses P, T, μ as variables and gets the phase equilibria directly. He finds this to be a good method for small systems, and uses it to study drops and clusters. He has applied it to small ionic clusters. They calculate μ(T,P,N) and get the critical cluster size, N_c. This takes 10 minutes on their computer, which is basically a copy of the IBM 360. He will send me a reprint on this method.

3 Odessa

3.1 Theory of Liquid Mixtures

Prof. L.Z. Boshkov together with another more junior colleague, came to Leningrad for my seminar and to discuss work on liquid mixtures. He is in an institute in Odessa (Doclady Academy Nauk) and was the doctoral adviser of Kalinichev (now at Chernenko, near Moscow) who I met at the Liblice conference in 1986. They use a perturbation theory of Lennard-Jones mixtures and say they can find Class VI behavior, and a new class they call VII, without using anisotropic intermolecular potentials.

4 Kharkov

In Kharkov I was at the Institute for Low Temperature Physics and Engineering of the Academy of Sciences of the Ukr. Most of the week was spent in discussions with various research group leaders there. They were particularly interested in the possibility of forming an exchange program or joint laboratory with Cornell, so that the discussions ranged over a variety of research areas. There was no research going on in computer simulation there, but there was an active group in the area of nonequilibrium statistical mechanics.

4.1 General

During the first day I met with:

- Prof. Manzhelii, Assistant Director of the Institute, Corresponding Member of the UkrSSR Academy of Sciences and Deputy Director of Research

- Dr. Shchelkunov, Head of Department (the dept Dr. Pozhar is in)

- Dr. L. Pozhar, leader of theory group

The Institute was founded in 1960, and has about 1400 professional scientists and engineers; about 700 are research scientists doing fundamental work, and 700 are engineers doing technical design and development. The Ukr SSR Academy of Sciences has generally more emphasis on applications to industry than the Soviet Academy of Sciences, though part of their effort is in fundamental areas. Manzhelii's responsibility is for these fundamental areas. Fundamental research areas include:

- Superconductivity
- High temperature superconductivity
- Liquid helium
- Other liquefied gases
- Solidified gases - cryocrystals, especially the quantum crystals He and H2, isotopes of H2, CH4
- Normal metals (electronic properties)
- Magnetism at low temperatures, especially magnetic ordering
- Spectroscopy, especially of solidified gases and magnetically ordered systems
- Mechanical properties of solids - plasticity, internal friction, etc., at low temperatures

They do not study very high pressures, but can explore temperatures down to 1 milliKelvin. They study thermal and mechanical properties down to 0.4 K, and their work on Helium goes down to 1 mK. Their work includes research in high magnetic fields.

Applied research areas include:

- Cryogenic equipment, refrigerators with LN_2 cooling
- Processing of foodstuffs and technical materials under low temperatures
- Medical science investigations; devices for cryosurgery, used by dental surgeons, oculists, gynacologists, etc.; freezing and preserving biological objects, human organs (e.g. kidney banks).

In addition to physicists and engineers, they also have mathematicians and biologists in the Institute. Most of their scientists (about 75%) are experimentalists; only 25% are theorists.

They publish the Journal of Low Temperature Physics of the USSR. Most of the papers are experimental. They publish 1000 copies of each issue, and the journal is translated into English, but appears only 9 months after the Russian version.

4.2 Transport Properties of Fluids

Dr. Pozhar is the head of a theory group doing studies of transport properties using kinetic theory and nonequilibrium statistical mechanics. In particular they are involved in the following:

1. The study of transport properties of mixtures of simple, dilute gases. They have shown that the Lennard-Jones model is quite good.
2. They calculate the collision integrals for dilute gases to high accuracy. They show that the existing tables are not accurate enough for their purposes.
3. They calculate the viscosity, diffusion coefficients, and thermal conductivities for Ar, O_2,N_2, CO_2, He, as pure components and binary mixtures. The theory is quite good for these mixtures over the range 100 - 300K for pressures in the range 1 - 10 bar.

5 Kiev

5.1 Simulations of Water and Molecules near Surfaces

Dr. V.P. Sokhan, of the Institute for Theoretical Physics, Academy of Sciences of the UkrSSR, Kiev, came over to Kharkov for 2 days to meet with me. He is in the group of Prof. V.Ya. Antonchenko (Head of the Computer Methods in Theoretical Physics there), along with V.V. Ilyin, N.N. Makovsky, V. Dailydonis, V. Chryapa, A.N. Pavlov, and V.N. Semyanovsky. He described the work of their group, much of which is on fluids in pores, and said he would send me reprints and preprints of their work. They use a computer which has a speed of about 1 MFlop. Much of their work is on water near surfaces. Among their studies are:

1. Investigations of water using the Jorgensen (TIPS) model. They include solute molecules in the water, and look at thin films using the GCMC simulation method. However, they have difficulties with GCMC because of the orientation of the molecules that are added. They confine the fluid between parallel, impenetrable walls. They use both hard, smooth walls and also walls with repulsive or attractive centers placed on a grid.
2. They have studied water confined between inclined plates; the plates were inclined at a 10° angle, with 50 water molecules.
3. Makovsky and Pavlov have studied spherocylinders in pores with cylindrical and square cross-section by MD. They investigated diffusion.

He also gave me a book on water by Antonchenko (Physics of Water, Kiev Naukova Dumka, 1986) which includes a good deal of their work on water in confined systems.

I asked him what other work was being done elsewhere in the USSR in these areas. He mentioned:

1. Novosibirsk. Naberuchkin studies water, both in bulk and near surfaces. He collaborates with Malenkov of the Institute for Physical Chemistry in Moscow. They have many institutes of the Academy of Sciences of the USSR in Novosibirsk, and he is at one of these.
2. Odessa. There are two people at the Institute of Food Technology who do density functional theory.
3. Vladivostock. Pavlov (of Kiev) is now there, in the State University of Vladivostock. He will return to Kiev in 1 or 2 years.

6 Lvov

6.1 Ionic Solutions, Molten Salts

Prof. M. Golovko and Dr. Orest Pizio of the Institute for Theoretical Physics Academy of Sciences of the UkrSSR, Kiev, came over to Kharkov to meet with me. Prof. Golovko is head of the Theory of Solutions section there. Dr. Pizio is a Senior Research Fellow in Golovko's group, and has unusually good English. This institute has a building and a small part of its scientific staff located in Lvov, and they are there. (In the English translations of many of their papers, Golovko's name has been incorrectly transliterated as Holovko). They are working in the area of theory of electrolytes and molten salts. We had lengthy discussions of what they were doing in the electrolytes area and how it related to our own work. Much of their work is written up as ITP reports, mostly in Russian with an English summary, but some in English. Not much is published in regular journals. They gave me a large number of these reports. They are eager to have some collaboration or contact with Western scientists. They are working in the following areas:

1. Metal-electrolyte solutions. They are studying an ion-dipole mixture in a neutralizing background. They also do ion-dipolar dumbell mixtures in a neutralizing background. (See their reprint ITP-87-40E about MSA for ion-dipole.)
2. Molten Salt Activities. They apply a cluster expansion to study the relation between the electronic structure of ions and the structure of the molten salt. Thus for AgCl, CuCl the Ag^+ and Cu^+ ions have d electrons, and they examine the effect of this on the molten salt structure. They also do metal-molten salt systems.
3. Electrolyte Structure. They study ion-multipole models of electrolytes, including ion-dipole and ion-quadrupole models.

They also study site-site hard ISM models for ions with diatomic dipoles. They use RISM theory for the hard molecule reference system. They use a MSA closure in the RISM framework for the charge forces. After this they consider the optimized cluster expansion (OCE). They are planning shortly to use the ST2 model for water in this theory. They work with Karl Heisinger in Mainz on the simulations via MD. They get the effects of the long-range tails via theory (OCE) instead of using Ewald sums in the simulation. They will do a conventional MD simulation with periodic boundaries, then add the tail via OCE.

4. Electrolyte Thermodynamic Properties. They use two methods for the ion-multipole models: cluster expansions and a Padé approximant. Their Padé approximant is similar to the Stell-Wu Padé. They find it to work well for the standard state. (See preprint ITP-79-119P (1979)). In addition, they have generalized Wertheim's renormalization theory for induction effects in polar fluids to the case of many-body induction effects in ion-dipole systems. They have also developed a non-restricted non-primitive model ($\sigma_i \neq \sigma_j$).
5. Ion-dipole mixture near a charged wall. They have studied the case of simple hard sphere ions mixed with hard sphere dipoles near a hard charged wall. They calculate the charge, potential, and polarization profiles near the wall, and also the differential capacity.

Their future research plans for studying the thermodynamic properties of ion-molecule systems include the use of MD, MC, and theoretical methods (MSA and Padé approximants) for ion-dipole mixtures, with the inclusion of quadrupoles and polarizability, and later H-bonding.

7 Moscow

I visited the Institute for Physical Chemistry of the Academy of Sciences of the USSR. Prof. Georgii Aleksandrovich Martinov was my host, but I also had discussions with Prof. N.V. Churaev, Dr. G. Malenkov, and Dr. A.G. Grivtsov. Prof. Derjaguin is the head of the Institute, but he was out of town; he is retiring this year, and they are looking for a new head.

7.1 Theory of Polar Liquids, Electrolytes

Prof. Martinov has recently been working in two areas, the dielectric constant of polar liquids, and the civilized model of electrolytes. In the dielectric work he has a new theory and is comparing the results with experiment. In the work on electrolytes he starts from the OZ equations. He models the polar molecules as spheres (HS or LJ) with a dipole.

When $x \to 0$ (dilute solution) these equations simplify. He solves these equations by using simple harmonic expansions, using an expansion for the bridge function, M_{ij}. He hasn't yet solved for the $g_{\alpha\beta}(r)$, but he has the large r limit. He hopes the results will be better than those of Nienhaus and Deutch. He first solves the equation for the dipole-dipole structure, then uses this to solve for the ion-dipole structure.

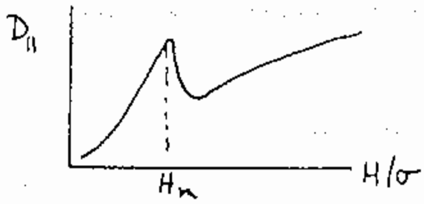
Martinov is writing a book called Statistical Theory of Simple and Semisimple Fluids, and expects to finish it by next year. It will be published by Nauka, Moscow. He gave me a detailed outline. It contains chapters on the fundamentals (physical foundations, mathematical foundations, thermodynamics and fluctuations), solving the BBGKY equations, integral equations, corresponding states, phase diagrams for pure fluids, critical phenomena, theory of solutions, theory of polar fluids, dielectric permittivity of polar fluids, solvation in polar solvents, Coulombic systems, and the civilized model of electrolytes.

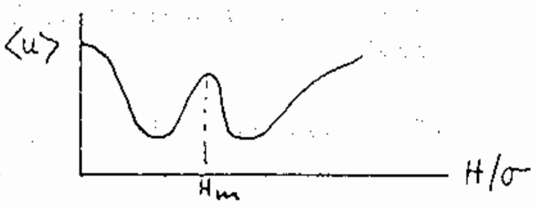
7.2 Monte Carlo for Water, and Water and other Molecules in Capillaries

Dr.G. Malenkov does MC for water in the bulk and in contact with surfaces. He also does simulations of biomolecules, together with the Institute of Biophysics. His main interest is in the structure of the fluid, in the bulk and also near the surface. He has done several simulations of water in a carbon pore, using a structured wall (about 100 atoms in each plate) and parallel plate geometry. He uses up to 20 water molecules. He uses a potential he devised himself (for details see his paper in the book Chemical Physics of Solvation, Volume A, Elsevier, 1985). It's a modification of ST2. He did not observe a phase transition. The plate separation was from 6-15 Å. He has also studied diffusion of this water fluid between parallel plates. He gets both D parallel and perpendicular using a formula

$$D \sim (kT)^{3/2} / \sqrt{\langle F^2 \rangle}$$

where $\langle F^2 \rangle$ is the mean squared force on a molecule. He also calculates the mean potential energy per molecule, $\langle u \rangle$. He finds the diffusion coefficient in the parallel direction to be much greater than in the perpendicular one, but both have a similar form when plotted against the plate separation H.





Thus there is a maximum in D at some separation H_m, and this separation also gives a maximum in $\langle u \rangle$.

