

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 44

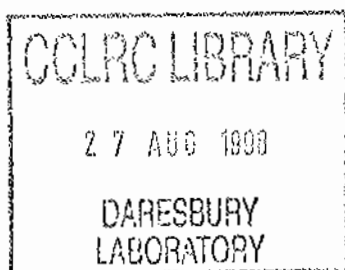
July 1995

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Editor: Dr. M. Leslie

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General News

CHAIRMANSHIP OF CCP5

Following a ballot by Email of UK members of CCP5, a new chairman and three new executive committee members have been elected. Professor M. Gillan has held the post of chairman for the past two and a half years. The executive committee members who have retired are

M. Allen (Physics, Bristol)
J. Goodfellow (Crystallography, Birkbeck)
W. Mackrodt (Chemistry, St. Andrews)

and the three members who will continue to serve are

G. Jackson (Chemistry, Sheffield)
G. D. Price (Geology, UCL)
S. Parker (Chemistry, Bath)

The result of the ballot is given below

CHAIRMAN		
Person nominated	Institution	Votes
M. Allen	Department of Physics, Bristol	23 (Elected)
J. Harding	AEA Technology, Harwell	5
N. Quirke	University of Bangor	13

EXECUTIVE COMMITTEE		
Person nominated	Institution	Votes
C. Care	Materials research Institute, Sheffield Hallam	21 (Elected)
M. Finnis	Queen's University, Belfast	25 (Elected)
J. Gale	Imperial College, London	15
R. Grimes	Department of Materials, Imperial College, London	13
J. Harding	AEA Technology, Harwell	19
M. Stapleton	MSI, Cambridge	23 (Elected)

FUTURE MEETINGS

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

TOPIC	DATES	LOCATION	ORGANISER
Structure and Order in Liquids	22-27 September 1995	Blankenberge	European Science Foundation / European Molecular Liquids group
Simulation of Molecular Materials	6 September 1995	Sheffield	Royal Society of Chemistry
Advanced Computer Simulation of Materials	20-22 September 1995	Daresbury	CCP5
Recent Advances in Molecular Simulation	6 December 1995	London	Royal Society of Chemistry

Full details of the ESF conference program may be obtained from

Dr. Josip Hendekovic, Email euresco@esf.c-strasbourg.fr
European Science Foundation,
1 quai Lezay-Marnésia, Tel. +33 88 76 71 35
67080 Strasbourg Cedex, Fax +33 88 36 69 87
France

CRAY NEWS

CCP5 participants are reminded that CCP5 has an annual allocation of Cray time at Rutherford Laboratory. This is available for the development of simulation programs which are of general use to the CCP5 community. Readers who wish to use some of this allocation should write to the CCP5 Secretary, Dr. M. Leslie.

INTEL NEWS

CCP5 also 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/44 directory: cd ccp5.newsletters/44
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.

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 publicize.

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.

Job vacancies

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

The section on other related information has been expanded, and I will add any further links notified to me.

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.

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).

REORGANISATION OF SCIENCE IN THE UK

Following reorganisation, Daresbury Laboratory is now part of "The Central Laboratory of the Research Councils", together with Rutherford Appleton Laboratory in Oxfordshire. The postal address is given below.

REQUEST FOR CONTRIBUTIONS

Contributors to the current issue

Our thanks go to:

Dr. M. Allen	Department of Physics University of Bristol
L. Kantorovich	Physics Department Keele University Keele, Staffordshire ST5 5BG, U.K.
F. Müller-Plathe	Laboratorium für Physikalische Chemie ETH-Zentrum Zürich Switzerland
D.M. Heyes	Department of Chemistry
P.A. Langston	University of Surrey
U. Tüüzün	Guildford GU2 5XH, UK
M. J. Gillan	Physics Department
F. Kirchoff	Keele University
J. M. Holender	Keele, Staffordshire ST5 5BG, U.K.

The deadline for contributions for the next 2 newsletters will be **1 September 1995** and **1 December 1995**. 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

RESEARCH CONFERENCE ON

<p style="text-align: center;">MOLECULAR LIQUIDS: Structure and Order in Liquids</p>
--

A European Research Conference run by the European Science Foundation in association with the European Molecular Liquids Group.

Blankenberge, Belgium, 22-27 September 1995

Chairman: R.M.Lynden-Bell (Cambridge)
Vice-Chairman: G.Palinkas (Budapest)

This meeting is the second Euroconference on Molecular Liquids held in association with the European Molecular Liquids Group. Although liquids are disordered on the large scale there is considerable order at the molecular scale. At this meeting there will be discussion of recent experimental and simulation results on local order in liquids and solutions. Both freezing into an ordered crystalline phase and glass formation are affected by the degree of local order and there will be sessions on these topics. The aim of the meeting will be to give a clear picture of the current state of theory and experiment and to highlight areas of future research. Participants are encouraged to contribute to the discussion and poster sessions.

Preliminary Programme

Order in Liquids

D.Frenkel	(Amsterdam):	Local order and molecular shape.
I.Cabaço	(Lisboa):	Neutron studies of benzene and perfluorobenzene.
MA.Ricci	(Roma):	The structure of water above its boiling point.
H.Versmold	(Aachen):	Investigation of local structure in fluids by light scattering.

Solvation

ADJ Haymet	(Sydney):	Calculating the dissociation of water.
E. Guardia	(Barcelona):	Computer Simulation of Ions in Solution.
H.Wengärtner	(Karlsruhe):	Liquid-liquid phase separation and criticality in electrolytes.
P.M.Rodger	(Reading):	Solvent induced structure of the solvation shell.

Freezing and Melting

D.Oxtoby	(Chicago):	Density functional theory of crystallization dynamics.
P.Madden	(Oxford):	Nucleation in hard sphere liquids.
C.Körber	(München):	Freezing of aqueous solutions - the advancing solid-liquid interface.
J-P. Hansen	(Lyon):	Studies of a sol-gel system.

Glass formation

L.Sjögren	(Göteborg):	Mode Coupling theory of glass formation.
D.Kivelson	(Los Angeles):	Supercooled liquids and glasses: A thermodynamic theory?
R.Vallauri	(Firenze):	Dynamics of supercooled liquids and glasses through normal modes.

SIMULATION OF MOLECULAR MATERIALS

Royal Society of Chemistry Autumn Meeting,
Sheffield,
6 September 1995.

Invited Speakers are:

Julian Clarke (Manchester)
Alejandro Gil (Sheffield)
Mike Klein (Pennsylvania)
Neal Skipper (University College, London)
Dominic Tildesley (Southampton)

There is space for short contributions.

George JACKSON Tel: (0114) 282 4781
Department of Chemistry Fax: (0114) 273 8673
University of Sheffield (0114) 275 0182
Sheffield S3 7HF E-Mail: G.Jackson@sheffield.ac.uk
United Kingdom

ADVANCED COMPUTER SIMULATION OF MATERIALS

The CCP5 Annual Meeting
20th - 22nd September 1995
Daresbury Laboratory, U.K.

The 1995 Annual Meeting of CCP5 has the theme of 'Advanced Computer Simulation of Materials'. Recent advances in computer power, particularly using parallel architectures, are enormously expanding the range of scientific problems that can be addressed by atomic-scale simulation. The meeting aims to review current research and to explore future possibilities. Ab initio and other quantum-based simulation methods as well as more traditional classical simulation techniques will fall within the scope of the meeting. There will be an emphasis on materials problems, but - as with all CCP5 Annual Meetings - general contributions will be welcome.

Invited speakers

The following speakers are confirmed. Details of the other invited speakers and titles of talks will be forwarded as they become available.

Dr. R. Jones,	Exeter University	The Importance of Combined Modelling and Experimental Studies for Characterising Semiconductors
Prof. U. Landman	Georgia Institute of Technology	To follow
Prof. R. Nieminen	Helsinki University of Technology	Defects, Interfaces and Metastability in Compound Semiconductors
Prof. D. G. Pettifor	Oxford University	To follow
Prof. K. Schwarz	Technical University Vienna	Molecular dynamics simulations of methanol in zeolites

Organising Committee

M. J. Gillan
M. Leslie

G. D. Price
P. J. D. Lindan

Further information may be found on WWW at
<http://www.dl.ac.uk/CCP/CCP5/meetings/1995.html>
or by contacting:

Dr. M. Leslie	Email	m.leslie@dl.ac.uk
CCL Daresbury Laboratory, Daresbury Warrington WA4 4AD UK	Tel. +44 (0) 1925 603334 Fax +44 (0) 1925 603634	

The meeting will start at 14.00 on Wednesday 20 September and finish at 16.00 on Friday 22 September. The closing date for registration and receipt of contributed papers is 31 August 1995.

REGISTRATION FORM

Advanced Computer Simulation of Materials

Daresbury Laboratory, UK

September 20th. - September 22nd 1995

SURNAME: (Prof , Dr , Mr , Mrs , Miss , Ms *) Male/Female*
(BLOCK letters please). * Please delete INITIALS:

ADDRESS:
.....
.....
.....
.....

Tel Fax

Electronic Mail Address

Accommodation will be on site at Daresbury Laboratory. The price below for accommodation will be limited to the first 50 delegates only in the order that registration and payment is received. Additional delegates will need to be accommodated in local hotels and will have to pay a supplement which will be about 15.00 pounds per night. Delegates wishing to stay on the night of September 19th. may also need to be accommodated in a local hotel. The accommodation fee includes the price of breakfast on the 21st. and 22nd. of September. Both hot and cold lunches may be purchased on all three days in the laboratory restaurant. Dinner on the 20th. and, for those not attending the Conference Dinner, on the 21st., may also be purchased at the restaurant. Please indicate if you have any special requirements (Diet, disability)

.....

CONFERENCE COSTS

(Prices in Pounds Stirling)

- 1) Conference Fees (please circle as appropriate) (Graduate students will need to send a supporting letter from the supervisor to qualify for the discount)
- | | | |
|------------------|-----|-------|
| Non-Student | £40 | |
| Graduate Student | £0 | |

- 2) Accommodation on night of Wednesday September 20th. (Bed and Break- £23.00
fast only)
- 3) Accommodation on night of Thursday September 21st. (Bed and Break- £23.00
fast only)
- 4) I will require additional nights accommodation on (please circle as
appropriate)
September 19th.
September 22nd.
(Payment for additional nights may be made at the conference)
- 5) Conference Dinner on Thursday 21st. September £15.00

I enclose a cheque for total £ (Payable to "Daresbury Laboratory").

CONFERENCE PRESENTATIONS

I would like to submit a presentation Yes/No*

I would prefer an ORAL/POSTER* presentation

Oral presentations will be 30 minutes including time for questions. Posters will be presented on display boards measuring 90cm x 115 cm.

TITLE

Lead author:

Affiliation:

Co-author(s):

Affiliation(s):

An abstract must be sent at the time of registration by electronic mail in an electronic format. The preferred formats are either LATEX or WORD. (If you use WORD, please send the file in RTF format). We may be able to accept other word processor formats; please contact the organisers. The abstracts will be published as part of an issue of the CCP5 quarterly newsletter. Delegates are also encouraged to submit a longer account of their work for publication in the newsletter. Postscript diagrams may also be accepted.

TRAVEL ARRANGEMENTS

I will arrive by car Yes/No* Registration number

Please send a map Yes/No*

If you are travelling by rail, the closest stations are Runcorn and Warrington Bank Quay on the main line from London, Euston. By air, Manchester airport is 15 miles away from the laboratory. Please return by 31 August to Dr. M. Leslie, CCL Daresbury Laboratory, Warrington, WA4 4AD, UK.

Royal Society of Chemistry: Theoretical Chemistry Group
Statistical Mechanics and Thermodynamics Group and
EPSRC Collaborative Computational Project No. 5:
Computer Simulation of Condensed Phases

THEORETICAL CHEMISTRY DAYS No. 3: RECENT ADVANCES IN MOLECULAR SIMULATION

A half-Day meeting to be held in the Department of Chemistry, University College, London on
Wednesday 6th December 1995, from 13.30 to 17.10.

Programme

1330	Chairman's Introduction	Professor J. N. L. Connor	(University of Manchester)
1340	Keynote Lecture: Molecular Simulation: Recent Advances.	Professor D. J. Tildesley	(University of Southampton).
1430	Simulation of Polymers: Recent Advances.	Professor J. H. R. Clarke	(UMIST).
1455	Tea		
1530	Plenary Lecture: Molecular Dynamics from First Principles: Recent Advances.	Professor R. Car	(Ecole Polytechnique Federale de Lausanne, Switzerland).
1620	Simulation of Stretched Crystals: Recent Advances	Professor R. M. Lynden-Bell	(Queen's University, Belfast).
1645	Simulation of Liquid Crystals: Recent Advances	Doctor M. P. Allen	(University of Bristol).

