Reference Copy

Daresbury Laboratory
INFORMATION QUARTERLY FOR COMPUTER SIMULATION OF CONDENSED PHASES

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

Number 45 May 1996

Contents

Editor: Dr. M. Leslie

CCLRC Daresbury Laboratory
Daresbury, Warrington WA4 4AD UK

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General News

FUTURE MEETINGS

A summary table is given below, further details may be found inside.

TOPIC	LOCATION	DATES	ORGANISER
CCP5 Annual Meeting CONDENSED MATTER SIMULATION: REALIZING THE POTENTIAL OF THE COMPUTER	Bristol	23-25 September 1996	CCP5
The 3rd International Conference on Computer Simulation of Radiation Effects in Solids	Surrey	22-26 July 1996	COSIRES'96
2nd European Cray MPP workshop	Edinburgh	25-26 July 1996	EPCC
Physics Computing '96	Krakow	17-21 September 1996	CYFRONET, Krakow and European Physical Society
Optical, electric and magnetic properties of molecules.	Cambridge	10-13 July 1997	
Solid State Chemistry: New Opportunities from Computer Simulations	University College, London	30 June - 2 July 1997	The Royal Society of Chemistry, Faraday Division

INTEL NEWS

CCP5 has an annual allocation of time on the Intel IPSC/860 at Daresbury. If any CCP5 member wishes to make use of some of this time please contact M. Leslie at Daresbury.

CCP5 FUNDS FOR COLLABORATIONS

CCP5 can make available funds of up to £200 per annum for groups of two or more UK researchers wishing to undertake a collaborative project within the scientific area covered by CCP5. The funds are intended to cover travel and subsistence costs. Researchers who wish to apply for funds are requested to submit a brief proposal (about 1/2 a page) describing the intended work to Dr. M. Leslie at the address below.

CCP5 VISITORS PROGRAM

CCP5 organizes a visitors program which funds the visit to the UK of overseas collaborators. We would normally expect a visitor to visit three sites in the UK and give a lecture at each site. These lectures would be open to all members of CCP5 as well as members of the host university. The visit would normally last between one or two weeks. CCP5 would pay for the cost of travel to the UK and within the UK between universities. CCP5 would expect some contribution towards accommodation expenses at the host university to be met by the university. We will also consider longer collaborations or visits just one place if this can be justified by the nature of the work to be done. If you have an overseas collaborator who you would like to invite under this program, please make a request to Dr. M. Leslie.

ELECTRONIC DISTRIBUTION OF CCP5 NEWSLETTERS AND WORLD WIDE WEB

All newsletters starting from issue 39 (October 1993) are now available on line, together with some articles from earlier newsletters. An index of recent newsletter articles can be found on the World Wide Web server: readers can access the individual articles by this means or by anonymous ftp. (Anonymous ftp will not access the index). The URL for the CCP5 home page is http://www.dl.ac.uk/CCP/CCP5/main.html

HOW TO GET THIS NEWSLETTER BY FTP

1.	move to the desired directory on YOUR machine	
2.	type:	ftp ftp.dl.ac.uk
	or	ftp 148.79.80.10
3.	enter userid:	anonymous
4.	enter passwd:	*enter your name and site*
5.	change to ccp5.newsletters/45 directory:	cd ccp5.newsletters/45
6.	change to postscript or latex subdirectory	cd ps
	or	cd latex
7.	to get the required files from the directory :	
	postscript from ps directory	get nl.ps
	compressed postscript from ps directory	get nl.ps.gz
	latex from latex directory	get nl.tex
8.		quit

Below is an index of the information held.

Readers may now **register** by filling in an on-line WWW form. Existing readers may also notify registration changes in this way.

In addition to notification of newsletters, we occasionally send other messages about meetings to the Email list. If you want us to send **notification of newsletters only**, let me know and I will place your Email address on a separate list. This will allow readers to restrict the amount of incoming Email if this will be a problem due to limited bandwidth or if readers are charged for incoming Email.

This newsletter is available by anonymous ftp either directly or by accessing the Daresbury World Wide Web server. The newsletter has been placed (in separate directories) both as postscript files and as the source latex files.

INFORMATION ON WWW SERVER
History of the project.
Organisation of the project.
Current research interests .
A library of computer software maintained by the project.
An index of future meetings and workshops which CCP5 is involved in organising or has been asked to
A list of proposed visitors sponsored by CCP5 with itinerary.
An index of articles from recent issues of the newsletter.
A copy of recently published newsletters commencing with Issue 39 (October 1993).
Registration and de-registration details.
Other related information on the Web.
Post-doctoral and lectureship vacancies
Doctoral studentship vacancies

Distribution of Information by Email

CCP5 will distribute by Email to the members on the mailing list (about 700 world wide) information which is of interest to our members. If you have information which you would like sent out in this way please send Email to M. Leslie. We also send out post-graduate, post-doctorate and lectureship positions notified to us. Normally post-graduate positions within the UK only are advertised in this way and the Email is restricted to UK members, however if the position is open to non-UK students then Email may be sent to the rest of Europe or the complete mailing list.

THE CCP5 PROGRAM LIBRARY

Copies of the newsletter no longer include a complete description of the program library. If readers wish to obtain a copy of the documentation it is available by anonymous ftp or through the World Wide Web page. The program library description is in ccp5.newsletters/library directory (postscript and ASCII text versions).

Version 1.5 and 1.6 of Shell-Dynamo are now available by anonymous ftp from hp2.kosmos.keele.ac.uk (160.5.15.131) in pub/dynamo/shell1.6.tar.Z. Alternatively you can obtain it via WWW using the first URL below.

Details of the release are appended

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URL (personal) http://www.keele.ac.uk/depts/ph/fincham/home.html

Changes from Version 1.4

There is an alternative representation for the short-range repulsive potential, of the form $(A/r)*exp(-r/\rho)$ instead of the usual $A*exp(-r/\rho)$. This gives greater anharmonicity. It can be used in conjunction with the breathing shell model. See command ERISINT. The breathing shell model can also have an anharmonicity parameter.

It is also now possible to use tabulated short-range interactions (commands TABINT and INTVAL)

A utility program tabulate can produce tabulated potentials of the general exp-6 form, but with some methods for fixing up the black hole at the origin.

The documentation now points out that the D/r^8 term in the potential is NOT implemented in the force routine.

There was a bug in the force routine which resulted in inaccurate forces at very large shell-core separations. This circumstance is unlikely to arise, but it has been corrected. To correct version 1.4 replace, in the file forces.f, the line

```
if (alphar.gt.0.01) then
```

by

```
if (alphar.gt.0.1) then
```

Other minor corrections include an error in the STATE AVBOX command, and in some instances an incorrect volume being set if UNITCELL was followed by FILLBOX.

See file "outline" for outline documentation

See file "commands" for command language details.

This program is copyright, (C) 1995 David Fincham. You are encouraged to make free use of it for academic purposes subject to the terms of the free academic licence in the file "licence".

REQUEST FOR CONTRIBUTIONS

Contributors to the current issue

Our thanks go to:

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The deadline for contributions for the next 2 newsletters will be **1 August 1996 and 1 November 1996** Readers are reminded that contributions are always welcome. Contributions may be sent by Email in LaTeX . WORD documents should preferably be sent in rtf format. We would be prepared to consider other formats on a trial basis.

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MEETING AND WORKSHOP ANNOUNCEMENTS

CONDENSED MATTER SIMULATION REALIZING THE POTENTIAL OF THE COMPUTER

Churchill Hall, University of Bristol
23–25 September 1996

The Annual Conference of CCP5† will take place at Churchill Hall, University of Bristol, from Monday 23 to Wednesday 25 September 1996. All areas of condensed matter simulation will be represented. The theme of the meeting will be the practical exploitation of the power of computer simulation in the fields of pure and applied research into condensed matter.

Many different approaches, from ab initio molecular dynamics to mesoscopic lattice models, are used to simulate condensed matter systems. In this rapidly-evolving field, cross-fertilization of ideas and techniques is vital. This conference provides an opportunity for experts within the UK simulation community to interact with each other, with representatives of UK industry, and with a number of visitors from overseas.

Invited speakers confirmed to date include:

- P. Cordero (Santiago, Chile)
- B. Dünweg (Mainz, Germany)
- M. Ferrario (Modena, Italy)
- J. Joannopoulos (MIT, USA)
- B. Smit (Shell, Amsterdam)
- M. Stoneham (UCL, UK)
- S. Toxvaerd (Copenhagen, Denmark)

The meeting will start at 9:00 a.m. on the morning of Monday 23 September (accommodation on the Sunday night will be provided) and will finish at lunchtime on Wednesday 25 September.

Registration information, and a general invitation to contribute talks and posters, will be made available shortly. For current information please see the CCP5 World Wide Web server:

http://www.dl.ac.uk/CCP/CCP5/main.html

† This conference is organized under the auspices of the Engineering and Physical Sciences Research Council Collaborative Computational Project # 5, on Condensed Matter Simulation.

The 3rd International Conference on Computer Simulation of Radiation Effects in Solids

University of Surrey, Guildford, UK
22-26 July 1996

Editors note - The details of this conference have already been distributed by Email: a summary is included here for the benefit of readers who receive paper copies of the newsletter.

Scope of the Conference

The International Conference on Computer Simulation of Radiation Effects in Solids (COSIRES'96) addresses the application of computer simulation methods to the study of the interaction of energetic particles with materials. It offers a forum for the presentation of the latest results and technique developments in this growing field of research. In recent years both the availability and power of computers has increased enormously, many developments have been made in producing more physically meaningful simulations of this subject. Topics will include:

Interatomic Potentials & Simulation Methods
Electronic Energy Loss
Electron-Phonon Coupling
Radiation Damage and Cascade Effects
Calculations of Implantation Phenomena
Energetic Cluster Impacts with Surfaces
Sputtering
Ion Beam Mixing
Low Energy Ion Beam-Surface Interaction
Plasma Processing of Materials
Electron and Laser Interaction with Solids
Comparisons of Models to Experiments
Simulation of Ion Beam Analysis Tools
Animation and Visualisation Techniques
Particle Surface Interactions
Radiation Effects in Biological Materials

For further information please contact

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http://www.ee.surrey.ac.uk/COSIRES

2nd European Cray MPP Workshop

A two-day workshop hosted by the Edinburgh Parallel Computing Centre and supported by the UK's High Performance Computing Initiative and Cray UK.
25-26 July 1996

Introduction

This meeting follows on from the very successful 1st European Cray T3D Workshop held by EPFL in Lausanne in September 1995. The workshop is intended for computational scientists and engineers working in applications development, systems administration or software support for Cray MPP systems (T3D's and T3E's) installed in Europe.

Talks and Posters

Anyone interested in making a presentation or poster on any of the following topics should indicate their Topic / Title on the registration form.

Applications in Science and Engineering
Cray MPP Systems Management
Programming Models
Performance Optimisation

Since time constraints limit the possible number of talks, we will have poster sessions in the conference foyer. The closing date for speaker registration is 17 May 1996: the programme will be circulated in late May.

Fees

There are no fees for attending the conference. Coffee and lunch will be provided, but all other expenses must be paid by the participants.

Details

The workshop will take place in the James Clerk Maxwell Building, The King's Buildings, Edinburgh, Scotland on 25-26 July 1996. The first session will start at 10:00, and the workshop will end by 17:00 on the second day.

The programme of talks will be selected by the Organising Committee. This is chaired by David Henty and comprises Stephen Booth, Caroline Neave and Alan Simpson from EPCC; Rob Allan from the Daresbury Laboratory; Zdenek Sekera from Cray Research Switzerland (CRAY-EPFL PATP project).

Further information on the background to this workshop is available.

Accommodation

Accommodation is extremely difficult to find in Edinburgh during the tourist season. We have pre-booked a number of rooms in convenient, low-cost accommodation at Pollock student halls of residence (the location is shown on the city centre map). The charge is 30 pounds per night for bed-and-breakfast and includes bus transport to the workshop. These rooms will be offered on a first-come first-served basis.

If you want to be sent an accommodation form, please indicate on the registration form. We think you will find it easier to use the accommodation we have arranged, and we urge you to register early as the number of rooms available is limited. However, if you prefer to make your own arrangements you can consult our accommodation list.

Travel

Edinburgh is easily accessible by air, rail and road. We have maps of the city and the King's Buildings campus.

Registration

Those wishing to speak and/or attend are invited to fill in the registration form. The deadline is 17 May if you want to give a presentation, 31 May otherwise. If you experience any problems registering, please email workshop@epcc.ed.ac.uk.

PHYSICS COMPUTING'96

Krakow, Poland
17-21 September 1996

Editors note - The details of this conference have already been distributed by Email: a summary is included here for the benefit of readers who receive paper copies of the newsletter. Full information about this meeting may be found at URL http://www.cyf-kr.edu.pl/pc96

Organizing institutions

The Conference is organized jointly by:

Academic Computer Centre CYFRONET - KRAKOW, Krakow, Poland
Interdisciplinary Group on Computational Physics of the European Physical Society
under the auspices of the European and the American Physical Societies.

Important dates

10 May 1996	deadline for receipt of contributed papers
31 May 1996	notification of acceptance of papers
15 June 1996	deadline for registration with reduced fee
17 September 1996	PC'96 Conference

Scientific Program

PC'96 Conference will be a forum for physicists throughout the world for whom the COMPUTER is the MAIN TOOL of RESEARCH. We hope that Conference will enable them to exchange ideas and research results relating to the fast-growing field of computational physics and to share experience with the most advanced developments in computer hardware and software. The scientific program of the conference will consist of invited lectures, contributed oral presentations, classical and virtual poster sessions, tutorials and vendor presentations.

Main topics of the meeting

Main topics of the meeting will cover:

various fields of computational physics, such as

- computer simulation in statistical physics
- simulation of specific materials
- surface phenomena
- percolation
- critical phenomena
- computational fluid dynamics
- classical and quantum molecular dynamics
- chaos dynamical systems
- self-organization and growth
- neural networks and their applications
- complex optimization

as well as contemporary trends in hardware and software development:

- recent developments in computer architectures
- modern programming techniques (parallel programming, object oriented approach)
- symbolic computations
- graphics, visualization and animation

together with industrial applications and teaching of computational physics.

Invited lectures

This is a partial list of those of most interest to CCP5, for a complete list refer to the URL given above.

Kurt Binder	University Mainz, Germany	Large scale Monte Carlo simulations: a powerful tool for material science?
Janos Kertesz	Technical University of Budapest, Hungary	Computer simulation of surface growth
Peter Lomdahl	Los Alamos National Laboratory, USA	Large scale molecular dynamics on MPPs
Mike Payne	Cavendish Lab., Cambridge, UK	Ab initio total energy pseudopotential calculations
Dennis C. Rapaport	Bar-Ilan University, Ramat-Gan, Israel	The art of molecular dynamics simulation

Up-to-date list of invited lectures is on the PC'96 www pages.

PC'96 www pages also has information on

Registration Fees Tutorials
Time schedule of PC'96
Papers Submission
Social program
Accommodation
Payment

Further Information

For more information about PC'96 contact:

http://www.cyf-kr.edu.pl/pc96	Marian Bubak
ftp: //ftp.cyf-kr.edu.pl/pc96	Physics Computing 96
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Optical, electric and Magnetic Properties of Molecules

Cambridge University, UK
10-13 July 1997.

Editors note - The details of this conference have already been distributed by Email; a summary is included here for the benefit of readers who receive paper copies of the newsletter.

This conference is being organised to celebrate the career of Professor A. David Buckingham.

Those interested in being placed on the mailing list should contact

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The Royal Society of Chemistry
FARADAY DIVISION

Divisione di Chimica Fisica, Societa' Chimica Italiana
Deutsche Bunsen Gesellschaft für Physikalische Chemie
Société Française de Chimie, Division de Chimie Physique

Faraday Discussion No: 106
Solid State Chemistry: New Opportunities
from Computer Simulations

University College, London
30 June - 2 July 1997

ORGANISING COMMITTEE:

Professor C R A Catlow	AND	Dr W C Mackrodt (Co-Chairman)
Dr N L Allan		Professor P W Fowler
Dr S L Price		Dr P A Madden

Over the past decade or so, one of the major developments in chemistry has been the increasingly important role played by high performance computing. Nowhere is this more evident than in solid state chemistry, where computer simulations are now a major source of understanding and interpretation and the generator of data which is either difficult or impossible to obtain by other means. The Discussion will highlight recent developments with a view to assessing likely directions for the future.

The meeting will embrace:

ab initio electronic structure methods
lattice statics and dynamics
molecular dynamics
Monte Carlo simulations

Systems for discussion will range in complexity from simple solids to high Tc superconductors, catalysts, microporous materials, molecular solids, glasses and fullerenes including surface properties and reactivity.

Contributions are invited for consideration by the Organising Committee. Titles and abstracts of about 300 words should be submitted no later than FRIDAY 26 JULY 1996 to Dr W C Mackrodt, School of Chemistry, University of St Andrews, Fife KY16 9ST.

Full papers for publication in the Faraday General Discussion 106 volume will be required by February 1997.

Updated conference information may be found on WWW at this URL: http://chemistry.rsc.org/rsc/farad106.htm

Chemical Database Service

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May 1996

The Chemical Database Service

Daresbury Laboratory provides a Chemical Database Service to the UK academic community. The aim of the service is to ensure that the growing body of information from chemistry research is conveniently accessible to the UK academic community in ways which foster the essential UK core competency in Chemistry. This is done by providing on-line access via Internet to a range of databases in the areas of crystallography, synthetic organic chemistry, spectroscopy and physical chemistry - see below. Three chemists provide help, support and advice to users of the service.

Components Presently Available

CSD The Cambridge Structural Databank. Crystal structure data for over 152,000 organic and organo-metallic compounds. Two releases of this databank are received and mounted annually (April and October). QUEST has 3D search capabilities.

ICSD Inorganic Crystal Structure Data File. Over 40,000 inorganic structures - the companion file to the Cambridge organic file (though in a different format).

MDF Metals Data File. Crystal structure data for over 55,800 metals and alloys.

PDB The Brookhaven Protein Data Bank containing bibliographic and coordinate details for over 4,400 proteins and other biological macromolecules.

CDIF Crystal Data Identification file. Crystal class and unit cell data for over 210,400 crystal structures.

FNMR A databank of about 6,000 19F NMR spectra and coupling constants.

ELYS Electrolyte Solutions Database. Thermodynamic and transport property data such as density, viscosity, diffusion coefficients etc. Currently contains about 10,000 entries.

