

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.

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## General News

This issue of the newsletter contains the abstracts of three meetings with which CCP5 has been involved during the summer.

### First Email Copy

This is the first copy of this newsletter which will not be distributed by ordinary post to all of our readers. (See Below).

### UK Telephone numbers

All telephone numbers in the UK have changed; however the existing numbers will continue to work until April 1995. To make the change, insert an extra digit 1 after the international code (44) but before the local area code. The Daresbury telephone number is noted in full below.

## FUTURE MEETINGS

A summary table is given below, further details may be found inside. CCP5 has been asked to publicize the University of Minnesota Supercomputer Institute meeting but is not involved with its organisation.

TOPIC	DATES	LOCATION
International Symposium on Computational Molecular Dynamics	24-26 October 1994	Minneapolis
METHODS IN MOLECULAR SIMULATION - SPRING SCHOOL	27-31 March 1995	Southampton

## 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

I now have one back issue available. All of the articles 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>

The World Wide Web server now has a page for job vacancies which have been notified to me, and can also be accessed by anonymous ftp in `ccp5.newsletters/vacancies`. I have also changed the page on "other related information" and divided these links into four categories.

1. General archives and mailing lists
2. Groups in the UK carrying out simulation work
3. Groups in other countries carrying out simulation work
4. Examples of simulation work

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

Starting with this issue, copies of the newsletter sent electronically will not 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).

## 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/42 directory: cd ccp5.newsletters/42
6. change to postscript or latex subdirectory  
or cd ps  
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

New versions of the NEMD programme, written by Professor D. Evans, are available and copies have been placed in the CCP5 program library. The programs are written for Apple Macintosh. There are copies of these programs in the CCP5 program library, or they are available by anonymous ftp from rschp1.anu.edu.au in directory /pub. There are two versions: the PowerPC version is in a self extracting archive NEMD\_v.84PPC.sea.hqx. The latest Motorola 68K version is NEMD\_v.83.sea.hqx - this will run on Mac II's through to Quadras.

The PPC programme now comes in 4 system sizes 56,224,896,3584 particles. In both v.83 and v.84 new changes include: A menu enables you to change from WCA to Lennard-Jones potential, on the fly. Students can find the triple point temperature where solid, liquid and gas can be simultaneously observed on the screen. The programme now runs over a much wider density range from  $\rho = 1.3$  to 0.05. The displayed particle size now scales with density.

Power Mac 6100/60 speeds (with cache) for the WCA potential ( $\rho=0.8, T=1$ ) are:

540,000 timesteps/hour for N= 56

178,000 timesteps/hour for N= 224

50,100 timesteps/hour for N= 896

19,500 timesteps/hour for N=3584

The Lennard-Jones potential is about 1/3 this speed.

## REQUEST FOR CONTRIBUTIONS

Contributors to the current issue

Our thanks go to:

Dr R.W. Grimes

The Royal Institution,  
London

Dr A.H. Harker,            AEA Technology,  
                                 Harwell

Andrew J.Masters        Department of Chemistry,  
                                 University of Manchester.

Mark R.Wilson            School of Physics and Materials,  
                                 University of Lancaster.

D. J. Cleaver            Sheffield Hallam University  
C. Care

The deadline for contributions for the next 2 newsletters will be **1 December 1994 and 1 March 1995** Readers are reminded that contributions are always welcome. Contributions may be sent by Email in **L<sup>A</sup>T<sub>E</sub>X** and we would be prepared to consider other formats on a trial basis.

### Address

Dr. M. Leslie	Email	
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## MEETING AND WORKSHOP ANNOUNCEMENTS

### METHODS IN MOLECULAR SIMULATION

Southampton University 27-31 March 1995

A Spring School organised by EPSRC Collaborative Computational Project number 5

This residential school is intended to provide a grounding in a wide variety of simulation techniques and is aimed at graduate students starting in the field. It will be limited to 32 students, with preference given to EPSRC/BBSRC-supported students in their first or second year of study. A knowledge of Fortran would be highly desirable, and the course is targetted at students who need to write and/or run their own simulation programs, or who would benefit from a knowledge of the simulation techniques used in molecular modelling packages.

The school will be organised by Professor D. J. Tildesley and Dr. M. P. Allen, and will consist of lectures and seminars given by invited guest speakers. There will also be extensive hands-on simulation workshops using Silicon Graphics workstations in the University of Southampton's Data Visualization facility: these will involve Fortran programming, the use of a range of scientific visualization utilities, and applications of molecular modelling packages.

Topics covered include:

- Introduction to Monte Carlo and molecular dynamics.
- Simulation of rigid and flexible molecules.
- Long-range forces.
- Calculation of thermodynamic, structural and dynamical properties.
- Methods for evaluating free energies.
- Mixtures, phase coexistence and the Gibbs ensemble.
- Simulation on parallel computers.

The cost for the week, including bed, breakfast, dinner, photocopied course notes and supplementary material will be 150 pounds per student. It is possible to apply for research council support to attend the Spring School, and further details will be provided on request.

For preliminary information and an application form please send an email message to [m.p.allen@bristol.ac.uk](mailto:m.p.allen@bristol.ac.uk) or [d.j.tildesley@soton.ac.uk](mailto:d.j.tildesley@soton.ac.uk). Information regarding this Spring School will also be available on the CCP5 World Wide Web server: <http://www.dl.ac.uk/CCP/CCP5/main.html>

International Symposium on Computational Molecular Dynamics  
sponsored by

University of Minnesota Supercomputer Institute  
Computers in Chemistry Division, American Chemical Society  
Division of Computational Physics, American Physical Society  
Division of Physical Chemistry, American Chemical Society

October 24-26, 1994

University of Minnesota Supercomputer Institute  
1200 Washington Avenue South  
Minneapolis, Minnesota

Symposium organizers: Jan Almlöf (University of Minnesota), Evelyn Goldfield (Cornell Theory Center), M. Katharine Holloway (Merck Research Laboratories), William Jorgensen (Yale University), Peter Rossky (University of Texas at Austin), George Schatz (Northwestern University), and Donald Truhlar (University of Minnesota)

The University of Minnesota Supercomputer Institute is hosting an international symposium on Computational Molecular Dynamics, Monday- through-Wednesday, October 24-26, 1994 (with a reception on the 23rd), at the Hubert H. Humphrey Center located on the University of Minnesota campus in Minneapolis. The coverage of the symposium will include all aspects of the dynamics of molecular systems and the use of molecular dynamics simulations-quantum and classical, few-body and many-body, physics and chemistry.

The organizing committee has developed a list of invited speakers that will insure that the program is at the forefront of the field. The list of confirmed speakers includes: Bruce Berne (Columbia University), Emily Carter (University of California, Los Angeles), Jim Chelikowsky (University of Minnesota), Paulette Clancy (Cornell University), Jean Durup (Universite Paul Sabatier), Michael Gillan (University of Keele), Trygve Helgaker (University of Oslo), Jan Hermans (University of North Carolina), Michael Klein (University of Pennsylvania), Ronnie Kosloff (Hebrew University), Uzi Landman (Georgia Tech), Claude Leforestier (Universite de Paris-Sud), Peter Lomdahl (Los Alamos National Laboratory), Paul Madden (Oxford University), Craig Martens (University of California, Irvine), Ken Merz (Penn State), Daniel Neuhauser (University of California, Los Angeles), Michele Parrinello (IBM-Zurich), David Pearlman (Vertex Pharmaceuticals), Montgomery Pettitt (University of Houston), Tamar Schlick (New York University), Terry Stouch (Bristol Meyers Squibb), Julian Tirado-Rives (Yale University), Steve Walch (NASA-Ames), and John Zhang (New York University).

In addition to the invited talks, there will also be poster papers to contribute to what we anticipate will be a fruitful exchange of information among a broader group of computational chemists and physicists than one usually encounters at a single meeting. Contributed poster papers are invited and strongly encouraged. Confirmed poster contributors at this date include Jan Almlöf, H. Ted Davis (University of Minnesota), David Ferguson (University of Minnesota), Evelyn Goldfield, J. Woods Halley (University of Minnesota), Lester Harris (Abbott Northwestern Hospital), Peter Rossky, George Schatz, and Donald Truhlar. Persons who wish to present a poster should send a one-page abstract by July 25, 1994. Late posters will be accepted on a space available basis.

The registration fee for the symposium is \$150 for registrations received prior to September 30, and \$175 after September 30. A 10 percent discount will be given to members of the cosponsoring divisions of the American Physical Society and American Chemical Society, listed at the top.



To receive more information regarding the meeting, including a list of lecture titles, contact the Symposium Administrator:  
Michael J. Olesen  
Supercomputer Institute  
University of Minnesota  
1200 Washington Avenue South  
Minneapolis, MN 55415  
phone: (612) 624-1356  
fax: (612) 624-8861  
electronic mail: olesen@msi.umn.edu

## THE COMPUTER PHYSICS COMMUNICATIONS PROGRAM LIBRARY

David Fincham (D.Fincham @ keele.ac.uk)

Many readers will be familiar with the North-Holland journal "Computer Physics Communications" which has published many papers relevant to the CCP5 fields of interest. Papers are usually computational in nature, discussing such issues as integration algorithms, neighbour search methods, efficient evaluation of long-range interactions, optimisation and vectorisation. For example the papers of Smith and Forester expounding the fundamental parallel algorithms of the DL-POLY project have recently appeared.

As a Specialist Editor of the journal I would like to encourage readers of the CCP5 Newsletter to submit more such papers, which may be sent directly to me. However, my main purpose in writing is to describe a unique feature of the "Computer Physics Communications", its associated program library. As well as papers on computational methods, the journal includes program descriptions, and the programs themselves are made available through a program library. An important point about this library, which distinguishes it from others such as the CCP5 program library, is that the programs themselves are refereed before being accepted into the library. The CPC library is therefore playing an important role in raising the standards of scientific software. Personally I attach great importance to this. Developments in computational methods will only receive the use they deserve if they are incorporated in robust, efficient and easy-to-use software.

At the moment the library is particularly weak in the area of molecular simulation. There is my very old Ewald sum program, Laaksonen's aqueous solution program, and a series of programs from Rycerz and Jacobs which primarily illustrate neighbour search algorithms, plus a few other rather specialised programs. We would really appreciate more programs from the CCP5 community. How about some rigid molecule programs, some Monte-Carlo and Gibbs ensemble programs, some multipolar and polarisable models, some stochastic dynamics? In the solid-state area there are some specialised lattice dynamics programs, but room for more, as well as for m.d programs in this area.

If you are writing simulation programs, please consider submitting them to Computer Physics Communications as well as to the CCP5 library. I know that bringing programs up to the required standards to get through the refereeing process, as well as producing documentation, is a very time-consuming process, but it is also a very useful service to the community which will be appreciated. And it will count as a refereed publication!

# HOW TO DERIVE THE INTERATOMIC POTENTIALS NEEDED FOR SIMULATION STUDIES

Mansfield College Oxford July 4th and 5th 1994

A meeting sponsored by the Collaborative Computational Programme CCP5 of EPSRC, with financial support from Biosym, Unilever plc, and the Polar Solids Discussion Group of the Royal Society of Chemistry

## Conference Organisers

Dr R.W. Grimes,  
The Royal Institution,  
London

Dr A.H. Harker,  
AEA Technology,  
Harwell

## ABSTRACTS OF ORAL PRESENTATIONS

### *Ab initio* databases for testing empirical potentials

M.C. Payne, I.J. Robertson<sup>1</sup>, D. Thomson and V. Heine

<sup>1</sup> Present address: J. Henry Schroder Wagg & Co. Limited, 120 Cheapside, London, EC2V 6DS.

Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE

A subjective view has always to be taken of the nature of the interatomic interactions for the purpose of constructing interatomic potentials so that a specific potential will embody particular forms of interactions such as two-, three- and higher-body interactions or many-body interactions. The strengths of these interactions are determined by fitting to the available experimental data. In many cases, such experimental data is extremely limited and may have only marginal relevance to the atomic environments modelled in the simulation. Hence, the accuracy of the resulting interatomic potential in the regions of phase space to be investigated is normally not known. Since one of the common difficulties associated with constructing interatomic potentials is the lack of a significant amount of reliable experimental data that can be used to parametrise the potentials, the use of *ab initio* methods to provide accurate energies and interatomic forces for any arrangement of atoms can obviously make a significant contribution to the process of constructing potentials by providing data in those regions of phase space which are most important for the processes to be studied. Several strategies have been adopted for using *ab initio* data in parametrising interatomic potentials. *Ab initio* molecular dynamics simulations provide enormous datasets for fitting interatomic potentials<sup>[1]</sup> but it is far from clear that fitting to such data for, say, a liquid will produce a potential that is accurate for a surface. Perhaps the more relevant, and demanding, question is whether a single interatomic potential is suitable for both the bulk and the surface. In our approach<sup>[2,3]</sup> we have generated a database of energies for 183 configurations of aluminium atoms with coordination numbers between 0 and 12. The database covers a range of interatomic separations and dimensionalities of structures. The size of the database is of significance because it allows the process of parametrising an interatomic potential and testing the accuracy of the resulting potential to be separated. This step is crucial in order to avoid the problem of overfitting

a potential to the dataset, which is liable to produce a potential which is not accurate for atomic configurations outside the original dataset.