7.3 MD for Fluids in Capillaries

Dr. A.G. Grivtsov has used MD to study argon between parallel plates. The wall-fluid potentials were either hard repulsions or a 9-3 potential. On these structureless walls they grew a structured crystal of 2 or 3 molecular layers. They then disrupted this crystal by pulling it laterally. Much of his work is with his wife, L.A. Grivtsova, and with N.V. Churaev. He gave me two reprints, one on simulations of chain molecules in the bulk phase (in English) and the other in Colloid Journal of the USSR on diffusion of simple fluids in cylindrical pores; the latter is in Russian but with an English summary (also this journal is translated), and looks quite interesting. Several people in Leningrad and elsewhere told me that Grivtsov was one of the earliest workers in MD, having applied it to study argon using a Lennard-Jones potential at about the same time (1964) as Rahman's work was published. His early work does not seem to be well known in the West.

7.4 Theory of Fluids near Surface and in Capillaries

Prof. N.V. Churaev has worked on the theory of diffusion in capillaries, and gave me two reprints. One is with Grivtsov and Grivtsova, and is the one referred to above in Colloid Journal of the USSR. The other is in Russian and is in the Engineering Physical Journal; this is translated and his reprint also has an English summary.

ADDRESSES: USSR

A. Leningrad

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Coping with the Pressure! – How to Calculate the Virial

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1 Introduction

In molecular dynamics, the pressure is one of the most important quantities one needs to calculate. In practice this means one must know how to calculate the system virial from any given form for the intermolecular potentials. In MD this is usually done by first obtaining pair forces $\underline{f}_{ij}$ and then calculating the sum of the scalar products:

$$\Phi = \sum_{i}^{N} \sum_{j<i} \underline{r}_{ij} \bullet \underline{f}_{ij} \tag{1}$$

For simple systems, such as Lennard-Jones, this is not difficult, but one finds that as the intermolecular potentials become progressively more complicated, it becomes increasingly more difficult to obtain the required formulae. As an example, consider a system of rigid molecules represented by fractional charges, in which the long range forces are handled via Ewald sums; how can allowance be made for the intramolecular interactions which are included in the Fourier part of the sum [1] ? In such circumstances one has to use intuition to derive the correct expression, and this is not always reliable.

The purpose of this note is to outline a general method for attacking this problem. The method has in fact been around for some time; it is mentioned in the book by T.L. Hill [2] and more recently it was described in a review by F. Abraham [3]. No doubt the method has appeared many times in the literature, in different guises. It is currently best known through the constant pressure algorithm of Andersen [4], though readers who are not familiar with constant pressure work may not have realised that it is also useful in constant volume MD. In the next section I will outline the theory of the method and in the subsequent section provide examples from some well-known systems.

2 Theory

The pressure in a thermodynamic system is given by the well-known expression:

$$P = kT\partial \log Z/\partial V \tag{2}$$

where Z is the configuration integral:

$$Z = \int \exp\{-\beta U(\underline{r}^N)\}\, d\underline{r}^N \tag{3}$$

and $U(\underline{r}^N)$ is the system configuration energy. In order to evaluate the pressure using these equations, a scaling relation is used, which is familiar to practitioners of Andersen's algorithm, *vis*:

$$\underline{r} = V^{1/3}\underline{\rho} \tag{4}$$

This equation represents a clever 'trick' by means of which we may make the volume dependence of any given function explicit. It has the interesting property that, if we expand or contract the system isotropically, the scaled coordinates of all the particles remains fixed. However, the *absolute* positions of the particles will, of course, be a function of the volume.

Substituting (4) into (3) gives

$$Z = V^N \int \exp\{-\beta U([V^{1/3}\underline{\rho}]^N)\} d\underline{\rho}^N \tag{5}$$

which on substitution into (2) provides the following expression for the pressure:

$$P = NkT/V - \langle \partial U([V^{1/3}\underline{\rho}]^N)/\partial V \rangle \tag{6}$$

By comparing (6) with the corresponding expression for the pressure according to the Virial Theorem [5], it can be seen that the virial is given by the following expression:

$$\Phi = 3V\langle \partial U([V^{1/3}\underline{\rho}]^N)/\partial V \rangle \tag{7}$$

which is the fundamental relationship of this method.

In the following section I give examples of its use in determining the virial for some commonly encountered systems. The reader is warned that, for the sake of brevity, the treatment is not fully rigorous. In particular, the above 'theory' is only valid for the case of monatomic molecules. However I hope that it sheds sufficient light on the method. Also, since this meant to be a note about the virial, I will not discuss the kinetic energy contribution to the pressure. This is not a trivial omission, since different models for a given molecule (e.g. rigid bonds or harmonic vibrational bonds) have different kinetic energies.

3 Examples

3.1 Systems of Monatomic Molecules

Assuming simple pair forces, the configuration energy is given by:

$$U = \sum_i^N \sum_{j<i} u(r_{ij}) \tag{8}$$

where $u(r_{ij})$ is a simple pair potential such as Lennard-Jones. Setting $r_{ij} = V^{1/3}\rho_{ij}$ and performing the differentiation in equation (7) gives

$$\Phi = 3V\langle\sum_{i}^{N}\sum_{j<i}(3Vr_{ij})^{-1}\partial u(r_{ij})/\partial r_{ij}\rangle \tag{9}$$

Which is more easily recognised when couched in terms of the pair forces:

$$\Phi = \langle\sum_{i}^{N}\sum_{j<i} -\underline{f}_{ij} \bullet \underline{r}_{ij}\rangle \tag{10}$$

with

$$\underline{f}_{ij} = (-r_{ij}^{-1}\partial u(r_{ij})/\partial r_{ij})\underline{r}_{ij}$$

(Notice how the volume V vanishes through cancellation from the final expression). This rather trivial example serves to show the essential simplicity of the method.

3.2 Rigid Polyatomic Molecules

For such molecules it is usual to assume a site model, in which the configuration energy is

$$U = \sum_{i}^{N}\sum_{j<i}\sum_{\alpha}^{on\,i}\sum_{\beta}^{on\,j} u(r_{ij}^{\alpha\beta}) \tag{11}$$

where $r_{ij}^{\alpha\beta}$ defines the distance between sites on different molecules and $u(r_{ij}^{\alpha\beta})$ is the corresponding site-site potential. The distance $r_{ij}^{\alpha\beta}$ is calculated as the modulus of vector $\underline{r}_{ij}^{\alpha\beta}$ with

$$\underline{r}_{ij}^{\alpha\beta} = \underline{R}_{ij} + \underline{d}_{ij}^{\alpha\beta}$$

and

$$\underline{R}_{ij} = \underline{R}_i - \underline{R}_j$$

$$\underline{d}_{ij}^{\alpha\beta} = \underline{d}_i^{\alpha} - \underline{d}_j^{\beta}.$$

Where $\underline{R}_i$ locates the centre-of-mass (COM) of molecule i and $\underline{d}_i^{\alpha}$ locates the α-th site relative to the COM of molecule i.

To determine the virial we must introduce the scaling relation. Since the molecules are deemed to be rigid, we cannot imagine them changing in size as the system volume fluctuates, therefore we use the following relation:

$$\underline{r}_{ij}^{\alpha\beta} = V^{1/3}\underline{\rho}_{ij} + \underline{d}_{ij}^{\alpha\beta} \tag{12}$$

(i.e. The scaling is applied to the space between molecules, but not to the molecular bonds.) From (12) we deduce that

$$\partial r_{ij}^{\alpha\beta}/\partial V = (3Vr_{ij}^{\alpha\beta})^{-1}\underline{r}_{ij}^{\alpha\beta} \bullet \underline{R}_{ij} \tag{13}$$

and hence via (7) and (11) that

$$\Phi = \langle \sum_i^N \sum_{j<i} \sum_\alpha^{on\, i} \sum_\beta^{on\, j} \chi(r_{ij}^{\alpha\beta}) \underline{r}_{ij}^{\alpha\beta} \bullet \underline{R}_{ij} \rangle \tag{14}$$

with

$$\chi(r_{ij}^{\alpha\beta}) = (r_{ij}^{\alpha\beta})^{-1} \partial u(r_{ij}^{\alpha\beta}) / \partial r_{ij}^{\alpha\beta}$$

Equation (14) can be written in a more recognisable form. Using the relation

$$\underline{R}_{ij} = \underline{r}_{ij}^{\alpha\beta} - \underline{d}_{ij}^{\alpha\beta}$$

we may, after some algebra, separate out two terms:

$$\Phi = \Phi_s + \Phi_c \tag{15}$$

with

$$\Phi_s = \langle \sum_i^N \sum_{j<i} \sum_\alpha^{on\, i} \sum_\beta^{on\, j} \chi(r_{ij}^{\alpha\beta}) \underline{r}_{ij}^{\alpha\beta} \bullet \underline{r}_{ij}^{\alpha\beta} \rangle$$

and

$$\Phi_c = \langle \sum_i^N \sum_\alpha^{on\, i} \underline{f}_i^\alpha \bullet \underline{d}_i^\alpha \rangle$$

The term Φ_s is usually called the site (or site-site) virial, since it takes into account the interaction between sites on different molecules. It is therefore the *intermolecular* contribution to the virial. Apart from ignoring the site-site interactions that can be classified as intramolecular, this term does not recognise the rigid structure of the molecules. The second term Φ_c may therefore regarded as a 'correction' for the molecular structure. ($\underline{f}_i^\alpha$ represents the net force acting on one of the sites.) It is a curious fact, but for an isotropic liquid, this second term is zero! This was shown by Ryckaert and Ciccotti recently[1] [6]. This is clearly not the case however, when the system being simulated is *not* isotropic (e.g. solids, liquid crystals etc.). It should also be recognised that at any given instant in the simulation the terms within the angular brackets $\langle\rangle$ are usually substantially different from zero, even in the isotropic case, and will contribute significantly to the pressure fluctuations.

3.3 Systems of Rigid Ions (Ewald Sum)

On the face of it, this would appear to be a rather trivial example of the method. It is well known that in a Coulombic system one may use the simple relation $\Phi = -\langle U \rangle$ to obtain the virial. Indeed one may use the example given in 3.1 above to show this easily (setting $u(r_{ij}) = q_i q_j / r_{ij}$). However, in the case of the Ewald summation method,

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[1] This may be seen in a hand-waving way if one realises that the net force on each site $\underline{f}_i^\alpha$ and the site displacement vector $\underline{d}_i^\alpha$ are uncorrelated over long times and an ensemble average of their scalar product is therefore zero.

things are not mathematically so obvious and some useful points emerge in a full treatment that are of value in more difficult cases.

The configuration energy for a system of point ions is given by the Ewald formula[7]:

$$U = \frac{2\pi}{V} \sum_{\underline{k}\neq\underline{0}}^{\infty} A_k |Q_{sum}|^2 + \sum_{j}^{N} \sum_{l<j} \frac{q_j q_l}{r_{jl}} \mathrm{erfc}(\alpha r_{jl}) - \frac{\alpha}{\sqrt{\pi}} \sum_{j}^{N} q_j^2 \tag{16}$$

with

$$A_k = \exp(-k^2/4\alpha^2)/k^2$$

and

$$Q_{sum} = \sum_{j}^{N} q_j \exp(-i\underline{k} \bullet \underline{r}_j)$$

and

$$\underline{k} = 2\pi V^{-1/3}(l, m, n)^{\dagger}$$

To determine the virial expression we again use the scaling relation (4). It is apparent at once that the third term of (16) makes no contribution to the virial (having no volume dependent terms) and henceforth disappears from our consideration. Also the second term (known henceforth as the *Real Space* term (U_R)) is short-ranged and is clearly in the same mould as the expression for monatomic molecules (Section 3.1). It may be dealt with in the same way. Proceeding as in Section 3.1 we obtain:

$$\frac{\partial U_R}{\partial V} = -\frac{1}{3V} \sum_{j}^{N} \sum_{l<j} q_j q_l \{\mathrm{erfc}(\alpha r_{jl})/r_{jl} + \frac{2\alpha}{\sqrt{\pi}} \exp(-\alpha^2 r_{ij}^2)\} \tag{17}$$

In which the identity

$$\frac{d}{dr}\mathrm{erfc}(\alpha r) = -\frac{2\alpha}{\sqrt{\pi}} \exp(-\alpha^2 r^2) \tag{18}$$

has been used.