ISIS/REACCS Chemical reaction information management systems allowing search, retrieval and display of molecules, reactions and their associated data. ISIS is a client/server system and is the replacement for REACCS. Currently ISIS can access over 605,000 searchable reactions and REACCS 240,000, from the following databases:

THEILHEIMER (Synthetic Methods of Organic Chemistry)

CHC mprehensive Heterocyclic Chemistry)

CLF (the Current Literature File)

CHIRAS (Asymmetric Synthesis)

METALYSIS (Transition metal-mediated transformation)

REACCS-JSM (Journal of Synthetic Methods)

CHEMINFORM (current awareness) only available via ISIS

CSM (Current Synthetic Methodology) a subset of CHEMINFORM, only available via REACCS

ORGSYN (Organic Synthesis) only available via ISIS

ORAC CORE (Established Literature) only available via ISIS

SPG (Protecting Groups) only available via REACCS

ISIS also allow access to ACDRX (Available Chemicals Directory), which is a database of suppliers of chemicals. It contains over 180,000 different compounds.

SPEC SpecInfo is a multi-technique spectroscopic database system which will cover NMR, IR and mass spectra. The package is designed to aid the chemist in spectral interpretation and structure elucidation problems. It contains spectral data sets with their associated structure connection tables. The database currently contains 72,000 13C, 15N, 17O, 19F and 31P NMR spectra and 20,000 infra-red spectra.

A variety of utility programs are also available, including chemical file format conversion, molecule viewers, gopher and World-Wide-Web browsers.

For further information contact:

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Email: cdsbb@dl.ac.uk

Report of the visit of Ronald Cohen to the UK

Ronald Cohen
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November 16, 1995

Thanks to partial support from CCP5 I was able to visit University College London, University of Cambridge, and Oxford University to present a series of seminars, exchange ideas, and form the basis for future collaborations.

I first attended the workshop "Developments in Mineral Physics–Collective Phenomena", a workshop in honor of Professor Desmond McConnell at Darwin College. Here is a brief summary of that meeting.

Professor McConnell (Oxford) first summarized several years of work on the nature of H and H_2O in quartz (SiO_2). It is well known experimentally that H_2O greatly weakens (lowers the shear strength of) quartz, and that H_2O greatly enhances diffusivity of O (measured via isotope experiments), but the microscopic reason was not previously understood. First principles calculations with Professor V. Heine and others showed that the hydrolytic weakening can be quantitatively understood in terms of depolymerization of the quartz structure by the formation of H_4 defects that aggregate together to form H_2O islands when a crystal is strained. These islands also become weak points for failure. The effect of H_2O on isotope exchange rates can be understood by the diffusion of H_2O into the channels in quartz, followed by exchange between the O in the channel water and the bulk. Large scale computations for supercells within the LDA and plane wave pseudopotentials gave good estimates of the relative energetics of different H and H_2O defects compared with calorimetry and T-dependent experiments.

Dr. Ross Angel (Bayreuth) gave a summary of recent work on isosymmetry phase transitions, especially recent work he has done on pyroxenes and feldspars. Within the resolution of the experiments, behavior is observed that is similar to that seen in displacive phase transitions, which usually involve changes in symmetry. Over a limited range of T or P, structural parameters vary rapidly, and very often P-T boundary bend sharply in the vicinity of one of these transitions. The phases are often structurally distinct, in spite of having the same space group symmetry. In the pyroxene example, one C2/c "phase" has kinked chains, whereas the other has straight chains. Other examples were discussed, including KTP, Ce, and H_2O.

Professor Volker Heine (Cambridge) gave an overview of a number of current research projects. M.H. Lee is working on γ–Al_2O_3, which is an fcc structure with disordered occupancies of T and O sites. They found that empirical potentials gave the wrong energy differences between the T and O sites, so LDA pseudopotential calculations are being performed. M. Gambhir is working on short range order in cristobalite. A. Pryde is studying diffuse scattering in low-tridymite from Rigid Unit Modes (RUM's). K. Hammonds is studying floppy modes in zeolites. R. Shav is using first-principles methods to study the reaction methanol $+ H^+ \rightarrow CH_3^+ + H_2O$, where the reaction is catalyzed by a zeolite, chabazite, which also provides the H^+. They are finding that a floppy mode is important to bring the H^+'s to the CH_3OH. Collaborations with Dr. M. Dove (Cambridge) involve studying Si-Al ordering using different order-disorder models.

In collaborative work in Professor Salje (Cambridge) Professor Heine also discussed the origin of tweed textures and how almost any non-equilibrium perturbation can cause tweed to set in when there are long-range elastic forces.

Professor Salje continued the discussed of tweed textures and discussed how new rocking geometry diffractometers at Cambridge are being used to map out the diffuse scattering due to twins, tweed, etc., and are being used to quantitatively describe the behavior.

Dr. R. Cohen (myself) gave an overview of research at the the Geophysical Laboratory (GL) using three different approaches 1) all-electron, full-potential LAPW (Linearized Augmented Plane Wave) computations within the LDA and GGA, 2) much faster Gordon-Kim like models, such as the VIB (Variationally Induced Breathing) model for ionic solids such as MgO, and 3) a new tight-binding total energy model which has accuracy rivalling that of the FLAPW when the model is used within the sphere of its parameterization, but which is many hundreds of times faster. Examples were given of studies using the different methods, and collaborative work with experimentalists at the Geophysical Lab were discussed. LAPW calculations on SiO_2 stishovite predicted a phase transition to the orthorhombic $CaCl_2$ structure at 45 GPa. High pressure Raman experiments at GL that showed the B_{1g} mode stopped softening at 50 GPa and begins to harden, in excellent agreement with predictions. LAPW calculations on FeO explain the origin of the observed rhombohedral strain and predict a loss of local magnetic moments with increasing pressure. The advantage of the VIB model is that long MD trajectories can be studied without sacrificing accuracy, at least for MgO. Recent equation of state studies (Inbar and Cohen) were discussed that show excellent agreement with the thermal equation of state. Melting of MgO was studied using both clusters (Cohen and Gong) and periodic boundary conditions (Cohen and Kluge) and obtain similar results, in disagreement with recent experiments (Zerr and Bohler) but consistent with systematics of alkaline earth oxides. Thermal conductivity simulations were mentioned. A new tight-binding total energy model (TBTE) was briefly discussed, and results were shown for Fe and Xe. The model accurately predicts properties over wide ranges of compression (within the bounds of the fit) and is being used for finite T simulations. The parameters are fit to LAPW total energies and band structures.

Dr. P. Ballone (MPI Stuttgart) discussed plane-wave pseudopotential simulations for three geophysically important polymorphs of Mg_2SiO_4, olivine (Pbnm, 28 atoms/primitive cell), β-spinel (Imma, 56 atoms/cell), and spinel (Fd3m, 14 atoms/cell) performing relaxations and studying the equations of state and phase transitions. Results are quite accurate. The olivine spinel transition is given at 12 GPa compared with 10 experimentally. He also discussed H in Fe_2SiO_4 (fayalite) and liquid fayalite which is an antiferromagnetic liquid. First-principles simulations were performed for 0.15 psec at 1800 K for 112 atoms. The difficulty of doing long trajectories with first-principles (i.e. self-consistent) methods was pointed out.

Dr. W. Schranz (Vienna) discussed recent progress on the central peak problem. He showed new results on homogeneous and inhomogeneous elastic measurements. He discussed different origins of central peak phenomenon, but concentrated on entropy fluctuations (heat waves) near phase transitions and gave a series of models to explain the observations. Extensive discussions were given of elastic and dielectric behavior near phase transitions, and gave an understanding of strong dispersion in elasticity observed around ferroelastic phase transitions.

Dr. D. Sherman (Bristol) discussed Hartree-Fock periodic CRYSTAL calculations of H_2O in diaspore, boehmite (α-AlOOH, γ-AlOOH) and brucite ($Mg(OH)_2$). He obtained deep potential wells for the H's, and claimed that tunneling is important even though the wells were 1 eV deep. He studied the equation of state of brucite and says that quantum delocalization sets in at high pressures. His conclusion was that there isn't much water in the Earth.

After the meeting, I traveled to University College London and presented a departmental seminar on similar topics to the above, but with the addition of recent work on the Earth's core. A combination of LAPW and TBTE calculations have been used to study the thermal equation of state and elasticity of Fe under core pressures. This work has been done in collaboration with Lars Stixrude and Evgeny Wasserman at the Ga. Inst. Technology. We find excellent agreement with seismological and free oscillation observations of anisotropy in the Earth's inner core if the inner core contains a huge single hcp crystal oriented approximately with the c-axis along the Earth's rotation axis.

At UCL I had extensive discussions with Professor D. Price and members of the department, including Drs. L. Vocadlo, J. Brodholt, N. Ross, and A. Patel. A. Patel et al. performed simulations of the thermal equation of state of $MgSiO_3$ perovskite. Vocadlo and Price have studied melting of MgO at high pressures using the THB2, Matsui, and Lewis and Catlow empirical potentials, and their results are almost identical to those we obtained recently (Cohen and Kluge) using the VIB model. We also discussed the melting of perovskite. We plan to form an active collaboration, and Dr. Vocadlo will visit GL for collaborative work. Discussions with Drs. J. Brodholt and N. Ross centered on the reported "kinks" (Chopela and others) in Raman frequencies versus pressure in olivine and perovskite.

On October 26 I presented a seminar for the TCM group at Cavendish on first-principles studies of ferroelectrics, and discussed work done at GL on bulk and slab $BaTiO_3$, $PbTiO_3$, $LiNbO_3$, and $LiNbO_3$. The goal is to understand the origin of ferroelectric behavior, the reasons for different behavior in similar materials, and the differences between the perovskite and $LiNbO_3$ families. I had extensive discussions with Dr. C. Molteni about first-principles simulations of grain boundary sliding and with N. Marzari on linear response computations for solid solutions, as well as with others.

On October 27 I gave a seminar for the Materials Department at Oxford on the new TBTE model and discussed applications to high pressure research. I visited the Modeling Laboratory and had extensive discussions with Dr. A. Bratkovsky on bond-order potentials and order N methods as well as with others.

On October 30 I gave a seminar at the Earth Science Department at Oxford primarily on on Fe in the Earth's core, and discussed in more detail the computations on Fe, the evidence that the inner core is largely a single crystal, and an overview of the geophysics of the core. I had extensive discussion with Dr. A. Jephcoat, and we have started two exciting collaborative theory and experimental projects on AlH_3 and $LiNbO_3$ at high pressures. I also had discussions with Prof. D. McConnell on effects of water on feldspar order-disorder, and extensive talks with Dr. K. Refson on LDA plane-wave pseudopotential methods and comparison with all-electron results and Hartree-Fock, which will probably lead to collaborative research and joint code development.

All in all it was a very fruitful scientific trip, and it is great that CCP5 can help bring such exchanges about. I should acknowledge my collaborators: B. Burton, Z. Gong, I. Inbar, D. Isaak, M. Kluge, I. Mazin, F. Marton, L. Stixrude, and E. Wasserman. I also thank the National Science Foundation, the Office of Naval Research, and the Carnegie Institution of Washington for supporting my research.

Report of Visit to UK by Professor Stefan Estreicher (Texas Tech University)

19-25 March 1996

Visit to London by Professor Stefan Estreicher

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In the London part of his trip, Professor Estreicher visited the Condensed Matter and Materials Physics group at University College London. He gave a talk on "Passivation processes in silicon" on 25 March, which was attended by an audience of about thirty people. The audience was drawn from the group at University College, from the Physics Department at King's College, from the Semiconductor IRC at Imperial College, and from the Rutherford Appleton Laboratory.

There was a lively discussion at the seminar and over the lunch following, which focussed (among other things) on

1. The role of basis-set superposition error in electronic structure calculations of defects;
2. The importance of zero-point energy in the free energies of defects involving light interstitials (particularly hydrogen);
3. The possible identity of rapidly-diffusing passivating species which are implied by recent developments in solar cell technology;
4. The candidate structures for various defect-hydrogen complexes, and their possible uses in passivation.

Visit to Edinburgh by Professor Stefan Estreicher

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Prof Eistreicher spent two days with us in Edinburgh, speaking with all members of the Condensed Matter Group involved with solid state simulation. We had very helpful discussions regarding the mechanism for neutral self-interstitial diffusion in silicon, a topic of mutual interest, and he had some interesting observations to make regarding our discovery of threefold rings of carbon atoms in amorphous carbon, in particular on the possibility that they might be remnants of C_3 clusters (stable as equilateral triangles) from the high temperature starting phase. His talk, on work carried out some time ago regarding diffusion in silicon, but excluding his very recent discoveries of hydrogen enhanced diffusion of oxygen, was delivered to a small audience of about 20.

Although, in the event, I was unable to arrange the good weather I had promised, Prof. Eistreicher also enjoyed a few days of being a tourist in Edinburgh. We also invited Stefan to a group meal which was well enjoyed by all, even the haggis pizza. The whole group found Prof Eistreicher's work of interest and him very approachable. In all it was a very successful visit, both scientifically and socially, and I should like to thank CCP5 for making it possible.

Report on CCP5-sponsored visit to UK of Professor Martin Schoen (TUB Berlin)

Professor Schoen visited the Department of Chemistry, University of Manchester, where his host was Dr. Andrew Masters; the Department of Chemistry, Imperial College London, hosted by Professor Dominic Tildesley; and the Department of Physics, University of Bristol, where his host was Dr. Mike Allen.

Martin arrived at Manchester from Berlin via Frankfurt on the morning of Tuesday 7 May. The journey was slightly jeopardized by the recent fire at Dusseldorf, which had made the originally scheduled route impossible; the revised connection at Frankfurt turned out to be very tight.

Martin mainly talked with Andrew Masters, his post-doc., Lena Akhmaskaya, and Julian Clarke from UMIST, with whom he shares many common simulation interests. He gave a seminar entitled *Phase transitions in confined films. Computer simulations and theoretical results* which covered shear-induced melting of confined solids, the microscopic structure of a near-critical fluid in a pore and some beautiful work on layering transitions in confined geometries. On Wednesday, Martin departed by train for London.

Martin arrived in London at about 5.30 p.m. on 8th May. We were able to find him accommodation in one of the Imperial College Guest rooms in Prince Consort Road just opposite the college. Ian Gould and David Nicholson took Martin to dinner at the Brasserie St Quentin in Knightsbridge, ensuing an auspicious start to his visit

We worked hard on the Thursday. Martin spent the first hour with Dominic Tildesley. They discussed Dominic's recent work on the calculation of the non-linear susceptibility and modelling of the second harmonic generation at the air/water interface and studies of flexible molecules dissolved in the Gay Berne fluid. Martin described his recent work on diffusion in confined monolayer films and a Taylor series Monte Carlo simulation method, which is reminiscent of the multiple time-step methods in molecular dynamics.

After coffee, Martin spent time with David Nicholson. David discussed his recent work on grand canonical simulations of mixtures in pores, his molecular dynamics studies of self-diffusion in slit geometries and new intermolecular potentials for zeolites. We introduced Martin to Dr Julian Gale, our Royal Society Research Fellow. Julian described his work based on the first density functional calculations of molecular adsorption on zeolite fragments. Recently this area has been extended to the use of plane-wave methods to study the binding of adsorbates in a periodic representation of a micro porous material.

We went to the Imperial College staff canteen for lunch and to take our mind off the food, we discussed the changes in Berlin since reunification. It is always a great pleasure to swap stories on the government's unusual approach to managing academic affairs. The chaos stretches across Europe.

In the afternoon Martin had an opportunity to meet the post-doc's and graduate students. He had an interesting session with Vladimir Sokhan discussing the adsorption of phenol at a water liquid/vapour interface and with Patrick Harvey on the penetration of oil into surfactant layers. Martin was full of ideas and questions and I think this session was enjoyed by all. We remembered to give him some time to think about his own talk and we had arranged tea for 4.00 pm in the old part of the Chemistry Building, which houses some magnificent Victorian lecture theatres.

We enjoyed an excellent seminar. Martin's observations on the significant changes in the lateral liquid structure of a fluid during pore filling gave rise to a large number of questions about the order and nature of the underlying phase transition. The seminar was much appreciated by a small but well-informed audience.

After a vote of thanks, we gave Martin a short seminar on the vagaries of the London Underground and delivered him with clear instructions for Paddington by way of South Kensington.

Martin arrived in Bristol shortly after 9 p.m., and had dinner with Mike Allen at Browns Restaurant, recently converted from the University Student Refectory into a place that serves decent food. An early start the next day saw Martin in detailed discussions with Mike and his students. Philip Camp described recent simulations of biaxial nematic ordering in rod-plate mixtures, and the mapping out of the isotropic-nematic coexistence line for uniaxial hard ellipsoids by Gibbs-Duhem integration. This work is directly connected with testing recent improvements to the classical Onsager theory. Julian Brown outlined work carried out in collaboration with the group in Seville, investigating the effect on the phase diagram of systematically varying parameters in the Gay-Berne model. Martin has recently begin work on the effects of confinement and simple models of molecule-surface interaction on this type of model, and there seems to be some scope for collaboration and exchange of information in the future. Mike Allen also described recent determinations of the Frank elastic constants for this system by his student Mark Warren. Martin spent some time discussing a range of simulations with Jeroen van Duijneveldt, a Ramsay Research Fellow in the group.

With Bob Evans, Martin discussed theoretical aspects of the effects of confinement on phase transitions, some of the related experimental work going on in the laboratory in the group of Ashraf Alam, and the effect of the long-range form of the pair potential on the asymptotic form of pair correlation functions and density profiles. With Bob, Mike Allen and Hector Dominguez, he discussed some simulation work of Hector's on the effect of confinement on the freezing transition, which involves some quite delicate free energy calculations.

The seminar was quite well attended, provoked much discussion, and was appreciated by all. Afterwards, Martin had the chance to talk to Margarita Rivera, a graduate student in the polymer group, who has performed a range of experiments on complex molecules adsorbed on surfaces using STM/AFM apparatus.

On Saturday, some time was devoted to tourism. Mike and Martin started by giving moral support to Philip Camp, who was playing in a two-day croquet tournament (more hard-particle dynamics). Then a guided tour of Bristol, part on foot, part by boat, followed. After lunch, Mike went home to watch the FA Cup Final on television, while Martin slept back at the University accommodation; it is debatable who had the more interesting time. A final dinner at the local Balti restaurant brought the visit to an end. Martin departed very early next morning for Heathrow by coach.

All those involved thought the visit worthwhile. Our thanks go to Martin Schoen for undertaking such a tour, talking to so many people, and being so interested in everything he encountered. CCP5 would like to thank the institutions who cooperated in this venture.

Book Review

The Art of Molecular Dynamics Simulation
by D. C. Rapaport
Cambridge University Press, 1995, £45 (hardback)
ISBN 0 521 44561 2

The author describes this as an introductory text, a recipe book, and a reference manual. The title recognises that simulation, like cooking, is as much an art as a science.

The approach is, within each chapter, to develop theory and methodology together, usually followed by examples and exercises. Algorithms are described using program listings which are integrated into the text, and it is this feature in particular which gives the book its practical flavour which will be much appreciated by beginners.