We have considered the ability of two- and three-body potentials and of many-body (glue model) potentials to accurately reproduce the energies of our database. We find that interatomic potentials with two- and three-body terms are totally incapable of describing the variation of energy over the whole range of coordination number, though they may work reasonably well over a small range. In contrast, glue models describe the trends over the whole range of coordination number extremely well. However, glue models still show significant errors for individual structures and, hence, they may give incorrect predictions for specific physical properties.

[1] F. Ercolessi and J.B. Adams, to be published in *Europhys Lett* (1994)

[2] I.J. Robertson, M.C. Payne and V. Heine, *Europhys Lett* **15**, 301 (1991)

[3] I.J. Robertson, V. Heine and M.C. Payne, *Phys. Rev. Lett.* **70**, 1944 (1993)

### A modern valence bond approach for interionic potentials

David.L. Cooper

Department of Chemistry, University of Liverpool

An attractive approach to intermolecular forces is to build the total wavefunction for a weakly-bound molecular complex from those of the unperturbed interacting fragments. A modern valence bond strategy is described which treats properly the overlap between the fragments whilst avoiding basis set superposition error. Recent results are presented for LiH..He. Analogous methodology has been employed to calculate two-body interionic potentials. Preliminary results are presented for binary oxides, chlorides and fluorides of alkali- and alkaline-earth metals. Factors discussed include the stabilisation of anions in a suitable Madelung potential, lattice symmetry, electron correlation in the fragments, and compression effects due to nearest neighbours.

### Bond order potentials for covalent systems

A.P. Horsfield <sup>1</sup>, D.G. Pettifor <sup>1</sup>, M. Aoki <sup>2</sup> and C. Goringe <sup>1</sup>

<sup>1</sup> Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH

<sup>2</sup> Department of Physics, Gifu University, 1-1 Yanagido, Gifu, 501-11, Japan

An angularly-dependent many-atom expansion has recently been derived for the bond energy within the Tight Binding model for electronic structure. It accounts properly for directional bonding in covalent materials. The background theory and essential concepts are presented. The method has been successfully applied to *sp*-valent systems, *d*-valent transition metals and refractory carbides. In particular, for silicon, structural energy differences, elastic constants, surface reconstruction, the Jahn-Teller distortion at a vacancy, defect formation energies, the structure of the liquid and small clusters have all been modelled.

The Bond Order Potential is compared with recent density matrix method <sup>[1]</sup>. The two methods are found to be comparable for semiconducting systems, though the Bond Order Potential is much more rapidly convergent for conducting systems.

[1] Li, X-P., Nunes, R.W. and Vanderbilt, D. *Phys. Rev. B* **47** 10891 (1993)

### Anisotropic atom-atom potentials for molecules

S.L. Price

Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ

The forces between polyatomic molecules are traditionally represented by the isotropic atom-atom potential model. However, the implicit assumption that the atoms interact as if they were spherical is a poor approximation for some elements. This paper outlines some of the progress being made in developing anisotropic atom-atom potentials, which can represent the effects of lone pair and  $\pi$  electron density on intermolecular interactions. It is difficult to determine the form of an atom's anisotropy empirically, and so it has to be derived from the molecular charge distribution, using recently developed theories of intermolecular forces. This can be done for each major contribution to the intermolecular potential for small polyatomics, resulting in more accurate intermolecular potentials. For organic molecules, at the moment, only the electrostatic contribution can be routinely described in this way, through a distributed multipole analysis. However, computational studies using such an accurate electrostatic model, in conjunction with simple approximations for the other contributions, have been useful for understanding the structures of van der Waals complexes, biochemical interactions and molecular crystal structures.

The development of new computer codes is gradually allowing anisotropic atom-atom potentials to be used routinely for an increasing range of types of simulation. Nevertheless, it will often be desirable, and adequate, to approximate an accurate potential by a simpler isotropic site-site form, with additional sites representing the anisotropic features. Assuming the isotropic atom-atom potential, without careful consideration of the distribution of charge in the molecule, can lead to problems in deriving quantitatively adequate potentials for many molecules, and can even lead to conceptual problems.

### Realistic description of many-body polarisation effects in simulations of ionic systems

P.A. Madden and M. Wilson

Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ

In order to represent the many-body aspects of polarisation interactions in ionic systems we have developed molecular dynamics algorithms based upon the Car-Parrinello strategy, in which distortions of the electronic structure of an ion due to interionic interactions are represented in a simplified way. Additional degrees of freedom which represent this structure are added to the ionic coordinates and the equations of motion extended accordingly, so that these variables are updated to their self-consistent, adiabatic values as the ions move, without the need for explicit energy minimisation<sup>[1]</sup>. The representation of the induced moments is not constrained by a particular model of the interionic interactions, as in the standard Shell Model. Short-range corrections to the asymptotic induction and dispersion terms are parametrised on the basis of *ab initio* electronic structure calculations.

The polarisable ion model accounts, *inter alia*, for the fact that  $\text{MX}_2$  systems (where M is a group II or IIB metal) crystallise into *layered* structures, for large radius ratios<sup>[2]</sup>. It also reproduces distinctive features of short- and intermediate-range order in  $\text{MX}_2$  melts, which have been detected in neutron scattering experiments, but eluded explanation<sup>[3,4]</sup>. The distinctive role played by the induction effects in pushing highly polarisable anions into asymmetric sites is also detected in a range of oxides. It seems that this simple extension of the ionic model accounts for many properties which have been regarded as 'covalent'. Besides simple dipole polarisation, recent extensions of the method allow a representation of induced quadrupoles and of the fact that some ions, like the oxide ion, change their effective radius in response to changes in their environment.

[1] M. Wilson and P.A. Madden *J. Phys. Condens. Matt.*, **5**, 2687 (1993)

[2] M. Wilson and P.A. Madden *J. Phys. Condens. Matt.* **6**, 159 (1994)

[3] M. Wilson and P.A. Madden *J. Phys. Condens. Matt.* **6**, A151 (1994)

[4] M. Wilson and P.A. Madden *Phys. Rev. Lett.* **72**, 3033 (1994)

## Derivation and properties of force related atomic multipoles

C.S. Ewig<sup>1</sup>, U. Dinur<sup>2</sup> and A.T. Hagler<sup>1</sup>

<sup>1</sup> BIOSYM Technologies, 9685 Scranton Road, San Diego, CA 92121 USA

<sup>2</sup> Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

“Force related” procedures refer to the use of atomic polar tensors (atp) and related quantities for predicting intermolecular electrostatic interactions. The parameters consist of atomic charges, multipoles, and charge-flux parameters obtained from quantum calculations of electrostatic properties. The derivation of parameters in this way provides a number of advantages over earlier procedures:

- (1) the parameters produce both interaction forces and energies simultaneously; accurate forces are of especial importance in molecular dynamics simulations or in optimising intermolecular geometries,
- (2) the derivation gives both multipoles and charge flux, the latter needed to reproduce the directional dependence of electrostatic forces about molecules and dependence of charges on molecular geometry,
- (3) they generally give accurate electrostatic potentials around molecules,
- (4) they are uniquely derivable from well-defined quantum observables, such as the atp,
- (5) the atomic multipoles reproduce the molecular multipoles exactly within the computational method employed, and
- (6) they correctly reproduce the asymptotic behaviour of the intermolecular interactions at large separations.

In this paper the general mathematical properties of force related multipoles, as well as charge flux, will be reviewed. The recently developed method for computing these parameters for molecules of arbitrary symmetry will be outlined. The computed values of the resulting multipoles for some simple molecules such as water and formamide may be compared directly to those predicted by other methods. For pairs of molecules the interaction energies retaining successively higher order terms in the multipole expansion are presented. The same comparison may be performed with the multipole expansions defined by other approaches. Finally the properties of molecular crystals (lattice vector lengths and angles, and lattice energies) are given for differing types of multipole expansions. We focus particularly on the formamide crystal. The results show that the force related formulation provides a general, consistent, and accurate procedure for modelling intermolecular electrostatic interactions.

### **Towards a general strategy for global interatomic potentials for elemental solids, surfaces and clusters**

J.N. Murrell

School of Chemistry and Molecular Sciences University of Sussex, Falmer, Brighton BN1 9QJ

Many problems of molecules and solids can be tackled within the Born-Oppenheimer approximation in which structure and dynamics are determined by a potential which depends on the internuclear distances. There is a hierarchy of assumptions that can be made about these potentials ranging from the simplest (optimistic), which is that the potential is pair-additive, to the

most complicated (pessimistic), that no useful analytical function can be found. Between these two extremes many functions have been investigated and the one we have been studying for elemental solids is a 2-body plus 3-body potential with simple analytical functions for each term.

We have been mainly concerned with the following question. If we fit with high accuracy the properties of a solid, taking more than one solid phase if these are known, will we obtain potentials which are useful for studying surfaces and clusters? We recognise that in this approach our cluster potentials are not electronic state specific, so for small clusters in particular they will have limited use.

The parameters in our potentials reproduce the following solid state data: cohesive energy, lattice constant, phonon frequencies, elastic constants and vacancy formation energy. In addition the potential must reproduce the correct order of cohesive energies of different solid structures where these are known, or, at the least, make the fitted structure the most stable.

Examples will be given to show the outcome of this procedure for simple metals and transition metals and for group 4 solids.

This work has been carried out in the School of Chemistry and Molecular Sciences at the University of Sussex with the help of several postgraduates and postdoctoral workers.

I acknowledge particularly the work of Dr R.L. Johnston, currently a Royal Society University Research Fellow.

### Interionic potentials for oxides

J.H. Harding

AEA Technology, 424.4 Harwell, Oxfordshire

Oxides are important materials. They range from the classical refractory ceramics such as MgO and Al<sub>2</sub>O<sub>3</sub> to complex mineral silicates. So diverse a range of materials has been tackled by a wide range of potential models. It is not proposed to review them all here. Rather, the objective of the talk is to discuss what criteria one might look for in a potential and what special features there are for oxides. Both empirical and calculated potentials will be considered. Questions of the meaning of ionicity will be reviewed and the modelling of oxide ions in the crystalline environment will be discussed.

### The computer modelling of oxide surfaces

M.J. Gillan, I. Manassis and S. Pugh

Physics Department, Keele University, Staffordshire ST5 5BG, U.K.

The talk will present the results of recent *ab initio* calculations on the surfaces of a variety of oxide materials. The results allow a critical examination of the predictions of interatomic potential models for the energetics and structure of oxide surfaces. The comparisons to be presented provide strong support for the reliability of current models.

### Future directions in empirical potential derivation

J.D. Gale

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London, SW7 2AY, UK.

Recent developments in the field of empirical potential derivation for ionic materials will be reviewed, with particular reference to the fitting of shell models. Examples of both "simultaneous" and "relaxed" fitting, as implemented in the program GULP will be given, indicating their merits over previous fitting methods.

Improved reliability of empirical potentials may be achieved by fitting many structures concurrently, rather than sequentially. The quality of a purely empirical oxygen-oxygen potential derived in this way will be examined for the energy of an oxygen interstitial in alumina, as compared with existing potentials and *ab initio* calculation. Compatibility of bulk and gas phase data for empirical fitting within the ionic model will also be addressed.

To date the majority of empirical potentials have been derived for application in athermal simulations. However, with the increasing use of free energy methods and molecular dynamics the future lies in fitting at finite temperatures. Results will be presented for the alkaline earth hydroxides in which potentials have been derived under the experimental conditions. The implications of lattice dynamics for theoretical calculations of interatomic potentials will be examined in this context.

I would like to thank Drs. Tim Bush and Andrew Rohl for their contribution in many of the examples that will be presented, and to thank the Royal Society for funding.

## ABSTRACTS OF POSTER PRESENTATIONS

### Polarisation effects on amino-acid and peptide conformation

D.A. Mac Dónaill and D.A. Morton-Blake

Department of Chemistry, Trinity College, Dublin 2, Republic of Ireland.