Differentiation of the first term of (16) (known henceforth as the *Fourier* term (U_F)), with respect to the volume is straightforward, and will not be given in detail. However, two points are worth making. Firstly, it should be noted that the term Q_{sum} is *independent* of the volume; since in the scalar products of $V^{1/3}\underline{\rho}_j$ and $\underline{k}$ in the exponentials the volume will cancel. Secondly, one should remember elsewhere the volume dependence of the $\underline{k}$ vectors, which arises independently of the scaling relation. (e.g. $\partial k^2/\partial V = -2k^2/3V$). These factors lead to the formula:

$$\frac{\partial U_F}{\partial V} = -\frac{2\pi}{3V^2} \sum_{\underline{k}\neq\underline{0}}^{\infty} A_k |Q_{sum}|^2 + \frac{2\pi}{3V^2} \sum_{\underline{k}\neq\underline{0}}^{\infty} A_k |Q_{sum}|^2 k^2/2\alpha^2 \tag{19}$$

Equations (17) and (19) may now be subtituted into (7) to give the virial expression. However a further simplification is possible. We rewrite the last term of (17) as:

$$\frac{1}{3V}\{-\frac{\alpha}{\sqrt{\pi}}\sum_{j}\sum_{l}q_j q_l \exp(-\alpha^2 r_{ij}^2)+\frac{\alpha}{\sqrt{\pi}}\sum_{j}q_j^2\} \qquad (20)$$

The first term of this expression is in fact identical (but for sign) with the last term of (19); since the latter represents a Fourier expansion of the former. Thus the addition of (17) to (19) results in the cancellation of these two terms. The final expression for the virial is therefore:

$$\Phi = -\langle\frac{2\pi}{V}\sum_{\underline{k}\neq\underline{0}}^{\infty}A_k|Q_{sum}|^2+\sum_{j}^{N}\sum_{l<j}\frac{q_j q_l}{r_{jl}}\mathrm{erfc}(\alpha r_{jl})-\frac{\alpha}{\sqrt{\pi}}\sum_{j}^{N}q_j^2\rangle \qquad (21)$$

Which is what we set out to derive. It is manifestly similar to the Ewald potential (16) as we expected.

3.4 Fractional Charge Molecules and the Ewald Sum

This represents a rather awkward hybrid of the systems described in sections 3.2 and 3.3 above. It is awkward because the expression for the configuration energy contains terms that describe *intramolecular* interactions, which arise because the Fourier part of the Ewald sum treats the fractional charges as though they were free point ions. Ideally, what we require is some simple relationship between the configuration energy and the virial, such as that arising in the case of point ions, but it is not immediately obvious what such a relationship might be. In such cases the scaling relation (7) becomes most useful, as it allows us to tackle the problem directly, without worrying about the complications suggested by the intramolecular effects.

The configuration energy for a fractional charge system is given by:

$$\begin{aligned} U \quad = \quad & \frac{2\pi}{V}\sum_{\underline{k}\neq\underline{0}}^{\infty}A_k|Q_{sum}|^2+\sum_{j}^{N}\sum_{l<j}\sum_{\beta}^{onj}\sum_{\gamma}^{onl}\frac{q_j^\beta q_l^\gamma}{r_{jl}^{\beta\gamma}}\mathrm{erfc}(\alpha r_{jl}^{\beta\gamma})- \\ & \frac{\alpha}{\sqrt{\pi}}\sum_{j}^{N}\sum_{\beta}^{onj}(q_j^\beta)^2+U_c \end{aligned} \qquad (22)$$

with A_k and $\underline{k}$ having the same meaning as before and

$$Q_{sum}=\sum_{j}^{N}\sum_{\beta}^{onj}q_j^\beta\exp(-i\underline{k}\bullet\underline{r}_j^\beta)$$

and

$$U_c=-\sum_{j}^{N}\sum_{\beta}^{onj}\sum_{\gamma}^{onj}\frac{q_j^\beta q_j^\gamma}{r_{jj}^{\beta\gamma}}\mathrm{erfc}(\alpha r_{jj}^{\beta\gamma})$$

But for the presence of the term U_c, which corrects for intramolecular interactions this form is very similar to equation (16). The derivation of the virial from this starting point parallels the cases in sections 3.2

and 3.3 above; indeed the same tricks may be performed to reduce the formulae. The algebra is, alas, lengthy and tedious, I shall therefore give the derivation in the briefest outline only, pointing out the new features unique to this case.

The scaling relation (12) appropriate to structured molecules is substituted into (22) and the differentiation with respect to volume performed. The third and fourth terms from (22) have zero derivatives; the former through the absence of volume dependent terms and the latter because of the absence of *intramolecular* scaling implicit in (12).

Differentiation of the Fourier term resembles that given in section 3.3 above with one important difference: The exponential terms now include volume dependent terms in the exponent; namely $\underline{k} \bullet \underline{d}_j^\beta$ and these provide extra terms in the differential:

$$\begin{aligned} \frac{\partial U_F}{\partial V} &= -\frac{2\pi}{3V^2} \sum_{\underline{k}\neq\underline{0}}^{\infty} A_k |Q_{sum}|^2 + \frac{2\pi}{3V^2} \sum_{\underline{k}\neq\underline{0}}^{\infty} A_k |Q_{sum}|^2 k^2/2\alpha^2 - \\ &\quad \frac{1}{3V} \sum_j^N \sum_\beta^{onj} \underline{d}_j^\beta \bullet (\underline{f}_j^\beta)_F \end{aligned} \tag{23}$$

Where $(\underline{f}_j^\beta)_F$ represents the force on site β of molecule j due to the Fourier terms. Its explicit form is

$$(\underline{f}_j^\beta)_F = -\frac{4\pi}{V} q_j^\beta \sum_{\underline{k}\neq\underline{0}}^{\infty} i\underline{k} A_k \exp(i\underline{k} \bullet \underline{r}_j^\beta) Q_{sum}^* \tag{24}$$

Differentiation of the Real Space term of (22) likewise follows straightforwardly from 3.2 and 3.3 above, with no additional complications.

$$\begin{aligned} \frac{\partial U_R}{\partial V} &= -\frac{1}{3V} \sum_j^N \sum_{l<j} \sum_\beta^{onj} \sum_\gamma^{onl} q_j^\beta q_l^\gamma \chi(r_{jl}^{\beta\gamma}) \underline{r}_{jl}^{\beta\gamma} \bullet \underline{r}_{jl}^{\beta\gamma} + \\ &\quad \frac{1}{3V} \sum_j^N \sum_\beta^{onj} \underline{d}_j^\beta \bullet (\underline{f}_j^\beta)_R \end{aligned} \tag{25}$$

with

$$\chi(r_{ij}^{\beta\gamma}) = \{\mathrm{erfc}(\alpha r_{jl}^{\beta\gamma})/(r_{jl}^{\beta\gamma})^3 + \frac{2\alpha}{\sqrt{\pi}} \exp(-\alpha^2 (r_{ij}^{\beta\gamma})^2)\}$$

and

$$(\underline{f}_j^\beta)_R = \sum_{\gamma\neq\beta}^{onj} q_j^\beta q_j^\gamma \chi(r_{jj}^{\beta\gamma}) \underline{r}_{jj}^{\beta\gamma}$$

where, $(\underline{f}_j^\beta)_R$ is the Real Space contribution to the force on site β.

We may now add the Fourier (23) and Real Space (25) components to obtain the virial. However, as before, the combined expression may be simplified further. The second term of (23) may be made to cancel the exp terms in (25), provided that a new term:

$$U_I = \sum_j^N \sum_\beta \sum_{\gamma<\beta} \frac{2\alpha}{\sqrt{\pi}} q_j^\beta q_j^\gamma \exp(-\alpha^2 (r_{jj}^{\beta\gamma})^2) \tag{26}$$

is both added to and subtracted from the combined expression. Thus the final form for the virial is:

$$\begin{aligned}\Phi &= \langle -\frac{2\pi}{V}\sum_{\underline{k}\neq\underline{0}}^{\infty} A_k|Q_{sum}|^2 - \sum_{j}^{N}\sum_{l<j}\sum_{\beta}^{onj}\sum_{\gamma}^{onl}\frac{q_j^\beta q_l^\gamma}{r_{jl}^{\beta\gamma}}\operatorname{erfc}(\alpha r_{jl}^{\beta\gamma}) + \\ &\quad \frac{\alpha}{\sqrt{\pi}}\sum_{j}^{N}\sum_{\beta}^{onj}(q_j^\beta)^2 + U_I + U_c\rangle \end{aligned} \tag{27}$$

where

$$U_c = \sum_{j}^{N}\sum_{\beta}^{onj}\underline{d}_j^\beta \bullet \{(\underline{f}_j^\beta)_F + (\underline{f}_j^\beta)_R\} \tag{28}$$

Once again we may assume that, in an *isotropic* system, U_c will make no net contribution to the ensemble average and may be set to zero. Thus we see that, but for the presence of the term U_I, which is a constant term for a given molecule (and thus needs to be calculated only once in a simulation) the final expression for the virial (27) is very closely related to the coulombic configuration potential energy (22) of the system.

4 Summary

The method of scaling the positions of molecules in a system is undoubtedly a powerful method for determining the virial in the system. It is hoped that the examples presented here offer some insight into that power. The method cannot, of course guarantee that the final expression will be simple and some further work may be necessary to bring it into an acceptable form. However, it is clear that it offers a direct route for even the most awkward of cases.

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Quantum Monte Carlo on the FPS T-Series Parallel Vector Processor

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The following is an abridged version of papers being prepared for submission to J. Chem. Phys. Some of the results are presently incomplete and conclusions must be regarded as preliminary.

1 Introduction

Quantum Monte Carlo (QMC) methods, with the short time approximaton (STA) [1,2,3] were originally applied to the solution of the electronic Schrödinger equation of atoms and molecules by Anderson [1,4]. Subsequently importance sampling was introduced to improve efficiency [5,6], the fixed node approximation (FNA) to correctly treat Fermi statistics [7] and methods to remove the STA by sampling from the exact Green's Function [8,9,10,11,12] and to remove the FNA by relaxing the nodal surfaces [10]. Extensions have also been proposed to allow the direct computation of energy differences [13] and the use of short time algorithms of second order in the time step [17,18,19,20]. Applications of QMC have been made to many few electron (2-10) systems (recent ones including F and F^- [14], CH_4 [15], LiH, Be, H_2O and BeH_2 [11], H_3, LiH, Li_2 and H_2O [10], H_3^+ [12], H_3 [16]) with varying levels of accuracy. Most recently core pseudopotentials have been used successfully [21] to eliminate the chemically unimportant, but computationally expensive, core electrons from the calculation. From hereafter we use QMC to refer to the all electron 'diffusion' quantum Monte Carlo method with both the short time and fixed node approximations and Green's Function Monte Carlo (GFMC) to refer to methods sampling from the exact Green's function [8,9,10,11,12].

All *ab initio* methods are computationally demanding but QMC stands out, being highly cpu intensive with zero I/O requirements, and as being remarkably simple to program when compared with the complex packages required for 'state of the art' conventional *ab initio* methods. The cpu requirement may be met by theoretical developments, through the use of more accurate trial wavefunctions, more sophisticated sampling techniques [12], the exclusion of core electrons [21], and by the exploitation of new computer technology and architechtures [10,22], in particular the cost effective parallel vector processors now becoming available.

A major overhead in the use of the STA is the need to extrapolate to the zero time-step limit, increasing not only the computation time but the statistical uncertainty. Use of GFMC methods which eliminate the time step error [8,9,10,11,12] is possible, but this increases both the complexity of the program (we have our own scalar serial implementation of the algorithm of Ceperley [9,10]) and the expense of the calculation, and does not address the major source of finite time step error for higher values of the nuclear charge (Z). This error is due to use of a finite time step with the FNA which is only exact in the limit of zero time step [14,2,10]. We observe below that use of an algorithm of second order in the time step reduces the systematic error for two electron atoms to well below either the statistical error obtainable for many electron atoms, or the error from inexact implementation of the FNA. In this regard the value of 'exact' GFMC methods is negated. Further the systematic study of these ionic and atomic systems reveals trends in the STA error not revealed in previous restricted or less systematic studies of higher order algorithms [17,18,19,20].