1710 Close

Organiser:

Professor J. N. L. Connor, Department of Chemistry, University of Manchester, Manchester M13
9PL.

Local Organiser:

Doctor Sally Price, University College London.

Post Doctoral Position
Oxford University Department of Earth Sciences
Postdoc in ab-initio Simulations of Alumino-Silicates

We are seeking to fill a position for a postdoctoral research assistant to work on Earth materials science problems involving alumino-silicate and oxide minerals. The work will use total energy pseudopotential methods and will form part of a program of study of order/disorder and water/mineral interaction processes, though there will be some flexibility regarding the specific problems to be tackled. The Earth Sciences department has substantial local computing equipment, although some parts of the work may require the use of national supercomputing facilities.

The exact duration will depend on which salary point the appointment is made at and therefore on the age and experience of the candidate, but will be approximately 16 months. The post will begin at a date in the near future by arrangement.

Candidates must have a sound theoretical background and a PhD in a relevant discipline. Experience with electronic structure calculations will be an advantage. To apply, please send your CV and letter of application to

Professor J. D. C. McConnell
Department of Earth Sciences
Parks Road
Oxford OX1 3PR

or by email (PostScript or LaTeX are acceptable but PLEASE make sure the document is portable!) to me, "Keith.Refsor@earth.ox.ac.uk".

Daresbury Laboratory
Modelling of the Physical Properties and Catalytic Activity of Zeolite
Materials

Applications are invited for a two-year fixed-term position within the Theory and Computational Science (TCS) Division at the CCL Daresbury Laboratory, Warrington, UK.

TCS Division works closely with experimentalists using the Synchrotron Radiation Source, with theoretical groups in Universities, and with industry. The Division is a recognised leader in the scientific exploitation of high performance computing; strong emphasis is placed on the development of effective parallelised scientific applications codes.

The position, which is part of a collaboration with Unilever Port Sunlight Laboratory, will involve the development and application of techniques for the modelling of the physical properties and catalytic activity of zeolite materials. Classical simulation, solid-state and molecular quantum-mechanical (HF, DFT) techniques will be used, with emphasis on models that link a quantum mechanical treatment of the active site with a classical molecular mechanical (MM) treatment of region of the surrounding zeolite lattice. With such models, it is possible to treat the active site with high-level quantum chemical methods, which are capable of dealing with the breaking of chemical bonds, while the long-range electrostatic effects of the zeolite framework and the flexibility of the lattice are accounted for using much cheaper classical approximations.

The appointee to the position will be expected to contribute both to the development of the methods required and in the application of these methods to problems of interest. The development aspect of the work will require the modification of existing codes and the writing of new

code modules as required, together with the design of test problems to validate and calibrate the new methods. The applications work will involve both the re-examination of problems from the experimental and computational literature using new methodologies, as well as work in close collaboration with Unilever on problems of more direct commercial relevance.

The successful candidates will be expected to have a PhD in a relevant area of computational science, with preference will be given to those candidates with experience in quantum chemistry of molecules and/or solid-state materials.

The salary will be in the range 13 025 - 18 911 pounds sterling depending on qualifications and experience. The laboratory operates a no smoking policy.

Further information may be obtained from Dr P. Sherwood (phone +44 (0)1925 603553, FAX +44 (0)1925 603634, email p.sherwood @dl.ac.uk), Dr N. M. Harrison (+44 (0)1925 603334 n.m.harrison @dl.ac.uk) or, at Unilever, Dr Steve Loades (s_loades @urpsl.co.uk, +44 (0)151 471 3191)

Application forms may be obtained from:

The Personnel Officer,
Daresbury Laboratory,
Warrington,
Cheshire, WA4 4AD.
Phone +44 (0)1925 603467 (24 hour answering service)

quoting reference DL321. The closing date for applications is Friday 11th August, 1995.

Daresbury Laboratory is part of the Council for the Central Laboratory of the Research Councils.

METHODS IN MOLECULAR SIMULATION

CCP5 Spring School 27-31 March
Mike Allen

The general format of this year's Spring School was similar to that adopted last year, with minor changes following the feedback we obtained at that time. As before, the event was held at Southampton University, with lectures in the Chemistry Department each morning, and a 'guest seminar' after lunch (plus a couple of extra seminars in the morning). The principal lecturers were Mike Allen (Bristol), Julian Clarke (UMIST) and Dominic Tildesley (Southampton), and guest speakers were Steve Parker (Bath), Tim Forester (Daresbury), Clive Freeman (Biosym), David Edwards (York), Jeremy Walton (NAG), Mike Gillan (Keele) and Dave Kofke (Buffalo). Hands-on computer workshops took place in the afternoon at the University's Data Visualization Suite; these were linked as much as possible to the material covered in lectures and seminars that day. Two poster sessions were held, to allow the students to explain in detail their research interests and the simulation techniques of most interest to them, and there was a round-table question and answer session on the last day which generated much discussion.

The majority of the students came from U.K. institutions, with one or two from continental Europe, and one from Canada. The course began with lectures and workshops on basic and advanced techniques in Monte Carlo and molecular dynamics, and then moved on to topics in parallel simulation methods, molecular modelling and scientific data visualization. Towards the end of the week, more specialized subjects were introduced: nonequilibrium methods, phase transitions, ab initio MD. For each afternoon, a selection of exercises was provided: enough to give a reasonable choice of new material, while still permitting the student to look back at work from earlier in the week. For almost every exercise, a 'solution' was provided about two-thirds of the way through the afternoon. This allowed students to look at problems that they did not wish, or have time, to attempt, as well as being able to check their own work. The early part of the week concentrated on programming and simulation algorithms using small programs and simple models, but the DL-POLY package was introduced on Tuesday, and molecular modelling using the Biosym suite on Wednesday. Collage (NCSA) was used to visualize large data sets, and Iris Explorer (SGI/NAG) was used to illustrate the modular approach to visualization. Finally, on the Friday, there was an exercise involving the progressive introduction of Fortran-90 constructs into a Fortran-77 molecular dynamics program.

This was an ambitious and intensive programme for both students and lecturers. The computer system worked almost faultlessly (a server failure caused one short-term glitch), and the software was also extremely reliable. After the course the students were allowed to copy their work, the original exercise programs, and the solutions to all the exercises, back home from a Web site set up at Bristol.

At the end of the course, the students filled in, anonymously, a set of questionnaires. These will provide some useful feedback and information essential to the planning of future courses, and they will be studied in detail. The overall tone was very positive indeed: all the students seem to have enjoyed their week, and gained something from it. The introduction of poster sessions and the round table were especially well received, while the food and accommodation at Glen Eyre hall of residence also met with general approval.

I would like to thank my co-lecturers, and all the 'guest seminar' speakers, for the effort they put in to present all this material in an interesting and informative way. Dominic Tildesley also deserves thanks for handling registration and all the domestic arrangements. Southampton University provided the lecture theatre and visualization suite free of charge. We could not have mounted

this course without the assistance of Southampton Computer Centre staff, notably Ian Hardy, who helped set things up on the DV Suite machines, and worked behind the scenes during the week to keep things running smoothly; Sean Jordan and Martin Bates also helped during the workshops. Thanks are also due to Allan Price, Clive Freeman and Glenn Mills of Biosym for allowing us to use their software, and (to Clive and Glenn) for coming to Southampton to supervise its use. We are grateful to Robert Morell of NAG for allowing us to use their Fortran-90 compiler. Finally, thanks to the students, who attended every lecture and workshop session, put on an impressive display of posters, and showed plenty of enthusiasm and good humour.

CCP1/CCP5 WORKSHOP
'Modelling of Localised States in Condensed Matter'
Keele University, 14th - 16th June 1995

In many different condensed-matter problems, one is interested in the properties of a highly localised group of atoms occupying a region perhaps less than 10 Å across, but which is strongly influenced by the surrounding medium. Examples include defects and impurities in crystals, molecules interacting with solid surfaces, and chemically reacting molecules in solution. The most effective strategy for tackling such problems theoretically should be to use an accurate quantum treatment for the small number of atoms of direct interest, and a simpler phenomenological treatment of the environment. However, the problem of matching the two very different kinds of treatment is highly non-trivial, and raises fundamental questions. This is the celebrated 'embedding problem'.

The three-day workshop, jointly supported by CCP1 and CCP5, brought together experts from a number of different fields, with the aim of comparing and analysing approaches to the embedding problem, and discussing ways of overcoming the difficulties that still exist. The following pages reproduce the workshop programme and the abstracts of the invited talks and the posters.

The organisers deliberately set out to invite participants from different backgrounds and with different research interests, and this led to extremely lively exchanges of views during the meeting. The participation of computational solid-state physicists, materials chemists and biochemists gave an almost unique opportunity to compare quantum chemistry methods based on the Hartree-Fock approach and solid-state methods based on density-functional theory, as well as semi-empirical and model-based methods, in the context of the embedding problem.

The meeting was generally agreed to have been highly successful. An obvious success was the setting up of entirely new contacts between research groups, which in some cases had been unaware of each other's existence. The opportunity to gain new perspectives on familiar problems from the vantage point of researchers in different fields was also invaluable. The meeting was also a chance to thrash out technical problems both in the formal discussion periods and outside the meeting. The organisers thank CCP1 and CCP5 for the financial support that made the workshop possible.

C. R. A. Catlow
M. J. Gillan
L. N. Kantorovich
A. L. Shluger

Combined density functional and configuration interaction method for the electronic structure of solids with impurities

I.V. ABARENKOV[†], V.L. BULATOV, R. GODBY, V. HEINE, M. PAYNE, A.V. TITOV,
I.I. TUPITSYN

[†]*Physics Department, St. Petersburg University, St. Petersburg 198804, Russia.*

The case of the open shells impurity atoms or molecules is considered.

The importance of correlation effects is discussed, and the relevant computational methods are briefly reviewed with examples from atoms and small molecules calculations.

The Local Density Approximation (LDA) can not be immediately applied for this case, as the wave function mixing several or many determinants is essential. The Many-Configuration Self-Consistent-Field (MC-SCF) method appropriate for the open shells atoms cannot be applied to a solid as it stands because the computing time scales very badly with the system size. The hybrid embedding scheme is proposed to incorporate the MC-SCF method for the impurity within solid state calculations done with LDA.

The idea is to introduce the intermediate region - a buffer (B) between the impurity (I) and the rest of the solid (S). The buffer should contain a comparatively small number of atoms so that MC-SCF calculation of the I+B can be practical. At the same time the one determinant wave function should make a good approximation to the buffer to enable the LDA calculations of B+S. The influence of S onto I+B is simulated with the embedding potential to be found from B+S calculations.

A simple model system was considered consisting of four pseudo-atoms, two one-electron pseudo-atoms representing I, one two-electron pseudo-atom representing B, and another two-electron pseudo-atom representing S. This system was calculated with LDA, HF, and MC-SCF methods. The local embedding potential was constructed and the proposed method was tested in comparison with the isolated I+B cluster approximation.

A hybrid shell-model/quantum mechanical treatment of defects in ionic crystals

A.H. HARKER

552 Harwell, Didcot, Oxon, OX11 0RA

The ICECAP computer code adopts a mixed model for defects in ionic crystals, in which a quantum mechanical core region is embedded in a semi-classical shell model of the surrounding crystal. This talk will discuss the reasons for the choice of this hybrid model, and describe the way in which the interface between the quantum mechanical and semi-classical models is implemented in the code.

Some results will be presented which demonstrate the internal consistency of the model, and examples will be given of the application of the model to a variety of defect systems and processes.

