

**CCP5 Annual Meeting 1998**  
**Making and Breaking Potentials**  
**Invited Talks**

**Model interatomic potentials for covalent systems.**

Jerry Tersoff.

IBM Watson Research Centre,  
PO Box 218, Yorktown Heights,  
New York 10598, USA.

This talk will describe one approach to constructing model potentials for covalent systems, with sample applications. The characteristic limitations of such potentials will be discussed, along with the obstacles and opportunities for constructing new and better potentials.

**Generalisation and augmentation of the  
Gay–Berne potential.**

Doug. Cleaver.

Materials Research Institute, Sheffield Hallam University,  
Pond St, Sheffield S1 1WB, UK.

The Gay–Berne potential involves pairwise-additive anisotropic interaction sites and can be viewed as a generalisation of the Lennard–Jones potential for non-spherical particles. It is mainly used in simulations of complex fluids (liquid crystals, amphiphiles and elastomers) where its simplicity makes accessible the considerable runtimes required for free assembly of the phases/structures of interest. This talk will illustrate the strengths and weaknesses of the Gay–Berne potential, some recent developments to it that have opened up new areas in liquid crystal simulation and some ideas for more diverse future applications.

**Atomistic aspects of cleavage fracture  
in crystalline materials.**

Peter Gumbsch.

Max-Planck-Institut für Metallforschung,  
Seestrasse 92, 70174 Stuttgart, Germany

The macroscopic failure of materials is ultimately determined by events on the atomic scale. This is particularly clear in the case of brittle fracture, where the crack at its tip must be atomically sharp and must break the bonds between atoms. It is therefore obvious that a detailed understanding of brittle fracture will ultimately require an understanding on the atomic scale. Atomistic modelling is a useful way to study such processes and is even more appealing if one acknowledges that it will naturally reproduce fracture by loading, whereas the widely used continuum models require explicit fracture criteria.

Similarly, the dynamics of the bond breaking, of dislocation generation and of dislocation motion in the crack tip field, which are the underlying physical processes in the so-called semi-brittle fracture regime are all linked to the atomic length scale and can all be studied atomistically. Semi-brittle fracture is usually observed in materials which undergo a brittle-to-ductile transition (below the transition temperature) and consequently we also need to develop deeper insight into these *dynamic* processes in order eventually to understand the brittle-to-ductile transition.

The talk will be centered around three main topics. First, the requirements for the construction of atomic interaction models which can be used in the atomistic modelling of crack tip processes will be briefly reviewed. Second, the importance of the discrete atomistic structure of the crack tip will be discussed together with the so-called lattice trapping effects. Third, the dynamics of the brittle fracture process and the critical velocities which can be attained by the crack and by emitted dislocations will be investigated.

**The importance of microscopic contributions  
to condensed phase macroscopic properties in  
empirical force field calculations.**

Alex MacKerell.

University of Maryland, School of Pharmacology,  
Department of Pharmaceutical Science,  
Baltimore, Maryland 21201, USA.

Empirical force field calculations apply simplistic mathematical models to study complex chemical systems. The results from such calculations are directly dependent on the quality of the empirical force field parameters used in the computations. We will present a methodology for the development of force field parameters that takes into account both microscopic (e.g. specific interactions between water molecules and model compounds) and macroscopic (e.g. heats of vaporization or free energies of solvation) properties. Examples from protein, lipid and nucleic acid calculations will be presented.

**Molecular dynamics simulations of the  $a \rightarrow b$**

## **pressure-induced reconstructive phase transformation in crystals of resorcinol.**

Samir Devani and Jamshed Anwar\*.

Department of Pharmacy, King's College London,  
Manresa Road, London SW3 6LX, UK.

The ability to predict new polymorphic phases of a substance as well as its phase stability is of considerable scientific interest and technological importance. The molecular dynamics simulation technique using the Parrinello–Rahman boundary conditions offers a potentially powerful approach for investigating both polymorphism and polymorphic phase transformations.

This study presents results of molecular dynamics simulations of a reconstructive polymorphic transformation in a strongly hydrogen-bonded molecular crystal, namely resorcinol. The focus has been on the  $a \rightarrow b$  transformation as a function of pressure, which has been successfully simulated. The effects of some of the important variables associated with simulations of crystals have been explored. Simulations were carried out using both a partially rigid and a flexible representation of the resorcinol molecule as well as different force-field parameters. In addition, the effects of variations in the temperature and pressure relaxation constants, system size and starting configuration were examined.