2 The Quantum Monte Carlo Method

This is more than adequately covered elsewhere [2,3] and we shall only sketch relevant details. The electronic Schrödinger equation in imaginary time with importance sampling is

$$-\frac{1}{2}\nabla^2 f + (E_L(\underline{R}) - E_T)f - \underline{\nabla}(f\underline{F}(\underline{R})) = -\partial f/\partial t, \tag{1}$$

where $f(\underline{R},t) = \psi_0(\underline{R},t)\psi_T(\underline{R})$, $\underline{F}(\underline{R}) = \underline{\nabla}\psi_T/\psi_T$ and $E_L(\underline{R}) = \hat{H}\psi_T/\psi_T$, ψ_T being a known trial wavefunction. The propagation of f forward in time according to equation (1) results in f converging to $\psi_0(\underline{R})\psi_T(\underline{R})$, where $\psi_0(\underline{R})$ is the groundstate eigenfunction of the same symmetry as the starting distribution. In practice the fixed node approximation is employed, where ψ_0 is forced to have the same nodal surfaces as ψ_T, the computed energy now being an upper bound to the exact energy [2].

Two propagation methods are used below. The first, denoted QMC1, corresponds to the usual short time Green's function

$$(2\pi t)^{-\frac{3N}{2}} \exp\left(-(\underline{R}' - \underline{R} - t\underline{F}(\underline{R}))^2/2t\right) \times \exp\left(-t\left[(E_L(\underline{R}') + E_L(\underline{R}))/2 - E_T\right]\right), \tag{2}$$

the propagation algorithm being

$$\underline{R}' = \underline{R} + \sqrt{t}\,\underline{n} + t\underline{F}(\underline{R}), \tag{3}$$

where $\underline{n}$ is a vector of gaussian random variables of zero mean and unit variance. Branching is according to the excess local energy

$$M = \exp\left(-t\left[(E_L(\underline{R}') + E_L(\underline{R}))/2 - E_T\right]\right) \tag{4}$$

The second method, denoted QMC2, is the second order method applied by Anderson to the H atom [17] and similar to those employed by Vbrik *et al* [18,19,20],

$$\underline{R}' = \underline{R} + \sqrt{t}\,\underline{n} + \frac{t}{2}\left(\underline{F}(\underline{R}) + \underline{F}(\underline{R} + \sqrt{t}\,\underline{n} + t\underline{F}(\underline{R}))\right) \tag{5}$$

with branching as for QMC1. QMC2 as described above requires two evaluations of ψ_T and $\underline{F}$ each step compared with one for QMC1. Vrbik *et al* [18,19,20] detail several related second order methods requiring one to three evaluations each step.

3 Parallel Vectorised Implementation

The Mk. I FPS–T20 consists of sixteen independent vector processors connected in a hypercube topology. Each processor or node comprises one T414 INMOS Transputer,

Table 1: Asymptotic Performance of Basic Mathematical Functions on the FPS T-20, FPS-164, Cray-1S and Cray-XMP/48.

	No. of Results per second / 10^6			
Function	FPS T-20[1]	FPS-164[2]	Cray-1S[3]	Cray-XMP[4]
SQRT	3.8	0.6	6.7	12.2
RECIP	5.5	0.9	13.7	33.3
COS	3.5	0.8	2.6	3.7
SIN	3.0	0.8	2.6	3.7
EXP	2.5	0.3	4.2	6.3
LOG	2.7	0.3	2.9	5.0
Matrix Multiply[5]	192	11	147	220

1Mbyte of memory and a floating point vector unit capable of 12Mflop which it can realise on simple vector operations due to a massive memory to vector register bandwidth. Communications between the nodes proceeds over the Transputer channels at 0.6Mbyte/s. QMC is an example of a perfectly parallel algorithm [22], which parallelises at the coarse grain level with essentially zero communications overhead; in addition it is also readily vectorised. Thus QMC is capable of demonstrating the peak performance of machines such as the FPS–T20.

In our implementation we have chosen to vectorise and parallelise over the independent configurations in a block of the simulation, each processor having a typical vector length of 128-384. For larger parallel machines it would be more efficient to vectorise over the independent configurations and parallelise over independent blocks. Very large calculations (e.g. H_9^+, DZP SCF trial wavefunction [28]) are dominated by function evaluations and matrix vector operations (see table 1) and the T20 is estimated to be performing at roughly half Cray-1S peak vector speed. Programming was done in occam-1b, an extremely simple parallel programming language with no internal representation of floating point numbers. More recent software releases include FORTRAN–77, C and PASCAL.

The random number generator used was that of the Cray vector function RANF (a 48 bit multiplicative congruential generator [23]), distributed so that V_L elements of the sequence were generated on one processor, the next (nprocessor-1)*V_L numbers being generated on other processors, V_L being the vector length. Thus the parallel machine behaves as one large serial processor with regard to random number generation. Numerical tests confirm that the identical sequence to RANF on a Cray is generated.

4 The helium isoelectronic sequence

The helium isoelectronic sequence is an ideal test bed for QMC since: the exact energies are known [24,25], being nodeless two electron systems QMC should converge to the exact result, and it is possible to employ trial wavefunctions of a uniform quality to to enable a systematic analysis of time step error as a function of nuclear charge. The trial functions used are the Hartree-Fock functions of Clementi and Roetti [26] multiplied by simple electron-electron Jastrow functions [27] optimised in variational calculations by correlated sampling techniques. These simple trial functions, used in variational calculations, are found to recover a uniform 67% of the correlation energy for this sequence.

Figure 1 displays the QMC1 and QMC2 energies of the sequence He-B^{3+} as a function of time step (results for C^{4+}-F^{7+} are presently incomplete). Calculations had an average population of 3300 configurations, a block size of $2E_h^{-1}$, averages being computed over 100 blocks after equilibrating for 50 blocks from the variational distribution. Displayed error bars are twice the estimated standard error. In all cases QMC1 and QMC2 computed energies extrapolate to within statistical error of the exact energy, thus any systematic error at zero time step is not resolved at the 0.0003 E_h level of accuracy even for F^{7+}.

The functional form aZ^b (Z, the nuclear charge) was found to provide a reasonable representation of the coefficients of polynomials least squares fitted to the data (*these preliminary results are based on incomplete data*). The QMC1 linear coefficients fitted to $0.0514Z^{3.312}$ and QMC2 to $0.0025Z^{3.212}$. The second order algorithm provides a 15-20 fold reduction in the linear time step error dependence compared to QMC1. Note that to reduce serial correlation the length of blocks over which averages are computed is inversely proportional to the time step.

The efficiency gained from reduction of the linear coefficient is offset by the additional complexity of the time step dependence with up to cubic terms being essential for correct fitting of the QMC2 data. The QMC1 and QMC2 quadratic coefficients fit to $-0.0053Z^{5.33}$ and $-0.184Z^{5.15}$ respectively; the QMC2 cubic coefficients to $0.0132Z^{7.44}$. The dependence of these coefficients on such evely spaced powers of Z suggests that a simple analytic model may be found, and must be related to the analysis of the short time Green's function given by Pollock and Ceperley [29] and to systematic deficiences of the trial functions at the nucleus.

No significant increase in the computed error for a given length of calculation is seen, the 1s core electrons' proximity to the nucleus not being directly responsible for the increased statistical error associated with similar calculations on many electron atoms. The latter is most likely due to comparatively poorer trial wavefunctions, additional singularites in the local energy associated with nodal surfaces and the higher dimensionality of the integrals being evaluated.

Higher order methods were not investigated since for these small systems the statistical error is beginning to dominate and for larger systems the error arising from use of the FNA with a finite time step swamps the STA error from within the nodal volumes, assuming this to be of the magnitude observed in the He isoelectronic sequence.

5 The first row atoms, He-F.

The trial wavefunctions were chosen as the DZ SCF functions of Clementi and Roetti [26] with the Jastrow functions used for the He isoelectronic sequence. For boron and beryllium small MCSCF expansions were also employed, as in a previous study [30], to improve nodal surfaces. These functions recover only the same fraction of the 1s intrashell correlation energy as in the He isoelectronic sequence, and essentially nothing else. The fraction of the total correlation energies recovered in variational calculations thus falls sharply from 66% in He and Li to 28% in B and then falls steadily to 19% in F.

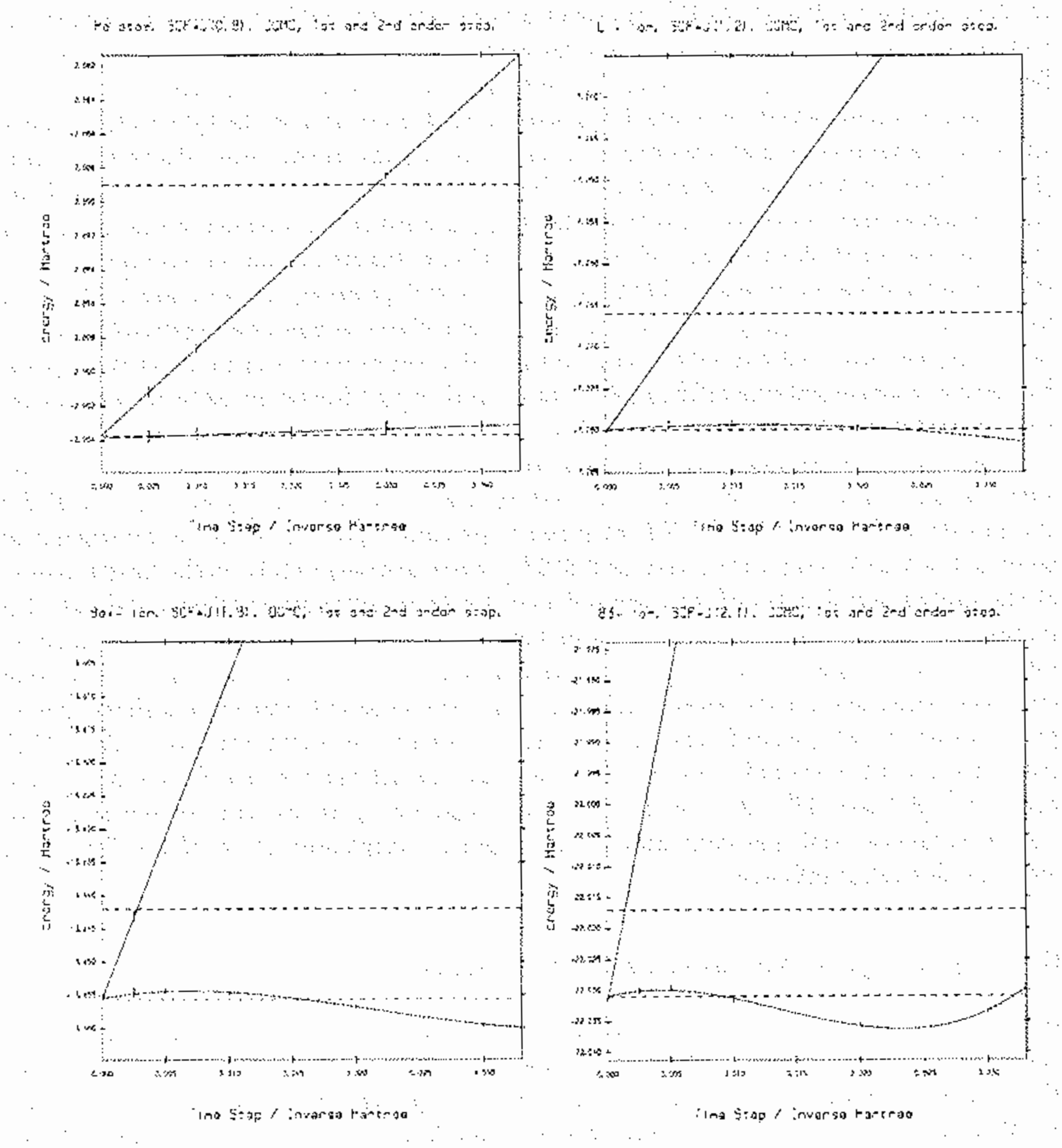

Figure 1: QMC1 and QMC2 Energies as a Function of Time Step for the Helium Isoelectronic Sequence He-B^{3+}.

For He and Li both QMC1 and QMC2 algorithms were used, QMC2 for the remainder.

Systematic beviour analagous to that in the He isoelectronic sequence is not observed, but of course we are now varying the number of electrons and the electronic state as well as the nuclear charge. The behaviour of the time step error is complex, with higher order terms more important than for the two electron atoms and extrapolation to the zero time step value is not as straight forward as in other calculations with models similar to QMC1 [14,15]. However a time step of $0.001E_h^{-1}$ is seen to reduce the time step dependent error below 0.1eV for all the atoms (with the possible exception of fluorine) this still being a tractable size of time step for a single calculation.