Notwithstanding recent advances in the simulation of polarisable environments <sup>[1,2]</sup>, in vacuo models are still widely employed in simulations involving supposedly "inert" solvents or environments <sup>[e.g.3]</sup>. In the calculations reported here a modified CNDO/2 method <sup>[4]</sup> was used to calculate the conformational energy surface of zwitterionic glycine and of the glycyl dipeptide in a simulated polarisable environment. The results were compared with in vacuo simulations.

While the calculated global minimum for the in vacuo glycine zwitterion corresponds to an eclipsed conformation, the allowance of even a small degree of environmental polarisability inverts the relative stabilities of the staggered and eclipsed forms. For the dipeptide, the C5 minimum resists small increases from zero polarisability, while the C7 minimum shifts to a nearby, related position. The latter result may explain apparently contradictory structural inferences drawn from i.r. and n.m.r. spectroscopy.

The calculations indicate that in vacuo models can be unreliable, even for supposedly "inert" media, and thus short-range potentials fitted to such calculations are also unreliable. Environmental polarisability should be explicitly considered in the calculation of short-range potentials.

[1] S. Ten-no, F. Hirata and S. Koto, *Chem. Phys. Lett.*, **214**, 391 (1993).

[2] S. Ten-no, F. Hirata and S. Koto, *J. Chem. Phys.*, **100**, 7443 (1994).

[3] C. Aleman and J. Percy, *Int. J. Pept. Prot. Res.*, **43**, 258 (1994).

[4] R. Constanciel and O. Tapia: *Theoret. Chim. Acta* **48**, 75 (1978).

### The search for global potential energy functions for metallic elements

Jason E. Hearn, Catherine R. Griffiths and Roy L. Johnston



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This poster presents some applications of the Murrell-Mottram type of 2-plus-3-body potential to metallic elements. For calcium, it has proven possible to derive a potential which gives a good fit to the phonon frequencies, elastic constants and vacancy energies of both the low temperature fcc and the high temperature bcc allotropes. This potential is currently being used to study the fcc-bcc phase transition of Ca. For sodium, which adopts the bcc structure at ambient temperature and pressure, a potential, derived by fitting lattice dynamical properties of the solid, has been used to predict the structures and relative stabilities of small clusters  $(\text{Na})_n$ , where  $n \leq 20$ . In agreement with other studies of sodium cluster growth icosahedral-based structures are generally found to be the most stable. The M+M potential has also been shown to give good results for transition metals such as iron (both the bcc and fcc forms) and Cu, Ag, Au. This is not surprising, since many-body forces are expected to be more significant for transition metals than for the simple Group 1 and 2 metals.

### **Empirical tight-binding parameters for silicon-boron, with applications**

Paul B. Rasband, Andrew P. Horsfield and Paulette Clancy

Department of Chemical Engineering, Cornell University, Ithaca, New York

Empirical Tight-Binding, when used with the recent developments in distance-scaling functions, is a very powerful tool for the study of point defects in semiconducting matter. Accurate information on relaxed structures, formation, binding, and migration energies and entropies, valence band structure, and more can be obtained through such potentials.

Our group has used the Goodwin-Skinner-Pettifor functional forms with Si-B ETB parameters to study the interaction between boron and silicon point defects, emphasising questions which deal with boron diffusion during semiconductor processing. The parameters were fitted to *ab initio* (LDA pseudopotential) data obtained using the Corning code. The structure of the occupied bands for zinc blende SiB are reproduced very well; the root-mean-square error for the 56 fitted band energies is 0.16eV. The three parameters involved with the repulsive potential have been fitted directly to formation energies for boron-defect pairs.

In addition to a description of the parameter fitting and evaluation, we will present results of migration energy studies for vacancy and interstitial mediated diffusion paths.

### **Empirical tight-binding parameters for silicon-boron, with application to boron-defect pairs in crystalline silicon**

Paul B. Rasband, Andrew P. Horsfield and Paulette Clancy

School of Chemical Engineering, Cornell University, Ithaca, NY

A set of Empirical Tight-Binding parameters for use with well-established functional forms has been produced to describe the interactions between Si and B atoms, complete with a quantum mechanical treatment of valence electrons. The functional forms adopted to describe the distance scaling of orbital interactions and ion-ion repulsion have been used successfully by other authors to treat Si-Si and C-C interactions. Here Si-B parameters are presented which have been chosen to reproduce ground-state band structures and total energies obtained from *ab initio* calculations. While the parameter fitting was done for tetrahedral configurations, the functions used have proven to be very flexible in the case of Si-Si interactions, suggesting that these Si-B parameters are

transferable to other structures. In addition to a discussion regarding the parameter development, this work also presents some examples of the application of the Si-B ETB model in studying defect-dopant pair formation. The ultimate objective of this ETB parameter development is to provide a means of accurately predicting formation and migration energies and entropies of neutral and charged species involved in the diffusion of boron during the production of semiconductor devices.

### Dynamics of adsorbed ammonia molecules on titanium dioxide (rutile) surfaces

Dietmar Paschek and Alfons Geiger

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The dynamics of adsorbed ammonia molecules on titanium dioxide (rutile) surfaces has been studied by molecular dynamics simulations in conjunction with  $^1H$ - and  $^2H$ -NMR measurements.

The  $^2H$ -spectra show an amazing dependence of the signal shape on the degree of coverage. At low coverage Pake-type solid state powder spectra occur. If the coverage becomes larger than about 0.75 monolayers, they change to orientationally averaged singlets, characteristic of a liquid-like mobility of the adsorbed molecules.

The results of our molecular dynamics simulations are consistent with these NMR measurements and give a simple explanation for the observed mobility increase. The  $\langle 110 \rangle$  surface consists of lines of  $Ti^{4+}$  adsorption sites, separated by linear walls of oxygen atoms. Because of the strong lateral repulsive interaction between ammonia molecules adsorbed on neighbouring sites, the lateral and orientational mobility increases drastically in the coverage range between 0.6 and 0.8 monolayers. In parallel, the distribution functions characterising the positions and orientations of the adsorbed molecules change strongly.

Our simulations serve as a practical tool for obtaining more detailed microscopic information from NMR data than would be possible by using conventional model calculations.

### Non-additive intermolecular forces in molecular systems: what can we learn from the spectroscopy of van der Waals trimers?

Andreas Ernesti and Jeremy M. Hutson

Department of Chemistry, University of Durham, Durham, DH1 3LE

Over the last few years, very accurate pair potentials have been developed for prototype systems such as Ar-HF and Ar-HCl by fitting to extensive high-resolution microwave, far-infrared and mid-infrared spectra of van der Waals dimers. These are now the best-characterised of all potential energy surfaces involving molecules (as opposed to atoms), and have been used very successfully to calculate collisional properties such as pressure broadening cross sections and molecular beam scattering results.

In order for accurate pair potentials to be useful in simulations, we need to understand many-body forces as well. Although there has been a great deal of work on non-additive forces in purely atomic systems, it has proved very difficult to find sources of information on non-additivity in systems containing molecules. Now, for the first time, the spectroscopy of van der Waals complexes is starting to provide such information.

Several experimental groups (Gutowsky, Saykally, Nesbitt) have now been able to measure high-resolution microwave, far-infrared and mid-infrared spectra of trimers such as  $Ar_2 - HCl$  and  $Ar_2 - HF$ . Since all the pair potentials are very well known, the spectroscopic results can be compared with calculations based on pairwise-additive potentials. We have developed the

computational methods needed to do this. We have shown that calculations using trimer potentials based on pairwise additivity give significant discrepancy with experiment (typically 2 to 3  $\text{cm}^{-1}$  error in the bending frequencies of the trimers). These discrepancies are about a factor of 5 larger than can be attributed to uncertainties in the pair potentials. We have investigated various sources of non-additive forces, including anisotropic triple-dipole dispersion forces and exchange overlap forces. We have concluded that the most important contribution to the changes in spectroscopic properties comes from a new type of non-additive force, which does not exist in purely atomic systems: this is the electrostatic interaction between the permanent multipoles of the HX molecule and an exchange quadrupole that develops on  $\text{Ar}_2$  at short range. This is a very general effect: in any system containing molecules, short-range exchange and overlap effects modify the charge distributions of the monomers, and thus modify the electrostatic interaction with a third molecule.

In future work, we hope to be able to *determine* details of the non-additive forces from the trimer spectra.

### **The effect of defects on the stability of heteroepitaxial ceramic interfaces using pair potentials**

D.C. Sayle <sup>1</sup>, T.X.T. Sayle <sup>2</sup>, S.C. Parker <sup>3</sup>, J.H. Harding <sup>4</sup> and C.R.A. Catlow <sup>1</sup>

<sup>1</sup> The Royal Institution, London

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<sup>3</sup> Department of Physics, University of Bath

<sup>4</sup> AEA Technology, Harwell

Static simulation techniques have been used to examine the defect chemistry in the heteroepitaxial ceramic interfaces  $\text{BaO}(100)/\text{MgO}(100)$  and  $\text{CeO}_2(111)\alpha - \text{Al}_2\text{O}_3(001)$ . Reduced ion density at the interface is seen to enhance the stability of the  $\text{BaO}(100)/\text{MgO}(100)$  interface. Interfacing  $\text{CeO}_2$  with  $\alpha - \text{Al}_2\text{O}_3$  promotes the migration of oxygen from the interfacial plane to the surface, a process that may be of importance in catalytic reactions.

### **Simulation of lithium insertion into metal oxides**

Andrew W.J. Smith, M.G.B. Drew, R.J. Hobson and V. Padyaychy

Department of Chemistry, University of Reading

Computer simulation techniques are an increasingly useful tool for various problems associated with solid state chemistry. They are most useful when used in conjunction with experimental techniques such as X-ray and neutron diffraction. However, they can also be helpful to investigate processes where there is little experimental information available, such as diffusion processes in solids.

Initially work was conducted to reproduce known crystal structures using a simple force field. The traditional Born model was used consisting of the electrostatic and non-bonded terms. The 6-12 Lennard-Jones potential (LJ) was used for the non-bonded terms containing the parameters  $\epsilon$  and  $R$ . However, for accurate reproduction of crystal data an in-house program, PARAM was developed which optimises the  $R$  parameter in the LJ potential. This has enabled more complicated structures to be studied by static relaxation methods and by Monte Carlo techniques. Starting values for  $\epsilon$  and  $R$  were taken from the Universal Force Field (UFF) <sup>(1)</sup>. A function  $F^2$  is defined as the sum of the square of the partial derivatives of the potential energy along the axes  $a$ ,  $b$  and  $c$

. During parametrisation  $F^2$  is minimised with respect to the  $R$  parameters. The Simplex method was used to perform the minimisation.

This work has provided parameters suitable to model diffusion of lithium in some metal oxide host structures such as  $\text{TiO}_2$  and  $\text{ReO}_3$  and these results will be presented.

This work has been supported by the Defence Research Agency.

[1] A.K. Rappe et al., *J. Am. Chem. Soc.* **114**, 10024-10035 (1992)

### Modelling of inorganic systems

Malcolm D. Shakesby and Michael G.B. Drew

Department of Chemistry, University of Reading

Potentials are being developed for rigid model and shell model calculations of a range of simple metal oxides using a variety of parametrisation procedures. We are particularly concerned with the interaction of gases within the oxides and therefore have concentrated upon development of potentials to evaluate the interaction of the gases within the solid. These potentials allow calculation of the preferred binding sites of the adsorbates in the system and their mobility through the system.

Of particular interest is the interaction of hydrogen with these solids and the problems encountered with deriving parameters for  $\text{H}_2$ ,  $\text{H}^+$ ,  $\text{H}^-$  and  $\text{OH}^-$  will be discussed. Many of the properties of absorption in metal solids are due to defects in the solid and the effect of such defects upon the calculations will be described.

### A periodic Hartree-Fock treatment of $\text{VO}_2$ : derivation of interatomic potentials

B. Slater and M.G.B. Drew

Department of Chemistry, University of Reading

We present central force potentials derived from an *ab initio* study of the metallic, rutile-type phase of  $\text{VO}_2$ . Relaxation of the unit cell at constant pressure reproduces the lattice constants to within 4%. These potentials have been used to study a first order semiconductor  $\rightarrow$  metallic phase transition which occurs at 340K. Below the transition temperature the regular rutile structure is significantly distorted, exhibiting alternate short and long metal-metal distances. We have performed Monte Carlo simulations using the derived potentials which are able to reproduce the subtle structural changes associated with this transition. Analysis of the configurations reveals that the phase transition is initially mediated by the oxygen anions.