This success with a hydrogen-bonded structure, along with a better understanding of the variables associated with molecular dynamics simulations of crystals opens up the possibility of exploring structure, phase stability, and kinetic aspects of polymorphic crystals of molecular systems.

## **Many-body effects in the interaction potentials of ionic materials.**

Paul Madden.

Physical and Theoretical Chemistry Laboratory,  
Oxford University, South Parks Road, Oxford OX1 3QZ, UK.

Anions in the condensed phase have profoundly different properties from their free counterparts. This is a consequence of the strong confining potential exerted on the anionic electron density by surrounding ions. Depending on the precise shape of the potential (which, in thermal motion, will vary from one instant to the next), the anion may be more-or-less compressed, deformed and polarized and hence its interaction potential with the other ions in the system will also vary. Only for the simplest ionic systems (*e.g.* alkali halides) can this variation be neglected and the interactions described by some average pair potential. Most other systems exhibit “covalent effects” in their structure and dynamical properties – that is to say that these properties are not describable as a consequence of pairwise additive ionic interactions.

For some time (see Chem.Soc.Rev., **25**, 339-350 (1996)), my group has been examining how to represent in computer simulations the *many-body* aspects of the interaction potentials, which arise as a consequence of the variation of the confining potential. Some of these effects (notably polarization and ion compression) can be unambiguously characterized by performing electronic structure calculations on ions in suitable idealized environments. These allow the partial parameterization of an “extended” ionic model, in which the variation in the ionic properties are represented by additional dynamical variables (alongside the ionic coordinates) which are handled by borrowing ideas from the Car-Parrinello method. For other effects, we have to resort to more empirical methods or to total energy calculations to characterize them. The calculations reveal that a surprisingly large range of “covalent” behaviour can be recovered within this extended ionic model.

In the talk I will illustrate these ideas by describing the development of many-body potentials for oxides by Adrian Rowley. The basic potential is refined in careful, quantitative studies of MgO (see J.Chem.Phys., **108**, 10209 (1998)). It is then shown how, by simply scaling some of the potential parameters to allow for the change of cation radius, this potential may be *transferred* to other oxides, even if this involves a change of stoichiometry. Applications to the surface relaxation of Cr<sub>2</sub>O<sub>3</sub> and to the different crystalline polymorphs of GeO<sub>2</sub> will be described.

## Oral Presentations

\* indicates speaker

### Parallelisation of molecular dynamics simulations: an introduction.

David Henty.

Edinburgh Parallel Computing Centre, Kings Buildings,  
University of Edinburgh, Edinburgh EH9 3JZ, UK.

Modern supercomputers are parallel machines, and these pose certain problems for the coding of simulations such as molecular dynamics. This talk aims to give insight into these problems, and how they are overcome for state-of-the-art machines. Those planning a career in high performance computation should appreciate how powerful these machines may be in the near future.

### Anticipating potential problems.

Graeme Ackland.

Department of Physics, King's Buildings,  
University of Edinburgh, Edinburgh EH9 3JZ, UK.

This introductory talk will discuss transferability of interatomic potentials. In particular the need to consider the types of interactions which are likely to be important in a given simulation is discussed. Selection of a functional form and appropriate fitting data for a potential is then investigated and a few examples are discussed.

### Mean-field and large-scale simulation approaches to the molecular design of liquid crystals.

Maja Nendel<sup>1\*</sup>, M.A. Glaser<sup>2</sup>, Y. Lansac<sup>2</sup>, N.A. Clark<sup>2</sup> and D.M. Walba<sup>1</sup>.

<sup>1</sup> Department of Chemistry and Biochemistry, Campus Box 215,  
University of Colorado, Boulder, CO 80309-0215, USA.

<sup>2</sup> Condensed Matter Laboratory, Department of Physics, Campus Box 390,  
University of Colorado, Boulder, CO 80309-0390, USA.