The EMBED project: recent results, problems and prospects

CESARE PISANI

*Department of Inorganic, Physical and Materials Chemistry, University of Turin, via Giuria 5,
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The EMBED project is being carried on for about eight years now by the Group of Theoretical Chemistry in Torino with several collaborations (Kantorovich, Catlow, Saunders, Sulimov, Allouche, Hess, Birkenheuer). Its aim is to produce efficient ab-initio computational techniques for the study of local electronic structures associated with point defects in otherwise perfect crystals. It is characterized by both the development of theories (based on the so-called perturbed-cluster (PC) approximation) and their implementation in a general-purpose computer program, whose first public version (EMBED93) has recently appeared [Pisani, Corà, Nada and Orlando, *Comp. Phys. Comm.* 82, 139 (1994)]. Because of this connection, the machinery employed for solving the fundamental equations is largely determined by the method adopted for determining the host crystal wavefunction. Our choice has been to refer to the Hartree-Fock LCAO technique as implemented in the CRYSTAL92 program [Dovesi, Saunders and Roetti, University of Torino and DRAL (1992)]. This communication illustrates the state of the project, its problems and prospects. Some recent results obtained with the use of the EMBED93 program (hydrogen adsorption and solution in lithium, ammonia protonation in zeolites, structural and chemical defects in ordinary ice) confirm that the approximation underlying the PC theory is well justified in many important cases, and that the code can provide useful results with acceptable computer requirements. On the other hand, the need for important improvements in both theory and algorithms has become evident. There are essentially two types of problems. Firstly, how to introduce simple corrections for taking into account changes induced by the defect in the 'external space' (flow of charge to or from the defect region, polarization of the medium, long-range atomic relaxation, etc.) which are disregarded in the basic PC theory. Secondly, how to make the code more efficient (reasonable initial guesses to accelerate convergence of the SCF process, and the use of pseudopotentials for heavy atoms) and more powerful (estimate the correlation correction to the defect formation energy, and the possibility to study open-shell and multi-determinantal configurations in the cluster, corresponding both to the defect ground state and to local excitations). Work is in progress on some of these points, and the solutions proposed are briefly discussed.

Unrestricted Hartree Fock Method for local defects in crystals and at their surfaces

UWE BIRKENHEUER

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In recent years the EMBED program has become a powerful tool for studying localised defects in crystals and adsorbates on well-ordered periodic surfaces. It is based on the Hartree-Fock method to determine the electronic structure of the defect systems under study. Up to now only the restricted Hartree-Fock technique has been implemented. Many important defects like core holes, open shell adsorbates and the description of bond breaking processes undergoing in the proximity of catalytic active surfaces, however, require an open-shell treatment. In the present communication the perturbed cluster equations underlying the EMBED program are presented and their extension for an unrestricted or restricted open-shell Hartree-Fock description of the electronic structure near the defect is discussed. The technique adopted to calculate the defect formation energy without subtracting two in principle infinite quantities and the impact of the open-shell method are presented too. To arrive at a self-consistent open-shell solution of the perturbed cluster equations during the SCF procedure several techniques have been introduced to properly initialise and control the parts of the density matrices recalculated in each SCF cycle. Preliminary results on typical open-shell defect systems are presented to demonstrate the range of applications which are now available with the new UHF option of the EMBED program.

The Relation Between Embedding and Linear Scaling

M.J. GILLAN AND E. HERNANDEZ

Physics Dept., Keele University, U.K.

In the last five years, there has been rapid progress in developing linear-scaling techniques for electronic-structure calculations - techniques in which the computer effort increases only linearly with the number of atoms. Many of these techniques are based either explicitly or implicitly on the approximation that the density matrix vanishes when the separation of its spatial arguments exceeds a chosen cut-off. But the embedding problem, if formulated in terms of the density matrix, also leads to the requirement that the latter be localized. This relation between embedding and linear scaling strongly suggests that recent linear-scaling ideas will be helpful for the embedding problem. The talk will outline an ab initio linear-scaling technique due to the present authors, and will suggest how it could be applied to the embedding problem.

New Tight-Binding Method (Molecule as Defect of Hilbert Space)

V.A. TELEZHKIN

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The main idea of the method consists in the 'embedding' of the finite basis set of localized functions into the space spanned on the plane waves basis (Free-Electron Continuum); the potential \hat{V} is assumed to have nonzero matrix elements only over that set. The problem is quite similar to one of the 'embedding' of a defect region into crystal but the fact that as a rule only the part of the spectrum below the level of vacuum will be of interest to us simplifies our following reasoning. Resonance states can be also described in this method as against the standard quantum chemical procedure.

In the new method a finite set of basis orbitals $\{N\}$ is chosen and eigenvalues ϵ and eigenvectors $|N\rangle$ are found from the standard one-particle Hamiltonian H projected on to this basis set

$$\hat{H}_N = \hat{P}_N \hat{H} \hat{P}_N = \hat{T}_N + \hat{V}_N \quad (1)$$

where \hat{V}_N is the self-consistent potential including coulomb and exchange interactions and \hat{P}_N is the orthogonal projector on to the subspace $\{N\}$. Inclusion of continuum states can be now realized by transforming from \hat{H}_N in eq.(1) to the Hamiltonian \hat{H}_1 ,

$$\hat{H}_1 = \hat{T} + \hat{V}_N \quad (2)$$

If the one-particle spectrum of the Hamiltonian \hat{H}_N is found by application of the Rayleigh-Ritz variational method then the spectrum of \hat{H}_N can be obtained by the degenerate perturbation technique of Lifshits or (equivalently) from the Kohn-Rostoker variational principle $\delta\Lambda = 0$ for the functional

$$\Lambda = \langle \psi_N | \hat{V}_N - \hat{V}_N \hat{G}_N^0 \hat{V}_N | \psi_N \rangle \quad (3)$$

where \hat{G}_N^0 is the projection of the free-electron Green function (or resolvent) for the kinetic energy operator $G^0 = (\epsilon - T)^{-1}$. This GF method is analogous to the embedding problem which occurs in the discussion of crystal defects in solid state physics but here the whole Hilbert space plays the role of the host crystal.

A complete exposition of the method, including mathematical details and computational peculiarities, such as the solution of the nonlinear eigenvalue problem and the estimation of Green-function matrix elements over Gaussian functions is given in ref.[1].

In ref.[2] we propose to estimate the total energy of a system in the new (Green-function) method as

$$E_{GF} = E_{HF} + 2 \sum_i (\epsilon_i^{GF} - \epsilon_i^{HF}) \quad (4)$$

where the summation is carried out over valence states. It seems that this supposition is reasonable for comparatively good bases, when 'charge' inside the given basis set $Q_N = Tr \rho_N$ converges to the number of electrons. It is possible that similar formulae will be true for methods which take into account electron correlation because the correction (4) concerns only the one-particle kinetic energy operator and does not involve the potential, which can be included in the correlation correction too.

Analysis of different ground state results of atoms and simple molecules allows us to formulate a semi-empirical correction to the one-particle energies

$$\epsilon = \frac{(2\epsilon_{GF} + \epsilon_{HF})}{3} \quad (5)$$

Using this correction improves the accuracy of the energy estimate by an order of magnitude. It seems that the correction must have a theoretical foundation which is so far not clear. A similar correction for the total energy can be proposed by the combination of eq.(4) and (5).

The GF method is more suitable than the HF one for the description of intermolecular interactions (see ref.3), including hydrogen bonding, because it gives the correct asymptotic behaviour of the tail of a wave function in the intermolecular space. In this space, where the potential is varying slowly, a corrected wave function will really be

$$\psi \sim \int G_N^0(\epsilon, \vec{r} - \vec{r}') \psi_N(\vec{r}') d\vec{r}'$$

where ψ_N is the HF wave function from the basis $\{N\}$. If $r \gg r'$ (ψ_N is localized at the origin of one of the molecules) then the asymptotic behaviour of ψ coincides with that of G^0 which corresponds to the correct quantum mechanical value

$$\frac{\exp(-\sqrt{-2\epsilon}r)}{r}$$

Thus the GF basis set obtained is corrected in the appropriate direction and we have to expect essentially a decrease in the basis-set superposition error which arises because the dimer basis set is larger than that of each monomer and this produces an artificial lowering of the dimer energy relative to that of the separated monomers.

REFERENCES

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Embedding Calculations based on Ab Initio Pseudopotential Techniques

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Plane-wave, pseudopotential methods, based on density functional theory, have become established as one of the most important techniques for the first principles simulation of condensed matter. Embedding methods have the potential to considerably extend the scope of current pseudopotential calculations. To illustrate this I will focus on one particular problem, the recovery of information about core states and true, as opposed to pseudo, valence wavefunctions from a pseudopotential calculation. The motivation is that an ab initio simulation of the core will enable us to calculate the fully relaxed crystal charge density (which can be compared with accurate structure factor determination by X-ray and electron diffraction) and to calculate properties which depend on the density near the nucleus, such as hyperfine interactions in magnetic systems.

The basic idea is to construct an embedding potential, using Green's function matching techniques, on a sphere around an atom which then acts as a boundary condition in a fully self-consistent atomic calculation inside the sphere. The main technical problem is the accurate calculation of the Green's function on the embedding sphere from a plane-wave representation. A number of

difficulties will be discussed, including completeness of the spectral representation and the need for accurate Brillouin zone integration. Results will be presented for the embedding potential and core reconstruction for the test case of bulk fcc Al.

The construction of accurate Green's functions from a plane-wave, pseudopotential calculation have many other applications and a number of these will be discussed, in particular in the context of surface embedding problems.

A combination of the Quantum-Mechanical Perturbed-Cluster and the Semiclassical Mott-Littleton techniques for the study of charged defects in crystals.

F. CORÁ†, C.R.A. CATLOW, M. LESLIE, R. NADA, R. ORLANDO, C. PISANI AND V.R. SAUNDERS.

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This talk focuses on defects that introduce long-range perturbations in the host crystal. Reference is made to the Perturbed-Cluster (PC) theory, presented earlier in this workshop by Prof. Pisani. The defect system is partitioned in a local zone, C, and an outer zone, D. In the standard PC theory both regions are treated quantum-mechanically (QM), with the approximation that the perfect crystal solution is used in zone D. The effects introduced by this approximation are now examined, and different levels of theory are proposed to overcome the limitations. In the case of charged defects, the long-range polarisation induced in the surrounding medium can be evaluated and included in the embedding procedure by means of a semiclassical (SC) treatment. This is based on the shell-model and on the Mott-Littleton theory. A new program, EMBRION, is being implemented, that includes this feature. In the new technique, at each cycle of the SCF procedure the polarising potential, V_q , created by the defect is computed with the QM method. The SC technique is used to describe how the ions in zone D polarise and displace under the effect of V_q , and how the field generated by zone D changes with respect to perfect crystal. This information is in turn used to correct the local QM Hamiltonian. The energetic contribution arising from the polarisation of the outer medium is also computed within the SC treatment. In the method proposed, the SC description of the outer zone is coupled to, and does not replace the QM. The requirements to make the two descriptions consistent are analysed.

Green function methods for surface state scattering studies and related problems

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As experimental surface science undergoes a transition from analysis to synthesis, theoreticians are posed new and challenging problems. Highlighting this are recent experiments which have demonstrated the controlled formation of surface structures, built atom-by-atom with the STM. Typical structures are comprised of c. 100 atoms, and cover an area of c. 1000 atoms. This is well beyond the capabilities of conventional electronic structure methods.

A particular feature of the experimental studies has been the observation of lateral standing electron waves on various surfaces of the noble metals, arising from the scattering by adatoms of electrons in Shockley surface states. Studies of this phenomena could offer insight into the two-dimensional electron gas, many-body effects at surfaces, electron localisation, and other fundamental and practical issues.

I will discuss recent progress on the development of theoretical methods for these problem. These include approaches based upon embedding techniques as well as multiple-scattering Green function calculations. The advantages and disadvantages of these approaches will be discussed, both in terms of ease of calculations, such as accommodating the large length-scale fixed by the surface state wavelength, and interpretive facility. Both approaches will be illustrated with recent results.

Simplified Electron Energetics in Car-Parrinello MD.

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In order to circumvent the computational cost of a full *ab-initio* description of the electronic structure in large-scale applications of Car-Parrinello MD, we have developed simplified representations of the electronic structure in the C-P scheme which are applicable to particular physical systems. These schemes could provide suitable embedding *environments* for more general quantum calculations since they are derived from the same well-specified electronic energy functionals which are used in the full quantum calculations.

For metals we use an LDA formalism which involves the use of the electron *density* as the basic variable and avoids the introduction of orbitals [*J. Phys. Condens. Matt.*, **5**, 3221 (1993)]. The form of the kinetic energy functional is chosen to incorporate several exact limits (uniform system, linear response and rapidly varying density) while the rest of the energy functional is exactly the same as in a Kohn-Sham calculation within the local density approximation. For metals the orbital-free scheme has particular advantages – the dynamics are stable and Brillouin-zone sampling is avoided. The electronic part of the algorithm scales linearly with system size and large simulation cells and long run times become possible. Good results for simple metals have been obtained.