### Computational sorption studies of alkanes in zeolites

Michael G.B. Drew and Paul M. Hobbs

Department of Chemistry, University of Reading

Alkane sorption in a pentasil zeolite has been studied through simulations. A series of alkanes, including methane, propane, n-butane, iso-butane and three hexane isomers, were studied in silicalite. Statistical mechanical principles have been employed to predict sorption equilibria at low occupancy. Henry's constants and isosteric heats of sorption were calculated, using the CERIOUS<sup>(1)</sup> software package from Molecular Simulations, through the evaluation of configurations with a Monte Carlo integration scheme. A range of Lennard-Jones parameters for carbon, hydrogen,

silicon and oxygen was used. The effects of using united atoms in the alkane and of removing the silicon atoms from the zeolite were estimated. An optimised set of parameters was obtained by fitting to experimental data for n-hexane and was then subsequently used with other alkanes. The results were in good agreement with experimental values in the literature [2].

[1] CERIOUS molecular modelling software for materials research from Molecular Simulations Inc. of Burlington, MA, and Cambridge UK.

[2] J.R. Hufton and R.P. Danner, *AIChE Journal* **39** (6), 945-961 (1993)

### RMC with interatomic potentials: modelling the structure and dynamics of an amorphous system?

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The Reverse Monte Carlo (RMC) method [1] has achieved significant success at modelling the structure of a range of disordered materials in recent years. One of the prime examples of this has been the simulation of experimental neutron diffraction, X-ray diffraction and EXAFS data simultaneously in the production of structural models of the four-component fast-ion conducting glass,  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  [2]. This study will show the progress currently being made in developing an *ab initio* determination of an interatomic potential from a final structural model created with RMC. The challenge to overcome and the potential benefits of this approach will be described.

[1] R.L. McGreevy and M.A. Howe (1992) *Ann. Rev. Mater. Sci.* **22**, 217.

[2] J.D. Wicks, L. Börjesson, G. Bushnell-Wye, W.S. Howells and R.L. McGreevy (1994) *Phys Rev Lett* in press.

### Significance of higher order many-body interaction energy terms in water clusters and bulk water<sup>1</sup>

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<sup>2</sup> Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy.

The magnitudes of the 2- through 6-body energy terms and their contribution to the interaction energy of small ring water clusters ( $n=2$  to 6) are computed at the Hartree-Fock (HF) and second through fourth order many-body perturbation (MP2, MP4) levels of theory. Each water molecule in the ring acts both as a proton donor and a proton acceptor resulting in one hydrogen bond per water molecule. This fact increases the polarisation of each fragment due to its neighbours and enhances, accordingly, the total as well as the individual many-body interactions. We have found that 3-body terms have a significant contribution (as high as 30%) to the interaction energy of the larger clusters and that 4-body and higher order terms are negligible. Electron correlation accounts for a 10 to 20% increase in the individual 2-body terms and a much larger increase of

75% for the 3-body and 200% for the small 4-body terms. The MP4 results are found to differ only slightly (<20%) from the corresponding MP2 results.

Many-body energy terms higher than two are, however, less significant for configurations resembling bulk water which have, on the average, two hydrogen bonds per water molecule.

### Deriving intermolecular potentials for predicting the crystal structures of polar molecules

D.S. Coombes

Department of Chemistry, University College, London

Most successful work on crystal structure modelling and prediction has concentrated on the crystal structures of non polar molecules. Attempts to extend the isotropic atom-atom potential method to polar molecules, however, have met with only limited success. This can be attributed to the fact that for polar molecules, the electrostatic contribution to the intermolecular potential will dominate the lattice energy, particularly if hydrogen bonding occurs within the crystal.

The electrostatic contribution to the intermolecular potential can be accurately described using a theoretically rigorous distributed multipole model for the charge distribution, which describes the molecular charge distribution as a set of point multipoles, usually on every atomic site.

The ability of a distributed multipole model, together with literature isotropic atom-atom repulsion-dispersion potentials, to model the crystal structures of a diverse range of polar organic molecules is investigated. This potential provides surprisingly good structure predictions and thus provides a benchmark and starting point for further optimisation.

This poster describes improvements on this set of isotropic atom-atom repulsion-dispersion potentials by least squares fitting to a set of crystal structures and lattice energies.

### Extracting and validating force fields for disordered polymeric materials from neutron scattering data

B. Rosi-Schwartz and G.R. Mitchell

Polymer Science Centre, J.J. Thomson Physical Laboratory, University of Reading

Many of the useful properties of polymeric materials ultimately depend on the connectivity and flexibility characters of the chain molecules. In general these features can be described in terms of 2, 3 and 4-body intramolecular potentials relating to bond stretching, valence angle bending and dihedral rotation respectively. For each of these contributions, the various force fields proposed to date depend on a number of "empirical" constants describing the detailed shape of the potential. These constants have been derived either from fits to spectroscopic and thermodynamic data or from *ab initio* calculations; in both cases the parameters are obtained on relatively simple model systems. The resulting force field expressions form the basis for the definition of the chain conformation in all theoretical predictions and atomistic modelling of polymer behaviour and properties. Although the assumption is made that these potentials work equally well for simple molecules and for systems as complex as polymers, such an assumption is not entirely justified and may seem somewhat arbitrary.

In this work we shall present a new approach that allows the determination of force field parameters from experimental neutron diffraction data obtained over a large  $Q$  range, through a tight coupling of computer modelling predictions with experimental neutron scattering results. The method is based on the generation of a model single chain through the assignment of analytical

expressions for the force fields of interest and on the systematic variation of the parameters constituting these analytical expressions to minimise the difference between predicted and experimental diffraction patterns. Particular attention will be devoted to the torsional term, since this is the term responsible for the degree of flexibility of the chain. We will present the sensitivity and the potential of this analysis strategy in a few case studies, specifically chosen for the varying level of stiffness of the polymer chains under investigation.

### Potential models for multi-component oxides: hexa-aluminates

Jae-Gwan Park and Alastair N. Cormack

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The phase equilibria and crystal chemistry of multi-component hexa-aluminates shows a considerable variation as a function of composition. Our interest is in rationalising this variation through an understanding of the structural stability as a function of stoichiometry and defect chemistry, which may be obtained from atomistic computer simulations. Our recent experiences in the use of interatomic potential models for the simulation of complex multi-component oxides are discussed with particular reference to alkaline earth hexa-aluminates,  $MA_{12}O_{19}$  ( $M=Ca, Sr, Ba$ ). We have found that simply transferring parameters from models of binary oxides is not necessarily valid, and that the usual test of reproducing the experimental crystal structural parameters is not by itself sufficient. A re-examination of the potential model for  $SrAl_{12}O_{19}$  revealed the need to include a consideration of cation coordination, as had been found desirable in simulations of spinels. Furthermore, it is also found that when the consideration of cation coordination is limited within the spinel-structured blocks in the structure of hexa-aluminates as well as when an appropriate set of binary oxide potential models is transferred, the thermodynamic stabilities of the related complex compounds are correctly predicted.

### The conformation of DNA containing chemically modified base pairs

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N-nitroso compounds are known to chemically modify normal DNA bases and result in mutations which either are corrected by repair proteins or lead to misreading of the code and possibly carcinogenesis. Molecular dynamics simulations of normal oligonucleotide sequences are commonly used to study conformation and dynamics. In order to undertake simulations of the modified sequences, we have extended the AMBER force field to allow for the  $O^6$ -methyl- and  $O^6$ -ethyl-guanine bases.

Our simulations show that the AMBER force field produces stable oligonucleotide double helices over 2,400 picoseconds. The normal sequence behaves as expected with Watson-Crick hydrogen bonds between the base pairs. The modified sequences with ethylguanine-cytosine base pairs leads to local disruption of the base pair because of the chemical modification of the guanine base but all other base pairs retain their normal conformation. The resulting modified base pair has only two hydrogen bonds and adopts the so-called wobble conformation. The resulting structure is likely to be less stable than the normal hydrogen bonding pattern and is likely to be recognised as different by a repair protein.

## Potentials for B-metal compounds: the stannates $M\text{SnO}_3$ ( $M=\text{Ca},\text{Sr},\text{Ba}$ ) and $\text{SnO}_2$

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Reliable potentials for B-metal oxides and halides have been notoriously difficult to obtain. We report a consistent set of potentials for alkaline earth stannates and tin (IV) dioxide. Results are presented relating to structure, defect properties and redox behaviour.

## Thermoelastic and dielectric properties of KCl and NaCl crystals in the quasi-harmonic approximation: fully automatic approach

L.N.Kantorovich

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Detailed general expressions are derived for the 1st and 2nd order derivatives of the Helmholtz free energy of an arbitrary crystal with respect to both internal and external strains in the quasi-harmonic approximation (QHA). This enables one to calculate a wide range of thermoelastic and dielectric properties of any non-primitive crystal for arbitrary temperature and general stress conditions by means of a single calculation since our final formulae contain just lattice summations similar to those used to study crystal phonon spectra and higher order elastic constants.

The pairwise potential energy of the crystal is taken from the theory of deformable dipoles by K.B.Tolpygo which includes the usual shell model as a special case. We prove by proper microscopic consideration that microscopic and macroscopic expressions for the elastic energy of any piezoelectric crystal coincide. The theory was implemented in a friendly computer code which fully exploits the crystal symmetry. Special attention is paid to the most efficient numerical realisation of the method.

Numerical results are presented for rock salts KCl and NaCl for which elastic and dielectric properties versus temperature and pressure were studied. The calculations clearly show that empirical pair potentials of Catlow et al are in reasonably good agreement with most of the zero-pressure data. However, these potentials must be revised if experimentally observed high-pressure properties of these crystals are to be reproduced. Our calculations in the vicinity of the melting point demonstrate that the transition is controlled only by the isothermal elastic constant  $C_{11}$ . It decreases so catastrophically rapidly with increase of temperature that it leads to an immediate violation of the stability condition  $C_{11} > C_{12}$  for isothermal elastic constants. In addition, we show that by means of the quasi-harmonic approximation physically correct qualitative results could be expected much further than half of the melting temperature.

## Parametrisation of empirical potentials in the presence of a distributed multipole electrostatic model

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The commonly used Buckingham form for the repulsion-dispersion potential can be parameterized in terms of its well depth, minimum energy separation and a steepness parameter. This gives an easy framework for the computer modeller to think about the significance of each potential in a given atomistic problem. Although formally called a repulsion-dispersion potential, the real function of the parametrised potential in a model is to account for all the interactions not explicitly calculated. In this paper it is shown how explicit treatment of the electrostatic term in polar organic crystals allows a better parametrisation of the potential to be made. Potentials are fitted to a set of experimental structures and sublimation energies. Different potentials are compared by the net deviation from the X-ray structure on relaxation for the crystals fitted.

### Pseudopotential for the excess electron in polar liquid

Mirosław Sopek and Maria Hilczer

Institute of Applied Radiation Chemistry, Technical University, Lodz , Poland

The methodology for building a pseudopotential between an excess electron and polar molecule in the electronic ground state is presented. The proposed form of the pseudopotential has four contributions:

$$V(r, R) = V_c + V_r + V_{ex} + V_p$$

The  $V_c$  term corresponds to the Coulomb potential,  $V_r$  term to repulsion according to the Pauli principle requiring the orthogonality of the wave function of the excess electron to all occupied orbitals of the molecule,  $V_{ex}$  term stands for exchange interaction whose origin lies in indistinguishability of the excess electron and molecular electrons. The last term  $V_p$  is the polarisation part of potential that results from polarisation effects due to excess electron charge.

The methodology is illustrated in a working example of the development of pseudopotential for the excess electron and methanol molecule. In this case the electrostatic part was approximated by a sum over partial charges located on sites of the molecule. The repulsion and exchange components were based on molecular electronic density while the polarisation part was proposed in a non-spherical form described by polarisation tensor. The electronic calculations were based on UHF *ab-initio* method with double-zeta (9s5p/4s) gaussian basis set.

### Application of pseudopotentials for the path integral simulation of excess electron in methanol

Mirosław Sopek and Witold M. Bartczak

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The question of how the excess electron is bonded to molecules or atoms in a medium in which it solvates still remains unanswered. The computer simulation techniques that rely on fully atomic description of the solvent and fully quantum description for the excess electron are in the best position to answer all questions about nature and behaviour of the excess electron. Despite many difficulties and uncertainties inherently bound to these methods, the main reason why these methods did not result in a full model is a fact that they were applied to a very narrow range of solvents. Regarding the electron in non-polar media, only atomic noble gases were investigated, while in polar media the simulations were performed for water, ammonia and quite recently methanol. In this poster we report some results of our Path Integral simulations of excess

electron in methanol. The simulations are based on the developed pseudopotential which describes the interaction between the excess electron and methanol molecule. Besides standard results of the simulation like the various radial distribution functions, we show the records that suggest that the electron in methanol is involved in a kind of bonding which fulfil the energetical as well as geometrical definition of the hydrogen bond. We conclude our contribution with the sketch of an investigation programme that should be undertaken to support or discard the hypothesis.