The Boulder model constitutes a mean-field approach to predict certain properties of tilted smectic liquid crystals, i.e. the spontaneous polarization density  $P$ , the non-zero second-order hyperpolarizability  $\chi^{(2)}$ , optical dichroism and refractive indices. In this model, a single liquid crystal molecule is placed into a bent cylindrical-shaped binding site, or mean-field potential, analogous

to the binding cavity in enzymes. The shape of the binding site is chosen to have a symmetry corresponding to that of the phase. The underlying hybrid force-fields are developed using *ab initio* and DFT calculations on small model systems, and they are parametrized to fit experimental data. The development of these force fields will be discussed, as will be the performance of the Boulder model in specific cases as compared to large-scale molecular dynamics calculations and to experimental data.

### Interaction laws used in the simulation of granular materials.

D.M. Heyes<sup>1\*</sup>, J. Baxter<sup>2</sup>, U. Tüzün<sup>2</sup> and P.A. Langston<sup>3</sup>.

<sup>1</sup> Department of Chemistry, University of Surrey,

<sup>2</sup> Department of Chemical Engineering, University of Surrey,

<sup>3</sup> Department of Chemical Engineering, University of Nottingham.

Molecular Dynamics simulation has been used many times to model the physical properties of granular materials since the pioneering work of Cundall & Strack (Geotechnique **29**, 47 (1979)). A wide range of processes, including simple shear, compaction, mixing by churning and vibration, transportation by conveyance, hopper filling and discharge and heap formation have been simulated. Highly idealised interaction laws have typically been employed (*e.g.* spring-and-dashpot, and Hertz – the classical solution for two elastic spheres in compressed contact) with the implicit assumption that the physical phenomena produced are insensitive to the interaction law between the grains. In recent years our MD work in this area has shown that this is far from the case. For example, the granular assembly structure, the stress distribution in the system and at its boundaries, and even the bulk flow characteristics are highly sensitive to the analytic form chosen for the interaction potential. We have established simple interaction laws that give a more realistic representation of granular system behaviour than those used in the past. A discussion of the terms in this interaction law, and the issues raised will be given. Examples of results taken from our simulations of hoppers and heap formation will be presented (Langston, Tüzün & Heyes, Chem.Eng.Sci. **50**, 967 (1995) & **51**, 863 (1995); Powder Tech. **85**, 153 (1995); Baxter, Tüzün, Burnell & Heyes, Phys.Rev.E **55**, 3546 (1997); Langston, Nikitidis, Tüzün, Heyes & Spyrou, Powder Tech. **94**, 59 (1997)).

### Effects of hard cores – purely viscous liquids?

J.G. Powles<sup>1\*</sup> and D.M. Heyes<sup>2</sup>.

<sup>1</sup> Physics Department, University of Kent, Canterbury,

<sup>2</sup> Chemistry Department, University of Surrey, Guildford.

It is shown that if an intermolecular potential has a hard core **of any sort**, the infinite-frequency shear modulus  $G_\infty$  and the bulk modulus  $K_\infty$  of the fluid are infinite (Powles & Heyes, in preparation). This is a generalisation and extended application of the analysis of Zwanzig (Zwanzig & Mountain, *J.Chem.Phys.* **43**, 4464 (1965); Schofield, *Proc.Phys.Soc.* **88**, 149 (1966)), which has recently been investigated in detail for hard spheres (Heyes & Aston, *J.Chem.Phys.* **100**, 2149 (1994)) and for increasingly steeply repulsive potentials (Heyes, *J.Chem.Phys.* **107**, 63 (1997); Heyes & Powles, *Molec.Phys.* in press) showing explicitly that  $G_\infty$  and  $K_\infty$  are infinite. This result has also been noted in passing, for hard spheres, elsewhere (Schofield, p.583 in *Physics of Simple Liquids*, ed: Temperley et al., North Holland (1968); Groot & Axtufof, *Macromolecules* **28**, 6284 (1995)).

According to Maxwell (*Phil.Trans.Roy.Soc.* **157**, 49 (1867)), and the experimental evidence, all real fluids are “viscoelastic”. However, if the infinite-frequency elastic moduli are infinite, the Maxwell relation time is zero and the fluid is purely viscous at all finite frequencies. Thus the non-physical assumption of a hard core interaction leads to non-physical behaviour and the repercussions of this demand further analysis (Powles & Heyes *loc. cit.*).

### Modelling aluminium clusters with an empirical many-body potential.

L.D. Lloyd.

