

# ABSTRACTS

## INDEX

- [INVITED TALKS](#)

The talk abstracts are in order of presentation.

- [Professor Alain Fuchs \(University of Paris-Sud\)](#)  
Thermodynamic Properties of Molecular Fluids Confined in Nanoporous Materials
- [Dr Douglas Cleaver \(Sheffield Hallam University\)](#)  
The importance of particle shape for controlling surface alignment: generating tilt and bistability in generic models of confined liquid crystals
- [Dr Fernando Bresme \(Imperial College London\)](#)  
Molecular Dynamics simulations of Newton Black Films
- [Dr Carl Dettmann \(University of Bristol\)](#)  
Chaos and statistical mechanics
- [Professor Chris Care \(Sheffield Hallam University\)](#)  
Mesoscale modelling of complex fluids: liquid crystals, blood and sludge
- [Professor David Brown \(University of Savoie\)](#)  
Molecular dynamics simulations of polymer nanocomposites and surfaces
- [Professor George Jackson \(Imperial College London\)](#)  
Simulation of the Macroscopic Pitch of Chiral Nematic Liquid Crystalline Materials
- [Dr Scott Owens \(British Nuclear Fuels plc\)](#)  
Multi-scale simulation of vitrification melter - from atomistic derivation of melt properties to a prediction of melter lifetime and melt mixing.
- [Professor Athanassios Panagiotopoulos \(Princeton University\)](#)  
Molecular and mesoscopic simulations of phase equilibria

- [CONTRIBUTED TALKS](#)

The talk abstracts are in order of presentation.

- [Nano and microscale simulation of exotic structures in zeolites](#)  
Ben Slater (Royal Institution, London)
- [Atomistic Simulations of Nanocrystals of Oxides and Minerals](#)  
Dino Spagnoli (University of Bath)
- [Chiral Discrimination by Chemical Force Microscopy: Simulations](#)  
Esther Haines (University of Cambridge)
- [Atomistic modelling of the structure and reactivity of Ionic Nanoparticles - Ceria.](#)  
Paul Martin (University of Bath)
- [Osmotic pressure calculation for dilute solutions of rod-like polyelectrolytes](#)  
Dmytro Antypov (Max-Planck-Institut für Polymerforschung)
- [Ab-Initio Simulations of Ionic Liquids](#)  
Mario Del Popolo (Queen's University Belfast)
- [Langevin Dynamics in non-Hamiltonian Systems : The NPT Ensemble](#)  
Mr David Quigley (University of York)

- [Packing of soft spheres: complex supramolecular assemblies](#)  
X. Zeng (University of Sheffield)
- [Molecular Dynamics Simulations of Fluids composed of Particles with Variable Softness](#)  
D.M. Heyes (University of Surrey)
- [Combination of Molecular Dynamics and SPH Methods in Simulation of Bi-Material Interface](#)  
Ken-ichi Saitoh (Kansai University)
- [Potential of Mean Force Between Colloidal Particles: Effect of Ion Polarizability](#)  
Frederico Tavares (Universidade Federal do Rio de Janeiro)
- [Computations of activated processes in biomolecules](#)  
Chandra Verma (Bioinformatics Institute, Singapore)
- [Modelling Liquid Crystal Display Cells Using Parametric Hard Gaussian Overlaps](#)  
F. Barmes (CECAM)
- [Order from disorder: crystal growth and inhibition in hydrocarbon/water mixtures](#)  
P.M. Rodger (University of Warwick,)
- [Computer simulation and perturbation theory for the solid-liquid-vapour phase behaviour of chain molecules: rigid and flexible models](#)  
A. Galindo (Universidad Complutense de Madrid)
- [The Role of Random Numbers in Computer Simulation, and Development of a Newly Combined Method Generating Random Numbers](#)  
Abdollah Aghaie (K N Toosi University of Technology)
- [Applications of computer modelling in the development of solid state materials for optical devices](#)  
Robert A Jackson (Keele University)

- [POSTER ABSTRACTS](#)

The poster abstracts are in alphabetical order.