After an introductory first chapter the author devotes four chapters to developing the fundamental methods used to study simple fluids. Topics discussed are force evaluation, including neighbour list and cell search methods; leapfrog and predictor-corrector integration schemes; measurement of thermodynamic and structural properties (including Voronoi polyhedra); transport coefficients; and dynamic structure factors. There are then chapters on constant temperature and constant pressure methods, and on non-equilibrium methods, before the author turns to molecular systems. Rigid molecule dynamics is described using a quaternion representation with a predictor-corrector algorithm; flexible molecules are also discussed, including the use of angle and torsion forces and the application of bond-length constraints. The next chapters cover the Ewald sum (applied to dipolar systems); three-body forces; and hard-sphere simulations. Finally there are two chapters which reflect particular research interests of the author: on the atomistic approach to fluid dynamics; and on algorithms for parallel and vector supercomputers.

The treatment is thorough and the style readable. A student who works through this book will gain an excellent grounding in molecular dynamics simulation. As a reference manual it is perhaps less successful, since its very thoroughness necessarily leads to omissions. Some of my favourite algorithms are missing (leapfrog rotational algorithms, loose coupling thermostat and pressurestat) and a weakness is the lack of consideration given to ionic materials.

An aspect of the book that will be controversial is the choice of the C language for the program listings. The author has avoided the use of C features that are not found in Fortran 77 but some will feel that he thereby ends up with the worst of both worlds. To keep the listings short he makes liberal use of global variables (which are listed in an appendix): a bad habit to encourage.

The book invites comparison with those by Allen and Tildesley (ISBN 0 19 855375 7) and Haile (ISBN 0 471 81966 2). Allen and Tildesley cover much more ground, with a deeper theoretical basis, more algorithms (including Monte Carlo) and more physical examples, but are less good on implementation details. Haile covers a few methods at a deep, almost philosophical, level but fails to get beyond the soft-sphere model, and relegates programming considerations to an appendix. Allen and Tildesley remains a very useful reference, Haile can be read with profit by beginners and experts alike, but Rapaport has provided the best introductory text.

David Fincham

Advanced Computer Simulation of Materials

The CCP5 Annual Meeting 1995,
sponsored by Biosym/Molecular Simulations.
Daresbury Laboratory,
Warrington WA4 4AD, UK.
20th–22nd September 1995

Introduction

M. J. Gillan
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The computer simulation of materials has been going through tremendously exciting changes recently. Two kinds of things are happening. More complex problems are being tackled than was the case a few years ago. But also, completely new kinds of problem are being addressed. The ability to simulate complex real-life problems is certainly due in part to improvements in computer power. Here, both the availability of local distributed hardware and the provision of leading-edge high-performance facilities are playing a major role. The installation of the Cray T3D at Edinburgh in 1994 has been crucial for the vitality of computational science in the U.K. But just as important as bigger computers has been the discovery of new techniques. I am thinking here particularly of the Car-Parrinello method of ab-initio simulation, which has so much expanded the range of problems that can be addressed.

The CCP5 Annual Meeting 1995 provides plenty of illustrations of both kinds of advance – both the importance of improved computer power and the increasing role of ab initio simulation. Indeed, some of the presentations combine the two themes, by reporting ab initio materials simulations performed on the Cray T3D or other high-performance machines. It is a well-worn cliché to talk about a conference giving a 'snap-shot' of the field. But in this case the phrase seems entirely appropriate. The following set of abstracts from the meeting gives a glimpse of what was happening in the advanced computer simulation of materials in late 1995. CCP5 can be proud to be participating in the exciting advances now going on.

Lecture abstracts

Bond Order Potentials: can they bridge the electron-atomistic length-scale gap?

D. G. Pettifor
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First principles linear scaling technique: the density matrix approach

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An algorithm for first-principles electronic structure calculations having a computational cost which scales linearly with system size is described. The method exploits the real-space localization of the density matrix, and is related to the technique of Li, Nunes and Vanderbilt. The density matrix is expressed in terms of localized *support* functions, and a matrix of variational parameters $L_{\alpha\beta}$ having finite spatial range. The total energy is minimized with respect to both the support

functions and the $L_{\alpha\beta}$ parameters. The method is variational, and becomes exact as the ranges of the support functions and L matrix are increased. The method has been tested on silicon systems containing up to 512 atoms. Some results will be presented, and future developments are outlined.

Monte Carlo simulation of electronic transport in advanced technology semiconductor devices

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Recent developments in semiconductor processing technology have enabled the fabrication of a range of complex device structures. Devices such as the High Electron Mobility Transistor (HEMT) consist of multiple layers of different semiconductor alloys, with minimum layer thicknesses of the order of 10^{-9}m. The active region of such devices has been continually reduced in size, in the quest for high operating speeds and frequencies. State-of-art field effect transistors (FETs) have been fabricated, on both silicon and gallium arsenide substrates, with gate lengths less than 100nm.

An accurate description of such devices requires the development of detailed microscopic models. The most successful approach to date involves the use of a Monte Carlo technique to simulate typical trajectories for an ensemble of electrons within the device. The energy and angle dependences of the electron scattering probabilities are calculated from time-dependent perturbation theory, and scattering events are selected stochastically during the simulation. Scattering by impurities (dopants) and all relevant phonon modes are considered. Consequently, the simulation represents an exact solution of the semi-classical Boltzmann transport equation for the device. The internal electric fields are self-consistently obtained by solving the Poisson equation (usually in two dimensions) on a frequent timestep. The energy band spectrum of the constituent semiconductor(s) can be represented to any desired precision. Usually, a many-valley effective mass scheme is sufficient, but, where high energy phenomena are to be studied, a complete energy band spectrum can be obtained from a pseudopotential calculation.

The purpose of this paper is to explain the key elements of the simulation method, to describe the current state-of-art in this field, and to show results from some of the recent work at Leeds on simulations of ultra-short gate multilayer FETs.

Ab-initio calculation of stacking fault energetics in silicate perovskite

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[2] TCM Group, University of Cambridge

Extended defects, namely dislocations and stacking faults are a common mechanism for creep in ceramic materials. (Magnesium) silicate perovskite is the major constituent of the Earth's mantle and its creep behaviour at high P and T controls the rheology of convective flow and consequently the motion of tectonic plates on the Earth's surface. Experiments are not practical at mantle pressure and temperature, but computer simulations using quantum mechanical methods based on density-functional theory can provide precise and reliable results irrespective of the extreme conditions.

Dislocations in analogous perovskites such as $CaGeO_3$ dissociate into partials separated by a [110] stacking fault, whose energy and activation energy of formation are an important constraint on the creep process. We have calculated the energetics of the [110] stacking fault in $CaSiO_3$ perovskite including a complete gamma-surface for the [110] shear. At 0GPa and 50GPa the stacking-fault energies are 1.1 and 1.77 J/m^2 respectively and the activation energies for the shear are 1.84 and 3.43 J/m^2.

Investigation of the Si(001) missing dimer defect structure

D. R. Bowler. C. M. Goringe and J. H. G. Owen.
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At low imaging voltage in STM pictures, single dimer vacancies are highlighted by a bright feature on neighbouring dimers. This contrast disappears at higher imaging voltages. For a number of proposed structures of the single dimer vacancy, *ab-initio* calculations of charge density as a function of energy have been used to simulate STM images. These images show a marked bias voltage dependence, and the low bias voltage images differ markedly between the structures modelled. On this basis, the rebonded structure is identified with the highlighted defects.

Energetic Particle Impacts with Graphite

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This paper will examine the effects of single particle and cluster (C60) impacts with a graphite surface at energies up to keV, by using classical Molecular Dynamics simulations and many-body potentials. It will be shown how single particle impacts can be responsible for bump formation on the graphite surface. These will be compared to experimental observations in the STM. Cluster impacts on the other hand produce waves on the graphite surface which are hexagonal in nature and little sputtering of material occurs at energies up to about 1 keV. The damage to the lattice as a result of these energetic impacts will be examined. Computer-generated simulation videos which illustrate the formation of the bumps and the waves will be shown.

Ab initio molecular dynamics calculations to study catalysis

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Density functional theory (dft) with the local density approximation (lda) was the basis of many solid state calculations, where a lot of experience has been gained. The modern versions of dft especially those using the generalized gradient approximation (gga), have reached (almost) chemical accuracy and thus such dft calculations can be applied to problems of real chemical interest, such as catalysis. The basic concepts for solving such problems are as follows, as a first step one must evaluate the dft and check and improve its form (lda, gga, etc) on small ideal systems of both, solids and molecules.

The ab initio molecular dynamics (md) method was initiated by Car and Parrinello, who started with a lagrangian combining the nuclear and the electronic degrees of freedom, where the forces acting on the atoms are determined within dft but the atomic motion is treated classically. The corresponding equations of motions are solved simultaneously for both, the atoms and the electronic wave functions, using a verlet algorithm. A very efficient implementation of this scheme is the projector augmented wave (paw) method developed

Enantioselective dehydration of butan-2-ol using modified zeolites

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The proton form of zeolite Y was modified with *R*-1,3-dithiane-1-oxide at a loading of one molecule per supercage to create a chiral acid catalyst. The enantiomeric discrimination of this catalyst was demonstrated using the dehydration of the separate enantiomers of butan-2-ol and over the temperature range investigated the *S*-enantiomer was always more reactive. This catalyst system was then studied using computational simulation methods. Molecular dynamics was used to investigate the thermal stability of the modifier molecule in the zeolite. In order to reproduce the experimentally observed thermal stability it was found that the dithiane oxide is probably present as a cationic species. With this model of the active catalyst the butan-2-ol enantiomers were then docked into the structure using a combination of Monte Carlo and energy minimisation techniques. The lowest energy structures for each of the enantiomers of butan-2-ol thus produced had binding energies of 64.7 $\mathrm{kJmol^{-1}}$ and 48.3 $\mathrm{kJmol^{-1}}$ for the *S*-enantiomer and *R*-enantiomer respectively. This difference in the adsorption of the two enantiomers is considered to be the origin of the enhanced reactivity of the *S*-enantiomer.

The transport of methane through shales

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Natural gas and oil are generated by the geochemical breakdown of dead organisms entombed within compacted sediments, known as source rocks. Unfortunately, it is seldom possible to extract todays commercial hydrocarbons directly from their source sediments. Instead, petroleum geologists must search for pools of oil and gas that have migrated out of low permeability source rocks, and then become trapped within a high permeability reservoir. A detailed knowledge of the diffusion of hydrocarbons through both source and trap rocks is therefore fundamental to petroleum exploration. Molecular dynamics computer modelling can now provide these diffusion data, and establish the microscopic mechanisms involved in hydrocarbon transport. As a first step we have calculated the mobility of methane within the most common group of source and trap rocks, namely clay-rich shales. Data are presented as a function of shale porosity, for burial depths of up to 6km. They show that molecular diffusion within nanometer scale pores is a dominant mechanism for the migration of methane through compacted shales.

Recent Modelling Studies of Molecular Ionic Materials

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K. J. Roberts
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Molecular ionic materials present challenges to computer modellers in that their cohesion involves both ionic and covalent interactions, both of which must be accounted for in any potential developed.

The talk will show how a consistent potential model has been used for a range of such materials, with parameters obtained by empirical fitting. The materials studied include carbonates, phosphates, perchlorates and chlorates, where in each case, potentials have been fitted to structural data, and tested by transfer to other materials in the same family. As well as calculating bulk crystal properties, morphologies have been calculated, using both attachment and surface energy approaches. Comparison is made with experimental data, where available.

Finally preliminary results will be presented of modelling studies of ammonium chloride, a molecular cationic material.

Alkali diffusion in alkali silicate glasses

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Molecular dynamics simulations of alkali silicate glasses have revealed a structure consistent with experimental determinations, which in turn are consistent with the modified random network model. Long-time scale molecular dynamics have yielded quantitative measurements of the alkali diffusion and demonstrated the mechanism of ion migration. The results show a pronounced 'mixed alkali' effect similar to that observed experimentally and thus promise to account for the observed behaviour in real glasses.

Dissociation of O_2 on Ag(110)

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The interaction of O_2 with Ag(110) provides a classic example of precursor-mediated dissociation, with a well-characterised molecular state existing between the gas-phase molecule and fully dissociated O atoms. We will present results of a first principles study of this system, based on density functional theory and using a plane-wave, pseudopotential method implemented on a Cray T3D parallel supercomputer. The calculations include full relaxation of the Ag substrate, gradient corrections and spin-polarisation. Results will be presented for the the structure and energetics of the chemisorbed O_2 state and the reaction pathways into and out of this state. The charge transfer from metal to molecule will also be discussed.

Tri-methyl-gallium adsorption on GaAs(001) β(2x4)

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The structure of the GaAs(001)-(2x4) surface has been the subject of considerable controversy. We have fitted tight-binding parameters to Local Density Approximation (LDA) results. Using a linear scaling tight-binding method we have been able to model sufficiently large unit cells to investigate the energetics of dimer row kinking, which provides strong evidence to support the identification of the β phase with the trench dimer model. Having done so, we returned to LDA calculations to investigate the interaction of the important CBE growth precursor tri-methyl-gallium (TMGa) with the surface, in order to identify both the mobile precursor structure and the final bonded structure.

First principles simulation of nanoindentation and Atomic Force Microscopy on silicon surfaces

Ruben Perez, Michael C. Payne

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Total-Energy pseudopotential calculations, implemented on a massively parallel computer, are used to study the interaction of a tip with a silicon surface in two relevant regimes: close mechanical contact in the nanoindentation experiments, and, weak attractive forces in the AFM operated in the non-contact mode.

In the case of nanoindentation, the goal is to understand the onset and development of plasticity in the indented material. Plastic flow of atoms towards interstitial positions and extrusion of material towards the tip walls, induced by the non-uniform volume strain and stabilized by the adhesive interactions with the tip, are the dominant mechanisms. The delocalization of the charge induced by the stress in the elastically compressed structure triggers these plastic deformations. The adhesive interactions, disregarded in many continuum approaches, are also shown to be responsible for the friction through the induced stick-slip motion of Si atoms along the walls of the tip, the hysteric behaviour observed in the simulations pulling the tip back from different stages of the indentation process, and the recovery of plastic strains during unloading. The onset of irreversible damage is related to the plastic deformation of the second double layer of the silicon slab. The effects of temperature and strain rate on the indentation process are considered by calculating the energy barriers between the different stable structures found in the total-energy diagram and their variation with strain.

The simulations of the non-contact AFM have been motivated by the recent report of atomic resolution images of the Si(111)-7×7 using this technique (F. J Giessibl, Science, 267 (1995) 68). Our results show that the range of operation, the values of the force, and the images determined experimentally, can be understood as a result of the interaction of the tip with the adatoms in the surface. Atomic resolution contrast is enhanced by the interaction between the dangling bonds of the adatoms and the apex atom in the tip. The contrast mechanism is related to the coupling between the tip and the charge transfer modes among the different dangling bonds in the surface.

Clusters, nanostructures and interfaces

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Computer-based modeling and simulations provide deep insights into the structural, dynamical, and mechanical properties of materials and the fundamental mechanisms of materials processes in various phases and degrees of aggregation. In this lecture we discuss computer simulation methodologies, including large-scale classical molecular dynamics (MD), ab-initio Born-Oppenheimer local-spin-0density (LSD) functional MD, and "all-quantum" simulations combining BO-LSD-MD with a path integral quantum mechanical treatment of the nuclei. These methods will be illustrated via investigations of:

- size-evolutionary patterns of materials properties, from molecules to clusters
- protonated water clusters
- fission of charged metallic and molecular clusters
- formation and properties of interfacial solid and liquid junctions

- studies of nano-elastohydrodynamics of complex liquids in lubricated sheared junctions

The importance of combined modelling and experimental studies for characterising semiconductors

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Defects in semiconductors can exist in unexpected structures and exhibit unusual properties dependent on charge state and mode of preparation. In addition, in many cases the defects are not in their lowest energy states but rather in a state of frozen equilibrium. their chemical composition is often unknown along with their crystalline state: ie the number of interstitial versus substitutional components. all this makes *ab initio* modelling extremely difficult. Real progress can come from combined experimental and theoretical investigations and examples of such investigations are presented. The important conclusion is that far from the *ab initio* modeller being able to do away with the experimentalist, the need for close collaboration is stronger than ever.

Chemical Potentials and Defect Energies in Ordered Alloys

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The calculation of defect energies in ordered alloys has been problematic because it is necessary to account for the chemical potentials of the species. These depend on alloy composition and three independent point defect formation energies. This is important for the comparison of energies of grain boundaries of alternative structures, even in the static limit (0 K). A consistent approach to dealing with the problem is described and illustrated by calculations of grain boundaries in NiAl. It is shown how the point defect formation energies determine the relative stability of boundary structures.

Defects and photo-induced processes in ionic nano-clusters

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We have developed a new computer code for studies of defects in clusters and their aggregates in order to model the mechanisms of defect processes in nanometer size clusters and highly dispersed powdered materials used in surface science and catalysis. In this approach a quantum cluster including several tens of ions is embedded in a much larger cluster (nano-cluster) which is treated using interatomic potentials and shell model for ionic polarisation within the GULP computer code. Polarisation of the nano-cluster is produced by an electric field due to ionic displacements and difference in the charge density distribution in the defect area treated quantum- mechanically, with respect to a 'reference system'. The polarisation potential is then included in the elements of the Fock matrix and the whole procedure is repeated until the total energy of the combined system does not change. The reference system may be a relaxed cluster of any form, with or without impurities. It is treated first completely quantum- mechanically to obtain an electronic structure and charge density distribution which is then used to calculate electrostatic interactions in studies of defects in this system. For quantum-chemical calculations we are presently using a semi-empirical technique based on an unrestricted Hartree- Fock method and the CLUSTER computer code. Optical transition energies are calculated using the configuration interaction technique for single excitations. We are currently working on implementation of the GAUSSIAN code within the same approach.

First applications include: i) studies of geometric and electronic structure and optical absorption of (MgO)n clusters (n=32,64,108) as a function of the cluster size and structure of cluster edges (number of steps, kinks and corners); ii) studies of geometric and electronic structure and optical absorption of [Li]0 centres at different positions within these clusters; iii) studies of decomposition of these clusters due to exciton excitation and hole trapping at low- coordinated sites. We suggest an interpretation for the optical absorption and photo-luminescence spectra of highly dispersed MgO. For the hole centres, we have determined the preferred

sites for the trapped holes and [Li]0 centres with respect to the edges and low-coordinated sites of these nano-clusters, and have calculated their optical transitions. We have also developed a new model for photo-induced decomposition of rough MgO surfaces based on exciton trapping and decomposition at low-coordinated sites at the surface.

Defects, interfaces and metastability in compound semiconductors

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The coupling between the electronic and ionic degrees of freedom in compound semiconductors leads to a wealth of interesting phenomena, such as metastable defects, self-compensation and negative-u effects. I present results of first-principles simulations of vacancies, antisites and dopants in these materials, as well as atomic structures and band offsets at planar interfaces. In particular, divacancies and dx/ax centers in GaAs, antisites in GaN and band offsets for interfaces between ZnSe and III-V alloys are discussed.