School of Chemistry,  
University of Birmingham, Birmingham B15 2TT, UK.

An empirical two-plus-three-body atomistic potential, derived by fitting experimental data pertaining to bulk aluminium, has been applied to the study of structures and growth patterns of small aluminium clusters. The high dimensionality of the nuclear configuration space for clusters results in an extremely large number of isomers and local minima on the potential energy hypersurface. Global optimisation (i.e. searching for the lowest energy structure) was carried out using Random Search and Monte Carlo Simulated Annealing methods, for  $\text{Al}_2$  to  $\text{Al}_{20}$ . The results of random searching have been used to put lower bounds on the number of minima for these nuclearities, and the efficiency of the Monte Carlo Simulated Annealing approach has been demonstrated. Comparisons have generally been in good agreement with results of previous calculations using electronic structure and empirical potential methods. While many of the global minima were also global minima for Lennard–Jones or Morse clusters, a number of new structures have been identified for  $\text{Al}_N$  clusters, notably for  $N = 9, 16, 17, 18$  and  $20$ .

### Cluster geometry optimization using genetic algorithms.

Roy L. Johnston\* and Chris Roberts.

School of Chemistry, The University of Birmingham,  
Edgbaston, Birmingham B15 2TT, UK.

Atomic clusters are aggregates of anywhere between 2 and (of the order of)  $10^6$  atoms. The atoms may all be of the same type (elemental clusters) or of different types (e.g. alloy clusters, ionic clusters). Clusters can be formed by nearly all the elements in the Periodic Table, such as the noble gases (e.g. argon), semi-conducting elements (e.g. carbon and silicon) and metals (e.g. sodium and iron). The bonding in these different types of clusters is very different, ranging from weak dispersion forces (noble gas clusters) to covalent (carbon and silicon clusters) and delocalized/metallic (metal clusters). Clusters are of interest from a theoretical viewpoint as well as for their possible application in the growing field of nano-electronics. For an  $N$ -atom cluster there are a very large number of possible structures (isomers), many of which correspond to local minima on the Potential Energy Hypersurface. The problem we face is trying to find the lowest energy isomer (Global Minimum). In this presentation, I will discuss the application of Genetic Algorithms to achieve this global minimization, giving examples ranging from argon clusters (bound by a simple Lennard-Jones potential) to metal clusters bound by Morse and many-body potentials and carbon clusters, including the fullerenes.

### The Road to Ammonium Nitrate.

K.A. Mort\*, R.A. Jackson, P.J. Wilde.

Department of Chemistry, Keele University,  
Keele, Staffs, ST5 5BG, UK.

Ammonium nitrate is an industrially important chemical which exists in several phases. A good starting point in trying to model this complex system is to develop potentials for the constituent molecular ions separately by using empirical fitting to ammonium halides and alkali nitrates. We have developed potentials for the ammonium ion and the nitrate ion using the GULP program developed by J. Gale (Imperial College). We present these results together with results from molecular dynamics simulations using these fitted potentials. We also present preliminary results for transferring these potentials into simulations of ammonium nitrate.

### How complex should a potential be?

Stuart Pawley.

Department of Physics, King's Buildings,  
University of Edinburgh, Edinburgh EH9 3JZ, UK.

We should always ask whether the potential function that we are using for a particular modelling task has sufficient mathematical complexity for the task, but does not have more complexity

than the task needs. Some examples will be presented, starting from the early days of lattice dynamics. Why is it that the Lennard–Jones atom–atom model, which was much maligned years ago, has now an enviable pedigree? Why is it that some molecular dynamics models need a time-step as small as a femto-second? And how can I somehow bring quaternions into my talk?

### *Ab initio* interatomic potentials of silica from a genetic algorithm.

T. Uchino<sup>1\*,\*</sup>, S.N. Taraskin<sup>2</sup>, S.R. Elliott<sup>2</sup>, and D.C. Clary<sup>1</sup>.

<sup>1</sup> Department of Chemistry, University College London,

<sup>2</sup> Department of Chemistry, University of Cambridge.

A new method to provide interatomic potentials from *ab initio* Hartree-Fock (HF) cluster calculations is proposed. We employ a cluster consisting of five SiO<sub>4</sub> tetrahedra. More than 250 *ab initio* points are calculated at the HF/6-31G(d) level on the basis of the normal coordinates of five different vibrational modes of the cluster. The force-field parameters are then determined based on a genetic algorithm. These parameters are tested in the molecular dynamics simulation of some silica polymorphs.