For ionic systems, the many-body aspects of polarization and dispersion interactions are included by adding additional degrees of freedom, which represent distortions of the electronic structure of an ion due to interionic interactions, to the ionic coordinates and extending the equations of motion accordingly [*J. Phys. Condens. Matt.*, **5**, 2687, (1993)]. Short-range corrections to the asymptotic induction and dispersion terms are parameterized on the basis of *ab-initio* electronic structure calculations. The polarizable ion model reproduces distinctive features of short- and intermediate-range order in MCl_2 melts (where M is a group IIA or IIB metal) and gives global energy minimum structures in agreement with experiment for the MX_2 crystals. Non-additive

dispersion effects become important for systems with highly polarizable anions and influence the structure of systems such as CsAu markedly.

Quantum Mechanical Embedding Methods to Study Solvation

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Models of solvent-solute interactions in which the solute is described using quantum mechanical methods, and the aqueous solvent is described using either a continuum model or explicit water molecules, are described. Their use is illustrated by studies of molecular shape, solvation energies and molecular reactivity.

Ab initio model potential (AIMP) embedded-cluster studies of localised ground and excited states in ionic crystals.

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The *ab initio* model potential method (AIMP) is presented as a useful embedding technique based in the Group-Function Theory proposed and developed by McWeeny and Huzinaga. The method is shown to be readily applicable to the calculation of the equilibrium geometry and electronic structure of localised ground and excited states in doped ionic crystals. Results of recent AIMP embedded-cluster calculations are presented which include (a) local structure properties and (b) electronic transitions (ground state absorptions, excited state absorptions, and fluorescence) in first-series transition metal doped oxide and fluoride crystals. The AIMP quantum embedding is shown to enable the calculation of the electronic structure of excited states with comparable accuracy to that attainable in the gas phase. This conclusion is illustrated along the AIMP study of mechanisms that compete with the laser activity in a family of tunable solid state laser materials.

Locality in the modelization and analysis of ionic materials

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The term locality is here interpreted to mean two rather different perspectives. On the one hand, localization of electrons in the orbital space is at the core of the Theory of Electronic Separability (TES). A hierarchy of models based on TES have been used to compute the geometry, vibrational and electronic spectra of Cu^+ centers in alkali halides, and the most relevant results will be reviewed.

On the other hand, Bader's *Atoms in Molecules* theory produces a detailed picture of the electronic distribution in the real space. Basic concepts such as the size, charge, energy and shape of an atom within a molecule or crystal come directly upon the wavefunction of the system. Recent application of this theory to ionic crystals is here presented and discussed.

Quantum cluster in polarisable crystal environment. Consistent microscopical approach

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During the last thirty years the molecular cluster model has been used quite extensively to study various point defects in a vast number of solids. At the same time, the complete understanding of approximations underlying this model are still lacking, and therefore most of the methods implemented so far are based on intuitive models. The talk will focus on the Embedded Molecular Cluster (EMC) method based on the Theory of Electronic Separability and the Arrow Diagram technique. These allow one to account for the overlap of the wave functions associated with different structure elements, namely the molecular cluster and the structure elements of the perfect crystal which are around it. We will demonstrate how a consistent quantum-mechanical approach developed in the EMC method confirms a model of 'a quantum cluster in the semi-classical environment' currently used in a number of *ab initio* and semi-empirical computer codes. Since the interaction of the cluster with the outside region and that within it are considered similarly, the short-range potential imposed on the cluster because of the perturbed outside region appears to be consistent with the way in which atoms in the outside region interact with each other. The problem of calculating the polarisation in the outside region will also be addressed and discussed.

Thermal effects on the localized solutions of the Fröhlich/Holstein/Davydov Hamiltonian.

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The Fröhlich/Holstein/Davydov model describes the motion of a quantum quasiparticle in a lattice which interacts with the quasiparticle. Because of the quasiparticle/lattice interaction, localised states can form at $T=0\text{K}$. As temperature increases, however, the localized states become less

stable. Important questions are the temperature at which the localized states become unstable and their lifetime in the unstable regime. While it is possible to answer the first question, the determination of the lifetime of localized solutions is still unresolved. A short review of this field, together with a discussion of the unsolved points and its possible relevance to biological processes, will be presented.

Self-consistent equations and gauge transformations of electron group functions

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Basic statements of the *Electron Group Functions* (EGF) method (known also as the *Theory of Electronic Separability*) are analysed, and general equations of the method are obtained.

The requirements of variational freedom of EGF's and their spatial separation are basic statements of the EGF method as they are necessary for taking into account the intragroup electron correlation while neglecting the intergroup one. But these requirements seem to be inconsistent with one another. This contradiction can be removed in certain cases using what we define here as the *Gauge Transformations* (GT) of EGF's. Particular examples are considered, one of them based on the notion of the *antisymmetrical annulment* of EGF [1]. The problem of existence of a general form of the GT is studied.

The total energy expression and self-consistent equations for arbitrary number of electron groups in the system with arbitrary numbers of electrons in the groups are written in the general form using an appropriate *Operator Technique* [2] and no approximation but the EGF one.

The transformation of the equations of the EGF method induced by some GT of EGF's is discussed. We also consider a possibility of applying GTs for constructing a pseudopotential produced by a correlated electron group as well as for localising EGF's.

[1] B.P.Zapol, V.E.Puchin. IJQC, v.41, 581-590 (1992).

[2] B.P.Zapol, L.N.Kantorovich. Latvian J.Phys.Techu.Sc. N5, 18-22 (1993)

Localised states in transition metal insulators; an Hartree Fock description

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The Hartree-Fock theory of transition metal insulators provides a qualitatively correct description of the ground state. The delicate balance between localised and delocalised behaviour will be discussed. In recent studies the response of the ground state to doping of electrons and holes has been examined. We present results of these calculations and their relationship to various spectroscopic measurements.

Interaction of Methane with a Surface V-Centre on MgO(100): ab Initio Cluster Model Study

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To describe the interaction of methane with a cation vacancy site in the (100) surface of MgO at ab initio level, a hierarchy of model clusters has been devised. The effect of the extended ionic system has been introduced to this localized description by the addition of a point charge (PC) array. Geometry relaxation of the substrate has to some extent been taken into account by optimizing the position of the oxygen ions adjacent to the V-centre. In a preparatory study of the bare (adsorbate free) site the effect of several factors have been compared (quality of basis set, correlation, size and shape of PC-array and of the model clusters). Based on the trends observed the models for the actual study was chosen. Introducing the adsorbate, a purely repulsive interaction was found using the smallest substrate cluster model.

Ab initio investigations of C-H and hydrogen defects in GaAs using a real-space cluster approach

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An understanding of carbon and hydrogen defects within III-V materials is crucial for the fabrication of efficient electronic devices with an adequate operating lifetime using MOCVD grown material. These defects are studied using the highly efficient serial and parallel versions of the local density functional cluster code AIMPRO both on workstations and on the T3D. The use of clusters offers certain advantages over a supercell method. It is found that the energy barrier to the dissociation of the neutral C(As)-H complex is 1.8 eV, but that this is drastically reduced in the presence of minority carriers. The barrier energy for the dissociation of C-H⁻ is reduced to less than half of that in the neutral case. This remarkable result explains recent experimental findings on the degradation of GaAs based heterojunction bipolar transistors.

The stability of the possible sites which H occupies in GaAs are investigated. The equilibrium site is found to be on a gallium-arsenic bond axis for H⁰ and H⁺ but at a Ga anti-bonding site

for H^- .

It is also shown that a H_2 molecule is stable and has a lower energy than the two possible H_2^- defects. These molecules could act as a reservoir for H within the material and the presence of interstitial hydrogen in GaAs has recently been experimentally identified as a precursor to the degrading of essential device characteristics. The stability of H_2 over H_2^- is similar to results previously obtained for Si, but contrasts with the situation in diamond.

Proton-ordered ice: periodic models and embedded-cluster study of impurities

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The use of 'periodic' models for determining the characteristics and chemical-physical properties of ice is of great interest for two reasons. Firstly, because they allow the taking into account of the cooperative effects of hydrogen bonds and long-range electrostatic interactions in a more complete way than is the case with cluster models. Secondly, they give a crystal solution which can be used for the study of local defects by adopting an embedded-cluster technique.

For this purpose, the adoption of a proton-ordered structure is required, though it is well-known that ice is intrinsically disordered. A proton-ordered structure, which is stable at low pressures and temperatures, has been detected experimentally. It is formed through an order-disorder phase transition of ordinary ice which occurs around $T = 70$ K and is catalyzed by KOH. Nevertheless, this orthorhombic phase of ice, symmetry Cmc21 (C), cannot be used in the study of adsorption phenomena with thin-film models because of the presence of a strong electric dipole moment normal to the surface. We have considered a different ice structure, also orthorhombic but with symmetry Pna21 (P), because it shows only a weak dipole moment parallel to the surface.

In the present work, preliminary results obtained with *ab initio* HF-LCAO methods on the two ice structures C and P are presented. The geometries have been optimized using the CRYSTAL program and a comparison between some bulk and surface properties of the two structures has been carried out. Calculations on the KOH defect in the two phases have been done using the EMBED program. In this way it was intended to verify whether the presence of KOH is fundamental in the formation of a local ordered structure of symmetry C rather than of symmetry P during the phase transition.

Embedded Cluster Modelling of Zeolite Catalysis

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An embedding scheme, designed to accurately model the electrostatic potential within a periodic zeolite is presented. In this model, a hydrogen terminated cluster is embedded within a set of point charges, designed to modify the electrostatic potential of the cluster to accurately represent the electrostatic potential of the periodic system, as derived from a periodic Hartree-Fock wavefunction. The computational implementation of the method is described, with applications to a number of systems of catalytic interest.

Some calculations relevant to Methanol Conversion over Acidic Zeolite Catalysts

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Two reaction pathways for acid catalysed methylation of lattice oxygen centres have been studied using *ab-initio* restricted Hartree-Fock and semi-empirical AM1 methods. Results using a 3-21G basis and a simple $\text{H}_2\text{O}.\text{Al}(\text{OH})_3$ model for a Brønsted acid site suggest that methylation involving two adsorbed methanol molecules is much more favourable than that involving only one. These results have been explained on the basis of the $\text{S}_\text{N}2$ nature and the greater transition state solvation of the route involving two methanols. The semi-empirical AM1 method was found to be unsuitable for study of this methylation reaction.

The effects of periodic boundary conditions on phonon calculations in sodium chloride

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In order to calculate the normal modes of a crystal, the force constants relating ionic displacement and the resulting forces must be found. In the framework of first-principles calculations, this is commonly done by calculating the Hellmann-Feynman forces on all the ions when one ion is displaced, using periodic boundary conditions. The dynamical matrix is then constructed, with the help of the symmetry of the crystal, and diagonalised to give the normal modes.

Two restrictions arise from the use of periodic boundary conditions. Firstly, in finite supercells, the 'force constants' found will be linear combinations of the true force constants of a crystal, so in all but very large supercells only phonons with wavevectors equal to the reciprocal lattice vectors of the supercell will be found accurately. Furthermore, periodic boundary conditions also preclude any macroscopic electric field. Since longitudinal optic phonons produce such a field at long wavelengths, splitting between longitudinal and transverse optical phonons near the zone centre will therefore not appear using this method.

We have illustrated these effects by calculating the Γ and X modes of sodium chloride using this simple technique, using density-functional theory in the local density approximation. The lack of LO-TO splitting at Γ is shown, but the displacement of pairs of ions rather than individual ions generates good agreement with experiment at X . The problems involved in calculating the correct longitudinal frequencies and various methods of improving the calculations are discussed, together with steps towards implementing these techniques in existing code.