#### **Developments in the surface descriptions of silicates**

Paul Baram

School of Chemistry, University of Bath

#### **Derivation of empirical potential parameters for oxide ferroelectric perovskites**

Martin Exner

The Royal Institution, London

#### **Modelling phosphate biominerals**

Marina G. Taylor

Department of Zoology, University of Reading

#### **Use of diamond anvil data in the derivation of potentials**

John Stuart

Department of Chemistry, University College London

#### **Derivation of potentials for molecular ionic materials**

Peter Wilde <sup>1</sup> and Gillian B. Telfer <sup>2</sup>

<sup>1</sup> Department of Chemistry, University of Keele <sup>2</sup> Department of Chemistry, Strathclyde University

#### **On the determination of force field parameters using weak coupling to experimental data**

S.L. Njo

Department of Chemistry, Swiss Federal Institute, Zurich

#### **Computational studies of supported platinum catalysts - developing interatomic potentials from *ab initio* calculations on model platinum clusters**

P. Wolohan

Department of Chemistry, University of Reading

#### **Modelling the hydrogen peroxide-water system**

Matthias Stein

Department of Chemistry, Manchester University

**DMA derived electrostatic charges from density functional methods**

Peter Winn

Department of Chemistry, University of Essex

**Simulations of nitroimidazole bio-reductive agents**

Jon Wright

Department of Chemistry, University of Essex

## Cellular Automata and their Applications to Molecular Fluids

Organised by the Statistical and Thermodynamics Group of the Royal Society of Chemistry, held in Manchester, U.K. on 19 - 20 July, 1994.

In recent years there has been growing interest in the application of cellular automata and lattice gas models to simulate complex systems. The basic operation of these methods is to move particles from one lattice node to another according to well-defined collision and propagation rules. By choosing these rules appropriately, a wide variety of phenomena can be modelled. Furthermore the methodology lends itself ideally to efficient parallelization on a computer, and thus complex systems may be studied which could not be investigated using more conventional techniques.

Approximately 50 people attended the conference, coming from this country and abroad and coming from both industry and universities. As intended, this was not a conference simply for the active practitioners of lattice gas simulations - throughout links were made with theoretical, experimental and conventional simulation work done on the systems of interest and the choice of invited speakers reflected this.

The talks covered a very wide range of topics and the abstracts, given below, illustrate quite how versatile cellular automata can be!

Finally, we would like to thank the sponsors of this conference (Schlumberger, Unilever, Shell and Courtaulds), and also CCP5 for their role in enabling Professor Tony Ladd to visit this country.

Andrew J. Masters  
Department of Chemistry, University of Manchester.

Mark R. Wilson  
School of Physics and Materials, University of Lancaster.

## Numerical Simulations of Particle Suspensions

Anthony J.C. Ladd

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Recent research has led to the development of a promising new technique for simulating hydrodynamically interacting particles [1-3]. The method combines Newtonian dynamics of the solid particles with a discretized Boltzmann model for the fluid; its most important feature is that the computational cost scales linearly with the number of particles. Suspensions containing up to 1000 spheres can be simulated on a desktop workstation; many more particles can be tracked on a massively parallel computer.

In this talk I will outline the basic ideas of the method and discuss two current applications: sedimentation of non-Brownian particles, and the development of hydrodynamic interactions in colloidal suspensions. Comparisons with experiment will also be discussed.

- [1] A.J.C. Ladd, Phys. Rev. Lett., 70, 1339 (1993)
- [2] A.J.C. Ladd, J. Fluid Mech., 271, 285 (1994)
- [3] A.J.C. Ladd, J. Fluid Mech., 271, 311 (1994)

## Numerical simulations of Colloidal suspensions via the Lattice Boltzmann method

Oliver Behrend

University of Edinburgh

In this talk, several methods of treating the solid-fluid boundaries in Lattice Boltzmann simulations of solid particle suspensions will be discussed. A novel and very simple method of adding fluctuations to the fluid will be presented as well as results from simulations of long-time diffusion in concentrated suspensions.

## Dynamics of Colloidal Suspensions

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At high concentrations, the dynamics of suspended colloidal particles are complicated by hydrodynamic couplings transmitted through the liquid suspension medium. Formally the hydrodynamic problem can be stated simply. In practical situations, due to the long range and intrinsic many-body nature of hydrodynamic interactions, its analytic solution has proved largely intractable. For these reasons, simulations, including both lattice gas and lattice Boltzmann modelling of the suspension medium, are proving valuable.

The talk will attempt a largely qualitative summary of the basic physics of colloidal suspensions. The forces (Brownian, direct and hydrodynamic) acting on the particles will be identified, and the relevant time scales discussed. Both quiescent suspensions, in which the particles undergo

interactive Brownian motions, and suspensions out of equilibrium, due to the application of external forces, will be considered.

### **Computer Simulation of Complex Fluid Flows**

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Research on complex fluids has great significance for a large number of industrial applications as well as for newly emerging technologies. A novel computer simulation technique, the Lagrangian/Eulerian method, for modelling complex fluid flows will be presented. The essential feature of our method is to explicitly track the motion of fluid elements in a Lagrangian fashion and to solve for the fluid fields on a co-moving grid in an Eulerian manner at each physical time step. The method is able to track the details of the fluid motion, e.g. deformation and stream lines, and it also can advance free surfaces in a physical way. The method has been applied to model continuum viscoelastic fluids, concentrated suspensions, foams and concentrated emulsions. The results of extrusion flows as well as simple shear and Poiseuille flows will be reported.

### **A Lattice-Boltzmann study of Dispersion in Porous Media**

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The value of the dispersion coefficient for a tracer particle present in a fluid flowing through a porous medium can differ substantially from its value in the static fluid. Essentially the fact that the diffusing particle experiences variations in the fluid velocity during its travels causes additional "hydrodynamic" dispersion. For this effect to be significant the ratio of the typical time taken by the particle to diffuse over some characteristic length scale must be large compared to the typical time taken to convect an equivalent distance. Otherwise the motion of the tracer becomes uncorrelated before it has time to sense the non-uniformity of the velocity field. The ratio of the two timescales defines the Peclet number. Here we describe a numerical study of this phenomenon.

The lattice-Boltzmann approach is well suited to the simulation of flows in complex geometries. There also exists a computational trick which allows one to calculate the velocity autocorrelation function (VACF) for tagged particle motion in the system, averaged over all the trajectories that a particle could possibly follow. The dispersion coefficient is then the integral over all time of this correlation function. By employing this approach we have been able to calculate dispersion coefficients as a function of Peclet number for flow through various three-dimensional structures. We describe results obtained for a periodic array of spheres, for which we can compare with the experimental results of Gunn and Pryce, and for random packings of spheres. The latter serves as a first approximation to a simple sandstone. By studying the the timescale for the decay of the VACF we are able to explain the Peclet number dependence of the dispersion coefficient in the two systems.

### **Polymer Melts as Complex Fluids**

**- current theoretical approaches**

T. C. B. Mcleish

IRC in Polymer Science & Technology

University of Leeds

Polymer melts are not immediately candidates for molecular simulation as the range of time-scales between molecular motion and viscoelastic relaxation is prohibitively wide. Instead a coarse-grained molecular model has proved to be the most fruitful approach, based on the topological interaction of the molecular segments. This "tube model" has been applied now to a wide range of molecular architectures - recent results on comb-polymers will be presented. The challenge is the application to non-linear flows, which demands an interface with the type of approach presented at this meeting by X-F Yuan. A set of calculational rules adaptable to numerical processing, and based on the molecular dynamics of branched polymers, is proposed.

**Molecular Level Simulations of Polymers**

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There is a growing current interest in the atomistic dynamical modelling of dense amorphous polymers in order to provide understanding of bulk properties such as stress/strain behaviour, the glass transformation and penetrant diffusion in terms of chain structure, chain motions and interchain forces. One of the major advantages of computer simulation is the control that one has over the parameters defining the problem and the external conditions that can be imposed. One of the major challenges is to relate the behaviour observed in computer simulations, which is obtained on small samples on ultrashort time scales, to behaviour of macroscopic samples obtained in the laboratory on time scales ten orders of magnitude longer.

In this talk we shall review what has been achieved to date and what is feasible for the near future using molecular dynamics and Monte Carlo simulations, with either coarse grain and "atomistic" force fields. In addition we shall discuss recent progress [1,2] in the use of parallel processing computers to extend the system size, simulation times and precision of data.

- [1] D.Brown, J.H.R.Clarke, M.Okuda and T.Yamazaki, J.Chem.Phys., 1994, 100, 1684
- [2] D.Brown, J.H.R.Clarke, M.Okuda and T.Yamazake, J.Chem.Phys., 1994, 100, 6011

**Long Range Correlations and Non-Gibbsian States in LGA's**

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Non-Gibbsian stationary states occur in dissipative non-equilibrium systems. They are closely connected with the lack of detailed balance, and the absence of a fluctuation-dissipation theorem. These states exhibit spatial and temporal correlations that are long ranged under generic conditions, even in systems with short range interactions, provided the system has slow modes, and there is

some anisotropy either in configuration space or in state space. The anisotropy may come from imposed fields (driven diffusive systems, temperature gradients). In the statistical mechanics of dissipative systems, such as stochastic cellular automata, the asymmetry is only in state space. Here the equilibrium states are non-Gibbsian, they may be spatially uniform with long range pair correlations,  $g(r) \sim r^{-d}$  (with dimensionality  $d$ ), and may even exhibit instabilities, and lead to the formation of clusters or patterns.

### **Topological Defects, Porod Tails and Growth Laws for Phase Ordering Kinetics**

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The concept of topological defects provides a unifying framework for the study of phase ordering kinetics. For  $n$ -component vector fields, we show that the structure factor exhibits the power-law tail,  $S(k) \sim A\rho/k^{d+n}$ , provided  $n \leq d$ , where  $d$  is the spatial dimension,  $\rho$  is the density of defect core (e.g. the area of domain wall per unit volume for  $n = 1$ ) and  $A$  is a calculable constant. Combined with the dynamic scaling hypothesis, this result can be used in a calculation of the energy dissipation rate to derive growth laws for general  $n$  and  $d$ , for both conserved and non-conserved dissipative dynamics.

### **Correlations and Renormalization in Lattice Gas Automata: Applications to a Model of a Chemically Reacting System**

Bruce M. Boghosian

Thinking Machines

USA

A method is described for calculating corrections to the usual Chapman-Enskog analysis of lattice gases due to the buildup of correlations. It is shown that these corrections can be expressed as a diagrammatic series, and closed-form expressions are given for the vertices in these diagrams. Subsets of these diagrams can be identified that correspond to the kinetic ring approximation or to truncations of the BBGKY hierarchy, and the relationship of this method to the more familiar Green-Kubo method is discussed. The method is then applied to a lattice gas for the Schloegl model chemical reaction. Corrections to the equilibrium densities and diffusivities are calculated and compared with numerical experiments. The impact of the correlations on the stoichiometry is elucidated.

### **Materials Science Applications: Cellular Automaton Simulations of Cement Hydration and Microstructure Development**

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Cellular automaton algorithms, which operate on a starting digital image of a water - cement suspension, are described. The algorithms simulate the microstructure development process due to



hydration reactions that occur between cement and water, converting the viscous water - cement suspension into a rigid porous solid. The processes modelled include dissolution, diffusion, reaction and aggregation.

Methods are presented for generating two and three dimensional images representing suspension initial conditions; these are derived both from micrographs of real cements and computer based algorithms. The 2D initial images are based on the processing of backscattered electron and X-ray images of real cement suspensions. The 3D images employ either spheres to represent cement particles, or, more realistic randomly shaped particles via an algorithm which smooths and thresholds a 3D lattice whose sites are initially populated with random white noise.

A convenient measure of the point at which the initial paste turns into a solid material is the percolation threshold of the solids. Consideration of these models led to the prediction and subsequent experimental observation of a sharply-defined onset of shear wave propagation, from ultrasonic measurements through hydrating cement slurries. The amount of hydration needed to reach the percolation threshold can be determined in the present simulation, and our results are compared with the time of shear wave onset in actual cement slurries.

Variants of the basic model provide insight into both early time behaviour that is of primary interest to oil-well cementing and the later time microstructural properties that are of interest in the construction industry.

It is hoped that this example will serve to highlight the potential range of applications of cellular automata within material science.