### The extended overlap model and its application to calculating anion polarizabilities in ionic solids.

Richard J. Wheatley.

Department of Chemistry, University of Nottingham,  
University Park, Nottingham NG7 2RD, UK.

The overlap model is based on the assumption that the intermolecular exchange-repulsion energy is proportional to the overlap between the ground-state molecular charge densities. It has been used successfully for obtaining semi-empirical potentials involving neutral molecules.

An extended overlap model has recently been introduced for ionic interactions, taking into account the effect of polarization on the anion charge density. In an A<sup>+</sup>B<sup>-</sup> dimer, a “monomer” *ab initio* calculation is performed on B<sup>-</sup>, using as a perturbation the electrostatic potential due to the interaction with A<sup>+</sup>, plus an effective potential due to the overlap of electrons between the two ions. This effective potential reduces the polarization of the anion, and can be regarded as providing an exchange–induction contribution to the potential, to infinite order.

The model can also be used for estimating the polarizabilities of ions in solids. Again, only a monomer calculation is required on the anion, perturbed by the electrostatic and effective potentials of the surrounding ions. The computational time required to calculate polarizabilities is

reduced by several orders of magnitude in this way. Basis set superposition error is also eliminated. Results for LiF and LiCl crystals indicate that the model provides in-crystal polarizabilities for the anions in essentially exact agreement with expensive direct calculations, at both the Hartree-Fock and MP2 levels of theory.

### **Deviations from the predicted behaviour of a polarisable and compressible ion model of zirconia.**

N.A. Marks\*, S. Fabris and M.W. Finnis.  
School of Mathematics and Physics,  
Queen's University of Belfast,  
Belfast BT7 1NN, Northern Ireland.

We examine a model of zirconia in which the ions carry formal charges and the anions are both compressible and polarisable. The compression aspect of the model is parametrised from *ab initio* calculations, while the polarisation effects are to the quadrupolar level and include the short-range damping effect demonstrated by Fowler and Madden. The paper which presents the zirconia model (Wilson *et al.* Phys.Rev.B **54**, 9147 (1996)) claims to reproduce both the experimentally observed monoclinic ground state as well as the tetragonal double well distortion. In attempting to break this model, we find that the ground state of the potential is a rutile-like structure, which has not been observed experimentally in zirconia. This situation can be explained as a manifestation of overly large quadrupole moments and a born-mayer term which is too repulsive. We examine how this has arisen and suggest ways in which the model can be corrected. One of these improvements is a new representation of the short-range damping.

### **Derivation of potential models for MgO from *ab initio* data.**

Maurice Leslie.

CLRC, Daresbury Laboratory, Warrington WA4 4AD, UK.

A number of models for ionic materials are compared using magnesium oxide as an example material. *Ab initio* Hartree Fock data are used as the observables in a least-squares fit. A number of different shell models will be presented and their limitations discussed. Particular emphasis will be placed on the L-point LA phonons which can only be adequately described by allowing the oxygen shells to become non-spherical.

## Posters

\* indicates presenter

### **First principles computer simulations of liquid crystal molecules.**

C.J. Adam\*, S.J. Clark, G.J. Ackland and J.Crain.

Department of Physics, King's Buildings,  
University of Edinburgh, Edinburgh EH9 3JZ, UK.

The molecular properties of the prototypical liquid-crystal molecule 4-4'pentyl-cyano- biphenyl (5CB) are investigated using an accurate first principles quantum mechanical method. A detailed study of the molecular structure and bonding in 5CB as well as the intra-molecular degrees of freedom is performed, which provide information on the conformational dynamics and vibrational molecular motions. Also investigated are the electrostatic properties of 5CB and the influence that the condensed phase may have on molecular properties.

### **Solvent polarisation and dynamics in hybrid QM/MM methods.**

R.A. Bryce\*, N.A. Burton, I.H. Hillier and R. Buesnel.

Department of Chemistry,  
University of Manchester,  
Manchester M13 9PL, UK.