Inexact implementation of the FNA with a finite time step is thought to be responsible for the increased time step dependence of the energy in the many electron systems [10,14]. The FNA is also responsible for the calculations only recovering 87-99% of the correlation energy. In some cases (e.g. Be atom) a substantial fraction of the remainder may be recovered through use of compact MCSCF functions but in general a larger (DZP) basis with an extensive MCSCF function will probably be necessary. However since most effort is expended in evaluating the one electron basis set modest CI expansions may be used without substantial additional expense once a large basis is adopted. Numerical representations of the molecular orbitals may provide an efficient alternative to transformation of the atomic orbitals.

The cpu time required per time step is empirically observed to rise quadratically with the number of electrons, the cubic matrix operations accounting for only 4% of the cpu in calculations on fluorine. The estimated cpu time required to reduce the statistical error below 0.1eV with a time step of $0.005E_h^{-1}$ rises approximately as the fourth power of the atomic number (quadratic dependence is seen in extending systems without also increasing the nuclear charge, such as in treating molecules not atoms). It is hard to estimate the Z dependance of the cpu time required to reduce both the systematic time step and statistical errors below 0.1eV, but since the required time step is theoretically proportional to Z^2 (argued [21] on the basis of current implementations of the FNA) then the cpu time should scale as Z^6. Previous suggestions for this dependence have been $Z^{5.5}$ [31] and $Z^{6.5}$ [21]. In practice the dependence is not this systematic, and higher accuracy trial functions and a more detailed implementation of the FNA will have a substantial influence.

6 Hydrogen Molecular Ion Clusters

High accuracy conventional *ab initio* and QMC calculations have been combined to generate essentially exact results for the binding energies of the molecules H_2, H_3^+, H_5^+, H_7^+ and H_9^+. Geometries were optimised with a 3s/3p (TZTP) basis set at the CEPA-1 level of accuracy. Comparisons with full CI calculations (in a DZP basis [33,34]) for H_5^+ indicate that CEPA-1 overestimates the total energy (and thus also the binding energy) by just 0.3kcal/mole. Basis set superposition error is estimated to be of similar magnitude in our TZTP basis.

All QMC calculations used the QMC2 algorithm, QMC being rigorously size extensive (unlike SDCI) and free of basis set superposition errors. Detailed analysis of time step error for H_2, H_3^+ and H_5^+ (given in figure 2) indicates that use of a time step of $0.01E_h^{-1}$ reduces errors in the total energies to of order 0.1kcal/mole. DZ SCF and DZP SCF trial functions (with electronic Jastrow factors [27] optimised in variational calcu-

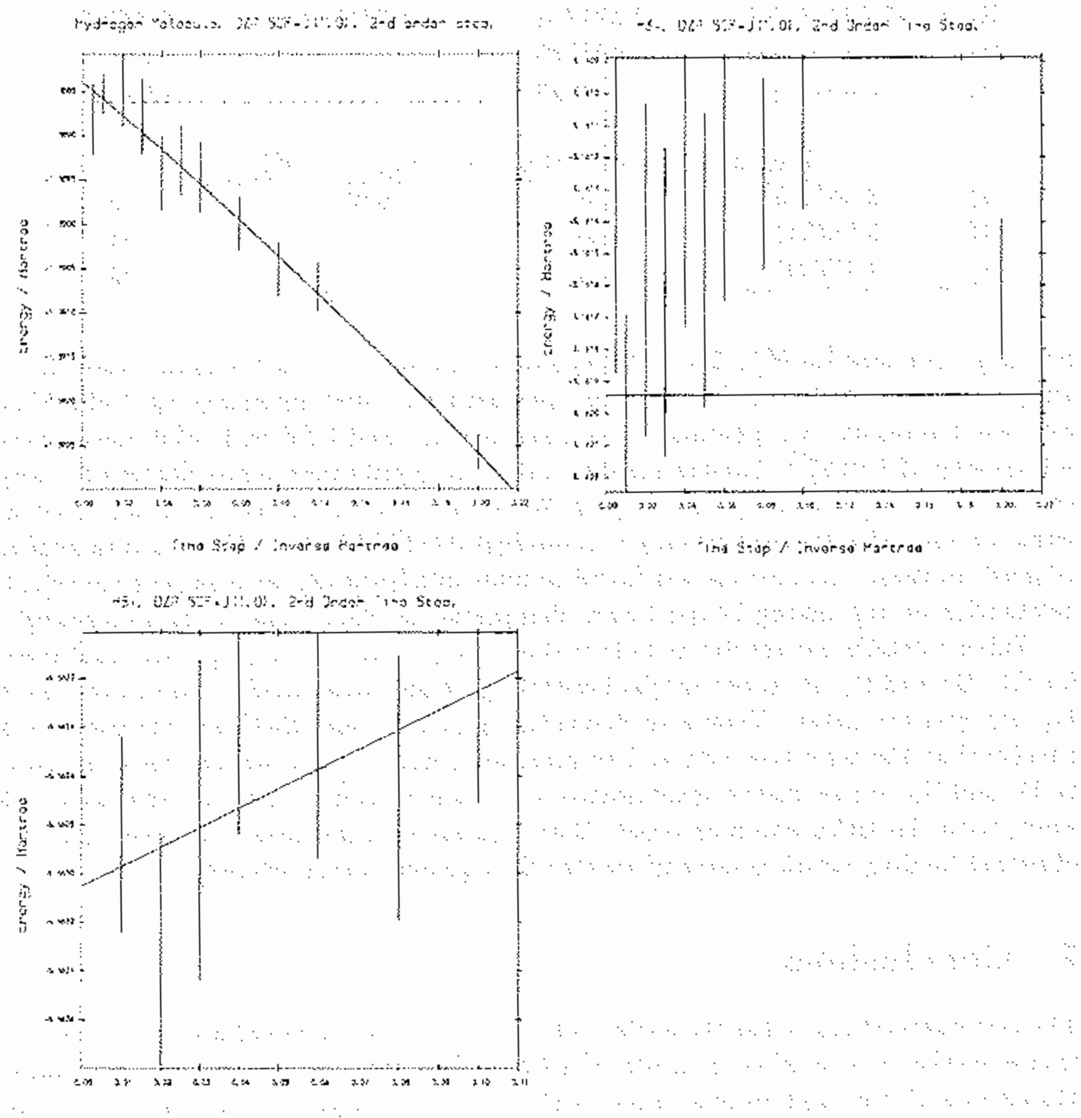

Figure 2: Analysis of QMC2 Time Step Error for H_2, H_3^+ and H_5^+.

Table 2: Total electronic energies and binding energies (removal of H_2) relevant to the hydrogen molecular ion clusters. Statistical uncertainties reported in parentheses.

	Total Energies / E_h			
	QMC (or exact)	TZTP CEPA-1	6s/3p CISD [33]	DZP CI [33,34]
H_2	-1.174475	-1.169727	-1.171430	-1.165705
H_3^+	-1.34371(16)	-1.338115	-1.340390	-1.334535
H_5^+	-2.53153(20)	-2.521331	-2.523150	-2.50987
H_7^+	-3.71405(33)	-3.698216		-3.67889
H_9^+	-4.89612(33)	-4.874655		-4.84678
	Binding Energies / kcal.mol^{-1} $H_{2n+1}^+ \rightarrow H_{2n-1}^+ + H_2$			
H_5^+	8.34(13)	8.46	8.02	6.75
H_7^+	5.05(24)	4.49		3.45
H_9^+	4.77(29)	4.21		3.26

lations) were used for H_5^+. The DZP function was found to be 1.5 times more efficient and, by improving the nodal surfaces, increased the binding energy by 1.5kcal/mole over the DZ result. All subsequent calculations employed DZP SCF trial functions and a time step of $0.01E_h^{-1}$. Calculations typically employed average populations of 4900, a block size of $4E_h^{-1}$, were equilibrated for 25 blocks from the variational distribution and were run until the desired accuracy was reached (50-150 blocks). The cpu time required to perform these calculations was found to scale quadratically with the system size, the calculation on H_9^+ taking 29 cpu hours, dominated by evaluation of the ao basis set.

Table 3 details our results and other theoretical values [32,33,34]. Our total enegies for H_5^+, H_7^+ and H_9^+ are substantially lower than all previous calculations and the H_2 and H_3^+ energies are exact. Time step dependent errors in our QMC binding energies are smaller than the statistical errors. The remaining errors in the binding energies relative to H_2 and H_3^+ are geometry optimisation at a lower level of theory and the fixed noded error, with the latter assumed small. Both will serve to increase the magnitude of the observed binding which is already greater than previous calculations.

7 Conclusions

The systematic study of the He isoelectronic sequence has displayed hitherto unobserved trends in the error arising from use of a finite time step. Comparison of propagation algorithms of first and second order in the time step suggests that the second order method has reduced errors in the energy from approximate solution of the electronic Schrödinger equation within nodal volumes to substantially below other errors for many electron atoms. The inexact forcing of the FNA boundary conditions is responsible for the large time step dependence seen in the many electron atoms, and the FNA is also responsible for the poor total atomic energies. Two possible solutions are improved release node techniques which currently seem insufficently stable [10] or improved trial functions with a more accurate enforcement of the FNA [10]. The second option is the least satisfactory, since it is still not exact in principle, but it may be the most readily achieved and will also permit larger time steps, increasing the efficiency of the simulation. Some evidence is also available to suggest that the substantial fixed node errors (10% or more of the correlation energy) cancel in taking chemical energy differences [14]).

We must also note that QMC remains extremely demanding of cpu time, the above and other calculations only being possible because of our dedicated parallel vector processor. The next few years will increase the power and cost effectiveness of such machines by several orders of magnitude compared to current supercomputers; if theory can also provide another factor of ten in speed and additional functionality (i.e. quantities other than total energies) then 'brute force' methods such as QMC may become attractive when compared with the more sophisticated established methods such as configuration interaction. At the moment QMC is only attractive for extremely highly accuracy single point calculations on light molecules and as an independent confirmation other *ab initio* calculations.

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The Ewald sum on the FPS/164 MAX

M. Leslie.

1 Introduction

Much has been written before about the Ewald sum and its application to both static and dynamic simulations [1] [2]. This article will therefore not attempt to repeat the theory. The aim is to show how the reciprocal space part of the sum may be reformulated such that the bulk of the floating point arithmetic is carried out as matrix multiplication operations. This allows the very fast matrix multiplication software provided with the FPS/164 MAX to be used. Although written with the FPS in mind, the method described is useful for any architecture where matrix multiplication may be performed at a much faster rate than ordinary FORTRAN. Overall the reciprocal space summation runs at 40 MFLOPS on the FPS/164 with 3 MAX boards at Daresbury. This should be compared with 200 MFLOPS on the CRAY XMP. The direct space part of the sum is slower on the 164 by a factor of 20 compared with the XMP. The MAX boards cannot be used for this part of the sum. However, it is possible to adjust the Ewald parameter α such that the bulk of the arithmetic is carried out in the reciprocal space sum with a larger reciprocal space cutoff and a smaller direct space cutoff. The direct space part of the sum will not be discussed further here.

The expression for the reciprocal space part of the energy and forces on a particle i is , following [1] equation (11b):

$$\phi_i = \sum_{\mathbf{k}} A(\mathbf{k}) \Re[(\sum_j q_j e^{i\mathbf{k}\bullet\mathbf{r}_j}) q_i e^{-i\mathbf{k}\bullet\mathbf{r}_i}] \tag{1}$$

$$-\mathbf{F}_i = \sum_{\mathbf{k}} A(\mathbf{k})\mathbf{k} \Im[(\sum_j q_j e^{i\mathbf{k}\bullet\mathbf{r}_j}) q_i e^{-i\mathbf{k}\bullet\mathbf{r}_i}] \tag{2}$$

Where:

$$A(\mathbf{k}) = \frac{\pi}{\alpha^2 V} e \left(-\frac{k^2}{4\alpha^2} \right) / \frac{k^2}{4\alpha^2} \tag{3}$$

$$\phi = \frac{1}{2} \sum_i \phi_i$$

The notation follows [1] except that V is the unit cell volume. The sum over $\mathbf{k}$ need only be carried out over half of reciprocal space and the final result doubled since reciprocal space is always centrosymmetric. The z component of the reciprocal lattice vector will always be taken as positive.