#### **Boundary conditions and interfaces in lattice gases and lattice Boltzmann equations**

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Lattice gases have been introduced by Frisch, Hasslacher and Pomeau [1] as an efficient way to simulate fluid flows with a simplified molecular dynamics. These models consider point particles moving synchronously on a regular lattice and obeying conservation laws during their collisions on the nodes of the lattice. The field as matured in the lattice Boltzmann equation [2], in which the particles are replaced by their occupation numbers. This latter step is the fundamental ingredient for the theoretical derivation of the Navier-Stokes equations and, at the same time, it has been proven an effective tool for the direct simulation of flows at low to moderate Reynolds numbers (up to several thousands).

Although the theory of these models is now well understood in the context of periodic boundary condition, the implementation of solid walls and of external flows relies on empirical or semi-empirical recipes such as the well known "bounce-back condition". An attempt to clarify this point will be presented in the context of a Couette flow for general orientations of the boundary with respect to the lattice. These results will be extended to Poiseuille flow oriented along one of the axis of symmetry of the lattice.

Some results will also be presented for systems with interfaces such as the two-color model introduced by Rothman et al. [3] or the liquid-gas model introduced by Appert and Zaleski [4].

- [1] U. Frisch, B. Hasslacher, and Y. Pomeau, "Lattice-gas automata for the Navier-Stokes equation", *Phys. Rev. Lett.* **56**,1505-1508 (1986).
- [2] F. J. Higuera, and J. Jimenez. "Boltzmann Approach to Lattice Gas Simulations." *Europhys. Lett.* **9**, 663-668 (1989).

- [3] A. K. Gustensen, D. H. Rothman, S. Zaleski, and G. Zanetti, "Lattice Boltzmann model of immiscible fluids", *Phys. Rev. A* **43**, 107-114 (1991).
- [4] C. Appert and S. Zaleski, "Dynamical liquid-gas phase transition", *J. de Phys. - France II* **3**, 309-337 (1993).

### A Cellular Automaton Model of Microbial Growth.

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A stochastic, cellular automaton model of diffusion controlled, two compartment, population growth is introduced. The behaviour of the model system has many features in common with the growth of bacterial populations. Automaton variables can be interpreted in terms of macroscopic properties of structured growth media and measured growth parameters for particular microorganisms. The automaton illustrates different growth regimes and structural properties of colony growth.

### Two dimensional Lattice Boltzmann simulation of immiscible fluid droplets in simple shear fields.

I Halliday

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In ([1]) Rothmann and Keller (RK) devised a simple rule which, when used to augment a Lattice Gas Cellular Automaton populated by particles of different species (colour) , segregates those particles and maintains an interface between them. Results from static simulations on Immiscible Lattice Gas Automata (ILG's) demonstrated that the Laplace Law governing fluid-fluid interfaces was recovered.

Subsequent work at Sheffield Hallam University on the original algorithm of [1] implemented in parallel on considerably larger lattices revealed certain disadvantages the method. However these were largely overcome when RK's idea was extended to Lattice Boltzmann simulations([2]) - results showed that interfaces with correct static properties might be produced and that these interfaces had (qualitatively at least) appropriate time-evolution behaviour.

This talk will review the various techniques used by workers over recent years to generate interfaces in LGAs, discuss their limitations, the parameters which influence their behaviour and the problems to be overcome in efficient implementation. It will present recent results from static simulations and from assessments of the dynamical, steady state properties of RK and RK-like interfaces in the context of fluid droplets under shear.

Possible modifications to the rule currently under development will be discussed.

- [1] Rothmann and Keller, *J Stat Phys* **52** (1988) pp1119
- [2] Gustensen, Rothmann, Zaleski, Zanetti, *Phys Rev A* **43** (1991) pp4320

## CCP5 ANNUAL MEETING - ORDER IN LIQUIDS

The annual meeting of CCP5 was held this year in Sheffield on the topic "order in liquids". The abstracts of the talks and posters are presented below.

### ORAL PRESENTATIONS

#### SURFACTANT SOLUTIONS

M.E. Cates

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Surfactants in solution self-assemble reversibly to form large aggregates. These may be either spherical micelles, locally cylindrical (wormlike) micelles, or else made of bilayers (vesicles, sponge phases...). Such systems show complex thermodynamics and flow behaviour with a variety of interesting static and dynamic phase transitions. Often, worthwhile information can be gained from models in which each surfactant occupies a small number (2-8) of bonds or sites. In contrast, truly microscopic level modelling is limited at present to questions involving small aggregates (or parts thereof) only. Here a feasible aim might be to predict parameters (such as elastic constants) which can then be fed into larger scale, phenomenological descriptions. As examples of the latter, we focus on two cases where a need for large-scale computation is apparent:

(1) The dynamical instability in entangled micellar systems under shear. Recent analytical predictions and experimental results will be presented and compared with a large scale numerical study [1] of the nonlinear flow equations in which the coarse-grained dynamics of the micelles is included by a Monte-Carlo algorithm.

(2) The role of defects in bilayer sponge phases. These are described by a lattice gauge model which ascribes a certain line tension to "edges" and "seams" in the bilayer. This connects smoothly with an Ising model in the limit of high line tensions (where the bilayer becomes a dividing surface); however, our understanding of the rest of the phase diagram remains very limited.

[1] X.-F. Yuan and N. Spenley, in progress

#### THE ESCAPE OF THE CRITICAL POINT

Daan Frenkel

FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands.

Novel Monte Carlo simulation techniques make it possible to study the phase behaviour of complex liquids such as polymeric systems and mixtures of colloids. These systems differ from

simple (atomic or molecular) systems mainly because the role of entropy is so much more important for the phase behaviour. In my talk I shall consider several entropic phase transitions. Of particular interest is the demixing transition that occurs when polymer is added to a colloidal suspension. Computer simulations allow us to predict how the phase diagram of these mixtures depends on the size ratio between polymers and colloids. Moreover, the simulations lead us to predict novel phase behaviour that has, thus far, not been observed experimentally.

## LIQUID STRUCTURE AND ORDERED SOLVATION CELLS

J. Fidler, A. Rodger and P.M. Rodger

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It is becoming recognised that the order imposed on a solvent by a solute can have important consequences in many situations. In particular, it is now being suggested that molecular recognition in biological systems (e.g. drug/receptor, or sweetness perception) have as much to do with the hydration structure of the molecules as with the chemical composition of the molecules themselves.

At present, direct probes of solvation structure are pushing the limits of experimental techniques. The problem is well suited to examination through computer simulations, but the development of analysis techniques for elucidating and interpreting the details of solvation effects is still in its infancy. Further, where simulations have probed solvation structure, their ability to link in with reliable experimental data has often been weak.

This talk will present the results of a combined simulation/experimental study of solvent effects on the circular dichroism (CD) spectra of various camphor derivatives in achiral solvents. CD is a chiral phenomenon, and no signal is generated for achiral species. By the same token, interactions with an achiral system should not alter the CD of a chiral species. Thus, for camphors in achiral solvents, any solvent influence on the camphor CD can only arise if the solute induces a chiral solvation structure, and so the phenomenon provides a direct probe of solvation structure. By combining the experiments with MD simulations using some extensions to existing structural analysis techniques, it has been possible to develop a detailed understanding of the structure of the solvation shell around the camphors, and how this depends on the solvent used. The results have some implications for solvent control of chiral phenomena such as asymmetric syntheses.

## DL POLY ON THE T3D

M.J. Gillan

Physics Department, Keele University, U.K.

The current CCP5 flagship project is the development and application of the general-purpose parallel molecular dynamics code DL\_POLY. The code is purpose-built to run on parallel machines, and has been developed at Daresbury Laboratory by W. Smith and T. Forester. The talk will outline the basic principles of the code, and will give some illustrations of the large-scale simulations

that have been performed on biomolecular and other systems over the last year. The DL-POLY project has an allocation of time on the 256-processor Cray T3D at the Edinburgh Parallel Computing Centre, and some of the timings and trial simulations done on the machine in the past two months will be described.

## THE PROTEIN-SOLVENT INTERFACE

Julia M. Goodfellow

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The interaction of proteins with aqueous solvent is important for their stability, conformation, dynamics and thermodynamics. In order to study structural aspects of protein-solvent interactions, we have adopted a multi-faceted approach in which we have analysed the experimental solvent data from protein crystallography and compared these analyses with energy minimisation calculations using traditional and novel electrostatic potentials and with molecular dynamics simulations aimed at the study of peptide stability. In this talk, I shall focus on apolar hydration especially for alanine, phenylalanine and leucine residues using these three approaches, and describe not only the protein-solvent interactions but the solvent-solvent interactions around apolar residues.

## MOLECULAR DYNAMICS SIMULATION OF TIME-RESOLVED SPECTRAL SOLVATION SHIFTS IN LIQUIDS

Ross Brown

Centre de Physique Moléculaire Optique et Hertzienne, u.a. 283 du C.N.R.S., Université Bordeaux I, France.

Classical molecular dynamics simulations are performed for the system 7-amino-3-methyl 1,4 benzoxazine 2-one (AMBO) in methanol at room temperature. The time dependent spectral shift of the fluorescence is estimated from non-equilibrium simulations, in which the charge distribution of the solute in ground state configurations of the solution is suddenly changed to that of the excited state (vertical transitions), and the transition frequency is calculated while the solvent cage adapts to the new distribution. The shift occurs mainly before 500 fs, with little broadening, reaching an asymptotic value of around  $2000\text{ cm}^{-1}$ .

Comparison with the linear response theory of solvation shifts shows that it correctly describes the large solute-solvent system, despite the apparently large perturbation (change of dipole moment  $\approx 5\text{D}$ ). Comparison is made with the orientational and energetic dynamics of the pure solvent to ascertain to what extent the solvation shift is representative of the dynamics of the solvent. The initial spectral relaxation is non-gaussian, contrary to recently studied small solutes, but is well correlated with the orientational motion. The influence of the internal degrees of freedom of this large solute is also assessed.

## PHASE EQUILIBRIA AND SURFACE TENSION OF MOLECULAR FLUIDS

Jose Alejandre

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The search for methods and interaction potentials with which to study fluid phase equilibria has academic and technological interest. In this work we present molecular dynamics simulations to study the liquid-vapour interface of molecular fluids. The systems are located in a rectangular cell with liquid in the middle and vapour on the left and right, with periodic boundary conditions in the three directions. Site-site effective potentials are used to describe the interactions between molecules. Chlorine,  $\text{CH}_2\text{F}_2$  and water are simulated. Water is simulated using the SPC/E potential and the Ewald technique is used for the long-range interactions.

The calculated properties are the orthobaric densities and the surface tension as a function of temperature. The orthobaric densities for the SPC/E water model are in better agreement with experimental data than those found with Gibbs ensemble for the SPC potential. We have shown that the differences are due to the different potential and not because of the difference in the simulation methods employed. The effect of long-range interactions on the surface tension of water is analysed in detail. Their inclusion is very important because the simulation is developed in a rectangular box. Excellent agreement with experimental results is found.

## STRUCTURE AND DYNAMICS OF HARD ELLIPSOIDS

Michael P. Allen

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The hard ellipsoid system is perhaps the most obvious generalization of the venerable hard-sphere model, and may serve as a reference system for molecular liquids in the same way as did hard spheres for atomic liquids. A programme of molecular dynamics and Monte Carlo simulations of hard ellipsoids has been in progress at Bristol for several years. This talk will review what we have learnt regarding the structure, single-particle and collective dynamics, and phase transitions exhibited by these systems.

## A NEW METHOD FOR DETERMINING THE CHEMICAL POTENTIAL FOR CONDENSED MATTER AT HIGH DENSITY

J.G. Powles, B. Holtz and W.A.B. Evans

The Physics Laboratories, The University, Canterbury, U.K.

We apply a space-dependent external potential to the fluid such as to produce both a high density, virtually homogeneous, region and a low density, not necessarily homogeneous, region.

We easily measure the chemical potential in the low density region by Widom's fictitious-particle-insertion method by computer simulation. By constancy of the chemical potential, the value is the same in the high density region, which is the difficult to measure directly by this or any other method. The method has been tested for Lennard-Jones fluids, for which independent values of chemical potential at high density are known. The method is quite general and can be used for molecular liquids, polymer melts, mixtures, etc.