Hybrid QM/MM potentials are now increasingly used in the study of dynamics and reactivity in the condensed phase. It is important to consider the mutual polarisation of the QM and MM regions. We have developed such a model of solvation to include these effects based on the principle of electronegativity equalisation (Bryce, Buesnel, Hillier & Burton, Chem.Phys.Lett. **279**, 367 (1997)). Here the partial atomic charges of the classical region are treated as dynamical variables and propagated in a fashion analogous to the Car-Parrinello method. Applications to the study of properties of ion-water clusters are discussed.

### **Calculation of helical twisting power for liquid crystal chiral dopants.**

Melanie J. Cook\* and Mark R. Wilson.

Department of Chemistry, University of Durham,  
South Road, Durham DH1 3LE, UK.

The helical twisting power (HTP) determines the pitch of the chiral nematic phase produced when a nematic liquid crystal is doped with a low concentration of chiral solute molecules. Molecules with large HTP values have major applications in electro-optic displays and in optical data processing.

We have developed a new simulation technique that allows accurate calculation of HTP values for a range of chiral dopant molecules. We employ twisted periodic boundary conditions, together with a Gay–Berne solvent, to produce a twisted nematic phase with a  $90^\circ$  rotation in the director across the simulation box. We then carry out a sequence of Monte Carlo fluid simulations to grow an atomistic model of a chiral dopant into the Gay–Berne solvent. Statistical perturbation theory gives a measure of the change in free energy for this process. Comparison of the free energy difference for an enantiomer and its mirror image allows us to calculate HTP values.

We find that we are able successfully to predict the direction of twist for each enantiomer. Within statistical errors the computed HTP values are in good agreement with experimental data.

### **A model potential for metal surface studies.**

Dr Hazel Cox<sup>1\*</sup>, Roy L. Johnston<sup>2</sup> and John N. Murrell<sup>1</sup>.

<sup>1</sup> School of Chemistry, Physics and Environmental Sciences,  
University of Sussex, Falmer, Brighton BN1 9QJ, UK,

<sup>2</sup> School of Chemistry,  
The University of Birmingham, UK.

An empirical potential energy function, comprising two- and three-body terms, has been derived for several cubic atomic solids (Pt, Pa, Yb, etc.) by fitting parameters to the phonon dispersion curves, elastic constants, lattice energy and lattice spacings of the most stable phase of the solid (fcc for the examples above), and the vacancy formation energy. These potentials reproduce the fitted structural data very well, and some other properties such as the Cauchy pressure (+ve and -ve) and phase changes along the Bain deformation path, which are not fitted. The potential is then used to calculate surface energies and relaxations of the high symmetry surfaces, which tend to agree well with experimental values. For example, the potential for Pt reproduces the energies and relaxations of the (111), (110) and (100) surfaces of fcc Pt to a high degree of accuracy, and correctly predicts the relaxation, pairing and buckling of the  $1 \times 2$  reconstruction of the (110) Pt surface.

### **Studies in the dissolution of calcite.**

N.H. De Leeuw<sup>1</sup>, S.C. Parker<sup>1</sup> and J.H. Harding<sup>2\*</sup>.

<sup>1</sup> School of Chemistry, University of Bath,

<sup>2</sup> University College, London.

Atomistic simulation techniques were used to model two stepped  $\{10.4\}$  surfaces of the calcium carbonate polymorph calcite. The obtuse monatomic steps were found to be more stable than the acute monatomic steps. The initial stages of growth at the steps were considered in vacuo and in water. In vacuo  $\text{CaCO}_3$  was shown to adsorb preferentially at the acute step. However, the energies of the adsorption were modified by the geometry of adsorbed water molecules. The calculations predict that including water molecules in the simulations causes the obtuse step to grow preferentially, in agreement with experimental findings of calcite growth in solution. On using potential parameters which reproduce experimental enthalpies of the dissolution of the calcite crystal, the addition of a full obtuse step is found to be exothermic in contrast to the endothermic process of adding an acute step. This explains why obtuse steps are experimentally found to grow faster than acute steps.

### **Molecular and bulk properties by molecular mechanics.**

Martin Grayson.

Department of Chemistry,  
University of Sheffield,  
Sheffield S3 7HF, UK.