The ab initio simulation of liquid semiconductor alloys

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In the last few years, dynamical ab initio simulation has become a major tool in the investigation of solids and liquids. This talk will outline the main features of ab initio simulation based on density functional theory and the pseudopotential method, and will show how it is giving important new insights into the structure and dynamics of real liquid semiconductors. Illustrations will be taken from recent work of the Keele group on the liquid alloys Ga/Se and Ag/Se.

Poster Abstracts

MD-Simulation and superhard materials: An empirical potential for Boron Nitride ?

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We discuss an empirical interatomic potential, which could be a promising candidate for MD-Simulations of c-BN thin film deposition. A cluster functional is proposed combining a modified Tersoff potential and a coulombic part. Results of first-principle calculations done by a DFT pseudopotential code are shown and discussed as data base for an optimal parametrization of the proposed potential.

Studies of tRNA^{Asp} Dynamics and Interactions - Part I: Solvated Molecular Dynamics Investigation of the Structuring Effects of Long-Range Hydration Forces on the Anticodon Loop

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A set of six independent 100 psec molecular dynamics trajectories of the fully solvated and neutralized anticodon loop of tRNA^{Asp} [1] were generated using the AMBER force field, SPC/E waters, mobile ammonium counterions and atomic charges from low temperature X-ray data of isolated nucleotides [2] starting from the same initial configuration, but with different initial velocity distributions. The protocol consisted of using a 16Å truncation distance for the electrostatic *solute-solvent* and *solvent-solvent* interactions and no cutoff for the *solute-solute* interactions. This led to an increased stabilization of the structural interactions of the anticodon loop over an earlier set of eight 100 psec simulations using an 8Å truncation distance for the interactions involving the solvent. [3] The results point to the importance of the inclusion of such long-range hydration forces in molecular dynamics. The increased stability of these trajectories allowed us to complete an extended analysis of the dynamical features of some of the main interactions stabilizing this RNA fragment. The observance of C-H ... acceptor hydrogen bonds located in structural strategic sites of the anticodon loop throughout the MD trajectory is presented, as well as dynamical global and detailed structural characteristics of the structure, its solvation, and some pertinent differences observed between the present set and the 8Å set. Additionally the relevance of running multiple molecular dynamics simulations is also discussed.

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Molecular Dynamics simulations on DEMOS

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The Delft Molecular Simulator (DEMOS) is a special purpose computer designed and build for large scale Molecular Dynamics simulations. It consists of a linear array of processor boards each equipped with a fast 40 MHz i860 RISC processor, and large on-board memory (32 - 128 Mb). Neighbouring boards are able to communicate through an asynchronous inter-processor bus (max 64 Mb per sec), independent of any other board, thus reducing latency to a minimum. Additional communication is handled by a global bus connecting all boards and the host computer, which provides for storage and program control. See figure.

Many potentials used for molecular modelling consist of short-ranged interactions between atoms. This fact can be exploited by linear domain decomposition of the computational box into slices of size larger than the potential cutoff radius. In that situation, only communication between neighbouring processor boards is required, which is extremely fast on DEMOS. In some cases long-range forces like Coulombic interactions are present and special techniques can be applied to handle these interactions correctly and still make use of the parallel architecture of DEMOS.

A molecular dynamics program has been written and is currently used for simulation of solid silicon-germanium superlattices and silicon-oxide structures. Focus is on growth and structural aspects. Preliminary results will be shown.

An Ab Initio Study of the Compressional Mechanisms of Forsterite at High Pressures

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The compressional behaviour of forsterite (Mg_2SiO_4) is of considerable interest to geophysicists since it is the major phase in the upper mantle and interpreting seismic data requires accurate values for bulk moduli. Forsterite is comprised of isolated SiO_4 tetrahedra linked by chains of edge-sharing distorted octahedra occupied by magnesium ions. Experimental data have led to the suggestion that there are discontinuities in the compressional mechanisms at about 8 GPa and 40 GPa. The low pressure change is thought to be due to one of the Mg-O bonds becoming essentially incompressible at about 8 GPa. In order to test this we have performed ab initio LDA calculations using the parallel code CETEP on the Cray T3D at Edinburgh. Extremely good agreement is found between the compressibility of the calculated cell parameters and the experimental data. In contrast to the experiments, however, we find no evidence for discontinuities in compressional mechanism at any pressure up to 70 GPa and suggest that the experimental data has been overinterpreted.

Molecular dynamics simulation of LaF_3 nano-clusters

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A new molecular dynamics code has been used to simulate the behaviour of *in vacuo* LaF_3 nano-cluster (i.e. no periodic boundary conditions). The method is based on a Gear 5th order predictor corrector algorithm with recursive generation of initial variables. Forces are calculated using a Born-like description of an ionic lattice.

Three clusters were simulated, consisting of 160, 552 and 3120 ions respectively. A linear heating rate was applied of 100K per ps starting from clusters equilibrated at 10K. Our interest is in three transitions. The first is at ~1100 K and corresponds to the onset of fast fluorine ion conduction. The second is at ~1600K at which point all clusters melt. Finally at much higher temperature (~4000K) evaporation occurs.

Despite the ionic description of forces, throughout the temperature range we observe short-range structures which are reminiscent of molecular-like behaviour.

An *ab initio* Study of a $\Sigma15$ (210)[001] Tilt Grain Boundary in the Transition Metal Dioxide TiO_2.

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The microscopic properties of a high-angle tilt grain boundary in rutile (TiO_2) have been investigated via the density functional pseudopotential approach. Combined electronic and ionic relaxation was performed using self-consistent Conjugate Gradient minimisation of the total energy functional. Optimised pseudopotentials were used for titanium and oxygen, at an energy cutoff of 500eV. The model supercell contained 60 atoms and two grain boundaries. The calculations confirm the stability of the experimentally observed translation state of the boundary. Under stoichiometric conditions, the structure can be characterised by an oxygen sublattice which is mirror symmetric across the boundary. The resulting density of electronic states indicates the presence of interface states spread across the forbidden band gap of the bulk material. The pseudovalence charge density is highly localized on the oxygen ions even in the boundary core. The effect of oxygen loss at the boundary on the atomic and electronic structure has also been investigated. All calculations were performed with the parallel code CETEP (Cambridge-Edinburgh Total Energy Package) running on the Cray T3D at Edinburgh Parallel Computing Centre.

Generation of Amorphous Silicon Structure on Si(110) Surface by a Continuum Monte Carlo Simulation

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A silicon structure is grown on a substrate of a two layer slab of crystalline silicon (110) surface using a semi-empirical potential energy function parametrized for simulating silicon systems. The growth is realized by means of continuum Monte Carlo at $600^0 K$. Radial distribution functions for the resulting amorphous structure are obtained and compared with experimental curves.

PACS Numbers: 61.40.Df , 61.55.Dc

Parallel Molecular Dynamics simulations of growth and structure of silicon-germanium superlattices

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Most potentials used for modeling of tetrahedral structures of silicon and germanium can be expressed as the sum of short-ranged pair- and triplet-interactions. Parallelization of an MD program using these potentials can be done by dividing the computational box into slices larger than the cutoff distance of the potential. Calculation of the forces in a slice then only requires communication with the two neighbouring slices. The special purpose computer DEMOS in Delft is especially designed and built for this kind of local environment problems which require optimized neighbour-to-neighbour communication (see poster by J. Beckers et al.).

An MD program for two- and three-body interactions has been written and its performance on DEMOS proved adequate. At the moment it is used to simulate the growth and structure of silicon-germanium superlattices (Si_nGe_m) for which the precise growth-mechanisms taking place at the germanium-silicon interfaces are being argued[1,2,3,4]. Preliminary results of the simulations will be shown.

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Molecular Dynamics Simulation studies of antibiotic mediated ion transport

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The selective transport of cations across biological membranes is a process of fundamental importance in cell biology. This transport is facilitated by the presence of small amounts of antibiotics, and broadly two modes of action have been identified involving channels and ion carriers. Valinomycin (VM) is an important example of a carrier antibiotic with high potassium selectivity. For ion carriers three distinct processes appear to be involved. (i) Complexation between the cation and a membrane bound antibiotic, (ii) transport of the complex through the membrane by diffusion or electrophoresis, and (iii) cation release at the membrane interface. Concentration gradients are thus ameliorated by the capture and release of cations on the two sides of the membrane.

We have developed a force field for the Valinomycin and used it to model crystalline phases of both VM and the potassium complex. Both VM and K^+-VM have been studied in water and a non-polar solvent along with the complexation process in free space. We also report large simulations of valinomycin and its potassium complex at a water/membrane interface. The simulations, involving almost 19,000 atomic sites, cover a total of over 500 ps and are used to examine both VM at the interface and the K^+ decomplexation reaction. The calculations demonstrate the feasibility of large scale simulations of complex systems. They were achieved using the recently introduced parallel supercomputing facility at Edinburgh as part of the work of the HPCI Materials consortium.

The studies show uncomplexed VM acts as a surfactant with hydrophobic groups embedding in the membrane while the hydrophilic carbonyl groups hydrogen bond with water. Consequently the conformers VM adopts at the interface are quite distinct from those seen in the solid state or in bulk solution where most experimental measurements are made. In contrast, the K^+-VM complex prefers the membrane interior and adopts a structure close to that seen in the solid state and in non polar solution. It remains embedded in the membrane until the decomplexation process is initiated by water attack through the HyV face. The decomplexation process at the interface is considerably faster than that in pure water and points to the role of the interface itself in the function of carrier antibiotics such as valinomycin.

Predicting growth processes; Atomistic modelling of metal atoms on ionic substrates

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We show that it is possible to use existing methods, well-tested for many other systems, to predict the key energies which determine the growth mode (layer, cluster, etc.) of metal deposited on ionic solids. The results agree well with experiment.

We show further that these energies can be used within a further theory of nucleation to predict the nucleation density and other properties as a function of deposition rate and temperature. In particular, this analysis shows how it is possible that Ag on MgO can form an (observed) metastable layer.

These developments suggest ways to influence the growth mode and morphology of metal on oxide, including the effects of the bulk doping of the oxide and the pre-treatment of the substrate surface, as well as control of deposition rate and temperature.

The approach already allows links to be made between metal morphology and interfacial energies between bulk metal and bulk oxide, though the link is not as simple as sometimes supposed. The models used have potential for understanding the operation and degradation mechanisms of operating sensors and catalysts.

A parallel conjugate gradient algorithm for ab-initio energy minimization

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The ab-initio molecular dynamics technique evolves simultaneously the ionic and electronic degrees of freedom in time. In the field of solid state physics, this method is now widely used to perform total energy calculations, i.e. to find the electronic ground state and to optimize the ionic geometry of a configuration.

The search for the electronic ground state is most efficiently done by employing a conjugate gradient algorithm. We present the implementation of such an algorithm on a distributed memory parallel computer. Our implementation divides the electronic states over the nodes, so that the gradients can be calculated in parallel (apart from a global summation to obtain the effective local potential).

Once the electronic ground state has been found a variety of interesting properties can be calculated. We will illustrate this for a Si(001) surface with an adsorbed Si dimer.

The ab-initio simulation of the liquid ga-se system

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Ab-initio dynamical simulation has been used to study the liquid Ga-Se system at several different concentrations including Ga_2Se, $GaSe$ and Ga_2Se_3 at the temperature 1300 K. The simulations are based on the density functional pseudopotential technique, with the system maintained on the Born-Oppenheimer surface by conjugate gradients minimization. We present results for the partial structure factors and radial distribution functions, which reveal how the liquid structure depends on composition. An analysis of the valence electron distribution allows us to examine how the chemical bonding depends on the apparent valence of Ga. Our calculations of the electrical conductivity σ using the Kubo-Greenwood approximation show that σ depends very strongly on composition, and is roughly three orders of magnitude lower at the stoichiometric composition Ga_2Se_3 than for pure $l - Ga$. We show how this variation of σ is related to the calculated electronic density of states. Comparisons with recent experimental determinations of the structure and conductivity will be presented.

Study of The Pressure Effects on Vibrational Properties of Layered Semiconductors

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The lattice dynamics of layered materials has been found to be different from 3- dimensional covalent crystals because of the coexistence of weak interlayer and stronger intralayer coupling. The weakness of the interlayer cohesion in layered semiconductors makes Raman- and infrared-active vibrations nearly degenerate and induces the very low-frequency optical phonons which are described by the rigid-layer (RL) model. It is expected that these vibrational properties of layered compounds will be affected dramatically under compression while the hydrostatic pressure preferentially enhances the interlayer interaction.

In this poster, the vibrational properties of prototypical layered semiconductors, GeS and GeSe, under pressure have been extensively studied using a combination of first principles calculation and experimental methods. Examination of *ab-initio* calculated phonon eigenvectors shows that the vibrational properties undergo a gradual transition from quasi-two dimensional to three-dimensional character. Also, the breakdown of RL approximation has been found to occur under modest compressions

The liquid Ag-Se system studied by ab-initio simulation

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The ab-initio dynamical simulation of liquids containing transition and post-transition metals presents a major technical challenge, because of the need to include d-electrons explicitly and because of the large basis sets required. We show how recent advances in computer power are making such systems accessible to simulation. We present ab-initio simulations of the Ag-Se system at three concentrations performed on the massively parallel Cray T3D machine. The simulations are performed on systems of 69 atoms at the experimentally interesting temperature of 1300 K, and have a duration of 3 ps, which is enough to ensure statistically reliable results. Results are presented for the partial radial distribution functions and structure factors, and we show that these are in excellent agreement with measured structural data.

Interstitial Carbon Defects in Silicon

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The C_i and $C_s - C_i$ defects in Si exhibit several unexplained properties. In the neutral charge state, the C_i defect possesses two almost degenerate vibrational modes suggesting a trigonal defect in disagreement with the C_{2v} symmetry deduced from several experiments. The B-form of the second defect is believed to consist of a Si interstitial, Si_i, located near a BC site between two C_s atoms, in apparent conflict with the results of PL experiments which show that the C-related vibrational modes are decoupled. The structure and vibrational modes of both defects are analysed using LDF cluster theory. The degeneracy of the modes of C_i is attributed to an almost $\mathbf{D}_{3h}$ structure, with a 3-fold axis along $[01\bar{1}]$. The modes of the di-carbon interstitial lead to a resolution of the long standing problem concerning the almost zero-shifts due to mixed isotopes in the 580 and 543 cm^{-1} local modes observed in PL studies.

Simulation of X-ray Scattering from $C_{10}H_{16}$

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Adamantane ($C_{10}H_{16}$) is an interesting archetypal plastic crystal which has been extensively studied. It undergoes transition from a low temperature ordered phase to a high temperature disordered phase at T=208.6K. The $C_{10}H_{16}$ molecule has tetrahedral symmetry and the orientational disorder in the plastic phase has been interpreted in terms of the distribution of the molecules between two equally preferred orientations.

Our simulation model consists of rigid molecules interacting with an (exp -6) atom-atom pairwise additive potential. We have looked in detail at the dynamics of the adamantane molecules in the plastic phase and have found results in general agreement with previous work [1],[2].

The molecular trajectories generated by our simulation are being used to evaluate the intensity of x-ray scattering from the crystal. Results are being compared with experimental data obtained from energy-dispersive diffuse x-ray scattering measurements made on Station 7.6 at the Daresbury SRS. Using a series of simplified models of the crystal we aim to investigate the relative contributions to the scattering intensity from translational and orientational disorder.

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Studies of tRNA^{Asp} Dynamics and Interactions - Part II: Conserved Interactions in Solvated Molecular Dynamics Simulations of the Thymine Arm

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The thymine arm fragment of transfer RNAs has been shown by chemical probing [1] and NMR [2] to be stable in solution, adopting the same secondary folding pattern as observed in the full tRNA molecule, and is postulated to possess an "intrinsic" tertiary structure. The thymine loop contains several unique tertiary structural motifs including a conserved reverse Hoogsteen ribothymine-adenine base pair, two uracil bulge residues and a U-turn in the phosphate backbone at the base of the loop. In the full tRNA molecule, eight additional potential hydrogen bonds, and two additional stacking interactions are introduced by the intercalation of two guanine residues from the D loop. The dynamical topology of the loop region of the thymine arm of tRNA^{Asp} [3], and the extent to which the D loop interactions stabilize the tertiary conformation of the loop topology, was studied via solvated molecular dynamics simulations using the AMBER force field, SPC/E waters, mobile ammonium counterions and atomic charges from low temperature X-ray data of isolated nucleotides [4]. A total trajectory of 600 psec constituted of six individual 100 psec simulations starting from the same initial configuration, but with different initial velocity distributions, was generated. Two of the simulations included the two guanine residue fragment of the D loop. The extent of conservation of the hydrogen bonding interactions preserving these structural elements is presented along with global characteristics of the simulations including solvation and counterion behavior.

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Full-potential and pseudopotential calculations on high pressure phases in CuCl.

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The ionic copper halide, CuCl, displays an unusual structural phase transition sequence under pressure. Using neutron diffraction experiments, two high pressure structures were observed. At ambient pressure, CuCl exists in the zincblende structure, while at elevated pressures it assumes the NaCl-type (rocksalt) structure via an intermediate simple cubic structure. This intermediate phase is the binary analogue of the metastable body-centered structure (BC8) seen in the elemental semiconductors Si and Ge. This is the first time this phase has been experimentally observed in a compound semiconductor, although it has been calculated to be a stable phase for the III-V semiconductors also.

Details of ab-initio total energy calculations on these three phases of CuCl will be shown here, using both the full-potential linearised augmented plane wave method (FLAPW) and the pseudopotential method. Band structures and charge densities will be shown for selected phases, along with details of recent work on the other copper halides, CuI and CuBr.

Computer Simulation of the Effect of Molecular Geometry upon the Formation of Nematic and Smectic Phases.

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Recent years have seen an upsurge of interest in ferroelectric and chiral smectic C^* phases in liquid crystals. The first example of an achiral anti-ferroelectric phase has been synthesised from which Goodby et al [1] infer that chirality may not necessarily stabilise the formation of a ferrielectric and antiferroelectric phase but that the structure may be stabilised by the biaxial nature of the liquid crystal. Over the last few years computer simulations have demonstrated the success of simple potentials such as the Gay-Berne or hybrid versions [2] in the simulation of smectic phases. However, the Gay-Berne potential is axially symmetric and real mesophases are not uniaxial. The smectic C phase is a tilted analogue of the smectic A and the Wulf theory [3] associates the driving force to tilt the molecules with the molecules having a zigzag rigid central core whilst the McMillan model [4] depends upon the molecules having two large oppositely directed outboard electric dipoles. Two derivations of a generalised form of the Gay-Berne potential to include the effect of two arbitrarily stretched uniaxial gaussians and to include the effect of non-equivalent biaxial particles been proposed [5]. However an alternative route to model the molecular geometry is to employ a multi-site Gay-Berne model. In this work we present preliminary results from molecular dynamics simulations of three-site molecules where each site is represented by a Gay-Berne mesogen spaced so that the repulsive core regions overlap. Various three site models have been compared : a cylindrically symmetric model, a zig-zag model with the central site twisted at an angle to the two end sites and a triangular model with one site displaced longitudinally form the other two. Results indicate a far more extensive nematic region for the triangular model compared with the zig-zag model indicating the importance of the molecular geometry in determining phase transitions.