## LOCAL ORDER IN FLUID LIPID-BILAYERS

Ole G. Mouritsen

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The fluid lipid-bilayer component of cell membranes is a mesoscopic system consisting typically of the order of  $10^8 - 10^{10}$  interacting molecules. In its capacity as an interacting many-particle system, the membrane sustains correlated dynamical modes and it may display cooperative phenomena such as static global phase separation and dynamical local heterogeneity on micro- and nano-scales of  $10 - 1000 \text{ \AA}$ . The microscopic manifestation of the cooperative modes consists in the formation of heterogeneous structures, such as lipid domains, that are dynamically maintained. The lipid domains may be seen as either lateral density fluctuations or compositional fluctuations. The macroscopic consequences of these fluctuations are anomalies in response functions, such as the specific heat and the lateral compressibility. Results from Monte models of planar lipid bilayers will be described and it will be shown how lipid domains and local structure arise under different thermodynamic conditions [1], [2]. It is proposed that the dynamically heterogeneous membrane states are important for passive and active membrane functions such as trans-membrane permeability, enzymatic activity and the in-plane aggregation of protein sub-units to functioning protein complexes. Membrane-associated functions may be manipulated by changes in the heterogeneous membrane structure that can be significantly altered in response to changes in compositional, thermodynamic, and environmental conditions. The diverse physical effects, and possibly some physiological effects of a variety of molecular compounds interacting with membranes such as cholesterol and drugs like anaesthetics, may be understood in terms of the ability of these compounds to affect and modulate the dynamic membrane heterogeneity.

[1] K. Jørgensen, M.M. Speretto, J.H. Ipsen, O.G. Mouritsen and M.J. Zuckermann, *Biochim. Biophys. Acta*, **1152**, 135 (1993).

[2] O.G. Mouritsen and K. Jørgensen, *Chem. Phys. Lipids*, in press (1994).

## SWIFT-HOHENBERG RELATIONS FOR THE DYNAMIC INSTABILITIES IN MICRO-PHASE TRANSITIONS OF ASYMMETRIC BLOCK COPOLYMER MELTS

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Density functional theory provides a general method for calculating the free energies in an inhomogeneous complex fluid. The present extension to off-equilibrium mixtures of copolymer chain molecules is essentially a generalisation of the dynamic RPA method, along the lines pointed out some years ago by de Gennes and others. These are time-dependent Ginzburg-Landau models with non-local and highly non-linear functional relations between densities and interaction fields. The method applies to systems in which the diffusion phenomena are slow enough to ensure, at any given moment in time (on a coarse-grained mesoscopic timescale), a *unique*, history independent, functional linkage between density profile and chain conformation distribution.

We present a few examples of numerical analysis of micro-phase transitions in block copolymer melts by numerical integration of the (stochastic) non-linear partial differential equations. Various predictions are made. An interesting result is that in a quenched asymmetric block copolymer melt, a symmetric defect leads to symmetrically propagating unstable dissipative waves. When these waves interact, interference is severely restricted due to non-linear interactions. In contrast, the interaction between the dissipative waves leads to the induction of new *asymmetric* propagations. In some cases, the interactions between these second order waves may lead to third order waves of yet another character. These effects can be understood by comparison with type  $I_s(\omega_0 = 0, q_0 \neq 0)$  pattern forming systems introduced in a recent magnificent review of pattern formation outside of equilibrium [1].

By means of some simple transformations of the original dynamic non-linear RPA equation, we derive a variant of the so-called Swift-Hohenberg equation. This equation was originally derived for pattern formation in hydrodynamic convection systems. The analogy leads to an amusing observation: experimental Raleigh-Bénard convection cells may provide effective natural simulation devices for the study of micro-phase formation in copolymer melts. This may seem a remote possibility, but it is clear that the Swift-Hohenberg equation points the way to efficient calculation methods.

[1] M.C. Cross and P.C. Hohenberg, *Rev. Mod. Phys.*, **65**, 851 (1993).

## ORDERING BEHAVIOUR OF CHAIN MOLECULES IN MODEL SYSTEMS: MONTE CARLO SIMULATIONS

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We have carried out athermal Monte Carlo model simulations of long chain molecules with several constraints on a simple cubic lattice. Our special interest was to investigate the ordering behaviour of linear flexible molecules with variation of both head density ( $0 < \Phi < 1$ ) and molecular length ( $2 \leq s \leq 15$ ).

First we investigated the influence of the dimensionality on the ordering behaviour. Therefore the heads of the molecules are confined to move along the x-axis whereas the chain segments could move *i*) in a plane *ii*) in the first quarter space and *iii*) in the upper half space. For two segment molecules the exact analytical solutions for all head line densities agree with simulation results. The ordering behaviour varies qualitatively within these different geometric cases. In case *i*) the degree of order shows a minimum behaviour at medium head line density and tends to unity when



the head line density approaches unity. In case *ii*) the degree of order behaves monotonously.

In the upper half space we investigated several flexible molecules of different topologies with heads confined to the plane  $z = 0$ . The order parameter for short linear molecules shows a minimum at medium head density.

The ordering behaviour of two-chain molecules with  $s_1 = 10$  segments in the main chain and  $s_2 = \{1, 2, 4, 6, 8\}$  segments in the side-chain has been investigated. The side-chain was connected to the second segment of the main chain. The degree of order varies with side-chain length: if the side-chain consists of one segment, the order parameter strongly decreases in comparison with molecules without a side-chain. In the cases of  $s_2 = 4$  and more segments in the side-chain, the order parameter is higher than for linear molecules.

The ordering behaviour of molecules with anisometric heads has to be described by two order parameters: one for the flexible chains and the other for the alignment of the heads. At high densities the heads form domains with preferred directions.

Work is now being undertaken to investigate the effect of including attractive interactions and non-zero widths for the heads in the  $z$ -direction. It is also intended to investigate other molecular topologies.

## COMPUTER SIMULATION OF SOME GAY-BERNE LIQUID CRYSTALS

Claudio Zannoni

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The talk will present some recent work on Gay-Berne models of liquid crystals. Some bulk systems in three and two dimensions will be examined and the resulting types of order and molecular organisations discussed. Gay-Berne systems confined to spherical and cylindrical cavities will also be investigated. In addition to the use of Gay-Berne systems in modelling, the effect of isotropic-nematic-smectic phase transformations on certain phenomena will be considered with the explicit case of Förster type energy transfer used as an example.

## LOCAL CLUSTER DYNAMICS AND ORDERING IN SHEARED LIQUID MIXTURES

W.C. Sandberg, U. Obeysekare

Naval Research Laboratory, USA

D.M. Hayes,

Department of Chemistry, University of Surrey, Guildford, U.K.

The momentum transfer and the associated relative motion between an atom and its immediate surroundings in sheared dilute atomic mixtures are examined using non-equilibrium molecular dynamics. We examine the variation in the momentum transfer, velocity and force autocorrelation functions as the dilute species mass is varied. The computations have been carried out for several shear rates. We also investigate the behaviour of the elements of the diffusion tensor under mass

and shear rate variation. The elements of the diffusion tensor are observed to be increasingly non-isotropic with increasing shear rate. A video has been prepared using the AVS system to visualise the evolution of the relative dynamics between an impurity atom and its surrounding near-neighbours. The variation in relative dynamics as the mass of the impurity atom is increased and as the magnitude of the shear field is increased is shown.

## **HYDROGEN BONDING IN AMPHIPHILIC SYSTEMS AND LIQUID CRYSTALS**

George Jackson

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Simple model molecules of amphiphiles will be used to examine the effect of hydrogen bonding on the phase behaviour of these systems. Aqueous solutions of amphiphiles are examined in some detail with particular reference to re-entrant phase behaviour. In this case the approach of Wertheim for molecular association will be used to describe the free energy. In the case of liquid crystal systems the effect of hydrogen bonding on the isotropic-nematic phase transition is examined by combining the Wertheim and Onsager approaches. The stability of the smectic and columnar phase relative to the nematic phase for associating systems is examined with a bifurcation analysis.

## **MOLECULAR DYNAMICS SIMULATIONS OF LIQUID CRYSTALS ON THE CRAY T3D**

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Molecular dynamics simulations of simple systems are often ideal candidates for parallelization. The main computational task of calculating the forces between pairs of atoms is an inherently parallel process, and a number of techniques exist for doing this efficiently on a range of different parallel computers. On the CRAY T3D a particular friendly environment for MD work exists. 256 DEC Alpha-processors are coupled to fast inter-processor communications providing the possibilities of long time-scale simulations of large systems, with a minimum of communication overheads.

For liquid crystal systems the T3D provides a useful means of tackling problems which would be intractable on most other machines. Large scale simulations are required to study the formation of defects and disclinations in nematic phases, the stability of smectic phases, the formation of biaxial chiral phases and the structure within polymer liquid crystals.

In this paper we present preliminary results of our liquid crystal simulations on the CRAY T3D. We discuss the efficiency of the algorithms used, the problems which arise in their implementation, and the range of problems which can be tackled. Initial results from simulations of chiral liquid crystals using twisted boundary conditions are presented.

## VIEWS ON PARALLEL PERFORMANCE IN COMPUTATIONAL CHEMISTRY

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Parallel computing is ideal for the biggest computational tasks in quantum chemistry, protein modelling, crystallography and studies of condensed matter and disordered systems. Microprocessor technology has enabled many groups to increase their computational power merely by buying the latest workstations. The problem sizes grow to fit the equipment. A more aggressive approach is possible with scalable parallel computing where the equipment can be selected to fit the problems.

### POSTER PRESENTATIONS

#### PARALLEL PROGRAMMING FOR HIGH PERFORMANCE IN COMPUTATIONAL CHEMISTRY

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Many parallel programs have been developed on the Daresbury Intel machines by CCP5 members. All of these can now be ported, without significant change, to any set of Unix workstations and any of the shared or distributed memory parallel supercomputers, using our Intel-to-pvm libraries. This includes Cray, DEC, HP, IBM, SUN, Silicon Graphics and Transtech PARAMID equipment.

We have ported three CCP5 codes, CASTEP, FUNGUS and PARION to our workstations and PARAMID with only 5 new lines to invoke our Intel library.

In many cases a group of workstations can give dramatic performance increases over one station. Our real life case does the iterative inversion of a large full matrix to solve a fluid flow problem. A large problem needed to use virtual memory on one DEC Alpha and was killed after 20 minutes. On a pair of Alphas the problem ran, in real memory, in 74 seconds.

Our machine independent toolset makes parallel code development quite straightforward. This was essential for us in handling so many different machines. The largest code we have handled had 180,000 lines of C and Fortran and was parallelised with about 400 new lines. Protein modelling codes spend about 95% of their time in one routine to evaluate the forces. Parallelisation is, therefore, almost trivial, requiring a few lines for the algorithm and a little more work for the protein setup.

In short, parallel programming can be very straightforward, large gains can be made on basic equipment, and the UK academic community now has many powerful parallel machines for the most massive problems. Details and demonstrations will be presented at the meeting.

#### MOLECULAR DYNAMICS SIMULATIONS OF HEXANE IN A GAY-BERNE FLUID

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Molecular dynamics simulations of a hexane molecule in isotropic, nematic and smectic phases are reported. The interaction between the solvent molecules is modelled using the Gay-Berne potential and the hexane-solvent potential is modelled as an explicit site-site interaction.

The conformational distributions are reported for a hexane molecule at a fixed temperature but at different densities in isotropic, nematic and smectic phases, and these are compared with the results from Monte Carlo simulations on an isolated molecule at the same temperature. The positions and orientations of the hexane molecule at each time step in the molecular dynamics simulations are used to calculate interproton dipolar coupling constants. These data are used to test the mean field models which have been applied with dipolar couplings obtained previously from nuclear magnetic resonance experiments to yield conformational distributions.

## **SIMULATION OF LIQUID CRYSTALS**

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We present some new results regarding the effects of periodic boundary conditions on the director distribution in liquid crystal simulations. We also give details of our attempts to simulate two-phase coexistence between liquid crystal and vapour phases.

## **COMPUTER SIMULATION OF ANISOTROPIC SYSTEMS. THE COLUMNAR NEMATIC PHASE ?**

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A necessary condition for a compound to form a mesophase is that its molecular shape must deviate from spherical symmetry, but molecular shape alone cannot determine whether a mesophase will be stable. Pure pentakis(phenylethynyl) phenoxydecane (D102) [1], for example, does not exhibit a liquid-crystalline phase. However, when doped with 2,4,7-trinitrofluorenone, which is also non-mesogenic, liquid-crystalline phases are induced. The reason why this phase induction occurs is not known. As there is a dramatic colour change on mixing, one possible explanation is that a charge transfer complex is formed, although charge transfer interactions are generally thought to be rather weak. Another possible explanation is that quadrupolar forces are important. In a pure system, these forces would tend to destroy face-to-face alignment between a pair of discs. However, in a mixture in which the components have opposite quadrupolar moments, face-to-face alignment between unlike molecules would be enhanced.