Molecular Mechanics uses a parameterized 2/3/4-body force-field to provide an estimate of the energy of an assembly of molecules. This work is concerned with the production of “property surfaces” to provide an estimate of quantities such as bulk magnetic susceptibility, NMR spectra from estimated shieldings and coupling constants, polarizabilities, or optical activity for the same assembly of molecules. This can also be expressed in parameterized 2/3/4-body form, 2-body forms being bond properties, their bond-length derivatives and their derivatives with respect to the surrounding coulomb field. Such bond properties have a very old pedigree right back to J.J. Thomson. A well-known 4-body parameterization is the Karplus Equation for the variation of spin-spin coupling constants with dihedral angle.

### **The renormalized potential for cubic crystals.**

Tomasz Gwizdalla.

Department of Solid State Physics,  
University of Lodz, Pomorska 149/153,  
90-236 Lodz, Poland.

The shape of the potential curve for some fcc and bcc crystals has been determined. Starting from the basic shape appropriate for the elastic properties for the temperature 0K and using the anharmonic renormalization method proposed by Siklos and Plakida, we obtained potentials for temperatures up to the melting point. These potentials were used for subsequent SLAB calculations of the dynamical properties of the samples studied, performing equally well for bulk as for thin film or surface calculations.

### **Conformational transitions in amylose strands.**

Michelle M. Kuttel\* and Kevin J. Naidoo.

Department of Chemistry, University of Cape Town  
Rondebosch, 7701, South Africa.

Development of a biodegradable alternative to imperishable plastic polymers is becoming increasingly necessary. A potential candidate is starch, a naturally-occurring and enzymatically degradable biopolymer comprising two polysaccharides: amylose (a linear polymer with  $\alpha(1\rightarrow4)$

linked D-glucopyranose units) and amylopectin (a branched polymer with short  $\alpha(1\rightarrow4)$  glucose chains connected by  $\alpha(1\rightarrow6)$  bonds).

However, in order to render starch-based plastics commercially viable, some undesirable physical properties of starch (eg. brittleness and rapid physical aging) should be eliminated. It is necessary to understand the underlying folding mechanisms of starch in a number of environments to determine which modifications should be made to the starch molecule to achieve this end. Our first approach is to explore the mechanisms of folding of a 6-unit amylose strand in vacuum. This strand constitutes a single turn in both the B and V helical form of amylose.

We compute the potential of mean force of the amylose strand as a function of the end-to-end distance (the distance between O4 on the first glucose residue and O1 on the sixth glucose residue), using an iterative constraining potential method, previously developed by us (Naidoo & Brady, *J.Am.Chem.Soc.*, submitted 1998). We use CHARMM (Brooks, Brucoleri, Olafson, States, Swaminathan & Karplus, *J.Comput.Chem.*, 4(2), 187) and a CHARMM-like force field for carbohydrates (Liang & Brady, unpublished, 1998), for all the molecular dynamics calculations.

### **Computer simulation of confined liquid crystal mixtures.**

R. Latham\* and D.J. Cleaver.

Materials Research Institute, Sheffield Hallam University,  
Pond St, Sheffield S1 1WB, UK.

We present preliminary results from a molecular dynamics study a confined liquid crystal mixture. This study uses a fluid composed of two species of rod-like particles of differing lengths confined between two solid substrates. The fluid interaction is modelled using a generalised Gay-Berne potential and a non-separable anisotropic molecule-wall potential is employed. The molecule-wall potential includes a term which breaks the azimuthal symmetry, in order both to aid equilibration and to simulate a "rubbed" surface.

### **Molecular dynamics simulations of particle bombardment induced desorption process: enhancement of Au-thiolate clusters by the use of a modified pairwise potential.**

K.S.S. Liu <sup>1\*</sup>, C.W. Yong <sup>2</sup>, B.J. Garrison <sup>3</sup> and J.C. Vickerman <sup>1</sup>.

<sup>1</sup> Surface Analysis Research Centre, Dept. of Chemistry,  
UMIST, P.O. Box 88, Manchester M60 1QD, UK,

<sup>2</sup> School of Biological Sciences, Stopford Building,  
The University of Manchester, M13 9PT UK,

<sup>3</sup> Dept. of Chemistry, The Pennsylvania State University,  
University Park, Pennsylvania 16820, USA.