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Ab-initio Predictions of Omega Phase Stability for Intermetallics of Transition Metal Based Alloys.

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It is well known that the directional nature of the covalent bonding between different atomic species tends to cause intermetallics of transition metal aluminides to be brittle. One strategy for overcoming the brittle behaviour has concentrated on the effect of ternary transition metal additions to intermetallic phases like Ti-Al and Nb-Al in order to induce more ductile alloys with the B2 structure. Unfortunately, it has been found recently that omega phase formation may drastically embrittle the parent B2 phase [1]. It is therefore it is very important to study the stability conditions under which this deleterious phase is likely to occur.

A data base for the theoretical structural trends of 3d and 4d transition metal aluminides has recently been generated using the first-principles Full-Potential Linear Muffin-Tin Orbitals (FP-LMTO) method [2]. Based on this systematic study of the bonding of intermetallics, we have carried out ab-initio calculations of the omega phase in transition metal based systems like Al(Ti, V, Zr, Nb) and Ti(V, Mo, Zr, Nb) and also in the related pure elements. Our calculations have greatly increased the amount of information we have on the microscopic mechanisms of structural B2-Omega transformation. We find that there are three important effects exhibited in this transition: (i)the presence of "soft phonon" modes, (ii) influence of high pressure and (iii) the size factor of the transition metal elements. The calculations have also demonstrated the importance of the omega phase as the most stable phase with 50:50 stoichiometry in NbAl. The predicted curves of the omega phase heats of formation versus an elementary electron/atom ratio are in good agreement with experimental data obtained from the measured diffuse omega peak shift versus e/a. As a result of these calculations, we are now able, for the first time, to make realistic calculations of the phase diagrams of useful intermetallic ternary alloys based on Nb3Al and TiAl for structural applications.

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Potential for a Novel Muon Experiment - Simulation Results

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Predicted results for a novel muon spectroscopy experiment are described. The results come from static and dynamic *ab initio* density functional calculations of ethanal + muonium, using the PAW technique [1]. The potential binding sites for the muonium are evaluated, along with the associated (stretching) vibrational frequencies and the Einstein coefficients for the vibrational transitions. These vibrational frequencies occur in the near IR, and so are well separated from other vibrational frequencies and also from any electronic transitions

This opens up the possibility of a new form of muon spectroscopy. If these vibrations were to be optically excited, then the resulting change in the environment of the muon should be detectable in the μSR signal.

[1] P. E. Blöchl *Phy. Rev. B* **50** (1994) 17953

The Interaction of the SO_2 Molecule with the TiO_2 Surface

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Ab initio calculations have been used to study the structure of the TiO_2 (110) surface in which surface oxygen has been replaced with sulphur, and to obtain preliminary estimates for the energy of reaction of the O2 and SO_2 molecules with the reduced surface. The work is motivated by experimental work which shows that SO_2 reacts very readily with the reduced TiO_2 surface. According to ultraviolet photoelectron spectroscopy (UPS) measurements, the reaction leads to the incorporation of sulphur into the surface crystal structure. The calculations are based on density functional theory and the pseudopotential method, and have been performed with the CETEP code on the Daresbury Intel parallel computer.

Model study of $[Li]_0$ -centres in MgO nano-clusters

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A common model in the study of surface defect sites is that of an infinite surface hosting the defect area. In cases of practical relevance (catalysis), however, one rarely encounters these extended low-index surfaces; rather the assumption of nano-clusters seems more appropriate. In this present study we follow this idea by embedding a quantum-mechanically treated cluster (QM-cluster) into a nano-cluster, which in turn is treated in the framework of interatomic potentials and the shell model for ionic polarisation (for technical details see also the paper by A. L. Shluger et. al., this meeting)

In the application to a $[Li]_0$-centre in MgO, clusters of various sizes have been tested to study the quality of the suggested model. The formation of a pair of substitutional Li and an electron hole localized on the adjacent oxygen anion was studied both in the bulk and on the surface of the nano-cluster. Cubic clusters $(MgO)_{64}$, $(MgO)_{108}$ and dimers of $(MgO)_{64}$ were used to model these situations. Geometric and electronic structure were determined as well as optical absorption properties.

In the study of the cubic clusters, a clear tendency of the hole to localize on the corner is established. Comparison with analog cases in a stepped dimer of two cubic clusters show, that the presence of the second cluster has little influence on the results obtained from the single cluster. There are, however, new possible sites arising from the presence of the step, namely at the bottom of the step. They are compared to the cases existing in the simple cubic model.

Chemical Modelling of Glassy Polymer and Composites with Flexible Bond Angles

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Molecular Mechanics Computer Simulation was applied to modelling of polymer glasses, i.e. the produced model structures represent minimum energy configurations. Atatic polypropylene was used as model polymer. Macroscopic density at -40 °C was guaranteed by three dimensional periodic boundary conditions. Unlike former works on this subject a model which includes not only torsion angles as degrees of freedom but bond angles too, was develloped. Both macroscopical and structural properties were examined. Structural properties like mean square of end-to-end distances were obtained directly by the minimum energy configuration. Elastic constants, internal pressure and thermal expansion coefficient were computed by deforming the originally simulated model structure. The results were compared with those of other model computations and experimental data. The method described above was also applied to polymer-graphite-systems. Results for structural and thermodynamic properties of the interface were shown.

Defects on the 90^o Partial Dislocation in Silicon

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Simulations of the motion of defects of the 90^o partial dislocation in Si are carried out using the Tersoff interatomic potential. Low energy paths corresponding to the motion of kinks, antiphase defects (APDs) and kink-APD complexes are found using a conjugate gradient elastic band method. This method gives the coordinates of the atoms as well as the energy of the system along the path and in this way we obtain the migration energy of these defects (energy at the saddle point configuration). The results obtained are a first step towards understanding the changes in the electronic structure associated with dislocation motion and the dependence of the mechanical properties of Si on its electronic structure.

Theoretical Studies of Implanted Muons in Organic Magnets

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Wholly organic ferromagnets are a new class of materials of great potential interest, but the early examples exhibit only very weak magnetic order at very low temperatures [1]. In these circumstances, muon spin rotation μSR is among the most sensitive sources of information about the magnetic structure and interactions on a molecular scale [2]. However, interpretation of the μSR data is complicated because of the large number of binding sites made possible by the relatively complicated molecular structure.

We have performed semi-empirical and *ab initio* density functional calculations of the electronic and molecular structure of muonium incorporated into the organic ferromagnets *para*-nitrophenyl α-nitronyl nitroxide (*p*-NPNN), 3-quinolyl nitronyl nitroxide (3-QNNN) and *para*-pyridyl nitronyl nitroxide (*p*-PYNN). We find evidence for a wide variety of possible muon binding sites including sites in the conjugated ring systems of the materials as well as in the nitronyl nitroxide group. Our calculations also suggest the formation of local triplet electronic states near the muon within the spin-1/2 magnetic system.

[1] M. Tamura et al. *Chem. Phys. Lett.* **186** (1991) 401
[2] F. L. Pratt et al.*Synthetic Metals* **61** (1993) 171

Full structural relaxation using density-functional theory

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The widely-used `CASTEP` and `CETEP` codes have been modified to allow full structural relaxation, enabling the unit cell to be optimised as well as the ionic positions. The equilibrium structure of complex triclinic crystals can now be found automatically. Further development will allow constant-pressure molecular dynamics simulations, offering the possibility of observing phase transitions.

Simulations are performed with a constant number of plane waves, to ensure that no charge is lost, but if the supercell changes then so will the energy of the highest plane wave, effectively altering the energy cutoff. A Pulay correction to the stress and total energy has thus been used: the practical implementation of this technique and the limitations to its use are discussed. We further modify the Parrinello–Rahman Lagrangian to work with the strain rather than the supercell vectors, to preserve the symmetry of the supercell.

Examples of simulations with cell relaxation are given, illustrating the applications and restrictions of the code, and explaining the choice of box mass and timestep. Further refinements to the code are suggested.

Dynamical instabilities in a-quartz and a-berlinite: A mechanism for amorphization

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Elastic instabilities have been used to explain the occurrence of amorphization in both α-quartz (SiO_2) and α-berlinite ($AlPO_4$). However, there is a dynamical instability at (1/3,1/3,0) in the Brillouin zone preceding the elastic instability for both structures which implies that distortion of a 3x3x1 supercell will form a more stable crystal structure. Simulations of distorted supercells of size 3x3x1 resulted in the collapse of the structures below the elastic instability pressures for both α-quartz and α-berlinite. A subtle difference between them was that the eigenvectors for phosphorus were smaller than those of silicon or aluminium and on 'amorphization' the PO_4 units in α-berlinite remained completely intact with only the aluminium changing coordination. This resulted in amorphization around the PO_4 units with no P-O-P links formed and a return to a crystalline phase on the release of pressure for α-berlinite, which was not found in the simulations of α-quartz.

Computer Simulation in the Physics of Contact Melting Phenomena

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Contact melting (CM) is a phenomenon at the interface of two heterogeneous bodies that occurs at a lower temperature than the melting point of each component. CM is the first-order transition with its specific distinctive indications, mechanisms and kinetics. Detailed studies of the contact melting phenomenon highlight the contact melting nature and allows wide application of the phenomenon in various technologies. Computer simulation is a powerful new technique that enable us to investigate the contact melting for the model system without cumbersome experiments. It allows us to obtain a connection between macroscopic CM phenomena and its microscopic characteristics, and dynamical properties of the constituent components, such as: the ion radius, the potentials of interactions in the system, the dynamic structure factor, the diffusion factor and other characteristics of the microstructure of the system.

In this paper the scientific software for the simulation of contact melting phenomena was developed. The software includes the direct Molecular Dynamic (MD) simulations and numerical solutions of the Nernst-Plank (NP) equation. In the MD experiments the data on ion coordinates and other results can be displayed on a monitor in the graphic form. The programs can be used for calculations of the mean square displacements, the diffusion coefficients, the radial distribution functions, the normalized velocity autocorrelation functions, and the contact melting temperature. The method was applied for the analysis of the KBr - NaBr, NaI - KI, NaI - NaCl and other typical ionic systems. The numerical solutions of the NP equations allows us to calculate the concentration distributions of ions in the melt. Investigations were conducted for different double nitrate, nitrite and alkali-halide systems.

From the Molecular Dynamics analysis the result was obtained that the form of the first maximum of the partial radial distribution functions are non-symmetrical, it means that the effects of anharmonicity are dominant in this region. The mean square displacements of Na and Cl ions in the NaCl-RbCl system grows faster than in the NaCl-KCl system and in the NaCl one component system. The calculated diffusion coefficients are sensitive to the CM temperature and can be used for its valuations. The mobility of ions in CM depends on the interface and arrangements of ions in the contacting crystal lattices. Local domains, consisting of mobile ions, of the size of 2 nm can be observed during a time of 10 ps. It reflects the appearance of the liquid phase in the interface. The results of the numerical calculations of the NM equations show a strong dependence of the interdiffusion coefficient on the concentration, on the external fields and on the charge of the diffusing ions. The results obtained lead to the elaboration of the methods for the control of the contact melting process and allows us to predict optimal conditions for the contact melting in practice.

Why the Car-Parrinello Method is too good to leave to the Electronic Structure Theorists

or

Molecular Dynamics with an Infinite Number of Timesteps.

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Introduction

Manipulating and thinning degrees of freedom are the jobs of the theorist. Computer simulation is becoming an increasingly useful tool for the latter: an extreme example will be the simulation, as part of the Grand Challenge in Colloidal Hydrodynamics, of a billion fluid particles plus a colloidal sphere, where one interesting output will be a single number – the effective Stokesian drag coefficient acting on the sphere.

As the number of degrees of freedom increases, so does the natural timescale of the slowest, collective modes of the system. These are invariably the modes of physical interest, so it makes sense to devote most of the simulation effort to the study of their energetics (how they contribute to the partition function, for example). Unfortunately, present molecular dynamics methods merely devote most of the simulation effort to ensuring that these modes evolve more slowly than shorter wavelength modes. This isn't quite the same thing as the goal mentioned above.

In this note I present a "novel" simulation method, which accomplishes the task of interest in computational Statistical Mechanics: to generate configurations according to a specific Hamiltonian in the most efficient possible manner. The method is in fact not completely new, as it uses ideas over 20 years old: however, these have been undeservedly ignored. My hope is that by rederiving the method via a currently popular route, its use may become more widespread.

The outline of this note is as follows: first I present a heuristic overview of the Car-Parrinello method, then consider variations on its main theme. I then examine one of those variations in more detail, and in doing so construct a novel algorithm for simulating a polymer, which is closely related to an old suggestion of C. H. Bennett. Finally, I pose some questions raised by this approach, and sketch out some directions for future research.

Electronic Structure Calculations in a nutshell

An excellent review, from the point of view of the molecular dynamicist, of the Car-Parrinello (CP) method for calculating electronic ground state properties has been given by Remler and Madden [1]. In this section I give an extremely condensed version of their description.

Consider a set of mass points (representing atomic nucleii) labelled by coordinates $\mathbf{R}_i$, and a smooth complex function (representing the electronic ground state wavefunction), labelled by the coefficients $\mathbf{C}$ of an expansion of this function in some basis set (here the boldface is meant to denote the complete set of coefficients; for the electronic structure problem these may be labelled as c_i^k, where i denotes an occupied electronic orbital and k denotes an element of a standard basis set (say, a gaussian) in terms of which each orbital is expanded).

Using the $\mathbf{R}_i$ and $\mathbf{C}$, one can construct a function which gives the energy of the system of nucleii and electrons. This is a difficult theoretical problem, and much use must be made of the local density approximation, where the electronic density is assumed to be slowly varying. At the end of the day, one arrives at an effective Hamiltonian which includes spatial kinetic energy, Hartree, exchange, correlation, and pseudopotential terms; minimising this Hamiltonian with respect to the $\mathbf{C}$, for fixed $\mathbf{R}_i$, gives estimates of the electronic ground state which are in good agreement with experiment in many important cases [2].

The minimisation may be accomplished by Molecular Dynamics methods. By giving the $\mathbf{C}$ a dynamics, i.e. including a term $\frac{\mu}{2}\sum_{i,k}\left(\dot{c}_i^k\right)^2$ in the Hamiltonian and solving Hamilton's equations as we usually do in molecular dynamics, then periodically withdrawing kinetic energy by setting the $\dot{c}_i^k$ to zero), the system is "annealed" into a configuration where the energy is minimised. This dynamics is fictitious, an evolution of the electronic state through computer time, and shouldn't be regarded as giving an accurate representation of the physical dynamics of electrons. The specific parameterisation which describes the ground state wavefunction isn't important – just the fact that it evolves with time.

The breakthrough of CP was to run this fictitious dynamics in parallel with the "real" Newtonian classical dynamics of the nucleii, which they simply implemented as above by including a term $\frac{1}{2}\sum_i M_i\left(\dot{\mathbf{R}}_i\right)^2$ and solving Hamilton's equations. This led to a constantly evolving electronic ground state wavefunction, which "followed" the nucleii in such a way that the system always remained on the Born-Oppenheimer (adiabatic electronic state) surface [3].

This breakthrough isn't simply a clever energy minimisation method; it is the realisation that what we regard as a real Newtonian dynamics, and a seemingly fictitious functional dynamics, can be put on an equal footing provided we have a good effective Hamiltonian linking the different degrees of freedom.

Variations on a Theme of Car and Parrinello

If we take this basic lesson of CP to heart, then we may play variations on a theme by simply examining different types of functions, providing we can construct an effective Hamiltonian which describes the degrees of freedom represented by that function (the Hartree-Fock Hamiltonian, while quite important, is to the theorist just another effective Hamiltonian)

For example, consider a function which maps the sphere onto an arbitrary closed surface in 3-dimensions. In this case there is an interesting Hamiltonian – the Helfrich Hamiltonian [4] – which gives the energy of such a surface in terms of an integral over its curvatures. This Hamiltonian describes a membrane, such as that surrounding an erythrocyte (red blood cell), whose properties are dominated by the energy required to bend it. Terms may be added to this Hamiltonian to describe effects due to surface tension and shear of the membrane, and osmotic pressure and compression of the gel in the underlying erythrocyte skeleton. Thus, a good effective Hamiltonian describing the the energetics of erythrocyte shape is available [5]. Using the CP method, a simulation of a collection of such cells, which dynamically change their shape, is possible (here the analogue of the nuclear coordinates $\mathbf{R}_i$ are simply the centre of-mass coordinates of the erythrocytes).

This type of simulation should be contrasted with a traditional molecular dynamics simulation of such a system, where all of the constituent molecules of each membrane and skeleton would be included, and changes in cell shape would only arise through collective excitations of these many degrees of freedom.

The CP method clearly promises a significant improvement in the size and complexity of the systems we can study by molecular dynamics, at the expense of additional theoretical effort in deriving accurate effective Hamiltonians. However, as a rule, theorists are cheap and plentiful.

A Detailed Example

In this section we fill in the details of the method outlined above for a particular system, in order to demonstrate how the method may be made to work. In doing so we will discover that the method isn't as different from "ordinary" MD as might at first seem; however, there will remain one absolutely crucial difference.

The system we consider starts with a function which maps the line segment [0, 1] onto n-dimensional space; in other words, a model of a polymer. In two dimensions, which lends itself to simple computations and nice pictures, we have our polymer $P \equiv (x(s), y(s))$; $0 \leq s \leq 1$ where x and y are "smooth" functions. As a result, these functions can be expressed as an expansion in coefficients **C** as with the electronic case; a reasonable choice would be Fourier coefficients:

$$x(s) = \sum_k c_k^x cos(ks) \ , \ y(s) = \sum_k c_k^y cos(ks) \tag{1}$$

where the upper cutoff on the sums will become clear in a moment.