To investigate the role of quadrupolar forces in a system of disc-like molecules, we have undertaken a computer simulation study based on the Gay-Berne potential [2], which has proved to be of considerable value in understanding the behaviour of pure systems composed of disc-like particles [3]. We have added a point quadrupolar term to the potential to account for the electrostatic interactions. Two systems have been studied using this model potential

- (I) a pure system of Gay-Berne quadrupolar discs, and
- (II) a binary mixture of such discs, differing only in the sign of their quadrupole moments.

Both systems were investigated by Monte Carlo simulations at constant volume as a function of temperature. In system I the quadrupolar forces were found to destroy the usual columnar packing exhibited by a model disc-like mesogen with no quadrupolar interactions<sup>c</sup>, although there is an indication that a tilted columnar phase may have been formed. System II was found to exhibit, in addition to an isotropic and a nematic phase, a columnar phase in which the discs pack more-or-less alternately.

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## MOLECULAR MODELLING OF INHOMOGENEOUS BROADENING IN SOLIDS

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The inhomogeneous broadening of the optical transitions of a probe molecule in a solid at low temperature is caused by fluctuations of the host-matrix stabilisation in the close surroundings (20Å), like short range repulsion, electric multipole interaction, dispersion forces and, in some cases, special forces like hydrogen bonding.

Estimation of inhomogeneous broadening thus poses two problems: calculation of the interactions for a given host-matrix configuration and proper accounting for the variety of configurations with suitable statistical weights. We approach this problem through molecular modelling. Molecular dynamics simulations supply the host-matrix configurations, including a large part of the intermolecular correlations present in the matrix because of steric effects or hydrogen bonding. A semi-empirical quantum calculation of the probe's spectrum, including the perturbation by the host molecules in each configuration, then yields the optical inhomogeneous lineshape.

## INHIBITION OF THE CRYSTAL GROWTH OF NATURAL GAS HYDRATES

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Gas hydrates form and cause blockages in natural gas pipelines - so resulting in inefficiency in the flow of gas and producing a potential hazard if the pipeline were to become plugged by the crystalline gas hydrate. This work has investigated the potential use of a water soluble polymer, polyvinylpyrrolidone (PVP) to inhibit this. PVP has the interesting property of structure-ordering in liquid water and has freeze-preservation properties.

Monte Carlo calculations were used to study the adsorption of the polymer on the hydrate surfaces. Various tacticities of PVP were considered and the polymer conformational trends analysed for these calculations. Adsorption sites have been identified and PVP chains were shown to lie flat on the surface rather than at an angle to it. Therefore, an inhibition mechanism is proposed whereby the hydrate growth sites, at which water molecules would add to the hydrate lattice, are covered by the polymer.

## **GENERALISATION OF THE GAY-BERNE POTENTIAL TO INCORPORATE HETEROGENEOUS PARTICLE-PARTICLE INTERACTIONS**

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In this poster, we derive a generalised form for the shape parameter governing the pair interaction between ellipsoidal particles. This generalisation is obtained by considering the overlap of two arbitrarily (i.e. differently) stretched gaussians. An interaction potential for heterogeneous particles is then obtained by importing this shape parameter into the standard Gay-Berne form. A parameterisation of this potential is obtained for a rod-disk interaction.

## **A COMPUTER SIMULATION OF THE MICROSTRUCTURE OF A PARTICULATE DISPERSION**

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We report on a computational simulation of a dispersion of iron particles undertaken to study the influence of the magnetostatic interactions on the microstructure of a particle ensemble. The simulation considers an equilibrium state derived from an initial random state by the force-bias Monte Carlo technique. We have studied a three dimensional ensemble in zero field and a saturating field.

The strong magnetostatic interaction gives rise to groups of energetically bound particles, known as clusters, which exhibit co-operative orientational and spatial migration. These associations are identified using a clustering method which attempts to maximise the configurational entropy and minimise the cluster self energy. The groups of particles so identified are temporarily identified as a rigid body.

This approach leads to the formation of extended networks consisting of particles in strongly bound clusters which themselves interact and give rise to an extended network. This is similar to the long-range order observed in practical dispersions.

## COMPUTER SIMULATION OF SURFACTANT SYSTEMS

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An NVT Monte Carlo simulation of a lattice model of a surfactant and solvent mixture is described. The work is an extension of an earlier model [1] in which surfactant chains are represented as a set of connected hydrophilic and hydrophobic segments lying on a cubic lattice.

In the work presented here, the lattice coordination number has been increased to 26 and chain flexibility is taken into account by associating an energy with each set of two consecutive bonds.

The extensions to the model are computationally demanding and it is necessary to use a more efficient sampling scheme than simple reptation. For this reason, a modification of the configurational bias Monte Carlo (CBMC) scheme is presented. This modification is closely related to the off-lattice system scheme of Frenkel et al. [2]. The efficiency of the new method is compared with standard CBMC [3] and simple reptation.

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## SIMULATION OF SELF-ORGANISATION AND SELF-ASSEMBLY IN DISCOTIC LIQUIDS

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A model discotic molecule, constructed from a planar hard core of bonded hard spheres and a central square-well attractive site, has been employed in a variety of simulation studies of self-organisation and self-assembly in complex fluids.

Monte Carlo (MC)  $NpT$  simulations of a monolayer of these molecules have been used to investigate the competition between standing-up states (condensed liquid) and lying-down states (expanded liquid) in adsorbed monolayers of insoluble disks [1].

MC  $NpT$  simulations of a bulk fluid mixture of these disks and square-well solvent are being used to map out regions of lyotropic liquid crystal behaviour and pre-transitional ordering for a

range of volume fractions. The simulations show trends similar to those observed for an analogous experimental system [2]. At lower volume fractions, we are studying the self-assembly of these disks into chain-like aggregates. Results can then be interpreted within the framework of 1-dimensional chemical association theory [3].

We have also begun initial studies of columnar adsorption onto square-well walls. Such studies of interfacial self-assembly require, in addition, control over the solvent chemical potential.

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## THE USE OF CHEMICAL SHIFT MEASUREMENTS TO PROBE THE ONE-DIMENSIONAL SELF ASSEMBLY OF AQUEOUS SOLUTIONS OF THE AMPHIPHILES TP6EO2M AND TP6EO3M

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The discotic amphiphiles TP6EO2M and TP6EO3M self-assemble in water by a simple stacking process. Proton chemical shift measurements in the isotropic phases of these amphiphile / water solutions were seen to be consistent with a thermodynamic model that describes the self-assembly of micelles in concentrated solution. The model was then adapted with a second virial approximation and the excluded volume interactions of the aggregates accounted for up to a volume fraction of 0.1. Thermodynamic parameters of aggregation are obtained as well as the intermolecular separation within the aggregates by modelling the aromatic ring current shift of a TP6EO2M dimer.

Hydration of the hydrophilic ethylene oxy side chains was seen to be an important consideration. Hydration numbers for ethylene oxy / water systems in the literature are dependent on the experimental technique used to obtain them, so careful consideration was required when applying them to these systems. Including the bound water to the side chains in the volume fraction of the aggregates leads to a better fit of the experimental data.

## COMPUTER SIMULATION OF HYDROPHOBIC EFFECTS IN ETHANE-WATER SYSTEMS

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Aqueous solutions of nonpolar solutes exhibit several unusual properties called hydrophobic effects. These can be subdivided into two categories. Hydrophobic hydration refers to the microscopic properties of the structure and dynamics of water molecules surrounding a nonpolar solute, and to the thermodynamic properties associated with these dilute solutions. Hydrophobic interaction refers to the solvent-induced forces between two or more nonpolar solute molecules. It is generally believed that these interactions are responsible for several phenomena like the folding



and stability of biopolymers and small molecules in solution, the stability of micelles and biological membranes, the aqueous association equilibria of different compounds, and the low solubility of species such as hydrocarbons and the inert gases.

The low solubility of nonpolar molecules in water is thermodynamically characterised by a positive standard Gibbs free energy of dissolution from the gas phase. The enthalpy of solution has been shown to be negative, thus indicating that the nonpolar solute increases the degree of hydrogen bonding of water molecules in the solvation shell so as to maximise the water-water attraction and avoid the solute's hard core, with a substantial unfavourable decrease in the entropy of water. This negative entropy change should be responsible for the observed decrease in the solubility of these solutes with increasing temperature near room temperature, and also for the entropy-driven force that drives such species together. Nonpolar solutes would tend to cluster together to have fewer ordered water molecules surrounding them, with an actual positive entropy change for this process. Since the enthalpy of association should be positive, the extent of hydrophobic aggregation should therefore increase with temperature near room temperature, but there should be a reversal of these trends, as for hydrophobic hydration, at high temperatures, due to the large heat capacity of solution.

This work reports on molecular dynamics simulations carried out on water-ethane mixtures to study the microscopic details of hydrophobic hydration and the extent of aggregation of these solutes in the range 280-350 K. The results on the hydrophobic hydration of a single ethane molecule in water show a temperature-independent structuring of the first hydration shell water molecules, but also an unexpected higher mobility, as revealed by shorter hydrogen-bond lifetimes and a broader distribution of coordination states. The hydrophobic interaction of four ethane molecules in water showed no difference in the tendency of aggregation in the range 280-300 K, but a clear increase in this tendency was observed at 320 K.

## WATER STRUCTURE IN AQUEOUS SOLUTIONS OF APOLAR SOLUTES

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Hydrophobic hydration effects are believed to be central to interactions in the aqueous environment involving macromolecular assembly and stability. However, the information on both solute-water and water-water structure at the atomic level in the liquid state is still sparse. We are using a combination of statistical analysis of crystallographic coordinates from protein databases [1], computer simulation [2] and neutron diffraction [3]; to build up a picture of apolar hydration structures. Neutron scattering is currently the best experimental method for getting this information because of the possibility of using H/D substitution difference methods [4]; these provide atomic partial pair correlation functions which can be compared directly with the same functions calculated from computer simulation. The poster presents neutron diffraction and simulation data on water structure around model compounds such as alcohols, tetraalkylammonium (TAA) ions and phenol. The experimental HH and XH correlation functions for the water in alcohol-water mixtures and TAA salt solutions show very little change with increasing "hydrophobicity" of the solute. They support the view that apolar solutes exist in cavities formed in the water but suggest

that such cavities have only a small effect in increasing the order in the water.

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## DIRECT FREE ENERGY CALCULATIONS FOR CLATHRATE HYDRATES

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In this work we present an extension of the quasi-harmonic method of calculating solid-phase free energies to make it applicable to molecular systems. The method has been used to calculate the phase behaviour of clathrate hydrates, and, in particular, to examine the validity of the assumptions that underlie the semi-empirical formulations that are currently used in engineering applications. Results will be presented for the free energies of various hydrate phases relative to ice, and calculated thermodynamic properties of clathrates as a function of state point. The method is cheap and quick, and makes it possible to contemplate full atomic free energy minimisation calculations on workstations.

## COMPUTER SIMULATION OF MODEL FERROELECTRIC PHASES

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Of late, much interest has been shown in ferroelectric mesophases. Ferroelectric chiral smectic- $C^*$  phases provide a molecular framework suitable for the production of a third generation of fast-switching liquid crystalline displays. However, a number of other molecular geometries have been proposed which may lead to useful ferroelectric materials. For instance, it has been proposed that molecules with a component of their molecular dipole parallel to the long molecular axes can form ferroelectric smectic phases (smectic- $A_p$  and smectic- $C_p$ ). Such phases rely on over-coming the natural tendency of molecules for anti-parallel dipole ordering, by careful manipulation of intermolecular forces.

In this work we present preliminary results from a Monte Carlo computer simulation study of ferroelectric formation in smectic mesophases. In our model we attempt to manipulate intermolecular forces to favour ferroelectric phases.

## LIQUID CRYSTAL ELASTIC CONSTANTS VIA COMPUTER SIMULATION

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A number of recent studies have shown the usefulness of computer simulation as a tool for studying liquid crystal phases [1]. Simulation provides an excellent technique to calculate bulk liquid crystal properties starting from only a molecular pair-potential. In particular, if molecular dynamics techniques are used, then simulations can yield both static (order parameters and elastic constants) and dynamic properties (diffusion constants) for the bulk fluid phases.

In this paper we present the results of a molecular dynamics simulation study of elastic constants in the nematic phase. The model molecules are based on chains of hard-spheres which are linked together by potential wells. The chains of spheres provide a convenient hard-particle mesogen [2] which can be tuned to allow differing amounts of molecular flexibility. Elastic constants are calculated for two systems with differing degrees of flexibility.

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