Molecular dynamics simulations have been used to model the process of Ar bombardment onto a system of n-alkanethiolate molecules adsorbed on a Au(111) surface. A blend of pairwise and many-body potentials are used for various interatomic interactions. Of note are the potentials for S-S and Au-S interactions which are essentially pairwise but with an energy parameter,  $D_e$ , which varies according to the heights of S and Au atoms above the surface. It is found that the modified Au-S potential enhances the formation of a variety of Au thiolate clusters. The ejected species calculated from the simulation correlate well with those recorded by the secondary ion mass spectrometry (SIMS).

### **Molecular dynamics simulation of flexible liquid crystal molecules.**

Carl McBride\* and Mark R. Wilson.

Department of Chemistry, University of Durham,  
South Road, Durham DH1 3LE, UK.

Molecular dynamics simulations have been performed for a liquid crystal molecule composed of a Gay–Berne core unit connecting a three-site and a seven-site Lennard–Jones flexible alkyl chain. Calculations have been carried out for 512 molecules in the NVT ensemble for simulation times of up to 8.0 ns at two distinct densities. The liquid crystal phases of the material have been fully characterised by measurements of orientational order parameters and structure factors in each phase. Results are also presented for conformational distributions and effective torsional potentials of the system as well as results for translational diffusion and reorientational dynamics. We conclude that models of this nature represent a powerful approach to the study of flexibility in mesogenic systems and open up possibilities for predicting both the phase behaviour and bulk properties of liquid crystals based solely on a prior knowledge of intermolecular interactions. See McBride, Wilson & Howard, *Mol.Phys.* **93**, 955 (1998); Wilson, *J.Chem.Phys.* **107**, 8654 (1997).

We also present results for a fully atomistic model of the mesogen 4,4'-dipentyl- 1,1'-bibicyclo[2.2.2]octane (5,5-BBCO) in which we show growth of a nematic phase directly from the isotropic liquid.

### **The structure of small gold clusters.**

Nicholas T. Wilson\* and Roy L. Johnston.

School of Chemistry, The University of Birmingham,  
Edgbaston, Birmingham B15 2TT, UK.

Molecular Dynamics Simulated Annealing techniques have been used to probe the structure of small gold clusters consisting of between 2 and 40 atoms. The interatomic interactions within these clusters are described using a Murrell-Mottram potential (Murrell & Mottram, *Mol.Phys.*, **69**, 571 (1990)) which is an empirical atomistic [2+3]-body potential energy function parameterised to bulk experimental data such as lattice energy, lattice separation and phonon frequencies.

The Molecular Dynamics Simulated Annealing protocol involves the slow quenching of a cluster from a high, usually molten, temperature into its lowest energy conformation. If the annealing is performed infinitely slowly then the cluster should be quenched into the global minimum of the potential. The efficiency of this method as a tool for probing the potential energy surface of this system is explored with relation to other methods of determining the global minimum.

### **The effects of segment-segment repulsion on model polymers.**

Cheng Xiao and David M. Heyes

Department of Chemistry, School of Physical Sciences,  
University of Surrey, Guildford GU2 5XH, UK.

The effects of segment-segment interactions on polymer solutions are examined by Brownian Dynamics simulation in the free-draining limit. The bead-and-spring model is used to describe polymer chains and the segment-segment interactions are modeled by a pair-potential of Gaussian type  $u(r)/kT = A \exp(-r^2/a^2)$ . The chain dimensions and viscoelastic properties of the system are studied as functions of chain-length and concentration.

### **Computer simulations of orientational behaviour of strained polymer networks.**

C.W. Yong\* and P.G. Higgs.

School of Biological Sciences, Stopford Building,  
The University of Manchester, M13 9PT, UK.

Monte Carlo simulations of dense polymer networks under uniaxial strain were carried out using a three-dimensional bond fluctuation chain model. A simple excluded volume (EV) rule is applied in order to take into account both inter- and intra-molecular interactions. Symmetrised distribution functions of segmental orientations are being calculated which show characteristic doublet structures as has also been observed in deuterium nuclear magnetic resonance experiments (D-NMR). The splittings are believed to be due to reorientations of polymer segments about a macroscopic axis parallel to the direction of the uniaxial strain. Such observations are in contradiction to the predictions of the classical "phantom" network theory. Different parts of interactions are systematically switched on or off in order to study in detail the factors which affect the orientational behaviour of a polymer segment. The uniformity of the average segmental uniaxial orientations along a chain will also be addressed.