In the zoology of polymer models [6], our model would be classed as "coarse-grained," but we will need to include information on the atomic level in order to make sense of the effective Hamiltonian. To see how this works, consider a term in the effective Hamiltonian which describes the self-interaction of our line segment, i.e. which makes it energetically impossible for the line to cross itself, and energetically unfavorable for the line to lie along itself. We could write such a self-interaction term as

$$H_{SI} = \epsilon \int_0^1 ds \int_0^1 dt f\left((x(s) - x(t))^2 + (y(s) - y(t))^2\right) \tag{2}$$

where f is a function which becomes large for small values of its argument, and represents a unit repulsion per unit length of the line segment. The integral in (2) of course diverges, and so we must regulate this and similar integrals, say, by discretising them. This we simply recognise as the requirement that the short distance properties of our theory must deal with the underlying physical chemistry of the polymer. Thus, we are quickly led back to a "bead-and-spring" model, where the terms in the effective Hamiltonian such as H_{SI} are given in terms of sums over "beads," labelled by coordinates $\mathbf{r}_i = (x_i, y_i), i = 1, N$, and the "springs" arise from the simplest expression for a term representing a polymer line tension. In fact, we could include as much physical chemistry as we wanted, in a sequence of successive improvements to our effective Hamiltonian. Extension to three dimensions is also straightforward.

So it seems that we are right back where we would have been had we decided to do "ordinary" MD on a model polymer. Have we gained anything by using the CP-based approach?

What we have gained is in fact tremendous, and constitutes nothing less that the complete elimination from our simulation of a large fraction of the degrees of freedom of our model polymer. The way this works is as follows: whilst describing the terms in the effective Hamiltonian of our polymer by beads and springs, we retain the CP expression for the kinetic energy:

$$H_{KE} = \frac{\mu}{2} \sum_k \left\{ \left(\dot{c^x}_k\right)^2 + \left(\dot{c^y}_k\right)^2 \right\} \tag{3}$$

This is again a fictitious dynamics, which should be regarded as providing us with polymer configurations which evolve in computer time, which may or may not be physically realistic. The most important thing about expression (3) is that it expresses the kinetic energy in terms of the *modes* of the polymer i.e. the Fourier coefficients) rather than the individual particles. In fact, expression (3) simply says that we give an equal effective timestep to each mode. It may thus seem that we are devoting no more computational effort to the long wavelength modes than to the short wavelength ones, but we must look more carefully.

Since each mode is given an equal timestep, we must set the value of the timestep by the criterion that the most unstable mode (typically the mode with shortest wavelength) isn't driven too hard. Then, as the *relaxation times* for the different modes depend strongly on their wavelength (they typically go like a power of $(1/k^2)$, the long wavelength modes will *evolve* very slowly on computer time scales. Thus, more computational effort is required to evolve a mode of long wavelength than one of short wavelength. Since the long wavelength modes are usually (but not always) the modes of physical interest, we have an inherently inefficient simulation mechanism.

The solution to this problem is made plain, however, simply by looking at (3). What we need is to give the modes an effective timestep in proportion to their relaxation times:

$$H_{KE} = \frac{\mu}{2} \sum_k \left\{ \frac{\left(\dot{c^x}_k\right)^2 + \left(\dot{c^y}_k\right)^2}{k^2 + m^2} \right\} \tag{3'}$$

where here as an example, the denominator is the spectrum of relaxation times for a harmonic system.

This will not give the modes equal timesteps, but it will give them an equal evolution in computer time, so the physical averages we are interested in will be generated with maximum efficiency. Roughly speaking, we can say the since the long wavelength modes will make the largest contribution to most quantities of interest, it is as if the short wavelength modes have been "integrated out" of the simulation. This rough way of speaking can be made more exact for the harmonic system, as we discuss later.

Expressed in terms of the velocities of the beads, (3') is nonlocal:

$$H_{KE} = \frac{1}{2} \sum_{i,j} \dot{\mathbf{r}}_i \, \mathbf{M}_{ij} \, \dot{\mathbf{r}}_j \tag{4}$$

where here the boldface **M** is meant to denote that as well as coupling different beads, this term can also couple the spacial indices (i.e. x and y). Expression (4) was first written down in 1975 by Charles Bennett [7], whom most of us know through other work (on calculating free energies). The name he gave the dynamics it generates was Mass Tensor Dynamics; the technique was revived in 1985 by K. G. Wilson [8] in the context of lattice gauge theory calculations, where it was renamed Fourier Acceleration.

Bennett performed Mass Tensor MD for a model polymer, by choosing a mass tensor $\mathbf{M}_{ij}$ which was the average over a region of phase space of the susceptibility matrix, i.e.

$$\mathbf{M}_{ij} \approx \left\langle \frac{\partial^2 V(\mathbf{r})}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \right\rangle \tag{5}$$

where $V(\mathbf{r})$ denotes the potential energy of the given Hamiltonian. Bennett found that this dynamics generated configurations effectively so long as the system remained near the region in phase space where the averages in (5) were calculated. In the limit that the system is harmonic, we can show analytically (for example using Hamilton Jacobi theory) that Mass Tensor Dynamics is optimal: basically, it eliminates N-1 modes and replaces them with copies of the remaining mode.

Alternatively, we can think of the method as providing a range of timesteps (one for each mode) given by the eigenvalues of $\mathbf{M}$. There are as many timesteps as degrees of freedom (hence my choice of subtitle). Bennett further suggested that a Mass Tensor which was an explicit function of the coordinates might fare better in systems which were anharmonic.

Such a Mass Tensor is indeed possible, by making a series of orthogonal transformations of a coordinate-independent Mass Tensor:

$$\mathbf{M}(\mathbf{r}) = \mathbf{A}_1(\mathbf{r})\mathbf{A}_2(\mathbf{r})\mathbf{A}_3(\mathbf{r})\ldots\mathbf{D}\ldots\mathbf{A}_3^T(\mathbf{r})\mathbf{A}_2^T(\mathbf{r})\mathbf{A}_1^T(\mathbf{r}) \tag{6}$$

where the $\mathbf{A}_i$ are orthogonal matrices, and we have for the moment suppressed the spatial indices. The orthogonal transformations ensure that the canonical phase space density of the system is the same as a system with normal dynamics and, if chosen correctly, can keep the Mass Tensor "up to date" as the system evolves through phase space, ensuring that the simulation continually expends minimal effort on merely generating collective modes, and so more effort on actually studying them.

In our simple 2D polymer model, where we have terms in the Hamiltonian describing the springs between beads, a bending energy, and a van der Waals repulsion between the beads, we can find explicit expressions for the $\mathbf{A}_i$ and $\mathbf{D}$. In this case, where there are harmonic terms in the Hamiltonian, one begins one's theory from this harmonic limit. Then $\mathbf{D}$ is a lattice laplacian, ∇_{ij}^2, with different coefficients for the directions along the polymer (spring energies) and across the polymer (bending energies), and the $\mathbf{A}_i$ are local rotations of the polymer into a coordinate system where $\mathbf{D}$ is tri-diagonal. Thus, this dynamics, which I call "accelerated molecular dynamics" AMD), can effectively evolve the long wavelength modes (including the reptation mode) of a polymer irrespective of its particular conformation. Of course, we have only dealt with the effects of entanglement on the dynamics in the simplest possible way; however, the approach is only limited by the quality of the theory used to determine $\mathbf{M}$. This places some of the burden of theory back on to the computational scientist, where it belongs.

In actual practice, there is a significant additional computational task in an accelerated molecular dynamics simulation over and above the force calculation (which is exactly the same as in "ordinary" MD). This is the solution of the equation

$$\mathbf{p}_i = \sum_j \mathbf{M}_{ij}\,\dot{\mathbf{r}}_j \tag{7}$$

or "$\mathbf{p} = \mathbf{M}\mathbf{v}$", which is now a matrix equation, which must be solved every timestep. In general, the matrix $\mathbf{M}$ shouldn't need to be dense in order to accelerate; in the polymer model it is sparse (in fact, block banded), and the time for the solution of this equation goes like N, the system size. This tradeoff in computation will in general be advantageous whenever the increase in cost due to solving (7) is less than the critical slowing down (i.e. the ratio of the largest to the smallest relaxation time) experienced with ordinary MD. Typically, collective relaxation times vary as a high power of N (N^2 for a purely harmonic model). So, the increase in efficiency given by the AMD algorithm can be very large. Conversely, there are few models without collective dynamics, whether they are harmonic or not – the method should thus provide an increase in efficiency for most models to which it is applied.

Finally, we note that the queasiness felt by some in modifying the dynamics of a perfectly innocent system such as this may be completely calmed by using accelerated molecular dynamics merely to generate configurations for input into a conventional Monte Carlo scheme. This is in fact the method of hybrid Monte Carlo, and it guarantees that the system configurations will be correctly Boltzmann distributed (according to the potential energy terms in the Hamiltonian) independent of the dynamics. More importantly it generates these configurations efficiently, in that it uses MD to only search out system dynamics along the "flat" directions (those along which the system energy varies the least). It also allows for the use of incredibly large (0.15 - 0.2) values of the timestep, as numerical integration inaccuracies are identically rendered inconsequential by the hybrid Monte Carlo method.

Alternatively, the dynamics is suitable for a quantum MD simulation.

Discussion

The polymer simulation discussed above is currently being implemented for a polymer melt. AMD is slightly more complex to implement than a standard MD, for reasons discussed above. As a result, data are currently lagging behind those I would have obtained via an "ordinary" MD implementation; however, I expect that the long timescales which plague such a conventional approach will soon allow me to "catch up". My purpose in writing this note is to trumpet the generality of the CP/Mass Tensor approach, which I believe will work for many more systems than the one I'm implementing.

In addition, there are several intriguing questions raised by the method, which point the way to its further use for nonharmonic systems, as well as giving us an understanding of what simulation does.

The first question is "Is accelerated molecular dynamics really possible?" In other words, is there a particle system in the laboratory with dynamics generated by nonlocal kinetic energy forms? The term in the energy which would be needed is one which couples the velocities of neighbouring particles. Such terms are thought to arise from effective two-body hydrodynamic forces, but the exact form of these interactions will have to await the results of the Grand Challenge mentioned previously.

A second question is "Can we recover MD from AMD?" Is there an analytical prescription for estimating dynamical quantities measured by the two methods? I suspect that a positive answer to this question may be needed before AMD gains general acceptance, even though many present MD calculations are only concerned with static properties.

A more practical question might be "How do we know that we have an optimal choice of M?" Here the CP approach may be of assistance, if we have an understanding of the expected modes of the system. If, for example, we want to simulate a dense melt, we may be more interested in a relative acceleration of the motions of the free ends of the polymers, in which case a reparameterisation of our function in terms of Jacobi or Chebyshev polynomials would be appropriate.

The more interesting questions are also more abstract in a mathematical sense. Ultimately, we know we are doing the best we can when locally in phase space,

$$\mathbf{M}_{ij} \approx \frac{\partial^2 V(\mathbf{r})}{\partial \mathbf{r}_i \partial \mathbf{r}_j}$$

For a harmonic system both sides are independent of $\mathbf{r}$, so the above relation can be easily satisfied. A more general criterion for when we can achieve this exists in the mathematical literature, and has generated recent interest amongst mathematicians and mathematical physicists, as it seems that large reductions in the number of degrees of freedom are possible even in non-harmonic theories [9]. The mathematical methods have been recast in the guise of statistical field theory calculations involving supersymmetry, in which one sees the cancellation of bosonic and fermionic degrees of freedom, even in models with complicated interactions. This usually results in a simpler theory than one with only bosons or only fermions. What we are doing with accelerated molecular dynamics is in a way similar, in that we are making the theory more complicated by coupling the momenta of different particles with each other and with the coordinates. Thus, the momenta, which are normally trivially integrated out of the partition function, now make a nontrivial contribution (proportional to the determinant of **M**). This is entirely at odds with the usual method of increasing the sophistication of a theory, which usually concentrates on making the potential energy more complicated. The hope is that our seemingly more complicated model may in fact be simple (or, more realistically, have a simple model imbedded in it), and so be more efficiently simulated once its simplicity is recognised. One of the hallmarks of supersymmetry is that the free energy is identically equal to zero; if the above relation for **M** can be satisfied then it is easy to show that the free energy of our more complicated system of coupled coordinates and momenta is indeed zero. Much more analytical work needs to be done to transform this handwaving into a prescription for actually choosing an optimal **M** for a given system; the links proposed in [9] are still tenuous. However, the potential benefits to simulation in general are enormous.

This brings us to our final point: that discussions of algorithm efficiency become increasingly important when computational resources are limited, as they are in this country now. The UK is so far down the league table of supercomputing that any simulation which wastes resources at the Gigaflop level seriously damages not only its own, but also neighbouring areas of computational science. Yet aren't many current simulations, which mindlessly increase the complexity of atom-atom potentials without putting in the simplest understanding of collective dynamics, guilty of a waste on precisely this scale?

Acknowledgements

I would like to thank David Heyes for early discussions about collective dynamics, and also for locating reference [7]. I would also like to thank Jon Keating for useful discussions.

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The Random Walk and the Mean Squared Displacement

W. Smith and M. J. Gillan

Introduction

The origin of this article lies in a research project of ours, in which it became important to quantify the errors in the calculation of the mean squared displacement (MSD) - putting the error bars on a MSD plot. This set us thinking about the simple random walk, which offered a theoretical model for the calculations. The exercise proved to be interesting and enlightening, and despite the almost certain probability that this has been published elsewhere, we present our findings to readers of the CCP5 newsletter, who perhaps have not thought about these matters before.

We begin with the calculation of the MSD from a single time origin, and proceed to the case of multiple time origins. In both cases we derive formulae for the MSD and the associated errors. In the final section we put the theory to the test with a computer simulation.

Single time origin

Consider a 1 D random walk. A particle starts at location 0 (the origin), from where it makes a random 'hop' of distance d in the positive or negative direction, to a location $\pm d$. It can subsequently make any number of similar hops in succession and by so doing move quite some distance from the origin. It is important to note that the direction of a given hop is completely independent of any preceding hop, which is to say that the hops are completely *uncorrelated*. Effectively, this manner of motion, confines the particle to sites on a regular 1 D grid with spacing d.

We next ask the question: where will the particle be after n hops? This will be given by the formula

$$x_n = \sum_{i=1}^{n} h_i \tag{8}$$

which simply sums the contributions to the overall particle trajectory made by each hop h_i, where

$$h_i = \pm d. \tag{9}$$

So in order to determine the position x_n we need to know the history of the particle hops. We call such a history the *trajectory*, for obvious reasons. Normally a single trajectory is of little interest, as it is only one of a potentially astronomical number of possible trajectories that can result from a random walk of n hops. This being so, it is obvious that we need a statistical approach if we are to derive anything useful from such a model.

If we regard a single trajectory of n hops as one statistical 'trial', we can easily consider the outcome of an infinite number of such trials[1]. We can represent this in the following way

$$< x_n >= \left\langle \sum_{i=1}^{n} h_i \right\rangle. \tag{10}$$

---

[1] Actually, this is a convenient fiction. While it is possible to imagine an infinite number of trials, there can only be 2^n possible independent trajectories. However, once n becomes sufficiently large, the conclusions drawn from the arguments above remain valid. We therefore assume that n is a large number throughout.

where the angular brackets $< \ldots >$ indicate an average over an infinite number of trials. The result of this elegance is disappointing: the average $< x_n >$ is zero, as can be seen from the following.

$$\begin{aligned} < x_n > &= \left\langle \sum_{i=1}^{n} h_i \right\rangle \\ &= \sum_{i=1}^{n} \langle h_i \rangle \\ &= \sum_{i=1}^{n} 0 \\ &= 0. \end{aligned} \tag{11}$$

On reflection, this result is obvious: the i'th step in any trajectory can be $+d$ or $-d$ with equal probability, so an average of an infinite number of i'th hops must be zero. However the result is useful in that in shows how we can separate out contributions to the average, something we are allowed to do because each hop is independent of all others.

A more useful average is $< x_n^2 >$, which of course is the *mean squared displacement*. We can calculate this as follows.

$$\begin{aligned} < x_n^2 > &= \left\langle \left(\sum_{i=1}^{n} h_i \right)^2 \right\rangle \\ &= \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} h_i h_j \right\rangle \\ &= \left\langle \sum_{i=1}^{n} h_i^2 \right\rangle + \left\langle \sum_{i=1}^{n} \sum_{j \neq i}^{n} h_i h_j \right\rangle \\ &= \sum_{i=1}^{n} \left\langle h_i^2 \right\rangle + \sum_{i=1}^{n} \sum_{j=1}^{n} \langle h_i h_j \rangle \\ &= nd^2. \end{aligned} \tag{12}$$

In obtaining this result we note that the loss of the cross terms ($i \neq j$) occuring after the fourth step above, results from the fact that the average $< h_i h_j >$ must be zero - since the product $h_i h_j$ is $\pm d^2$, with equal probability for both signs, and once again an average of such terms must be zero.

The result (12) is of immediate interest to molecular simulators on at least two accounts. Firstly if it is imagined that each hop occurs after a regular time interval Δt, then it is apparent that n is directly proportional to the elapsed time t, which in turn means that the MSD is *linear in time*. Secondly in circumstances where the diffusional motion of atoms really is due to hops from one site to another, the model immediately reveals the average relationship between the hopping distance and the time interval between hops.

This simple model can be taken further. For example, a question often asked in molecular simulation is: how accurate is the MSD calculated in a simulation? The model offers insight into this issue also.

Since we know the MSD, as given by equation (12), we can proceed to determine the uncertainty in the result by calculating the *variance* for each point on the MSD, which we denote by σ_n^2. This given by the standard statistical formula:

$$\sigma_n^2 = \left\langle \left(x_n^2 - \left\langle x_n^2 \right\rangle \right)^2 \right\rangle, \tag{13}$$

which can be manipulated as follows

$$\begin{aligned}\sigma_n^2 &= \left\langle \left(x_n^2\right)^2 \right\rangle - 2\left\langle x_n^2 \right\rangle \left\langle x_n^2 \right\rangle + \left\langle x_n^2 \right\rangle^2 \\ &= \left\langle x_n^4 \right\rangle - \left\langle x_n^2 \right\rangle^2, \end{aligned} \tag{14}$$

where

$$\left\langle x_n^4 \right\rangle = \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{\ell=1}^{n} h_i h_j h_k h_\ell \right\rangle \tag{15}$$

and (of course)

$$\left\langle x_n^2 \right\rangle^2 = (nd^2)^2. \tag{16}$$

Computing the term on the right of (15) is greatly simplified by recognising that since h_i, h_j, h_k, and h_ℓ, are uncorrelated when $i \neq j \neq k \neq \ell$, the only terms that survive the averaging process are those with:

(a) $i = j = k = \ell$;
(b) $(i = j) \neq (k = \ell)$;
(c) $(i = k) \neq (j = \ell)$;
(d) $(i = \ell) \neq (j = k)$;

where we note that the indices are equivalenced *in pairs* to guarantee a positive product for $h_i h_j h_k h_\ell$. We also note that the conditions (b), (c) and (d) are equivalent.