In general, the unit cell may have any shape and in the above expressions $\mathbf{k}$ is $2\pi \times$ a reciprocal lattice vector in orthonormal coordinates and $\mathbf{r}$ is an atom position in orthonormal coordinates. It is more convenient to work in a coordinate system defined relative to the unit cell lattice vectors. Let $\mathbf{L}$ be a matrix in the orthonormal coordinate system whose columns are the unit cell lattice vectors. Then the coordinates of an atom $\mathbf{R}$ in the non-orthogonal crystallographic reference frame may be defined as

$$\mathbf{r} = \mathbf{L} \bullet \mathbf{R}$$

The reciprocal lattice vectors in the new reference frame transform to

$$\mathbf{k} = \mathbf{K} \bullet \mathbf{L}^{-1}$$

where $\mathbf{K}$ is now 2π times an integer vector. Hence

$$\mathbf{k} \bullet \mathbf{r} = \mathbf{K} \bullet \mathbf{L}^{-1} \bullet \mathbf{L} \bullet \mathbf{R} = \mathbf{K} \bullet \mathbf{R}$$

Equations (1) and (2) may be written in terms integer reciprocal lattice vectors and non-orthogonal atom positions.

$$\phi_i = \sum_{\mathbf{k}} A(\mathbf{k}) \Re[(\sum_j q_j e^{i\mathbf{K}\bullet\mathbf{R}_j}) q_i e^{-i\mathbf{K}\bullet\mathbf{R}_i}] \tag{4}$$

$$-\mathbf{F}_i = \sum_{\mathbf{k}} A(\mathbf{k}) \mathbf{k} \Im[(\sum_j q_j e^{i\mathbf{K}\bullet\mathbf{R}_j}) q_i e^{-i\mathbf{K}\bullet\mathbf{R}_i}] \tag{5}$$

2 Description of method

The calculation is divided into seven sections.

2.1 Step 1. Calculate $A(k)$

The $A(\mathbf{k})$ factors are calculated according to (3). Note that these do not depend on the positions of the atoms in the unit cell, so only need be calculated once if the unit cell shape is not allowed to change.

2.2 Step 2. Factorization

The second step is to factorize the complex exponential. This greatly reduces the computation time since the factors may be evaluated by complex multiplication rather than a complex exponentiation.

$$q_j e^{i\mathbf{K}\bullet\mathbf{R}} = q_j e^{iK_x R_x} e^{iK_y R_y} e^{iK_z R_z}$$

The complex exponentials $e^{2\pi i R_x}$, $e^{2\pi i R_y}$ and $e^{2\pi i R_z}$ must be calculated. Then the higher values of K are calculated by complex multiplication.

$$e^{2(2\pi i R_x)} = e^{2\pi i R_x} \times e^{2\pi i R_x}$$

If the maximum reciprocal lattice vectors in the x, y and z directions are N_x, N_y and N_z respectively and there are M atoms in the unit cell, the factors are stored in three matrices $\mathbf{V}_x$, $\mathbf{V}_y$ and $\mathbf{V}_z$. $\mathbf{V}_x$ is a M by $2N_x$ matrix with columns alternately the real and imaginary parts of the complex products. The $K_x = 0$ vector is not stored. The elements of $\mathbf{V}_x$ are multiplied by q_j. $\mathbf{V}_y$ is a M by $2N_y$ matrix. $\mathbf{V}_z$ is a M by $2N_z + 1$ matrix. Column 1 of $\mathbf{V}_z$ is the real part of the $K_z = 0$ vector and has all elements set to 1.

2.3 Step 3. Calculation of the xy product matrix

The complex product of the factors $e^{iK_xR_x}e^{iK_yR_y}$ is now calculated and stored for all K_x and K_y. In this calculation allowance is made for $K_x = 0$ and $K_y = 0$, as well as calculating the complex conjugate product.

1 Row The real part of $K_x = 0$, $K_y = 0$ is set equal to q_i.

$2N_y$ Rows These rows are the transpose of $\mathbf{V}_y$ multiplied by q_i, and are for $K_x = 0$.

$2N_x$ Rows These rows are the transpose of $\mathbf{V}_x$.

$4N_xN_y$ Rows These rows are the complex product of two non-zero K_x and K_y vectors followed by the complex conjugate product. The products are calculated in the same DO loop since they have the same multiplications in them. This gives a matrix $\mathbf{V}_4$ of dimension $(1 + 2N_x)(1 + 2N_y)$ by M.

2.4 Step 4. First matrix product.

The matrix product $\mathbf{V}_4\mathbf{V}_z$ gives a matrix $\mathbf{W}$ whose elements contain the real and imaginary parts of $\sum_j q_j e^{i\mathbf{K}\bullet\mathbf{R}}$. $\mathbf{W}$ is a $(1 + 2N_x)(1 + 2N_y)$ by $(1 + 2N_z)$ matrix. Henceforth the following notation will be used:

C_{xy}	is the real part of	$\mathbf{V}_4$
S_{xy}	is the imaginary part of	$\mathbf{V}_4$
C_z	is the real part of	$\mathbf{V}_z$
S_z	is the imaginary part of	$\mathbf{V}_z$

$$
\begin{aligned}
&\sum_j (C_{xy} + iS_{xy}) \times (C_z + iS_z) \\
&\quad = \sum_j C_{xy}C_z - \sum_j S_{xy}S_z + i \times \Big(\sum_j C_{xy}S_z + \sum_j S_{xy}C_z\Big) \\
&\quad = W_{CC} - W_{SS} + i \times (W_{CS} + W_{SC})
\end{aligned}
$$

The product of the complex conjugate of the xy vector with z will also be needed, giving the reciprocal lattice vector $-x - yz$.

$$
\begin{aligned}
&\sum_j (C_{xy} - iS_{xy}) \times (C_z + iS_z) \\
&\quad = \sum_j C_{xy}C_z + \sum_j S_{xy}S_z + i \times \Big(\sum_j C_{xy}S_z - \sum_j S_{xy}C_z\Big) \\
&\quad = W_{CC} + W_{SS} + i \times (W_{CS} - W_{SC})
\end{aligned}
$$

Equations (4) and (5) may be rewritten using this notation:

$$\begin{aligned}\phi_i &= \sum_{xyz} A(xyz)\Re\{[(W_{CC}-W_{SS})+i\times(W_{CS}+W_{SC})]\times\\ &\quad [(C_{xy}-iS_{xy})\times(C_z-iS_z)]\} \qquad (6)\end{aligned}$$

$$\begin{aligned}-\mathbf{F}_i &= \sum_{xyz} A(xyz)\mathbf{k}(xyz)\Im\{[(W_{CC}-W_{SS})+i\times(W_{CS}+W_{SC})]\times\\ &\quad [(C_{xy}-iS_{xy})\times(C_z-iS_z)]\} \qquad (7)\end{aligned}$$

2.5 Step 5. Setup for second matrix product

Equations (6) and (7) are now rearranged so that another matrix product may be carried out. First the terms in xyz and $-x-yz$ are written explicitly.

$$\begin{aligned}\phi_i &= \sum_{xyz,z>0} \Re\{\{A(xyz)[(W_{CC}-W_{SS})+i(W_{CS}+W_{SC})]\times\\ &\quad (C_{xy}-iS_{xy}) + A(-x-yz)[(W_{CC}+W_{SS})+i(W_{CS}-W_{SC})]\times\\ &\quad (C_{xy}+iS_{xy})\}\times(C_z-iS_z)\}\\ &= \sum_{z,z>0}\sum_{xy}\Re\{\{\\ &\quad [A(xyz)(W_{CC}-W_{SS})+A(-x-yz)(W_{CC}+W_{SS})]\times C_{xy}\\ &\quad +[A(xyz)(W_{CS}+W_{SC})-A(-x-yz)(W_{CS}-W_{SC})]\times S_{xy}\\ &\quad +[A(xyz)(W_{CS}+W_{SC})+A(-x-yz)(W_{CS}-W_{SC})]\times iC_{xy}\\ &\quad +[-A(xyz)(W_{CC}-W_{SS})+A(-x-yz)(W_{CC}+W_{SS})]\times iS_{xy}\}\\ &\quad \times(C_z-iS_z)\}\\ &= \sum_{z,z>0}\sum_{xy}\Re\{\{X_{CC}C_{xy}+X_{CS}S_{xy}+iX_{SC}C_{xy}+iX_{SS}S_{xy}\}\\ &\quad \times(C_z-iS_z)\} \qquad (8)\end{aligned}$$

$$\begin{aligned}-\mathbf{F}_i &= \sum_{z,z>0}\sum_{xy}\Im\{\{\mathbf{Y}_{CC}C_{xy}+\mathbf{Y}_{CS}S_{xy}+i\mathbf{Y}_{SC}C_{xy}+i\mathbf{Y}_{SS}S_{xy}\}\\ &\quad \times(C_z-iS_z)\} \qquad (9)\end{aligned}$$

Where:

$$\begin{aligned}\mathbf{Y}_{CC} &= A(xyz)\mathbf{k}(xyz)(W_{CC}-W_{SS})+\\ &\quad A(-x-yz)\mathbf{k}(-x-yz)(W_{CC}+W_{SS})\\ \mathbf{Y}_{CS} &= A(xyz)\mathbf{k}(xyz)(W_{CS}+W_{SC})-\\ &\quad A(-x-yz)\mathbf{k}(-x-yz)(W_{CS}-W_{SC})\\ \mathbf{Y}_{SC} &= A(xyz)\mathbf{k}(xyz)(W_{CS}+W_{SC})+\\ &\quad A(-x-yz)\mathbf{k}(-x-yz)(W_{CS}-W_{SC})\\ \mathbf{Y}_{SS} &= -A(xyz)\mathbf{k}(xyz)(W_{CC}-W_{SS})+\\ &\quad A(-x-yz)\mathbf{k}(-x-yz)(W_{CC}+W_{SS})\end{aligned}$$

In the above equations, allowance must be made for the terms for which x, y or z are zero.

2.6 Step 6. Second matrix product

The elements of X and Y in equations (8) and (9) are written into one large matrix $\mathbf{V}_5$. For each pair of reciprocal lattice vectors $\mathbf{k}(xyz)$ and $\mathbf{k}(-x-yz)$ 8 elements of the array $\mathbf{V}_5$ are written. These are shown below, together with two elements from the array $\mathbf{V}_4$.

$$\begin{array}{rrl} X_{CC} & X_{CS} & C_{xy} \\ X_{SC} & X_{SS} & S_{xy} \\ Y_{SCx} & Y_{SSx} & \\ -Y_{CCx} & -Y_{CSx} & \\ Y_{SCy} & Y_{SSy} & \\ -Y_{CCy} & -Y_{CSy} & \\ Y_{SCz} & Y_{SSz} & \\ -Y_{CCz} & -Y_{CSz} & \end{array}$$

The following notation will now be used

$$\begin{array}{lcl} V_{511} = X_{CC} & \text{or} & Y_{SC\alpha} \\ V_{512} = X_{CS} & \text{or} & Y_{SS\alpha} \\ V_{521} = X_{SC} & \text{or} & -Y_{CC\alpha} \\ V_{522} = X_{CC} & \text{or} & -Y_{CS\alpha} \end{array}$$

Where $\alpha = x$, y or z. Fewer elements will need to be written for the special cases of $x = 0$, $y = 0$ and $z = 0$. It may be shown that the array $\mathbf{V}_5$ has dimensions $4(1+2N_z)$ by $(1+2N_x)(1+2N_y)$. The matrix product $\mathbf{V}_5\mathbf{V}_4 = \mathbf{V}_6$ then gives the sum over xy in equations (8) and (9). The matrix product is carried out as one large product rather than four smaller products as this reduces the overheads on the FPS associated with loading the MAX boards with one of the matrices.