- [Modelling of Glassy State Relaxations in Polymers: The Rotation of the Methoxy Group in PVME](#)  
J.C. Berthet (Univeristy of Leeds)
- [Determining the structure of zeolite catalysts through a distributed computing strategy](#)  
Ms Rosemary Coates (University College London)
- [Preparation and Characterization of Porous matrices by computer Simulations](#)  
Hector Dominguez (Universidad Nacional Autonoma de Mexico)
- [Temperature-accelerated dynamics of alumina](#)  
J.H. Harding (University of Sheffield)
- [Multi-scale modelling of membrane materials for fuel cell applications](#)  
Dr J. A. Elliott (University of Cambridge)
- [Modelling of Glassy State Relaxations in Polymers: The Linear Polymer Problem](#)  
Taining Liang (Univeristy of Leeds)
- [Molecular Modelling of Self-Assembling Amphiphilic Systems](#)  
David Michel (Sheffield Hallam University)
- [The Influence of Poly\(ethylene oxide\) Oligomer End-Groups on their Interface With a Silica Nanoparticle](#)

S. Neyertz (Université de Savoie)

- [High-temperature glass transition in model C60.](#)  
Romina Ruberto (Università degli Studi di Messina)
- [Sensitivity of the Thermal Diffusion Factor of Diatomic-diatomc and Monoatomic-Diatomc Mixtures to the Details of the Intermolecular Potential by DNEMD Simulation](#)  
Saeed Yeganegi (University of Mazandaran)

## INVITED TALKS

### **Thermodynamic Properties of Molecular Fluids Confined in Nanoporous Materials**

Alain Fuchs<sup>1</sup>, Sophie Sacquin-Mora<sup>1</sup>, and Martin Schoen<sup>2</sup>

1. Physical Chemistry Laboratory University of Paris-Sud Orsay, France
2. Martin Schoen Stranski-Laboratorium für Physikalische und Theoretische Chemie Technische Universität Berlin Berlin, Germany

When a fluid phase is confined to spaces of nanoscopic dimensions by solid substrates, confinement adds a new relevant length scale to the system, namely the separation of the solid surfaces (or pore width). As a consequence, fluid properties are markedly altered from those of a corresponding bulk fluid at the same temperature and chemical potential. This has led to numerous studies concerned either with simple fluids or with more complex ones such as alkanes or liquid-crystal films. However, if these fluids are constrained by either chemically or physically decorated substrates, additional length scales competing with the pore width become relevant. These length scales are associated with the pattern with which the solid surfaces are endowed. In addition to liquid-gas coexistence, bridge phases may form in these systems, as a third morphology of confined fluids. We show that a bridge phase can be established as a generic thermodynamic phase. We investigate in this paper the phase behaviour of simple fluids confined in a variety of chemical and physically heterogeneous slit pores by means of Monte Carlo simulations in the grand canonical ensemble. We develop a thermodynamic integration scheme to calculate the grand potential of the system. Torsion-induced phase transitions are also investigated.

---

### **The role of particle shape in controlling surface alignment: generating tilt and bistability using generic models of confined liquid crystals.**

Dr Doug Cleaver

Materials Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, UK

It is recognised that particle shape is the main factor in determining the structure (e.g. the radial distribution function) of bulk liquids. Similarly, the structures of fluids adsorbed at substrates or in narrow pores depend crucially on the wall-particle contact function. To illustrate this, this talk will use results from generic model simulations to examine the signatures of various adsorption behaviours. Following on from this, it will be shown that these shape considerations can be used to control the orientational anchoring properties of ordered fluids.

---

### **Chaos and statistical mechanics.**

Carl Dettmann

Department of Mathematics, University of Bristol, UK

Despite the gulf in system size between research in chaos (usually  $N$  about 2) and statistical mechanics (usually  $N \rightarrow \infty$ ) there has been a significant interaction between the two in recent years, involving relations between Lyapunov exponents (measures of chaotic instability), fractal dimensions and phase space contraction on one hand, and macroscopic transport coefficients, fluctuations and correlation functions on the other. I will give a general overview emphasizing directions of current active interest.

---

## Molecular Dynamics simulations of Newton Black Films

Dr Fernando Bresme

Department of Chemistry, Imperial College London, SW7 2AZ, London, United Kingdom

Newton Black Films (NBFs) are the thinnest equilibrium states of soap films, with typical thicknesses of the order of 4 nm. These surfactant bilayer structures constitute the basic building blocks of foams, emulsions and they are relevant to understand the physics of biological membranes. The NBFs stability determines the stability of foams and emulsions. Despite their importance there is not a clear and satisfactory explanation of the physical origin of the repulsive forces stabilising NBFs. Some theories claim that electrostatic forces induce a modification of the water structure inside these films (hydration forces) [1], whereas others claim that the entropic repulsion of thermally excited molecular groups are responsible for the stability of the films [2].