Modelling of Localised States in Condensed Matter

(Keele, June 14-16, 1995)

Wednesday June 14th

- 10.00- Registration
13.00-13.45 Coffee/tea
13.45-14.00 Welcome (C.R.A. Catlow and M.J. Gillan)
14.00-15.00 I.V. ABARENKOV*, V.L. Bulatov, R. Godby, V. Heine, M. Payne, A.V. Titov,
I.I. Tupitsyn (* Sankt-Peterburg, Russia)
*Combined density functional and configuration interaction method
for the electronic structure of solids with impurities.*
15.00-16.00 A.H. HARKER (AEA Technology, Harwell, UK)
*A hybrid shell-model/quantum mechanical treatment of defects
in ionic crystals.*
16.00-16.30 Coffee/tea break
16.30-17.30 C. PISANI (University of Torino, Torino, Italy)
The EMBED project: recent results, problems and prospects.
17.30-18.00 U. BIRKENHEUER (University of Torino, Torino, Italy)
*Unrestricted Hartree-Fock method for local defects in crystals
and at their surfaces.*

Thursday June 15th

- 09.00-10.00 M.J. GILLAN, E. Hernández (University of Keele, Keele, UK)
The relation between embedding and linear scaling.
10.00-11.00 V.A. TELEZHKIN (Donetsk Institute of Physics and Technology of
the Ukrainian Academy of Sciences, Donetsk, Ukraine)
New Tight-Binding Method (Molecule as a Defect of the Hilbert Space).
11.00-11.30 Coffee/tea break
11.30-12.30 D.M. BIRD, S. Crampin, R. James
and J.R. Trail (University of Bath, Bath, UK)
Embedding calculations based on ab initio pseudopotential technique.
12.30-13.00 F. CORÁ*, C.R.A. Catlow, M. Leslie, R. Nada,
R. Orlando, C. Pisani and V.R.Saunders
(* The Royal Institution of Great Britain, London, UK)
*A combination of the Quantum-Mechanical Perturbed-Cluster
and the Semiclassical Mott-Littleton techniques for the study
of charged defects in crystals.*
13.00-14.30 Lunch
14.30-15.30 S. CRAMPIN (University of Bath, Bath, UK)

*Green function methods for surface state scattering
studies and related problems.*

- 15.30-16.30 P.A. MADDEN (University of Oxford, UK)
Simplified electron energetics in Car-Parrinello MD
- 16.30-17.00 Coffee/tea break
- 17.00-18.00 I.H. HILLIER (University of Manchester, Manchester, UK)
Quantum mechanical embedding methods to study solvation.
- 18.00-18.30 General discussion
- 18.30-20.00 Wine reception, posters.
- 20.00 Workshop dinner

Friday June 16th

- 09.00-10.00 Z. BARANDIARAN (Universidad Autonoma de Madrid, Spain)
*Ab initio model potential (AIMP) embedded-cluster
studies of localised ground and excited states
in ionic crystals.*
- 10.00-11.00 V. LUÑA (University of Oviedo, Spain)
Locality in the modelisation and analysis of ionic materials
- 11.00-11.30 Coffee/tea break
- 11.30-12.30 L.N. KANTOROVICH (University of Keele, Keele, UK)
*Quantum cluster in polarisable crystal environment.
Consistent microscopical approach.*
- 12.30-13.00 L. CRUZEIRO-HANSSON (Birkbeck College, London, UK)
*Thermal effects on localised solutions of the
Fröhlich/Holstein/Davydov Hamiltonian.*
- 13.00-14.00 Lunch
- 14.00-15.00 B.P. ZAPOL (Latvian University, Riga, Latvia)
*Self-consistent equations and gauge transformations of
electron group functions.*
- 15.00-15.30 N.M. HARRISON (Daresbury Laboratory, Daresbury, UK)
*Localised states in transition metal insulators; an Hartree Fock
description.*
- 15.30-16.30 General discussion and closing

Posters should be displayed at the beginning and remain until the end of the workshop.

Singularity-free Treatment of Linear Bond Angles

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(for submission to the *CCP5 Newsletter*, version February 21, 1995)

Using a harmonic potential energy function

$$E(\phi) = \frac{K}{2}(\phi - \phi_0)^2 \quad \text{Eqn. 1}$$

to describe valence bond angle deformations, one encounters a technical problem if the bond angle ϕ becomes 180 degrees. This normally does not happen if the equilibrium angle ϕ_0 is far away from this value. The problem is caused by the transformation of the force acting along ϕ

$$f(\phi) = -dE/d\phi = -K(\phi - \phi_0) \quad \text{Eqn. 2}$$

to Cartesian forces \mathbf{f}_i , \mathbf{f}_j and \mathbf{f}_k acting on the three atoms i , j and k defining the angle, j being the central atom. Using the chain rule, the transformation becomes

$$\mathbf{f}_i = f(\phi) \left(\frac{\partial \phi}{\partial \cos \phi} \right) \left(\frac{\partial}{\partial \mathbf{r}_i} \cos \phi \right), \quad \text{Eqn. 3}$$

and similarly for the other atoms (for details, see ref. 1). The second factor in Eqn. 3 is equal to $-1/\sin \phi$ and causes the transformation to become undefined for $\phi = \pi$. The problem has been overcome in many forcefields by using a bond angle interaction term harmonic in $\cos \phi$, rather than in ϕ

$$E(\cos \phi) = \frac{K'}{2}(\cos \phi - \cos \phi_0)^2, \quad \text{Eqn. 4}$$

in which case the factor $\left(\frac{\partial \phi}{\partial \cos \phi} \right)$ disappears from Eqn. 3.

However, for $\phi_0 = \pi$, there is a simpler solution: The sine function is linear around π to a very good approximation, so we can rewrite Eqn. 2

$$f(\phi) = K \sin \phi \quad \text{for } \phi_0 = \pi. \quad \text{Eqn. 5}$$

(In fact, Eqn. 2 is just the first non-zero term in a Taylor expansion of $\sin\phi$ around $\phi_0 = \pi$.) The $\sin\phi$ term in Eqn. 5 exactly cancels the $1/\sin\phi$ term arising in the transformation (Eqn. 3). Integrating Eqn. 5 gives the expression for the potential energy

$$E(\phi) = K(1 + \cos\phi) \quad \text{for } \phi_0 = \pi. \quad \text{Eqn. 6}$$

The force constant K has the same numerical value in the trigonometrical form of the interaction terms (Eqn. 5 and Eqn. 6) as in the harmonic form (Eqn. 1 and Eqn. 2), under the condition that its unit in the trigonometric form is an energy unit (i.e. kJ mol^{-1}) and in the harmonic form it is the same energy unit per radians squared (i.e. $\text{kJ mol}^{-1} \text{rad}^{-2}$). This equivalence is sometimes more convenient than the more complicated relationship between K (Eqn. 1) and K' (Eqn. 4).

I decided to report this little technical trick in this place for three reasons: (i) I believe it has not been described before. (ii) My original description is hidden in the appendix of a paper dealing with something completely different [2]. (iii) It has been implemented in the latest version of the YASP program [3].

References

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2. F. Müller-Plathe, *J. Chem. Phys.* (submitted).
3. F. Müller-Plathe, *Comput. Phys. Commun.* **78**, 77 (1993).

A Novel Application for Molecular Dynamics - The Simulation of Powder Flow

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1 Introduction

The purpose of this short note is to bring to the attention of the atomistic simulation community an interesting application of molecular dynamics, MD, that has been attracting increasing interest in the chemical engineering and applied physics communities over recent years.

Molecular Dynamics is being applied to investigate transport of dry granular materials. The particles modelled are typically $\sim mm$, across so they are considerably larger than the particles normally dealt with in atomistic simulation, in fact, *i.e.*, $\sim 10^7$ larger in length scale! Powders are formed, stored and transported in a wide variety of industrial processes as an intermediate stage or as the final product itself. A wide range of materials is encompassed, for example, agricultural grains (*e.g.*, wheat and barley seeds), foodstuffs (*e.g.*, sugar), solid fuels (*e.g.*, coal), and pharmaceutical products. The applications are wide in scope and enormous in terms of monetary value. Small improvements in the efficient handling of these materials can reap significant financial rewards. These materials are often heaped up in piles (*e.g.*, agricultural produce in the farmyard and sand in a builder's yard). An alternative method of storage is to convey the powder into tall bins (called 'hoppers' or 'silos') that have a narrow hole at the bottom which can be opened to discharge the material in a controlled manner. (The hopper design is popular in chemical engineering practice as it readily fits into an engineering unit process.) A hopper is designed in two shapes, either (a) with a converging nozzle, like a soft-drinks bottle upside down, or (b) without the converging nozzle, so that the vertical wall meets a flat bottom containing the hole in the centre. There are many important issues that need to be considered when deciding on a process for handling a powder through to the final product. Often the composition of the material is required to change as little as possible. In unfavorable circumstances, the particles can fragment owing to excessive stresses ('attrition') and segregate if a size or shape range distribution of granules is present. In pharmaceutical pills, for example, the active component may only be a small proportion of the bulk of the pill, and hence it is important to dispense the drug and the filler powder within well-defined bounds to form the pill.

Powders undergo quite distinct classes of flow, much more than for a liquid. Powder granules can be in a highly 'thermalised' state, for example, in agitated flow during conveying, fluidised beds or in free fall under gravity. Indeed theories based on the kinetic theory of gases have had some success at describing these 'lean-phase' flows. In contrast, in other situations there is very slow motion of the granular assembly, so that the particles flow in a highly cooperative manner, as in a hopper during discharge. This latter type of flow is called 'quasi-static' flow. These two types of flow are quite different, and the granular assembly goes through a kind of phase transition between the two 'states'. Any realistic simulation model must be able to cope with these two extremes as

they are induced by external forces and positional constraints on the particles.

Cundall & Strack [1979] [1] first applied Molecular Dynamics to granular systems. They developed the program BALL to simulate assemblies of discs, out of which grew the widely used and modified program, TRUBAL. The 'granular dynamics', GD, shares much in common with MD, in that it numerically integrates Newton's equations of motion to produce a chronologically ordered set of particle positions from which the particle forces can be determined. (These are needed to evolve the assembly through time.) Constant or linearly varying conditions are assumed over the time interval, and hence the time interval must be small enough so that the mechanical state of the system changes only marginally from 'frame' to 'frame'. Although the interactions between the particles are treated at a pair-wise additive level, the technique follows the highly cooperative movement of the particles so that the complex coupled motion in a real assembly can be reproduced.

The GD technique differs from MD in certain important respects:

- Each particle in the simulation represents a granule of the powder, which can contain many millions of atoms. The atomic level detail is not included in the model description, rather the distance scale in the model is that of the granule itself.
- The interactions ('pair potentials') between the particles are not elastic but include an inelastic damping term to reflect kinetic energy loss when two macroscopically sized particles collide. Energy can be dissipated as heat within the particle assembly, and through frictional and elastic-plastic work when enduring contacts between the particles slide against each other. The energy lost from the system by this mechanism plays no further part in determining the trajectories of the particles.
- As a consequence of the above point, the 'natural' state of a granular assembly is to come to rest in a state of mechanical stability with essentially no relative motion between the particles. There is no meaningful concept of 'temperature' in these systems, as the particle velocities, \underline{v} , are not related to the physical temperature of the particles (which is largely irrelevant). The concept of a 'granular' temperature is sometimes invoked, by applying $T \propto m \langle \underline{v}^2 \rangle$, although its significance is still rather uncertain.

What are the objectives of any granular dynamics simulation? Well, they are very similar to those of atomistic simulation - in helping develop a particle-level understanding of these systems to improve models and ultimately establish design criteria (although the relevant time and distance scales are much larger). In the context of powders they are,

- to test and improve theories of the flow of powders and the accompanying stress states within them. Most theories of powders in this category are, in fact, continuum theories based on application of mass and momentum conservation - with a minimum of particle-level information. There is very little in the realm of particle based theories, as no useful statistical mechanical description of powders has emerged.
- to model effects that cannot be incorporated in analytic theories, *e.g.*, particle segregation (the separation of the bed into regions rich in one size), inhomogeneous flow fields (particularly prevalent in quasistatic flow).

- to explore the effect of the geometry of the enclosing boundaries container on the flow and stress fields.

In recent years, we have made a granular dynamics study of flow in hoppers during the filling and discharging stages. The bed in hoppers has a particularly rich range of phenomena associated with it. Storage and flow of granular materials in hoppers is characterised by a series of flow regimes: erratic flow out of the orifice, blockage of the orifice, stagnant or ‘dead’ zones in corners, material ageing, segregation and derived effects including attrition, wall adhesion (which has an influence on wear of the hopper wall). These phenomena can have dramatic consequences, even leading to hopper collapse and dust explosions. We have explored some of these effects, placing particular emphasis on establishing the sensitivity of derived properties on the analytic form of the particle interactions.

We have found that it is not necessary to consider very large systems to explore the physics of hopper flow (several thousand particles are usually sufficient). Also stresses on the walls of the hopper and discharge rates from the hole at the bottom are comparatively insensitive to the form of the particle normal interactions, and in line with semiempirical formulae based on analytic continuum analyses. However, the *internal* state of the powder bed *i.e.*, stresses on and deformation of the granules (which has implications for the quality of the granules at the end of the process) are quite sensitive to the interaction law. Details of the simulations can be found in our publications [2] [3]. However, here we discuss one important aspect of the model before illustrating some representative results from the simulations.

Normal Interaction Force

As with all discrete particle simulations, the central force law that keeps the particles from overlapping significantly, must be chosen with care. (The interaction potentials themselves and derived total interaction energies are not of great interest for granular systems, so we concentrate on the forces.) The ‘normal’ force $F_n(r)$, between two granules is a function of the particle centre-centre separation, r .