Thus from (a) we obtain the result:

$$\left\langle \sum_{i=1} h_i^4 \right\rangle = nd^4, \tag{17}$$

and from (b), (c) and (d) we obtain:

$$\left\langle \sum_{i=1} \sum_{j=1} h_i^2 h_j^2 \right\rangle = (nd^2)^2, \tag{18}$$

from which it follows that

$$\left\langle x_n^4 \right\rangle = (3n^2 + n)d^4, \tag{19}$$

or if n is extremely large, we may approximate this by

$$\left\langle x_n^4 \right\rangle = 3n^2 d^4. \tag{20}$$

Finally, combining this result with (16) gives

$$\sigma_n^2 = 2n^2 d^4. \tag{21}$$

We may thus quote the error in the MSD of the random walk as $\pm\sigma_n$, with

$$\sigma_n = \sqrt{2}nd^2. \tag{22}$$

This is an interesting result. It shows that the error in the MSD is directly proportional to the MSD itself (at least for a random walk). It is also quite large! However, this outcome is easily improved upon by calculating the MSD of many particles simultaneously. Then if the particles are independent, it is easy to show that the MSD remains the same, but the error is reduced to

$$\Sigma_n = \sqrt{\frac{2}{N}} n d^2, \tag{23}$$

where N is the number of particles. Even so 100 particles are necessary to improve the accuracy by an order of magnitude.

In 3 D, the corresponding results are easily shown to be

$$\begin{aligned} \left\langle r_n^2 \right\rangle &= 3nd^2, \\ \sigma_n &= \sqrt{6} n d^2, \\ \Sigma_n &= \sqrt{\frac{6}{N}} n d^2. \end{aligned} \tag{24}$$

While these results are interesting in themselves, they do not fully reflect how MSDs are calculated in simulations. The most obvious difference from practice, is that the results are obtained from a *single time origin* and consequently each point on a trajectory contributes only once to the overall averaging process. In practice it is usual to use many points on a trajectory, each as a time origin in its own right. The MSD is then calculated as an average over origins, as well as an average over trajectories. What are the statistical consequences of this?

Multiple time origins

For a single particle making M hops in 1 D, (where M is assumed to be a very large number,) we may take a point s on the trajectory as an origin and calculate the displacement of the particle from this origin after a further n hops using the formula

$$x_{n:s} = \sum_{i=s}^{n+s-1} h_i, \tag{25}$$

which is seen to be a generalisation of equation (8). It is important to note that $x_{n:s}$ does not represent an absolute location of the particle on the grid, but its displacement from the point labelled s. The squared displacement is given by

$$x_{n:s}^2 = \left(\sum_{i=s}^{n+s-1} h_i \right)^2. \tag{26}$$

The average of $x_{n:s}^2$ over N_o origins taken from the same trajectory is given by the equation

$$\bar{x}_n^2 = \frac{1}{N_o} \sum_{s=1}^{N_o} \left(\sum_{i=s}^{n+s-1} h_i \right)^2. \tag{27}$$

(Note that we have not assumed that every point on the trajectory has to be used as an origin.) We now recall that this is the result of averaging over just one trajectory. The average for an infinite number of trajectories is

$$\left\langle \bar{x}_n^2 \right\rangle = \left\langle \frac{1}{N_o} \sum_{s=1}^{N_o} \left(\sum_{i=s}^{n+s-1} h_i \right)^2 \right\rangle$$

$$
\begin{aligned}
&= \frac{1}{N_o}\sum_{s=1}^{N_o}\left\langle\left(\sum_{i=s}^{n+s-1} h_i\right)^2\right\rangle \\
&= \frac{1}{N_o}\sum_{s=1}^{N_o} nd^2 \\
&= nd^2, \qquad (28)
\end{aligned}
$$

which is precisely the result obtained previously. It is perhaps gratifying to discover that the process of averaging over origins does not alter the expected result, but is it more accurate? To find out we must again calculate the variance, which is given by the same formula as before:

$$\bar{\sigma}_n^2 = \left\langle\left(\bar{x}_n^2\right)^2\right\rangle - \left\langle\bar{x}_n^2\right\rangle^2, \qquad (29)$$

where

$$\left\langle\bar{x}_n^2\right\rangle^2 = n^2 d^4, \qquad (30)$$

and

$$
\begin{aligned}
\left\langle\left(\bar{x}_n^2\right)^2\right\rangle &= \left\langle\left(\frac{1}{N_o}\sum_{s=1}^{N_o}\left(\sum_{i=s}^{n+s-1} h_i\right)^2\right)^2\right\rangle \\
&= \frac{1}{N_o^2}\left\langle\sum_{s=1}^{N_o}\sum_{t=1}^{N_o}\sum_{i=s}^{n+s-1}\sum_{j=s}^{n+s-1}\sum_{k=t}^{n+t-1}\sum_{\ell=t}^{n+t-1} h_i h_j h_k h_\ell\right\rangle. \qquad (31)
\end{aligned}
$$

Once again we can reduce this expression if we recognise that h_i, h_j, h_k, and h_ℓ, are uncorrelated when $i \neq j \neq k \neq \ell$ and the only terms that survive the averaging process are those with:

(a) $i = j = k = \ell$;

(b) $(i = j) \neq (k = \ell)$;

(c) $(i = k) \neq (j = \ell)$;

(d) $(i = \ell) \neq (j = k)$;

where we note that (c) and (d) give rise to equivalent terms, but (a) and (b) are distinct.

Applying the condition (a) we obtain

$$\left\langle\left(\bar{x}_n^2\right)^2\right\rangle_{(a)} = \frac{1}{N_o^2}\left\langle\sum_{s=1}^{N_o}\sum_{t=1}^{N_o}\sum_{i=max(s,t)}^{min(n+s-1,n+t-1)} h_i^4\right\rangle, \qquad (32)$$

in which the peculiar limits of the third summation specify the points shared by the two sub-trajectories originating at s and t respectively. This can be made more explicit if we separate terms for which $s = t$ from those for which $s \neq t$, giving

$$\left\langle\left(\bar{x}_n^2\right)^2\right\rangle_{(a)} = \frac{1}{N_o^2}\left\langle\sum_{s=1}^{N_o}\sum_{i=s}^{n+s-1} h_i^4\right\rangle + \frac{2}{N_o^2}\left\langle\sum_{s=1}^{N_o-1}\sum_{t>s}^{N_o}\sum_{i=t}^{n+s-1} h_i^4\right\rangle. \qquad (33)$$

The first term on the right deals with points on the *same* sub-trajectory only, while the second term deals with points *shared* between *different* sub-trajectories. It is now that we must recognise an important fact: if we are to calculate the true statistical error, we cannot admit into the calculation data that are correlated, which means we must use only those sub-trajectories that have no points in common. (Put another way, the average over origins must be an average over statistically independent quantities, as is the average over trajectories.) It is obvious that the second term is comprised entirely of such points and should be ignored. Thus the result of this part of the calculation is

$$\begin{aligned}
\left\langle \left(\bar{x}_n^2\right)^2 \right\rangle_{(a)} &= \frac{1}{N_o^2} \left\langle \sum_{s=1}^{N_o} \sum_{i=s}^{n+s-1} h_i^4 \right\rangle \\
&= \frac{1}{N_o^2} \sum_{s=1}^{N_o} \sum_{i=s}^{n+s-1} \left\langle h_i^4 \right\rangle \\
&= \frac{1}{N_o^2} \sum_{s=1}^{N_o} \sum_{i=s}^{n+s-1} d^4 \\
&= \frac{nd^4}{N_o}. \qquad (34)
\end{aligned}$$

Proceeding with condition (b) we obtain

$$\begin{aligned}
\left\langle \left(\bar{x}_n^2\right)^2 \right\rangle_{(b)} &= \frac{1}{N_o^2} \left\langle \sum_{s=1}^{N_o} \sum_{t=1}^{N_o} \sum_{i=s}^{n+s-1} \sum_{k=t}^{n+t-1} h_i^2 h_k^2 \right\rangle \\
&= \frac{1}{N_o^2} \left\langle \left(\sum_{s=1}^{N_o} \sum_{i=s}^{n+s-1} h_i^2 \right)^2 \right\rangle \\
&= \frac{1}{N_o^2} \left(N_o n d^2\right)^2 \\
&= n^2 d^4. \qquad (35)
\end{aligned}$$

In this case there is no difficulty with shared points, the sub-trajectories are independent.

Condition (c) gives

$$\begin{aligned}
\left\langle \left(\bar{x}_n^2\right)^2 \right\rangle_{(c)} &= \frac{1}{N_o^2} \left\langle \sum_{s=1}^{N_o} \sum_{t=1}^{N_o} \sum_{i=max(s,t)}^{min(n+s-1,n+t-1)} \sum_{j=max(s,t)}^{min(n+s-1,n+t-1)} h_i^2 h_j^2 \right\rangle \\
&= \frac{1}{N_o^2} \left\langle \sum_{s=1}^{N_o} \sum_{t=1}^{N_o} \left(\sum_{i=max(s,t)}^{min(n+s-1,n+t-1)} h_i^2 \right)^2 \right\rangle \\
&= \frac{1}{N_o^2} \left\langle \sum_{s=1}^{N_o} \left(\sum_{i=s}^{n+s-1} h_i^2 \right)^2 \right\rangle + \frac{2}{N_o^2} \left\langle \sum_{s=1}^{N_o-1} \sum_{t>s}^{N_o} \left(\sum_{i=t}^{n+s-1} h_i^2 \right)^2 \right\rangle. \qquad (36)
\end{aligned}$$

Once again we recognise that the second term right of the above equation is concerned with correlated origins, and so is discarded. Thus proceeding we obtain

$$\begin{aligned}
\left\langle \left(\bar{x}_n^2\right)^2 \right\rangle_{(c)} &= \frac{1}{N_o^2} \left\langle \sum_{s=1}^{N_o} \left(\sum_{i=s}^{n+s-1} h_i^2 \right)^2 \right\rangle \\
&= \frac{1}{N_o^2} \left(N_o \left(nd^2\right)^2 \right) \\
&= \frac{n^2 d^4}{N_o}. \qquad (37)
\end{aligned}$$

And finally, for condition (d) we have

$$\left\langle \left(\bar{x}_n^2\right)^2 \right\rangle_{(d)} = \frac{n^2 d^4}{N_o}, \tag{38}$$

which follows from its equivalence to (c).

Combining the results (34), (35), (37) and (38) into (31) and substituting with (30) into (29) gives the final result for $\bar{\sigma}_n^2$:

$$\bar{\sigma}_n^2 = \frac{2n^2 d^4}{N_o}. \tag{39}$$

From this we obtain the error as

$$\bar{\sigma}_n = \sqrt{\frac{2}{N_o}}\, nd^2. \tag{40}$$

So the error in the MSD calculated using a sum over *statistically independent* origins is just what might have been expected: the error for a single time origin, divided by $\sqrt{N_o}$. The error in an N particle average is then

$$\bar{\bar{\Sigma}}_n = \sqrt{\frac{2}{N_o N}}\, nd^2. \tag{41}$$

In 3 D, the corresponding results are

$$\begin{aligned} \left\langle \bar{r}_n^2 \right\rangle &= 3nd^2, \\ \bar{\sigma}_n &= \sqrt{\frac{6}{N_o}}\, nd^2, \\ \bar{\bar{\Sigma}}_n &= \sqrt{\frac{6}{N_o N}}\, nd^2. \end{aligned} \tag{42}$$

As before, it is noticeable that the error is directly proportional to the MSD, which provides the following useful mnemonic formula

$$\bar{\bar{\Sigma}}_n = \sqrt{\frac{2}{3N_o N}} \left\langle \bar{r}_n^2 \right\rangle \tag{43}$$

as a general formula for estimating the error in the MSD.

In the following section we test these formulae against a simulated random walk, but beforehand we need to make some additional comments.

Firstly, for a full trajectory comprised of M data points, then the maximum number of statistically independent origins for sub-trajectories of length n is

$$N_o = Int(M/n). \tag{44}$$

Thus the value of N_o appearing in the formulae for the error will differ according to where we are on the MSD curve. This will cause the error to grow more rapidly with increasing n than equations (43) and (42) at first suggest.

Secondly, while the formula (43) may be used to estimate the error in the general case, its use hinges on the assumption that the underlying diffusional motion is a random walk (i.e. the motions of the atoms are independent and uncorrelated). One cannot therefore quote the results of this formula as the error if the MSD is non-linear. The best that can be said if the curvature of the MSD is outside the bounds defined by these errors is that the MSD is *inconsistent* with the random walk model. This may be a significant observation in some circumstances.

Thirdly, we have been careful in our calculation of the MSD and the associated errors to use uncorrelated origins, meaning that for sub-trajectories of length n, the origins are taken n points apart. What would be the consequences of ignoring this requirement and simply using every possible data point on the full trajectory of M points to calculate these? It turns out that the MSD is the same (as one might have expected). The error calculated in this way however, is quite different. The derivation is tedious, but it follows the lines outlined above, and we simply quote the(3-D) results.

$$\begin{aligned} \left\langle r_n^2 \right\rangle &= 3nd^2, \\ \Sigma_n^* &= \frac{d^2}{N_o}\sqrt{\frac{n^3(4N_o' - n)}{N}}. \end{aligned} \tag{45}$$

(Where we have used the asterisk to distinguish this formula from (42).) In this case as many as $M - n$ points on the trajectory can be used as origins for a sub-trajectory of length n. Thus the relationship between the number of origins (N_o'), M and n is

$$N_o' = M - n. \tag{46}$$

We should also note that in the derivation of (45) we have made the assumption that $N_o' \geq n$. The equality $N_o' = n$ shows that $n = M/2$ is the longest sub-trajectory for which the analysis holds. This is not an unreasonable condition to impose, and it greatly simplifies the final formula.

The formula (45) is very different from (43), but what difference it makes in practice is best shown by an example in the next section.

Example simulation

As an example we have performed a random walk simulation using a system of 100 'atoms' with cubic periodic boundaries. The atoms had no mutual interaction and the trajectory of each is therefore completely independent. Each atom was initially placed in a random position in a 1 × 1 × 1 cubic cell from which it underwent 16400 random hops in 3 D. Each hop was ±0.1 units in the x, y and z directions simultaneously. The random number generator used for this purpose was that of Marsaglia *et al* [1].

The resulting MSD is presented Figure 1, with error bars calculated using formula (43) as an example. It is easy to see that the plot is linear and precisely the magnitude predicted by the formula (42).

In Figure 2 we present the estimated errors calculated by a number of different methods:

(a) the variance obtained from direct calculation (see below);

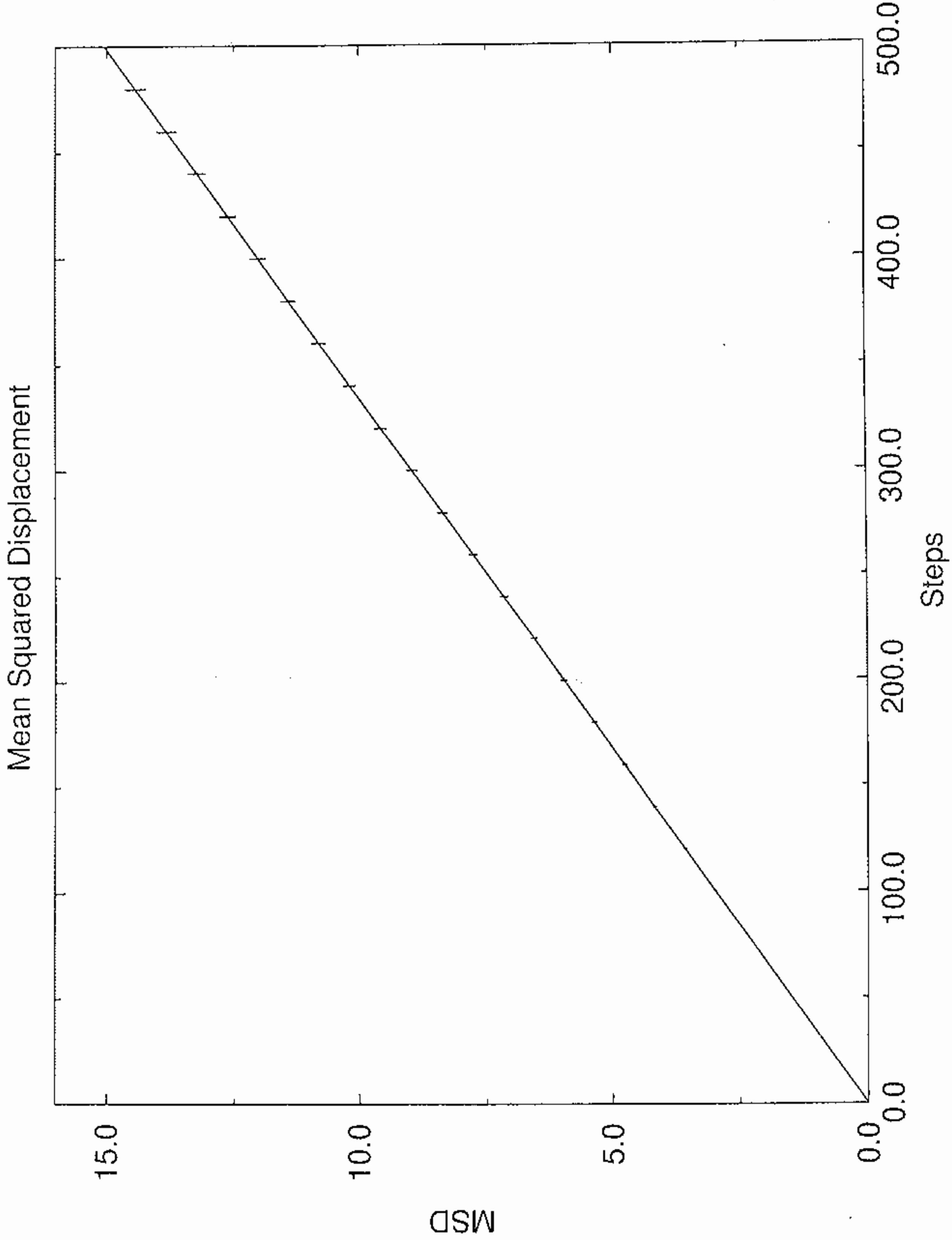
(b) the error calculated using formula (45);

(c) the error calculated using formula (42);

(d) the error calculated using the 'blocking method' [2].