Using Molecular Dynamics computer simulation we have investigated Sodium Dodecyl sulfate Newton Black Films (SDS-NBF). The SDS-NBF system has been studied in the past using X-Ray reflectivity experiments [3], and represents a suitable system to test computational models [4]. In order to advance in the understanding of the physical origin of the forces stabilising NBFs, we have studied the electrostatics of the SDS-NBF. We show that water exhibits an anomalous dielectric response [5], which plays an essential role in determining the stability of the NBFs. By computing the electrostatic Helmholtz free energy we show that the anomalous dielectric behaviour results in a repulsive force that can be identified with the "hydration" force measured in experiments [6].

### References

- [1] D.W.R. Gruen and S. Marcelja, *J. Chem. Soc. Faraday Trans.* , **2** , 79, 225 (1983).
  - [2] J. Israelachvili and H. Wennerstrom, *Nature (London)* , **379** , 219 (1996).
  - [3] O. Belorgey and J.J. Benatar, *Phys. Rev. Lett.* , **66** , 313 (1991).
  - [4] F. Bresme and J. Faraudo, *Langmuir* (2004).
  - [5] J. Faraudo and F. Bresme, *Phys. Rev. Lett.* (2004).
  - [6] J. Faraudo and F. Bresme, submitted (2004).
-

## Mesoscale modelling of complex fluids: liquid crystals, blood and sludge

Professor C. M. Care

Materials Research Institute, Sheffield Hallam University, Howard Street, Sheffield, S1 1WB, UK

The lattice Boltzmann (LB) method is a well established method for modelling simple fluids at the mesoscopic length scale [1]. The method has been adapted to represent complex fluids such as liquid crystals, dense colloidal suspensions and more recently the flow of blood cells.

In the first part of the talk, a brief review will be given of the different ways in which the LB method has been extended to model the flow of a nematic liquid crystal [2,3]. The motivation for using a mesoscopic approach and the problems associated with modelling the slow and fast degrees of freedom within the same simulation framework will be discussed. Results will be presented from a lattice Boltzmann solver for a full liquid crystal device. The solver is able to correctly model the influence of flexo-electricity and surface structure on liquid crystal device switching.

In the second part of the talk, a number of different physical problems will be presented to illustrate the way in which the LB method can be modified to correctly include additional physics. The problems considered will include (i) solid colloidal particles embedded in a nematic liquid crystal (ii) a droplet of an isotropic fluid embedded in a nematic (iii) colloidal suspensions of multiple deformable droplets (iv) the flow of blood.

### References

[1] S. Succi “The lattice Boltzmann equation for Fluid Mechanics and Beyond” (Clarendon Press; Oxford) (2001)

[2] Care, C M, Good, K and Halliday, I (2000) *J Phys: Cond Matter* **12**, L665; Care C M, Halliday I, Good K and Lishchuk S V (2003) *Phys Rev E* **67**, 061703

[3] Denniston C, Orlandini E and Yeomans JM (2000) *Euro Phys Let* **52** 481; Denniston C, Orlandini E and Yeomans J M (2001) *Phys Rev E* **63**, 056702.

---

## Molecular dynamics simulations of polymer nanocomposites and surfaces

David Brown

Laboratoire Matériaux Organiques à Propriétés Spécifiques (LMOPS), UMR 5041 Université de Savoie - CNRS, Campus Scientifique, 73376 Le Bourget-du-Lac, France

This talk will present the application of classical simulation methods of molecular dynamics (MD) and Monte Carlo (MC) to polymers from studies of bulk amorphous systems through to more recent advances in the preparation of inhomogeneous systems such as composites and films.

Amorphous polymer systems present a challenge for the simulator because of the broad range of relaxation times. Although many techniques exist in the literature for preparing samples of amorphous polymers, very few have actually been verified. It will be shown here that the use of the hypothesis of Flory has allowed the development of a robust hybrid Pivot MC-MD technique [1] which can be used to prepare polymers of arbitrary connectivity in the amorphous state. The method's reliability stems from the systematic confrontation of the results of single-chain sampling, using Pivot MC-MD, with those of brute force MD calculations of a bulk melt of oligomers of the same length, for which equilibrium can be obtained within time scales available to atomistic level simulation.