A serious limitation with many of the simulations carried out to date is that it has not been clear what the particle interactions used in the model are actually representing in the real system (if anything realistic at all!) and therefore the model may not represent any real assembly at all. Until recently this issue has not been adequately confronted. To this end, we have explored three analytic forms for $F_n(r)$,

1. Hooke

The most simple is a Hooke’s law spring,

$$F_{N_{Hooke}} = k(\sigma - r), \quad (6)$$

where k is the Hooke’s Law spring constant, σ is the particle diameter and r , is the separation distance between the centres of the two particles. .

2. Hertz

This is the force law that applies when two macroscopic spheres with high elastic modulus are pressed together [4].

$$F_{N_{Hertz}} = \frac{4}{3}E^* \sqrt{R}(\sigma - r)^{3/2}, \quad (7)$$

where the elastic modulus, of the two particles is E^* and R is the contact radius of curvature.

3. Continuous Interaction

We have also used a force law, in which the rate of change of repulsive force varies more rapidly than the other two, as the particles overlap. This we have called the Continuous Interaction, *CI*, is a generalisation of the sphere-sphere interaction,

$$F_{N_{CI}} = n\epsilon\left(\frac{\sigma}{r}\right)^n/r, \quad (8)$$

where n is an arbitrary index, m is the mass of the granule, $\epsilon = \sigma mg/n$ and σ set the force and distance scales. The coefficients are chosen so that the force is equal to the gravitational force, mg , when the particle centre to centre separation equals σ . The advantage of this form in favour of the other two is that over a large ‘overlap’ distance range, the normal forces are initially relatively low, enabling particles to interact, restructure and consolidate better, if under stress, before the forces become too large and the assembly ‘locks’ into a particular arrangement in space. Most of the simulation studies to date have chosen the constants for these normal force laws which are very “soft” when compared with equivalent elastic contacts for real particles. In a sense, the CI interaction is an ‘effective’ potential in the best MD tradition, which this time takes into account the irregular shapes and slight polydispersity of real granular materials in a mean-field manner. From a purely computational perspective, a soft potential also has advantages; interestingly the results have been found to be relatively insensitive to the choice of these parameters, above a certain stiffness, underscoring the fact that these normal interactions should be considered to be ‘effective’ *i.e.*, including the essential physics of the interactions but in a manageable ‘mean field’ sense.

An important issue in any particle assembly representation of a granular material is: what is the most appropriate analytic form and distance scale (‘scale of description’) for the particle interactions? During attrition and compaction the particle normal loads are high, which lead to significant particle deformation and a realistic description at the microcontact ($\sim \mu\text{m}$) scale should be included. A Hertz or appropriately modified form of this interaction which varies significantly on a μm distance scale is appropriate in these circumstances.

In a hopper, in contrast, the loads on the particles are comparatively low and the mechanism of assembly evolution is quite different to that which takes place in compacted granular assemblies. In this case the granules execute highly cooperative movements of the particles through sustained quasi-static flow. Many particles undergo a relative ‘sliding’ action with large bulk shear deformations whereas other regions of particles move *en masse* with relatively small relative displacements. In this situation, issues of particle and system geometry are most influential in determining the evolution of the system. The most pertinent scale of description for the particles is one that scales with the particle size, rather than with the component microcontacts. The interaction law must be able to include the effects of particle shape and topography, at least in a mean field sense. An interaction law based on surface forces and contact mechanics of ideal spheres is inappropriate in this context. This is why we consider (and indeed have shown) that the CI interaction force law gives the most realistic representation of powders in a hopper.

Sliding or Tangential Interaction Force

In addition to normal interactions, the granules interact through relative sliding movements which must be incorporated in a model interaction law. This tangential interaction, F_t , represents the elastic-plastic deformation of the contact region. We have chosen the following analytic form for F_t .

$$F_T = \mu F_N (1 - (1 - |\delta_t|/\delta_{max})^{3/2}), \quad (9)$$

where δ_t is the total tangential displacement executed by the two surfaces, measured from the point where they initially come into contact. If $|\delta_t| > \delta_{max}$ then gross sliding is deemed to have started and the frictional force assumes a constant value given by Amonton's law, $F_T = \mu F_N$ where μ is the coefficient of friction (we typically chose $\mu = 0.6$ between the particles and $\mu = 0.3$ between particle and wall). This equation has a generic functional form that represents deformation and sliding of a contact (*i.e.*, an elastic-plastic force curve smoothly going to the gross sliding limit). Although it is the same analytic form as derived by Mindlin and Deresiewicz (1953) [5] for micromechanical contacts, the δ_{max} here is typically several orders of magnitude larger than that for a typical micromechanical contact, and consequently the physics represented in the two cases is quite different. We have adopted the prescription $\delta_{max} = a\delta_n$ where a is a constant and δ_n is the extent of overlap of the particles, which is $\delta_n = \sigma - r$ for Hertz and Hooke, and $\delta_n = b\sigma - r$, where b is a constant, for the CI interaction. As the CI particles have no unambiguous diameter, we have deemed that the two particles 'overlap' when they are separated by $b\sigma$. We have explored a range of coefficients, b , and shown that $b \sim 1.2$ give most realistic results *vis à vis* experiment.

2 Simulation Details

We have written MD programs to model hopper flow in $2D$ and $3D$. The simulations follow the filling and discharge of a model hopper in $2D$ for discs and $3D$ for spheres. The model granules are introduced at the top of the hopper a few at a time and allowed to fall under gravity to a settled state, and then discharged under gravity through an orifice at the base of the hopper. Translational and rotational motion of the particles are followed using a time-stepping numerical integration of the equation of motion, details of which are given in [2] [3].

3 Typical Results and Conclusions

Fuller details of our work can be found in refs. [2] [3]. For illustrative purposes we consider here the important hopper properties of wall stress and discharge rate.

In figure 1 we show the normal and tangential wall stresses of a consolidated bed of material containing 2000 CI particles in $2D$ flat-bottomed hopper under discharge. These are represented by scaled lines in the direction the forces act on the wall. (The tangential wall stress lines have been reorientated by 10° for clarity.) A theoretical prediction, called the 'continuum differential slice force balance' method, which is based on mechanical stability stress balance considerations, is given for comparison.

Figure 1

Flat bottomed hopper

Soft-sphere (CI) potential ($n = 36$)

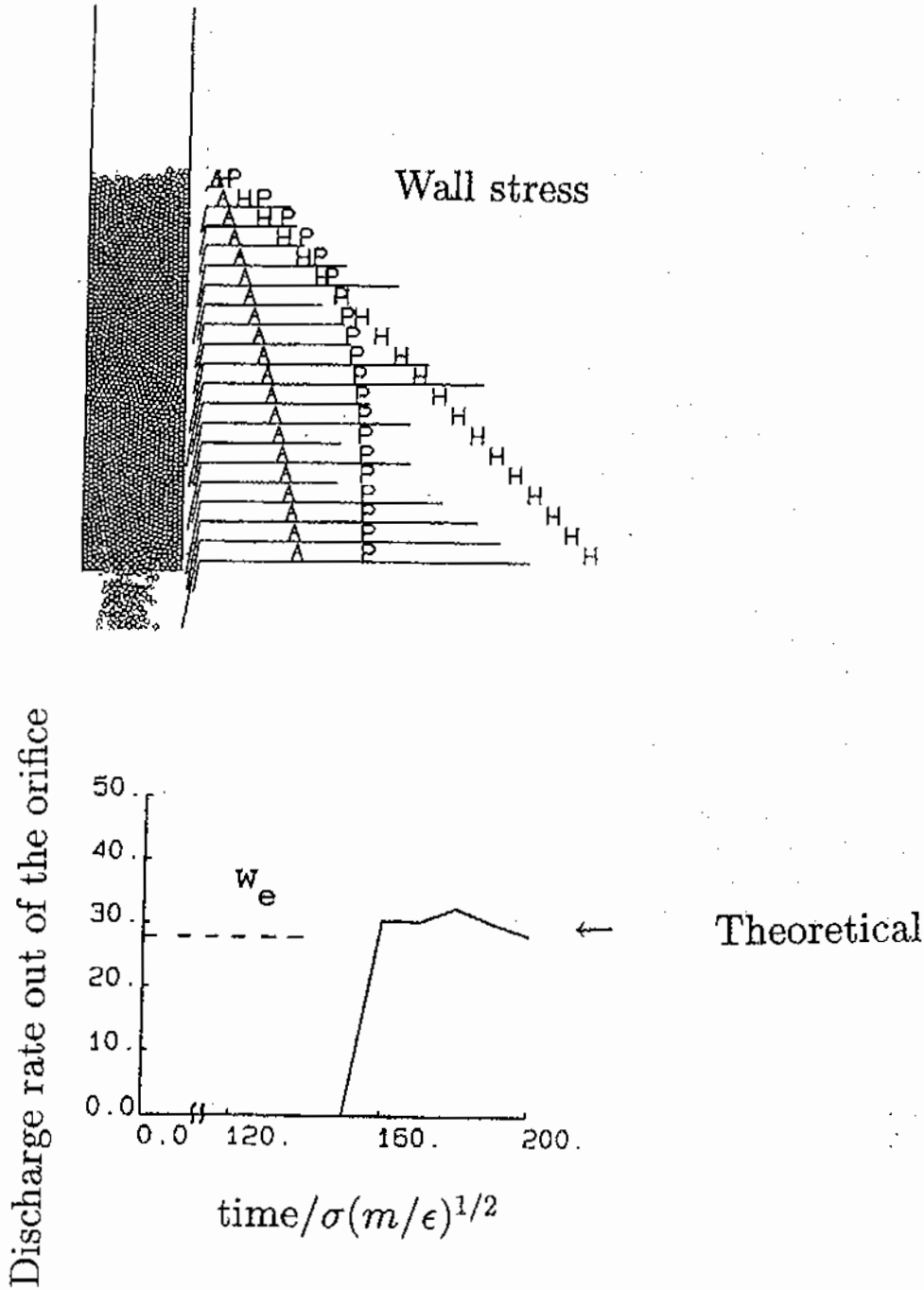


Figure 1: A 2D granular discharge event from a flat bottomed hopper using continuous interaction eq. (8) with $n = 36$ showing, the wall stresses in the discharging state.

This approach predicts a series of most likely states called the ‘active’ state, A on the figure, which is most appropriate to a static bed, and the ‘passive’ state, P , on the figure, which is most appropriate to a discharging hopper. [6]. The figure reveals that the normal stresses on the wall are statistically indistinguishable from the predicted passive state profile. (The symbol H on the figures represents the hydrostatic equivalent stress.)

The lower diagram of figure 1 shows the discharge rates as a function of time from the beginning of the simulation. The solid line is the computed discharge rate and the dashed line marks a semi-empirical theoretical prediction called the ‘Beverloo’ equation [6] [7]. The agreement is very good, once a steady flow has become established.

In figure 2 we show the corresponding figures for a conical shaped hopper, which is called a ‘mass flow’ hopper. This type of hopper has a number of interesting features. There is a ‘spike’ in the normal wall stress at the point at which the vertical wall section joins to the conical section. This peak, sometimes called a ‘switch’ stress is a feature observed in real hoppers. As a result, this transition region of the hopper needs to be especially strengthened. The discharge rates for a mass flow hopper are greater than the corresponding flat bottomed hopper, which is what we find in our simulations. Agreement with the continuum theoretical prediction is again very good.

In general, we find that in both $2D$ and $3D$ simulations, the wall stresses and discharge rates are relatively insensitive to the form of the normal interaction. However, the wall stresses are *very* sensitive to details of the tangential interaction.

In contrast, we find that internal ‘local’ properties within the bed are sensitive to both normal and tangential interactions. In order to generate realistic conditions within the bed it is necessary to have ‘good quality’ particle interactions to produce these effects. For example, distributions of contact tangential displacement vectors are very sensitive to the form of F_n . Let us define a normalized tangential displacement vector as the ratio of tangential displacement to the maximum displacement required for the onset of gross sliding at that normal load. It can be used as a measure of how close a local region within the flow field is to “rigid plastic failure” or “rupture”. In figure 3 we see that “rupture zones”, regions of high bulk shear deformation, are present in the CI case. There are regions in-between in which the granules hardly move relative to one another, and flow essentially *en masse*. These are regions of high strain which dominate the overall flow field, and where particle degradation is most likely to occur. Note that the rupturing is large near the walls. The corresponding Hertz and Hooke interaction maps show a much more random distribution of displacement vectors, with no evidence of rupturing. These model materials will flow much more like a classical liquid. We find this in both plain-strain ($2D$) and axial symmetric ($3D$) flows. Rupturing has been observed in experiment, for example, Bransby *et al.* [8] [9] report rupture zones during the flow of cohesive sand particles in a rectangular silo using x-ray radiography.