2.7 Step 7. Final scalar product

The final step is to carry out a scalar product over all of the real and imaginary parts of $\mathbf{V}_6$ with $\mathbf{V}_z$. The following notation will be used.

$$\begin{aligned} V_{6C} &= \sum_{xy} [V_{511}C_{xy} + V_{512}S_{xy}] \\ V_{6S} &= \sum_{xy} [V_{521}C_{xy} + V_{522}S_{xy}] \end{aligned}$$

Equations (8) and (9) now become:

$$\begin{aligned} \phi_i &= \Re \sum_z (V_{6C} + iV_{6S})(C_z - iS_z) \\ &= \sum_z V_{6C}C_z + \sum_z V_{6S}S_z \qquad (10) \\ -F_i &= \Im \sum_z (iV_{6C} - V_{6S})(C_z - iS_z) \\ &= \sum_z V_{6C}C_z + \sum_z V_{6S}S_z \qquad (11) \end{aligned}$$

3 Cutoffs

The choice of Ewald parameter α determines the cutoffs used in the direct and reciprocal space sums. The expressions used are taken from [3]. Let A be an accuracy parameter with the direct and reciprocal space sums calculated to this accuracy. Then

$$f = (-\ln A)^{1/2}$$

The direct space cutoff is $r_{max} = f/\alpha$ and the reciprocal space cutoff is $k_{max}/2\pi = \alpha f/\pi$. The value of α chosen to give approximately equal numbers of terms in the two series is:

$$\alpha = (M\pi^3/V^2)^{1/6}$$

However, this value of α may be changed to make the reciprocal space cutoff larger and the direct space cutoff smaller. The maximum reciprocal lattice vectors in the x, y and z directions N_x, N_y and N_z are determined from the formula given below.

$$N_x = (k_{max}/2\pi)/|\mathbf{l}_x|$$

where $\mathbf{l}_x$ is the x column of the $\mathbf{L}$ matrix defined in the introduction.

Usually all vectors outside the spherical cutoff are omitted from the calculation. The method as described so far includes all vectors within a cube (parallelepiped in general). Hence the number of vectors calculated is approximately twice the number within the spherical cutoff. This may be improved by omitting those lines in reciprocal space in the z direction which do not intersect the cutoff sphere. The ratio of the total number of points calculated to the number in the cutoff sphere is now reduced to 1.5. The cutoff is applied in step 3 above, the row dimension of the matrix $\mathbf{V}_4$ will be less than $(1 + 2N_x)(1 + 2N_y)$.

4 Timings

The times given below are for 1000 basis atoms with a reciprocal space cutoff $N_x = N_y = N_z = 9$. This gives 3429 reciprocal lattice vectors within the cube. Of these, 1559 are within the spherical cutoff. There are 181 lines of reciprocal space points in the z direction, of which 131 intersect the cutoff sphere. This gives a total of 2489 reciprocal space points calculated by the matrix method.

Timings on FPS and XMP in seconds				
STEP		FPS	XMP	FPS/XMP
1		0.051	0.0016	32.0
2		0.153	0.0031	50.0
3		0.218	0.0056	39.0
4	MAX	0.211	0.0493	4.3
5		0.019	0.0020	10.0
6	MAX	0.650	0.1977	3.3
7		0.053	0.0016	33.0
Total		1.354	0.2650	5.3

The total time on the XMP using the full spherical cutoff without any matrix multiplication was 0.330 s. This is slightly greater than the matrix multiplication time despite there being fewer vectors calculated. Steps 2, 3 and 7 are all memory limited on the FPS. They could all be speeded up by a factor of 2-3 if the table memory were used, but this part would need to be programmed in assembler. On the XMP, vector loops can carry out three vector memory references simultaneously, so the loops are not memory limited.

References

[1] N. Anastasiou and D. Fincham Comput. Phys. Comm. 25 (1982) 159

[2] W. Smith. CCP5 Newsletter 21 (1986) 37

[3] C. R. A. Catlow and W. C. Mackrodt in Computer simulation of solids. Lecture notes in Physics Vol. 166. Berlin Springer-Verlag (1982) C. R. A. Catlow (ed.)

CRAY VECTORISED LINK CELL CODE

D.M. Heyes and W. Smith

September 21, 1987

1 Introduction

In the last issue of the CCP5 Newsletter one of us presented a 'speculative' method for handling moderately large numbers of particles on the CRAY-1, using approximately 1000 particles [1]. Since then the need to go to yet larger numbers of particles, ca. 5000, has arisen! This motivated us to adapt the Link Cell, LC, method to run on the CRAY. This method is the only scheme feasible in such a regime we believe (unless CCP5 readers can inform us to the contrary!). It involves breaking the MD cell into smaller sub-cells, each of minimum side-length greater than the truncation radius for the interactions. This enables us to modify the double FORTRAN DO-loop where one evaluates the forces so that one can pre-eliminate interactions beyond the interaction truncation radius. The two-particle sum becomes essentially a two sub-cell sum. For each sub-cell pair one finds the contents using a rather elegant scheme which chains the particle indices together. The unvectorised version has been amply discussed elsewhere by both of us [2,3]. We only give the essential code here, other MD details can be found in [1,2,3]. Notation is reasonably consistent between these.

We find this code is marginally faster than the method given in [1] for N=1372 . At LJ reduced densities of 0.6 and 0.8442 the time steps are 0.26 and 0.45 sec for this method, whereas it was a density independent 0.5 sec in [1]. It is for much larger N that the real benefits of the LC method become evident. For N=2048 the method described here takes 0.37 and 0.57 sec CPU, respectively. For N=6912 we have 1.22 and 1.59 sec, respectively . (NLX=9 and 8, respectively in the last case.)

This is undoubtedly not the last word on this subject! We felt that this preliminary report was warranted to spur a move towards the most efficient codes in the MD field. (PS If you discover any improvements, please let us know!)

References

[1] D.M. Heyes, "Information Quarterly for Computer Simulation of Condensed Phases", June 1987, No. 25, p. 57.

[2] D. Fincham and D.M. Heyes, "Recent Advances in Molecular Dynamics Computer Simulation", Advances in Chemical Physics, 1985, J. Wiley Sons, pp 493-575.

[3] W. Smith, "Information Quarterly for Computer Simulation of Condensed Phases", March 1986, No. 20, p. 52

2 The Vectorised Code

```
      PARAMETER (N=2048,NVECT=500,NDOUB=1000)
      DIMENSION LTOP(NDOUB),LINK(N),NIX(14),NIY(14),NIZ(14),
     1 RX(N),RY(N),RZ(N),FX(N),FY(N),FZ(N),JADDR(NVECT),
     2 FXI(NVECT),FYI(NVECT),FZI(NVECT),RXX(NVECT),
     3 RYY(NVECT),RZZ(NVECT),POTRI(NVECT),POTAI(NVECT),
     4 PRI(NVECT)
      DATA NIX/ 0,-1,-1,-1, 0, 0,-1, 1,-1, 0, 1,-1, 0, 1/
      DATA NIY/ 0, 0,-1, 1, 1, 0, 0, 0,-1,-1,-1, 1, 1, 1/
      DATA NIZ/ 0, 0, 0, 0, 0, 1, 1, 1, 1, 1, 1, 1, 1, 1/
      NLX=S/CU ! S IS THE WIDTH OF THE MD CELL IN LJ SIGMA
C     THE MORE LINK CELLS YOU CAN SQUEEZE INTO THE MD
C     CELL THE FASTER THE CODE WILL RUN.
      CX=S/FLOAT(NLX) ! THERE ARE NLX LINK CELLS ACROSS THE
      NCELLS=NLX*NLX*NLX ! BOX. THIS IS A CUBIC MD CELL
      FNLX=FLOAT(NLX) ! CU IS THE INTERACTION CUT-OFF
      FNI=1.0/FLOAT(N) ! THERE ARE N PARTICLES IN THE MD CELL
      CU2=CU*CU
      .......... ! A LOT OF MD CODE, BASICALLY INITIALISATION.
C
C     THIS IS THE FORCES LOOP.
C
C     CALCULATE LINK CELL INDICES
      DO 110 L=1,NCELLS ! NCELLS IS THE NUMBER OF LINK CELLS
110   LTOP(L)=0 ! LTOP CONTAINS THE LEADING INDEX FOR EACH LC
      DO 1654 I=1,N
      FX(I)=0.0
      FY(I)=0.0
      FZ(I)=0.0
      IX=INT(FNLX*RX(I)/S) ! EACH TIME STEP WE FILL THE
      IY=INT(FNLX*RY(I)/S) ! CONTENTS OF EACH LINK CELL
      IZ=INT(FNLX*RZ(I)/S)
      ICELL=1+IX+NLX*(IY+NLX*IZ)
      J=LTOP(ICELL)
      LTOP(ICELL)=I
      LINK(I)=J ! THE END OF THE CHAIN IS WHEN LINK(I)=0
1654  CONTINUE
C
C     PRIMARY LOOP OVER ALL CELLS
C
C     SET CONTROL VARIABLES FOR LOOP OVER CELLS
      IX=1
      IY=1
      IZ=1
```

```
C
C     PRIMARY LOOP OVER ALL CELLS
      DO 5001 IC=1,NCELLS
      I=LTOP(IC)
C
C     BYPASS CELL IF EMPTY
      IF (I.EQ.0) GOTO 5001
      M=0
99    M=M+1
      JADDR(M)=I ! THIS IS A CONTIGUOUS ADDRESS LABEL ARRAY
      RXX(M)=RX(I) ! TO PROMOTE VECTORISATION
      RYY(M)=RY(I) ! THESE ARE TEMPORARY POSITION ARRAYS
      RZZ(M)=RZ(I)
      I=LINK(I)
      IF (I.GT.0) GOTO 99
      MSTART=M
C
C     SECONDARY LOOP OVER NEIGHBOURING CELLS
      DO 4001 KC=2,14
      SX=0.0
      SY=0.0
      SZ=0.0
      JX=IX+NIX(KC)
      JY=IY+NIY(KC)
      JZ=IZ+NIZ(KC)
C
C     MINIMUM IMAGE CONVENTION
      IF((IX.EQ.NLX).AND.(JX.GT.IX))THEN
      JX=1
      SX=S
      ELSEIF((IX.EQ.1).AND.(JX.LT.IX))THEN
      JX=NLX
      SX=-S
      ENDIF
      IF((IY.EQ.NLX).AND.(JY.GT.IY))THEN
      JY=1
      SY=S
      ELSEIF((IY.EQ.1).AND.(JY.LT.IY))THEN
      JY=NLX
      SY=-S
      ENDIF
      IF((IZ.EQ.NLX).AND.(JZ.GT.IZ))THEN
      JZ=1
```

```
            SZ=S
            ELSEIF((IZ.EQ.1).AND.(JZ.LT.IZ))THEN
            JZ=NLX
            SZ=-S
            ENDIF
C
C           INDEX OF NEIGHBOURING CELL
            JC=JX+NLX*((JY-1)+NLX*(JZ-1))
            J=LTOP(JC)
C
C           BYPASS CELL IF EMPTY
            IF (J.EQ.0) GOTO 4001
199         M=M+1
            JADDR(M)=J
            RXX(M)=RX(J)+SX
            RYY(M)=RY(J)+SY
            RZZ(M)=RZ(J)+SZ
            J=LINK(J)
            IF (J.GT.0) GOTO 199
4001        CONTINUE
C           WE HAVE NOW FINISHED FINDING ALL NEIGH. PARTICLES OF BOX IC.
            MAX=M
            IF (MAX.GT.NVECT) STOP
            MSTART1=MSTART
            IF (MAX.EQ.MSTART) MSTART1=MSTART-1
            IF (MSTART1.LE.0) GOTO 2748
C
C           NOW DO THE PARTICLE-PARTICLE INTERACTIONS
            DO 6001 IM=1,MSTART1
            RXI=RXX(IM)
            RYI=RYY(IM)
            RZI=RZZ(IM)
            MM=0
C           DO THE INNER VECTORISED LOOP
            DO 6002 M=IM+1,MAX
            X=RXI-RXX(M)
            Y=RYI-RYY(M)
            Z=RZI-RZZ(M)
            RR=X*X+Y*Y+Z*Z
            RRI=1.0/RR
            RRI=CVMGP(RRI,0.0,CU2-RR)
            MM=MM+1
            R6I=RRI*RRI*RRI
```

```
         R12I=R6I*R6I
         POTRI(MM)=4.0*R12I ! LENNARD-JONES POTENTIAL USED HERE
         POTAI(MM)=-4.0*R6I
         FF=24.0*(R12I+R12I-R6I)*RRI
         PRI(MM)=RR*FF
         FXI(MM)=X*FF
         FYI(MM)=Y*FF
         FZI(MM)=Z*FF
6002     CONTINUE
         MMAX=MM
         IF (MMAX.LE.0) GOTO 2748
         I=JADDR(IM)
         FX(I)=FX(I)+SSUM(MMAX,FXI,1) !SUMMATION ROUTINE
         FY(I)=FY(I)+SSUM(MMAX,FYI,1)
         FZ(I)=FZ(I)+SSUM(MMAX,FZI,1)
         UR=UR+SSUM(MMAX,POTRI,1)*FNI
         UA=UA+SSUM(MMAX,POTAI,1)*FNI
         PRES=PRES+SSUM(MMAX,PRI,1)*0.3333333*VI
         DO 3422 KK=1,MMAX !PART NOT YET VECTORISED (!)
         J=JADDR(IM+KK)
         FX(J)=FX(J)-FXI(KK)
         FY(J)=FY(J)-FYI(KK)
         FZ(J)=FZ(J)-FZI(KK)
3422     CONTINUE
2748     CONTINUE
6001     CONTINUE
C
C        PRIMARY CELL INDEX CONTROL SECTION
         IX=IX+1
         IF(IX.GT.NLX)THEN
         IX=1
         IY=IY+1
         IF(IY.GT.NLX)THEN
         IY=1
         IZ=IZ+1
         ENDIF
         ENDIF
5001     CONTINUE
```

.... LOTS MORE MD CODE...