The above approach has recently been used to prepare polymer matrices into which have been inserted inorganic spherical nanoparticles using a novel technique [2]. In composite systems, questions arise as to the influence of interactions at the polymer-filler interface on the molecular mobility and structure of neighbouring chains and the consequences this has on macroscopic properties. These effects are amplified in the case of objects of small dimensions as the relative amount of material in the vicinity of the interface is inversely proportional to the size of the inclusions. Thus, although some experimental work points to a reduction in molecular mobility in the region of the interface, little is known about the origin of this immobilisation, the possible accompanying changes in structure or the spatial extent of these two effects. In this presentation, results for a long-chain generic model [2] are compared to those obtained for a more detailed model of the PBMA-water-silica nanocomposite system; this latter system has recently been the subject of an extensive experimental and simulation study [3]. In both these cases the chains are too long to come into complete equilibrium with the silica surface and the consequences of this will be discussed. In a related work, which will be presented at this meeting in the form of a poster, short PEO oligomers were relaxed completely to equilibrium in the presence of a silica nanoparticle [4].

Although the above approach allows spherical interfaces to be studied, introducing a planar interface into an amorphous long-chain polymer system has long been a problem for simulation. The complete relaxation of a polymer at a planar interface must resort to more sophisticated techniques and recent advances using a combined coarse-graining and back-mapping approach [5, 6] will be outlined and their application to the construction of an atomistic model of a  $\sim 300$  Å thick polymer film illustrated.

(For more information see <http://www.univ-savoie.fr/labos/lmops/brown/db.html>)

### References

- [1] S. Neyertz and D. Brown, "Preparation of Bulk Melt Chain Configurations of Polycyclic Polymers", *J. Chem. Phys.*, **115**, 708-717, (2001).
- [2] D. Brown, P. Mélé, S. Marceau and N. Albérola, "A Molecular Dynamics Study of a Model Nanoparticle Embedded in a Polymer Matrix", *Macromolecules*, **36**, 1395-1406, (2003).
- [3] S. Marceau, Architecture Multiéchelle et Propriétés Mécaniques de Nanocomposites, Ph.D. Thesis, Université de Savoie, 2003, available in PDF format at:- <http://www.univ-savoie.fr/labos/lmops/people/smarceau/these/these.html>.

- [4] D. Barbier, D. Brown, A.-C. Grillet and S. Neyertz, "Interface between End-Functionalized PEO Oligomers and a Silica Nanoparticle Studied by Molecular Dynamics Simulations", *Macromolecules*, **37**, 4695-4710, (2004).
- [5] S. Queyroy, "Simulations moléculaires dynamiques de surfaces de polymère amorphe: cas de la cellulose", Ph.D. Thesis, University of Savoie, 2004.
- [6] S. Queyroy, S. Neyertz, D. Brown and F. Müller-Plathe, "Preparing Relaxed Systems of Amorphous Polymers by Multi-scale Simulation: Application to Cellulose", *Macromolecules*, (2004), in press.
- 

## Simulation of the Macroscopic Pitch of Chiral Nematic Liquid Crystalline Materials

Szabolcs Varga<sup>1,3</sup>, and George Jackson<sup>1,2</sup>

1. Department of Chemical Engineering and Chemical Technology, Imperial College London, South Kensington Campus, LONDON SW7 2AZ, UK
2. Affiliated to the Molecular Systems Engineering Group of the Centre for Process Systems Engineering
3. Department of Physics, University of Veszprém, H-8201 Veszprém, PO Box 158, Hungary