Figure 2

Conical shaped ('mass flow') hopper

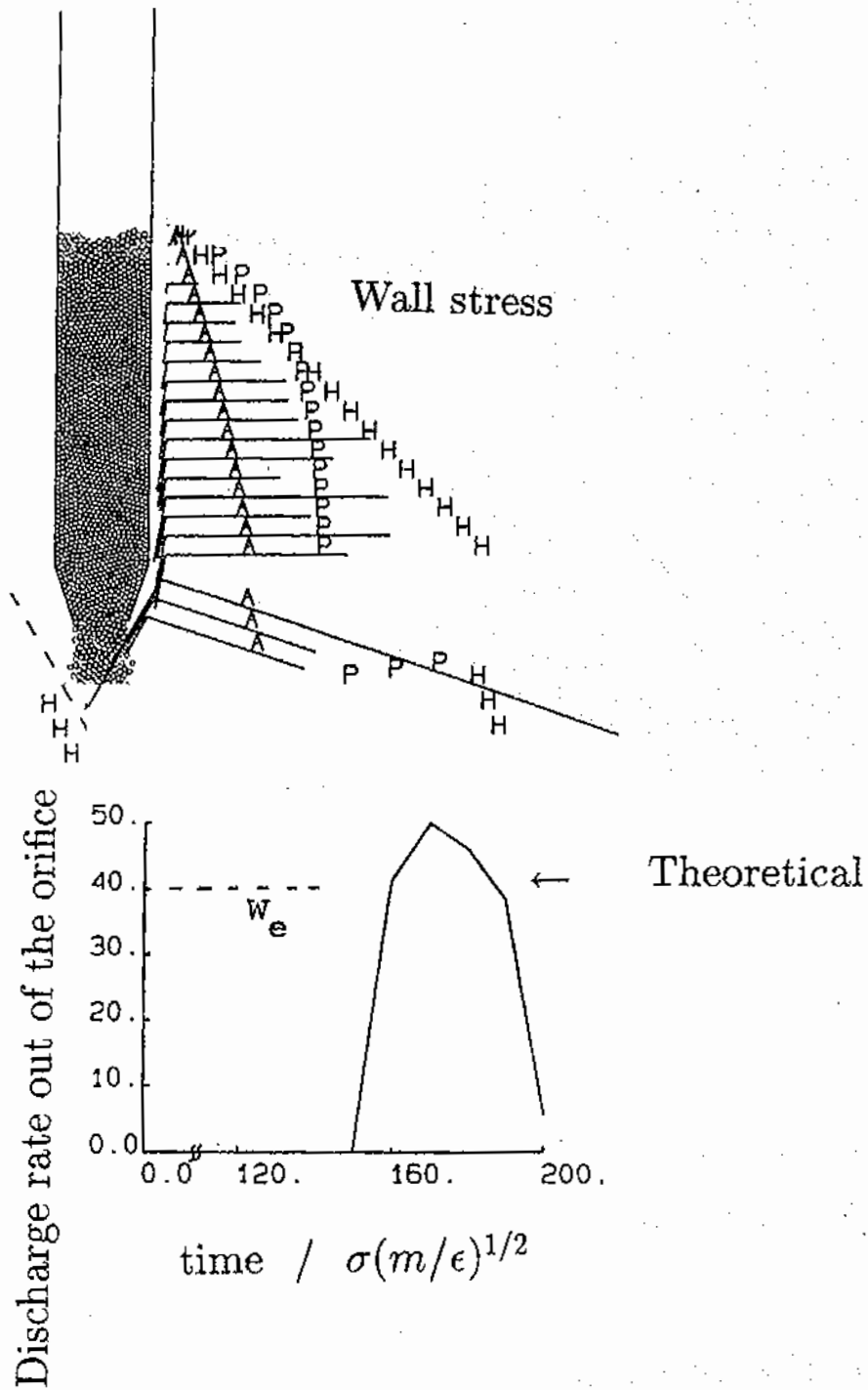
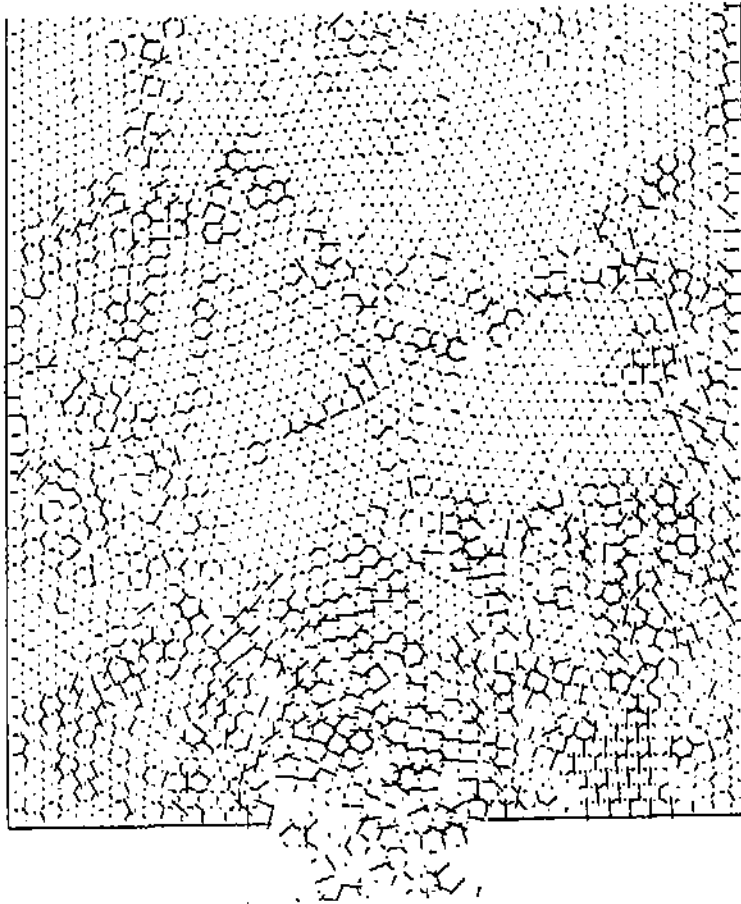


Figure 2: The discharge rates from figure 1, except that a mass flow hopper is considered.

Soft-sphere (CI) potential ($n = 36$)



Discharge

Map of tangential contact displacement vectors
at the base of a flat bottomed hopper.

Note the inhomogeneous distribution.

Figure 3: Contact tangential displacement ratio map during discharge in 2D for the CI model.

To summarise, the Molecular Dynamics model for quasi-static flow in hoppers is, at this stage, a useful research tool, which will help us formulate microstructurally sound models for quasi-static flow in hoppers. The power of the present simulation studies is that we are, for the first time, able to test directly the validity of now traditional assumptions and identify the strengths and weaknesses inherent in continuum analyses. The exercise is one of instruction and illumination of the key processes. Relatively small systems can be used to fulfil this purpose. Eventually we envisage that, out of this type of work, will emerge design packages along the lines of fluid mechanics CAD/CAM packages, which will, however, have as input, microstructural parameters appropriate to, and be able to distinguish between different granular materials *e.g.*, corn seeds *vs.* sugar!

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Car-Parrinello Simulation Reveals Complex Ions in Liquid Semiconductors

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One of the major developments in condensed matter simulation over the last ten years has been the ability to study real chemical effects involving the making and breaking of covalent bonds. This has been made possible by the arrival of first principles dynamical methods, originally proposed by Car and Parrinello, in which the valence electrons are explicitly included in the simulation. This approach to simulation has brought a huge expansion in the range of materials and problems that can be addressed. For example, the reconstruction of semiconductor surfaces, the dissociative chemisorption of molecules at solid surfaces, the structure and dynamics of liquid metals and semiconductors, the equilibrium structure of exotic molecules, the structure and dynamics of water, and many other classic problems in condensed matter science have all been tackled by the new techniques. At Keele, we have recently been using first principles simulation to study the properties of liquid semiconductor alloys in collaboration with the experimental group of Enderby at Bristol. This article gives a brief overview of some of the work we have been doing, and of the new insights we have obtained into the formation of complex ions in these systems.

But first, a few words about first principles simulation. Traditional molecular dynamic simulation is based on a model for the interactions between the atoms, which is derived either by fitting some reasonable functional form to experimental data or by using quantum mechanical calculations on pairs of atoms or molecules. For some systems, this approach is surprisingly successful, but the condition for it to work is that electron redistribution effects should be small. This is the reason why it works for closed-shell systems like rare gases, simple ionic materials and simple molecules. The approach breaks down if electron redistribution is important, as in the deformation of highly polarisable ions, the transfer of electrons, or the rupture of chemical bonds. The basic idea of Car and Parrinello is to avoid completely the need for interaction models by determining the total energy and the forces on the atoms by a quantum mechanical calculation on the valence electrons at each time step. There are many ways the quantum mechanics can be done, ranging from semi-empirical tight-binding methods to full blown *ab initio* calculations. For the greatest realism and reliability, *ab initio* is the way to go, and that is what I am talking about in this article.

The most effective way of doing *ab initio* dynamics, at least at present, is based on density functional theory, which treats the exchange and correlation energy of the electrons in a simple approximation. Only the valence electrons are included explicitly, and their interaction with the atomic cores is represented by a pseudopotential, which itself is constructed by *ab initio* calculations on single atoms. The other important feature of this approach is that the valence orbitals are generally expanded in plane waves, in other words as Fourier series. As in traditional molecular dynamics simulation, periodic boundary conditions are used, and this makes the Fourier approach particularly convenient. The price you pay for avoiding the use of empirical models by doing *ab initio* dynamics is obviously substantial. What you pay depends a lot on the system you are looking at, but typically *ab initio* dynamics can be a thousand times as costly as traditional M.D. The price is worth paying if it allows you to tackle problems that are out of reach of any other method. It is also worth remembering that the speed of computers has increased at least a thousand-fold since the early days of M.D. simulation, so we are in very much the same situation as the M.D. simulators were in the late 1960s.

We are working on liquid alloys at Keele because we want to understand the relationships

between the liquid structure and the electronic properties of these systems. It has been known for many years that the electrical conductivity of alloys often depends dramatically on the composition. A celebrated case is the liquid Cs-Au system, which behaves like an excellent metal at the two ends of the composition range, but is an insulator at the equiatomic composition. Many other alloys show the same kind of effects, and everyone agrees that they are caused by changes of chemical bonding. For example, in the Cs-Au system, the elements have different electronegativities, so that at the equiatomic composition there is a strong tendency for charge transfer from Cs to Au. The bonding is basically ionic, and the system behaves like a molten salt. Clearly there is little chance of describing the change from metallic to ionic bonding as one crosses the composition range by any kind of simple empirical model. One of the systems we have been studying at Keele is the Ag-Se system where the problems are even worse: liquid Ag is an excellent metal, and liquid Se is a covalent semiconductor, and there is strong evidence for ionic bonding at the stoichiometric composition Ag_2Se , so that all the three main types of bonding are involved as the composition is varied. We picked on this system because it is currently being studied by Enderby's group, and their diffraction work will soon give results on the three partial radial distribution functions, but all that is available at present is the total neutron weighted structure factor.

So far, we have done *ab initio* simulations of this $\text{Ag}_{1-x}\text{Se}_x$ liquid system at three different compositions corresponding to $x = 0.33, 0.42$ and 0.65 , and we have also done some simulations on the pure liquid Se system. As far as the structure is concerned, all we can do at present is to compare with the measured neutron weighted structure factor, but this comparison is extremely encouraging as can be seen in Figure 1. The agreement is about as good as could be wished, and is probably within the experimental errors. It is worth remembering that there are no adjustable parameters in the calculations at all - they are truly *ab initio* in the sense that the only experimental input consists of the electronic charge and mass, and the value of Planck's constant. What the comparison is testing is the reliability of the approximations used in applying density functional theory, and the adequacy of the system size.