In order to calculate the errors according to (a) and (d) the atom-averaged contributions to each point on the MSD arising from every possible time origin were stored - thus for example for the j-th point on the MSD, $16400 - j$ contributions were stored. The straightforward variance

Figure 1



of all these contributions constituted the error (a). In the case (d) the blocking method [2] was used to calculate the error. This method attempts to eliminate correlation from the data and at worst determines the *lower bound* of the error. In Figure 2 we have plotted the maximum error

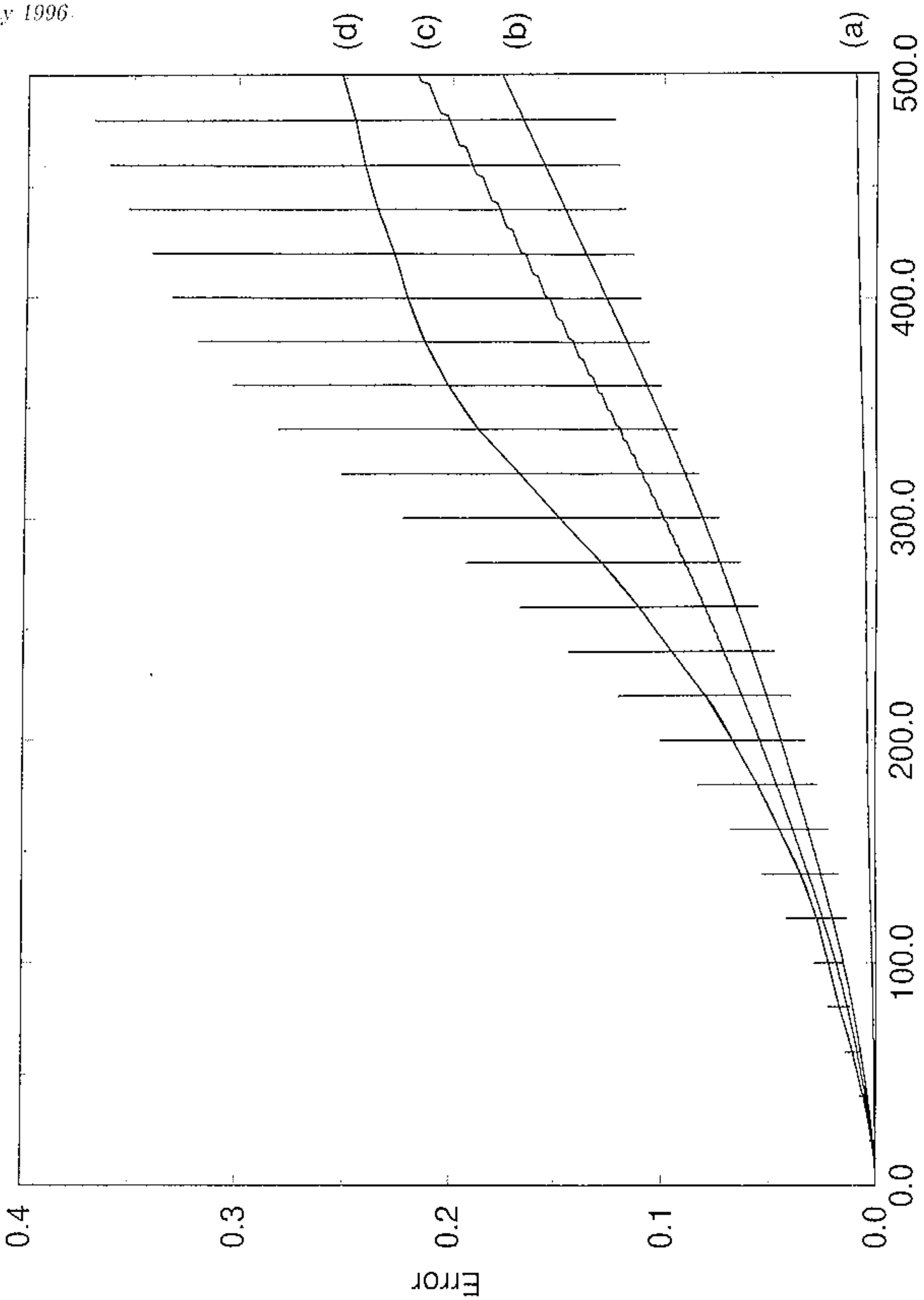


Figure 2

Estimated Errors

determined by this method along with the associated uncertainties plotted as error bars. (Using the maximum error is by no means the only option, but it has the merit of simplicity. An analytical fit of th error as a function of the 'blocking factor' would undoubtedly yield a better estimate.)

The results in Figure 2 show clearly that method (a) offers a very poor estimate of the error, as might be expected given its complete disregard of correlation. Methods (b) and (c) give very similar results, which at first glance is surprising, but a closer inspection of formula (45) reveals why. If is is assumed that the number N_o' dominates the formula, we can write the approximation:

$$\tilde{\Sigma}_n^* \simeq nd^2\sqrt{\frac{4n}{NM}}, \tag{47}$$

which closely resembles the formula (42), if the definition (44) is taken into account. By this reckoning, the formulae (42) and (45) should differ only by a factor of $\sqrt{3/2}$, as is borne out by Figure 2. We note that the error according to (42) is larger because it has no correlation in the origins.

Lastly, the error calculated by the blocking method is seen to be a similar order of magnitude as the theoretical estimates. One hoped for a closer agreement than this, but it must be noted that the estimate of the error is itself subject to considerable uncertainty [2]. These errors grow rapidly with the 'blocking index' as the error bars in Figure 2, for some representative points, reveal. Nevertheless the results here show that the error obtained in this way agrees with the theoretical estimate to within the calculated uncertainties. Thus it follows that the blocking method can be used to obtain the error in a general case (i.e. not just for random walks.)

Conclusions

We have shown that estimates of the error in the MSD are easily obtained from the random walk model. Simple formulæ have been provided. The key requirement in calculating the error is to eliminate, as far as possible, any correlation from the data. The blocking method is recommended as a model-independent method.

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Some further notes on linear bond angles

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Introduction

This note is a follow up to the article by Florian Müller-Plathe from the previous issue. [1] It describes an alternative procedure for dealing with the problem of linear bonds in molecular mechanics and dynamics programs, and also gives detail of the mathematics which is not included in the original literature reference. [2] Most of this article will be concerned with the case where the equilibrium angle ϕ_0 is not equal to π. The analysis is also extended to consider second derivatives of the energy function with respect to particle positions. This energy function has been included in the CCP5 static lattice simulation programs for a number of years.

For simplicity the valence bond angle deformation energy is assumed to be a function of the bond angle ϕ only: i.e. cross terms with the bond lengths are omitted.

Starting from this energy expression

$$E = f(\phi) \tag{48}$$

the first and second derivatives with respect to particle coordinates are found using the chain rule

$$\frac{\partial E}{\partial r_{i\alpha}} = \frac{dE}{d\cos\phi}\frac{\partial\cos\phi}{\partial r_{i\alpha}} \tag{49}$$

$$\frac{\partial^2 E}{\partial r_{i\alpha}\partial r_{j\beta}} = \frac{d^2 E}{d\left(\cos\phi\right)^2}\frac{\partial\cos\phi}{\partial r_{i\alpha}}\frac{\partial\cos\phi}{\partial r_{j\beta}} + \frac{dE}{d\cos\phi}\frac{\partial^2\cos\phi}{\partial r_{i\alpha}\partial r_{j\beta}} \tag{50}$$

where i, j, k label the three particles in the bond and α, β, γ the Cartesian axes. i is the label of the particle about which there is a bond angle ϕ.

First and second derivatives of $\cos\phi$ are easily found by the chain rule using bond length derivatives. Also, this part of the calculation does not depend on the functional form of $f(\phi)$. Thus:

$$\begin{aligned}\frac{\partial\cos\phi}{\partial r_{i\alpha}} &= 2\frac{\partial\cos\phi}{\partial r_{ij}^2}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}} + 2\frac{\partial\cos\phi}{\partial r_{ik}^2}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}} \\ &= 2\frac{\partial\cos\phi}{\partial r_{ij}^2}r_{ij\alpha} + 2\frac{\partial\cos\phi}{\partial r_{ik}^2}r_{ik\alpha}\end{aligned} \tag{51}$$

$$\begin{aligned}\frac{\partial^2\cos\phi}{\partial r_{i\alpha}\partial r_{j\beta}} &= \left\{\left[\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{ij}^2} + \frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{jk}^2}\right]2\frac{\partial\cos\phi}{\partial r_{ij}^2}\right\}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}} + 2\frac{\partial\cos\phi}{\partial r_{ij}^2}\frac{\partial}{\partial r_{j\beta}}r_{ij\alpha} \\ &\quad + \left\{\left[\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{ij}^2} + \frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}}2\frac{\partial}{\partial r_{jk}^2}\right]2\frac{\partial\cos\phi}{\partial r_{ik}^2}\right\}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}} \\ &= 4\frac{\partial^2\cos\phi}{\left(\partial r_{ij}^2\right)^2}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}} + 4\frac{\partial^2\cos\phi}{\partial r_{ij}^2\partial r_{jk}^2}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}} - 2\frac{\partial\cos\phi}{\partial r_{ij}^2}\delta_{\alpha\beta}\end{aligned}$$

$$
\begin{aligned}
&+4\frac{\partial^2 \cos\phi}{\partial r_{ij}^2 \partial r_{ik}^2}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{ij}^2}{\partial r_{j\beta}} + 4\frac{\partial^2 \cos\phi}{\partial r_{ik}^2 \partial r_{jk}^2}\frac{1}{2}\frac{\partial r_{ik}^2}{\partial r_{i\alpha}}\frac{1}{2}\frac{\partial r_{jk}^2}{\partial r_{j\beta}} \\
= \quad &-4\frac{\partial^2 \cos\phi}{\left(\partial r_{ij}^2\right)^2} r_{ij\alpha} r_{ij\beta} + 4\frac{\partial^2 \cos\phi}{\partial r_{ij}^2 \partial r_{jk}^2} r_{ij\alpha} r_{jk\beta} - 2\frac{\partial \cos\phi}{\partial r_{ij}^2}\delta_{\alpha\beta} \\
&-4\frac{\partial^2 \cos\phi}{\partial r_{ij}^2 \partial r_{ik}^2} r_{ik\alpha} r_{ij\beta} + 4\frac{\partial^2 \cos\phi}{\partial r_{ik}^2 \partial r_{jk}^2} r_{ik\alpha} r_{jk\beta} \qquad (52)
\end{aligned}
$$

Where

$$r_{ij} = r_i - r_j \qquad (53)$$

The other first and second derivatives follow similarly. Derivatives of $\cos\phi$ with respect to bond lengths are found using the cosine rule; the derivation is straightforward and is left to the reader. The results are given below.

$$2\frac{\partial \cos\phi}{\partial r_{ij}^2} = \frac{1}{r_{ij}r_{ik}} - \frac{\cos\phi}{r_{ij}^2} \qquad 2\frac{\partial \cos\phi}{\partial r_{ik}^2} = \frac{1}{r_{ij}r_{ik}} - \frac{\cos\phi}{r_{ik}^2} \qquad 2\frac{\partial \cos\phi}{\partial r_{jk}^2} = -\frac{1}{r_{ij}r_{ik}} \qquad (54)$$

$$4\frac{\partial^2 \cos\phi}{\left(\partial r_{ij}^2\right)^2} = \frac{1}{r_{ij}^3 r_{ik}} - \frac{3}{r_{ij}^2}\left[2\frac{\partial \cos\phi}{\partial r_{ij}^2}\right] \qquad 4\frac{\partial^2 \cos\phi}{\left(\partial r_{ik}^2\right)^2} = \frac{1}{r_{ij}r_{ik}^3} - \frac{3}{r_{ik}^2}\left[2\frac{\partial \cos\phi}{\partial r_{ik}^2}\right] \qquad (55)$$

$$4\frac{\partial^2 \cos\phi}{\left(\partial r_{jk}^2\right)^2} = 0 \qquad 4\frac{\partial^2 \cos\phi}{\partial r_{ij}^2 \partial r_{jk}^2} = \frac{1}{r_{ij}^3 r_{ik}} \qquad 4\frac{\partial^2 \cos\phi}{\partial r_{ik}^2 \partial r_{jk}^2} = \frac{1}{r_{ij} r_{ik}^3} \qquad (56)$$

$$4\frac{\partial^2 \cos\phi}{\partial r_{ij}^2 \partial r_{ik}^2} = -\frac{\cos\phi}{r_{ij}^2 r_{ik}^2} - \frac{1}{r_{ik}^2}2\frac{\partial \cos\phi}{\partial r_{ij}^2} - \frac{1}{r_{ij}^2}2\frac{\partial \cos\phi}{\partial r_{ik}^2} \qquad (57)$$

Difficulties arise with the cosine derivatives of the energy from equations (48) and (49), $\frac{dE}{d\cos\phi}$ and $\frac{d^2E}{d(\cos\phi)^2}$. These may be calculated as follows:

$$\frac{dE}{d\cos\phi} = \frac{dE}{d\phi}\frac{d\phi}{d\cos\phi} \qquad = -\frac{dE}{d\phi}\frac{1}{\sin\phi} \qquad (58)$$

$$\frac{d^2E}{d\left(\cos\phi\right)^2} = \frac{1}{\sin^2\phi}\left[\frac{d^2E}{d\phi^2} - \frac{dE}{d\phi}\frac{\cos\phi}{\sin\phi}\right] \qquad (59)$$

Problems will arise with the appearance of $\frac{1}{\sin\phi}$ and $\frac{1}{\sin^2\phi}$ in the denominators of the above expressions, and their behaviour as $\phi \rightarrow \pi$. Conventionally the explicit form of the function f will be

$$E = \frac{1}{2}k\left(\phi - \phi_0\right)^2 \qquad (60)$$

where k is the force constant and ϕ_0 is an assumed equilibrium angle. The overall derivative of E with respect to particle coordinates in this case may be either singular or indeterminate. A Cartesian axis system may be defined with respect to the directions of the bonds with x along ij, y in the plane of the three atoms and z normal to the plane. In this reference frame it is possible to show that the first derivatives with respect to particle positions all tend to finite limits as $\phi \rightarrow \pi$, i.e. the method used to calculate the first derivatives leads to an indeterminate. However, the second derivatives involving two z directions diverge. So there is a singularity in the function only in its second derivatives. This derivation is left to the reader.

It is possible instead to use a quartic function for E [2] of this form:

$$E = \frac{1}{4} A B^2 \tag{61}$$

where

$$A = \frac{1}{2} \frac{k}{(\phi_0 - \pi)^2} \qquad\qquad B = (\phi_0 - \pi)^2 - (\phi - \pi)^2 \tag{62}$$

This function has the following properties.

1. There is a minimum at $\phi = \phi_0$ (and also at $2\pi - \phi_0$)
2. The second derivative of E with respect to ϕ at this point is k, i.e. the same as the conventional expression.
3. There is a maximum, not a cusp, at $\phi = \pi$
4. As shown below all the first and second derivatives are easily calculable.
5. As $\phi \rightarrow 0$ difficulties arise with singularities, although this situation is unlikely to occur in real systems which are treated by molecular mechanics or dynamics.

The first and second derivatives will now be obtained.

$$\frac{dE}{d\phi} = -ABC \qquad \frac{d^2E}{d\phi^2} = A\left(2C^2 - B\right) \qquad \text{where} \quad C = \phi - \pi \tag{63}$$

The appearance of $C = \phi - \pi$ in the numerator make the calculation tractable. From (58),

$$\frac{dE}{d\cos\phi} = \frac{ABC}{\sin\phi} \tag{64}$$

Now

$$\begin{aligned}
\frac{C}{\sin\phi} &= -\frac{\phi - \pi}{\sin(\phi - \pi)} \\
&= -\frac{\sin^{-1} S}{S} \qquad \text{where} \qquad S = \sin(\phi - \pi) \\
&= -\frac{1}{S}\left[S + 1/6S^3 + 3/40S^5 + \frac{(2n)!S^{2n+1}}{2^{2n}(n!)^2(2n+1)} + \ldots\right] \qquad \text{for small S} \\
&= -\left[1 + 1/6S^2 + 3/40S^4 + \ldots\right] \\
&= -\left[1 + 1/6\sin^2\phi + 3/40\sin^4\phi + \ldots\right] \\
&= T_1
\end{aligned} \tag{65}$$

where the expansion for $\sin^{-1} S$ for small S has been used and may be calculated to the necessary accuracy. Hence

$$\frac{dE}{d\cos\phi} = ABT_1 \tag{66}$$

From (59),

$$\begin{aligned}
\frac{d^2E}{d(\cos\phi)^2} &= \frac{1}{\sin^2\phi}\left[A\left(2C^2 - B\right) - \frac{\cos\phi}{\sin\phi}(-ABC)\right] \\
&= \frac{A}{\sin^2\phi}\left[2C^2 - B\left(1 - \frac{C}{\tan\phi}\right)\right]
\end{aligned} \tag{67}$$

Now

$$
\begin{aligned}
& -\frac{1}{\sin^2\phi}\left[1-\frac{\phi-\pi}{\tan\phi}\right] \\
= & -\frac{1}{\sin^2(\phi-\pi)}\left[1-\frac{\phi-\pi}{\tan(\phi-\pi)}\right] \\
= & -\frac{1}{S^2}\left[1-\frac{\tan^{-1}T}{T}\right] \qquad \text{where} \qquad T=\tan(\phi-\pi) \\
= & -\frac{1}{S^2}\left[1-\frac{1}{T}\left(T-1/3T^3+1/5T^5+\frac{(-1)^nT^{(2n+1)}}{(2n+1)}+\dots\right)\right] \qquad \text{for small T} \\
= & -\frac{1}{S^2}\left[1-\left(1-1/3T^2+1/5T^4-\dots\right)\right] \\
= & -\frac{1}{S^2}\left[+1/3T^2-1/5T^4+\dots\right] \\
= & -\frac{1}{3\cos^2(\phi-\pi)}+\frac{\sin^2(\phi-\pi)}{5\cos^4(\phi-\pi)-\dots} \\
= & -\frac{1}{3\cos^2(\phi)}+\frac{\sin^2(\phi)}{5\cos^4(\phi)}-\dots \\
= & \; T_2
\end{aligned}
\tag{68}
$$

where the expansion for $\tan^{-1}T$ for small T has been used and may be calculated to the necessary accuracy. Hence

$$\frac{d^2E}{d\,(\cos\phi)^2}=A\left[2T_1^2+BT_2\right] \tag{69}$$

This procedure breaks down if the equilibrium angle ϕ_0 is π as in this case A is infinite. However, a similar procedure may be followed using a harmonic potential of the form

$$E=\frac{1}{2}k\,(\phi-\pi)^2 \tag{70}$$

Now

$$\frac{dE}{d\phi}=kC \qquad \frac{d^2E}{d\phi^2}=k \qquad \text{where} \qquad C=\phi-\pi \tag{71}$$

and

$$\frac{dE}{d\cos\phi}=-k\frac{C}{\sin\phi} \tag{72}$$

which may be expanded as above. Also

$$\frac{d^2E}{d\,(\cos\phi)^2}=\frac{k}{\sin^2\phi}\left[1-\frac{\phi-\pi}{\tan\phi}\right] \tag{73}$$

which again may be expanded in the same way as above.

References

[1] F. Müller-Plathe CCP5 Newsletter No. 44, July 1995 Page 40.

[2] M. Leslie Physica **131B** (1985) 145-150