CCP5 Literature Survey - Addendum 2

S.H. Lee, J.C. Rasaiah and J.B. Hubbard
Molecular dynamics study of a dipolar fluid between charged plates.
J. Chem. Phys. **85** 5232-5237 (1986)

S.H. Lee, J.C. Rasaiah and J.B. Hubbard
Molecular dynamics study of a dipolar fluid between charged plates II.
J. Chem. Phys. **85** 2383-2393 (1987)

CONFERENCE FEES

	1 day	3 days
Non-Member	£38.00	£64.00
Member+	£31.00	£48.00
Student/Retired Member*	£22.00	£30.00

\+ Members of Institute of Physics (all grades) or those with Membership applications pending. This fee also applies to Members of EPs.

* Members as defined above who are bona fide full-time students. Their application must be countersigned by their Head of Department/Supervisor. This fee also applies to members over the age of 60 who have retired from active business and to Members who are unemployed because of redundancy.

THERE WILL BE A CONCESSIONARY DISCOUNT OF £10 FOR APPLICANTS WHOSE REMITTANCES ARE POSTED BEFORE 1 NOVEMBER.

PAYMENTS

All payments must accompany the registration form. Fees CANNOT be invoiced. Please make cheques payable to 'University of Bristol'.

GRANTS FOR YOUNG SCIENTISTS

Bursaries to assist young scientists to attend the Conference will be available. Preference will be given to non-tenured academic and industrial scientists under 30 years of age. Applications, which should include a brief CV and an estimate of expenses sought, should be sent to the Conference Secretaries (address above) as soon as possible and certainly before 1 OCTOBER to guarantee consideration.

CANCELLATIONS

No refunds are guaranteed to those cancelling their registration or accommodation after 20 NOVEMBER.

SATELLITE MEETING ON 'HIGH TEMPERATURE SUPERCONDUCTIVITY'

This will be held on 14 and 15 DECEMBER. Further details are enclosed. SEPARATE REGISTRATION is necessary for this meeting - see white registration form.

OTHER EVENTS

There will be an IoP Open Meeting at 20.45 on Wednesday 16 December. This will be followed by a presentation by the Chairman of the SERC Physics Committee.

LOCAL ARRANGEMENTS

The Conference Sessions will take place in the University of Bristol. Residential accommodation, which will be in two adjoining Halls of Residence, consists of single study bedrooms with wash-basins. The Halls are approximately 3 miles from the City Centre/Temple Meads Station and 2 miles from the University. Coaches will transport participants between the Halls and the Conference. Participants requiring hotel accommodation should request a list from the Conference Secretaries as soon as possible and then make their own arrangements with the hotel of their choice. Lunches in the University will be available by ticket only which must be purchased in advance. Dinner will be available in the Halls of Residence except on Thursday, 17 December when the Conference Buffet Dinner will be held in the City Museum. This will follow a Reception. All figures quoted on the attached form are fully inclusive.

TRAVEL

There is a frequent and fast (1hr 30m) train service from London Paddington to BRISTOL TEMPLE MEADS. Direct coach services operate between both Heathrow and Gatwick airports and Bristol. Car parking is available at the Halls of Residence but NOT at the University. Participants are strongly advised to use the transfer buses provided. Maps will be sent with confirmation of application.

The Institute of Physics

Solid State Physics Sub-Committee

1987 SOLID STATE PHYSICS CONFERENCE

16–18 December 1987

University of Bristol

H H Wills Physics Laboratory

CLOSING DATES

ABSTRACTS: 2 NOVEMBER 1987

ADVANCE REGISTRATION: 2 NOVEMBER 1987

LATE REGISTRATION: 20 NOVEMBER 1987

CONFERENCE SECRETARIES: Drs R.Evans and B.L.Gyorffy, H.H. Wills Physics Laboratory,

University of Bristol, Bristol, BS8 1TL, U.K.

(TELEPHONE ENQUIRIES: MRS L MURPHY (0272)303603)

PROVISIONAL PROGRAMME

The final programme, Abstract book and local information will be distributed at the Conference. Confirmation of registration and accommodation will be mailed.

MOTT LECTURE

G.G.Lonzarich (Cambridge) - 'The Nature of Heavy Fermion Quasiparticles'

PLENARY LECTURES

S.Berko (Brandeis) - 'Positron Annihilation Studies in Condensed Matter Physics'

M.V.Berry (Bristol) - 'The Adiabatic Phase: Four Years After'

S.Chandrasekhar (Bangalore) - 'Recent Progress in the Physics of Liquid Crystals'

J.M.Gibson (Bell Labs.) - 'Molecular Beam Epitaxy of Metal Films on Si; in situ Electron Microscopy Characterization of Growth'.

M.Bart (Manchester) - 'Characterization of New Materials by Diffraction Methods'

C.Janot (ILL Grenoble) - 'Neutron Diffraction of Quasi Periodic Structures: Contrast Variation, Isomorphism and Pseudo Structures'

C.M.Varma (Bell Laboratories) - 'Progress in High Temperature Superconductivity'

EXHIBITION

An exhibition of books and manufacturers equipment and services will take place throughout the conference. For details please contact Dr.M.G.Priestley, H.H.Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, immediately.

SYMPOSIA

The Conference will be based on ten Symposia. These will run on the days listed below:

(D) DIFFRACTION STUDIES OF NEARLY PERFECT CRYSTALS (Wed,Thur)
Speakers will include **R.A.Cowley** (Edinburgh), **P.F.Fewster** (Philips), **P.J.Halfpenny** (GEC), **C.J.Humphreys** (Liverpool), **J.R.Schneider** (Berlin), **J.N.Sherwood** (Strathclyde).
Organiser: Mrs M.A.G.Halliwell, British Telecom Research Labs, Martlesham Heath, Ipswich IP5 7RE.

(ES) SPECTROSCOPY OF ELECTRONIC STATES IN METALS AND SEMICONDUCTORS (Wed,Thur)
Speakers will include **U.von Barth** (Lund), **J.C.Fuggle** (Nijmegen), **R.Godby** (Cambridge), **K.Nash** (RSRE Malvern)
Organisers: Dr.P.J.Durham, Theory Group,SERC,Daresbury Laboratory, Daresbury, Warrington WA4 4AD and **Prof.J.C.Inkson** (Exeter).

(P) POLYMERS AND LIQUID CRYSTALS (Wed, Thur)
Speakers will include **H.Finkelmann** (Freiburg), **J.M.F.Gunn** (Rutherford), **A.Keller** (Bristol), **H.Ringsdorf** (Mainz)
Organiser: Dr.M.Warner, TCM,Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE.

(HP) PHYSICS OF SOLIDS AT HIGH PRESSURES (Wed)
Speakers will include **A.R.Adams** (Surrey),**J.M.Besson** (Paris VI)
Organiser: Prof.C.H.L.Goodman, S.T.C.Technology, London Road, Harlow, Essex CM17 9NA.

(SP) PHYSICS OF THE SPUTTERING PROCESS (Wed)
Speakers will include **H.H.Andersen** (Copenhagen), **A.Benninghoven** (MUnster), **G.Carter** (Salford), **B.Sundqvist** (Uppsala)
Organiser: Dr.R.Webb, Dept.of Electronic and Electrical Engineering,University of Surrey,Guildford,Surrey GU2 5XH.

(NS) SCATTERING OF NEUTRONS FROM DISORDERED SYSTEMS (Thur)
Speakers will include **J.E.Enderby** (ILL,Grenoble), **P.Gaskell** (Cambridge), **R.McGreevy** (Oxford), **A.K.Soper** (Rutherford).
Organiser:Dr G.W.Neilson,H.H.Wills Physics Laboratory,University of Bristol,Bristol BS8 1TL.

(SI) SURFACE AND INTERFACE PHYSICS OF ADVANCED SEMICONDUCTORS (Thur,Fri)
Speakers will include: **R. Egdell** (Imperial), **M.J.Kelly** (GEC), **J.B.Pethica** (Oxford), **W. Richter** (Aachen), **F. van der Veen** (Amsterdam), **J. Venables** (Sussex), **R.Vincent** (Bristol)
Organisers: Dr.D.Cherns,H.H.Wills Physics Laboratory, University of Bristol,Bristol BS8 1TL and **Prof.R.H.Williams** (Cardiff).

(SM) STATISTICAL MECHANICS OF DISORDERED AND INHOMOGENEOUS SYSTEMS (Fri, Posters Thur)
Speakers will include **D.J.Amit** (Jerusalem), **M.Gillan** (Harwell), **P.R.King** (B.P.), **I.R.McDonald** (Cambridge), **D.W.Oxtoby** (Chicago).
Organisers: Dr R.Evans,H.H.Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL and **Dr R.Ball** (Cambridge).

(M) MAGNETIC INFORMATION STORAGE (Fri, Posters Thur)
Speakers will include **R.Carey** (Coventry), **P.J.Grundy** (Salford), **J.C.Lodder** (Twente), **D.Mapps** (Plymouth), **B.K.Middleton** (Manchester), **D.E.Speliotis** (Burlington: to be confirmed)
Organiser: Dr P.J.Grundy,Dept. of Applied Physics, University of Salford, Salford M54WT.

(G) GENERAL TOPICS (Thu,Fri)
Organiser: Dr.D.A.Greenwood, H.H.Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL.

CONTRIBUTED PAPERS

Abstracts are invited for contributions to the symposia. These should be typed in single-line spacing with the title in capital letters. The complete abstract, including title, authors' names and addresses should occupy an area **NOT EXCEEDING 165mm** wide and **110mm** high. Please send them directly to the appropriate **symposium organiser** listed above, **BEFORE 2 NOVEMBER 1987.**

PROVISIONAL PROGRAMME

Monday 14 and Tuesday 15 December
SATELLITE MEETING ON HIGH T_c SUPERCONDUCTIVITY (see separate notice).

Wednesday, 16 December
09.40 OPENING ADDRESS **by Sir Charles Frank**
09.45 PLENARY **(Varma)**
10.30 COFFEE
11.00 SYMPOSIA (D,ES,SP,HP)
12.40 Lunch
14.00 PLENARY **(Chandrasekhar)**
14.45 POSTERS (D,ES,SP,HP,G) and Tea
16.15 SYMPOSIA (D,ES,SP,P)
19.00 Dinner in Halls of Residence
20.45 IoP Open Meeting; SERC Presentation

Thursday, 17 December
09.00 MOTT LECTURE **(Lonzarich)**
09.45 PLENARY **(Bart)**
10.30 Coffee
11.00 SYMPOSIA (D,ES,P,NS)
12.40 Lunch
14.00 PLENARY **(Janot)**
14.45 POSTERS (P,NS,SI,M,SM,G) and tea
16.15 SYMPOSIA (P,NS,SI,G)
18.15 Reception
19.15 Conference Buffet Dinner

Friday, 18 December
09.00 PLENARY **(Berko)**
09.45 PLENARY **(Berry)**
10.30 Coffee
11.00 SYMPOSIA (SI,M,SM,G)
12.40 Lunch
14.00 PLENARY **(Gibson)**
15.00 SYMPOSIA (SI,M,SM,G)
16.30 Mulled Wine
17.00 Conference Closes

MEMBERSHIP OF CONFERENCE

The Conference is open to all interested. The enclosed (yellow) Registration Form and a remittance for fees and other charges should be sent to:

MRS L MURPHY (Solid State Conference)
H.H.Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL

THE CLOSING DATE FOR APPLICATIONS IS 20 NOVEMBER 1987. After this date there is no guarantee that applications will be accepted or that accommodation will be available.