The partial RDFs and the electronic density of states that emerged from the simulations confirm that the system is partially ionic at the composition, Ag_2Se . However, as the Se content is increased the picture changes rapidly. The first clue that something interesting is happening comes from the Se-Se RDF, which is shown for three compositions in Figure 2. At the Ag_2Se composition, the first peak in this RDF is at about 4 \AA , but as the Se content is increased a peak at much smaller distances develops until it becomes the dominant feature. The distance of this peak is 2.4 \AA , which is almost exactly the covalent bond length in crystalline Se. This hint that covalent bonding is beginning to occur is fully confirmed by snap-shots of the atomic configurations, some examples of which are shown in Figure 3. What we have done here is to plot the atomic positions with sticks joining pairs of atoms that are less than 3 \AA apart. At the Ag_2Se composition, there is almost no covalent bonding at all, but as the Se content is increased, chain-like clusters immediately begin to form. The formation of these complexes is, of course, completely spontaneous. The *ab initio* calculations themselves produce the redistribution of electrons responsible for this bonding.

A striking feature of the covalent bonding we are observing is its extremely rapid dynamics. We know that the covalent bonds are very well defined, because of the sharp peak they produce in the RDF. Nevertheless, the bonds turn out to be extremely short lived, with bonded pairs typically surviving for less than 1 ps . In fact, remarkably the Se diffusion coefficient actually *increases* with increasing Se content.

From one point of view, what we have been observing here is a kind of primitive chemical reaction: the association of single atoms to form complexes. An exciting prospect now on the horizon is the idea of using these *ab initio* dynamical methods to study more interesting condensed-

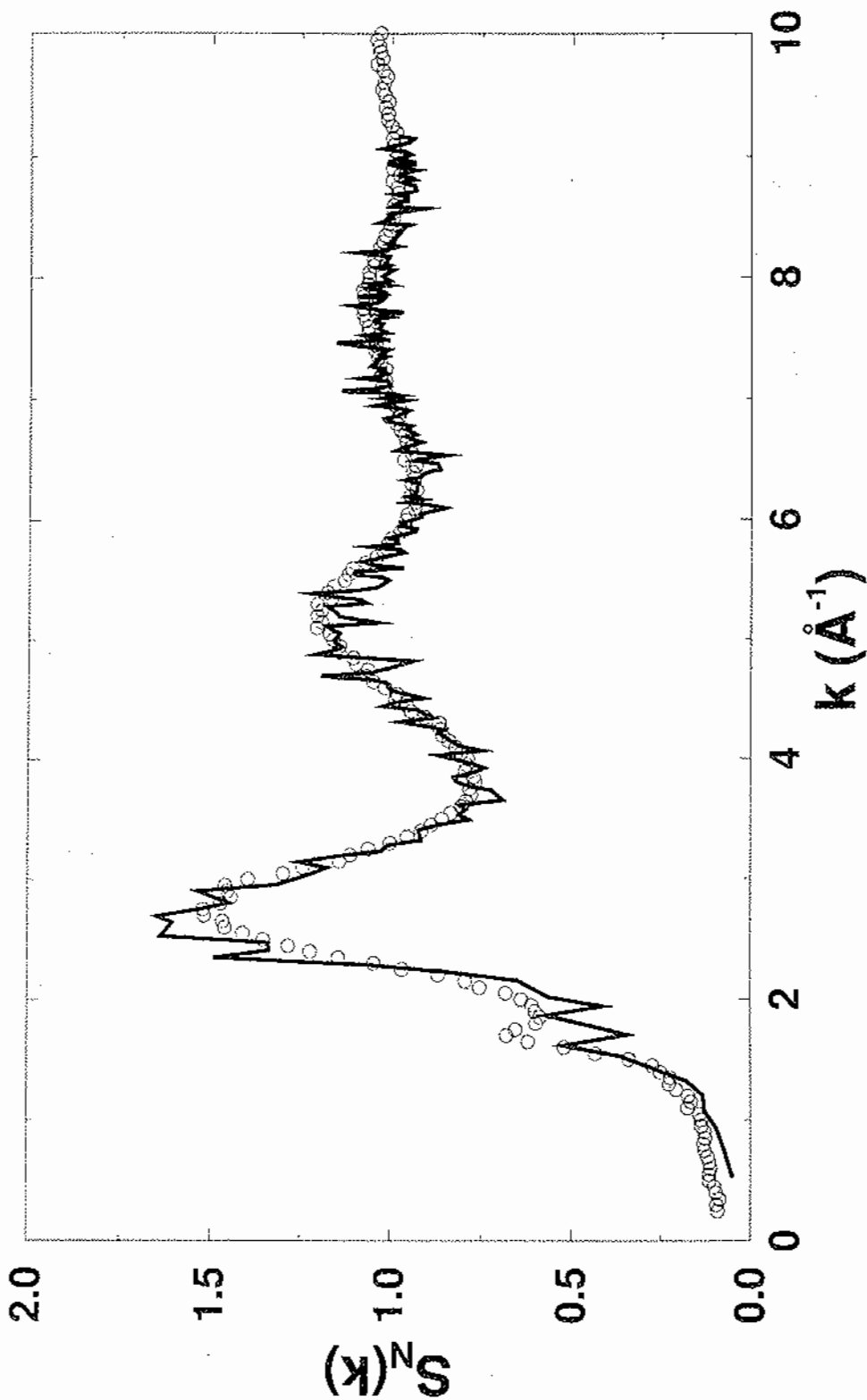


Figure 1: The total neutron-weighted structure factor $S(k)$ of Ag_2Se . Solid lines and circles show simulation and experimental results respectively.

phase chemical reactions. Even the study of reactions in aqueous solution may not be so far off, because the possibility of doing ab initio molecular dynamics on liquid water has already been well established. Preliminary attempts to study polymerisation reactions under high pressure have also been reported recently. The next few years will surely bring exciting new developments in the application of these ideas.

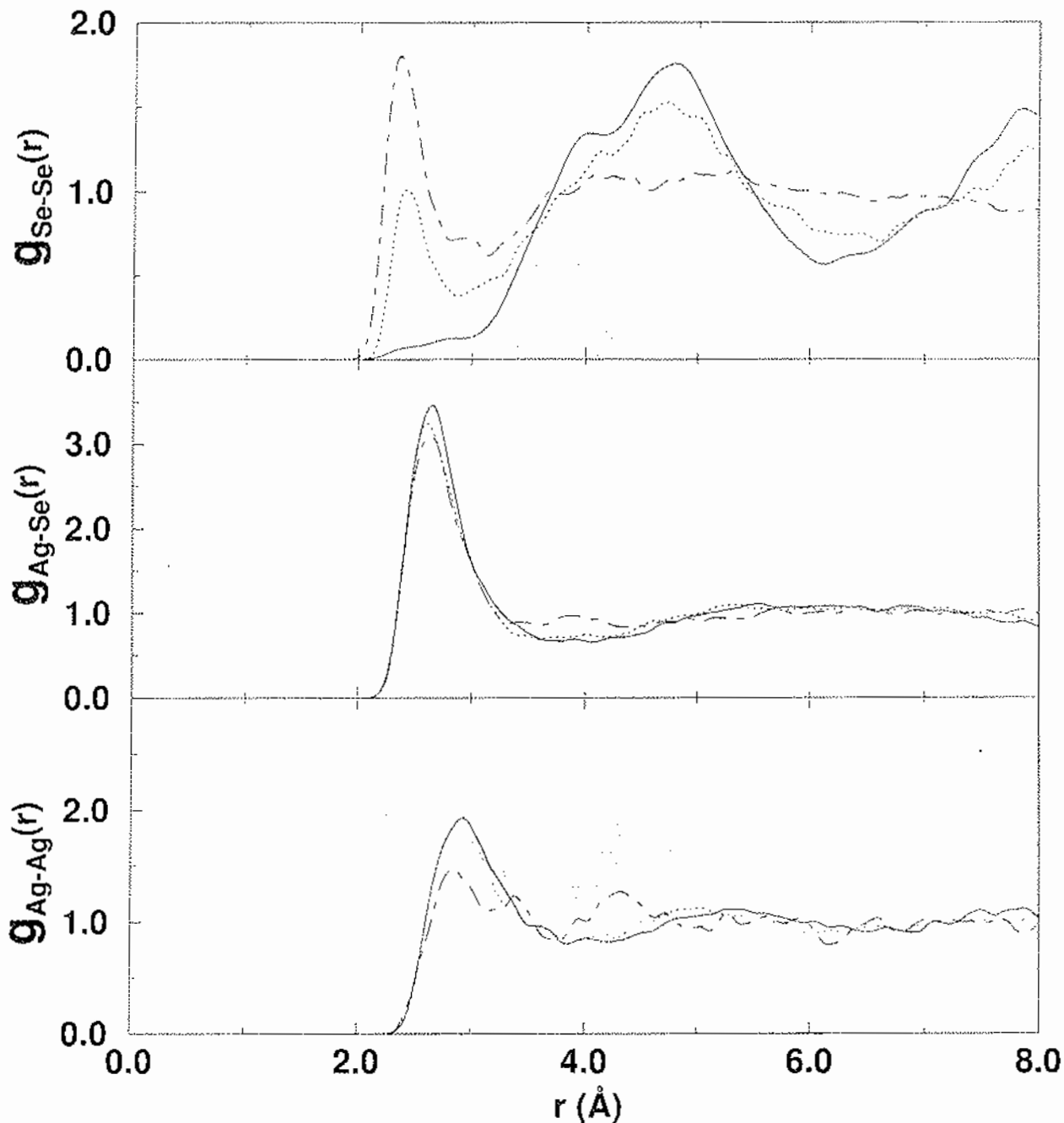


Figure 2: Partial radial distribution functions $g_{\alpha\beta}(r)$ of $l\text{-Ag}_{1-x}\text{Se}_x$ at concentrations of $x = 0.33$ (full line), $x = 0.42$ (dotted line) and $x = 0.65$ (dot-dashed line).

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More information about the ab initio work of the Keele group can be found on the World Wide Web at URL:

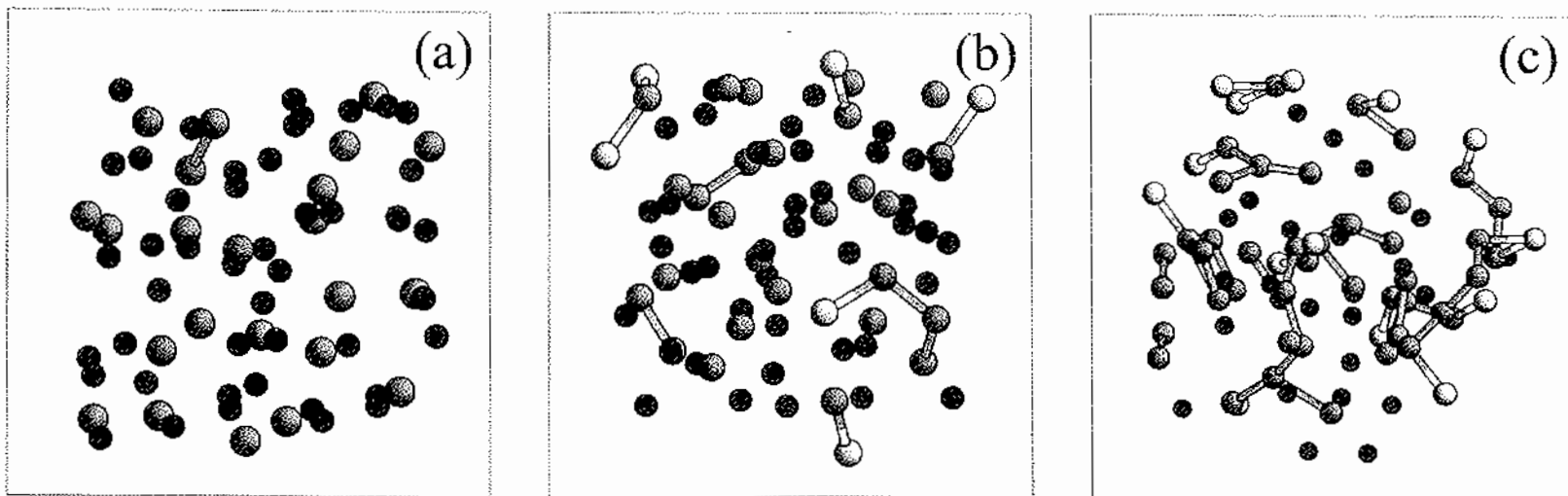


Figure 3: Snap-shots of typical configurations of $t\text{-Ag}_{1-x}\text{Se}_x$ at concentrations of (a) $x = 0.33$, (b) $x = 0.42$ and (c) $x = 0.65$. Silver atoms are shown as black spheres, selenium atoms as grey spheres. Bonds are drawn between Se atoms with separation $< 3.0 \text{ \AA}$.