An important class of mesogenic molecules possess a chiral geometry which imparts a chirality on the bulk phase. The effect of molecular chirality on the cholesteric phase behaviour is examined for a fluid of hard spherocylinders of aspect ratio  $L/D=5$  with a central chiral dispersion potential [S. Varga, and G. Jackson, *Chem. Phys. Lett.*, **377**, 6 (2003)]. Canonical Monte Carlo (MC-NVT) simulations are performed for the system under conventional three dimensional periodic boundary conditions, and for the system confined between two parallel hard walls (two dimensional periodic boundary conditions). In both cases a chiral nematic phase is found for sufficiently large values of the chiral interaction parameter. Our studies highlight the unphysical nature of the use of standard periodic boundary conditions in simulations of such systems: the pitch of the resulting chiral nematic phase is constrained to be commensurate with the dimension of the simulation box. As a consequence the pitch shows no dependence on the strength of the chiral interaction (temperature), which is in stark contrast with experimental findings. It is gratifying to see that in the case of the confined system the pitch decreases as the strength of the chiral interaction is increased. For values of the chiral interaction which are of the order of thermal energy (kT), a pitch of a few hundred nanometers is observed; this is particularly encouraging as the approach has allowed the simulation of an equilibrium pitch which is many times greater than the dimension of the sample. A connection is made with the temperature dependence of the pitch that is observed for cholesteric liquid crystals, and for biological systems such as solutions of cellulose, viruses and DNA.

---

## **Multi-scale simulation of vitrification melter - from atomistic derivation of melt properties to a prediction of melter lifetime and melt mixing**

Dr Scott L Owens

Nuclear Sciences and Technology Services, BNFL, Risley Warrington, Cheshire, WA3 6AS

Vitrification (encapsulation in a glassy material) is a process that is used commonly world-wide for immobilising radioactive and toxic elements. The process as it is used in the nuclear industry involves mixing the waste components in oxide form with borosilicate glass and melting and rapid quenching to form a glass monolith. The mixing is achieved by fluid mixing due to thermal buoyancy effects and sparge.

In order to achieve a homogeneous product, the melter design must allow optimal flow of the melt, such that there is sufficient mixing of the melt, and that stagnant regions of the melter are not created. However this flow must not be at the cost of excessive thermal gradients in the surrounding plant - as this will result in stressing of the melter vessel and early failure.

The study presented will describe an integrated simulation of the melter that encompasses all of the components required to describe the process. Computational fluid dynamics (CFD) simulations have been used to describe the glass flow patterns inside the melter, and these have been coupled to simulations of thermal stress in the melter to investigate the resultant strains, and identify possible design issues with the melter itself, or it's mode of operation.

As input, the melt properties are calculated from atomistic simulations, particularly simulation of melt viscosity and melt thermal conductivity are novel in applications of this type. These properties are very difficult to measure experimentally and hard to extrapolate for the range of compositions found in a nuclear waste glass melt (which may contain over half of the elements in the periodic table in measurable quantities).

The novel "confined shear" simulations used to estimate viscosity and the non-equilibrium dynamics simulations used to estimate thermal conductivity will be described, and their consequences on the fluid dynamics flow patterns and resultant stresses on the melter will be shown.

---

## **Molecular and mesoscopic simulations of phase equilibria**

Professor Athanassios Z. Panagiotopoulos

Dept. of Chemical Engineering, Princeton, University, Princeton, NJ

This presentation summarizes recent work on modeling phase transitions in ionic, surfactant and colloid/polymer systems in the author's group. The unifying characteristic of these complex fluids is the close interplay between microstructure and macroscopic properties and the existence of strong interactions or multiple relevant length and time scales. Two complementary approaches are used to render the computational problem tractable, namely drastic simplification of the model studied to retain only essential physical characteristics and development of powerful Monte Carlo sampling methodologies to avoid getting trapped in local free energy minima and to cover large regions of parameter space in an efficient way. In the area of ionic systems, we have recently expanded the range of charge and size asymmetries that can be handled and have initiated studies of strongly coupled polyelectrolytes and polyampholytes.

---

## CONTRIBUTED TALKS

### **Atomistic Simulations of Nanocrystals of Oxides and Minerals**

Dino Spagnoli and Steve Parker

Department of Chemistry, University of Bath, Bath BA2 7AY UK

Nanocrystals are attracting much public and industrial interest. Everything needs to be smaller and better than the last device. The aim of this work is to develop a simple and yet robust approach for modelling nanocrystals of minerals and oxides with different shapes. Ultimately we aim to be able to predict the conditions that control the size and morphology of nanocrystals. In earlier work different mineral surfaces were created by cutting them along different Miller Indices and calculating the surface energies. Using these surface energies as guideline different mineral habits can be simulated via a Wulff construction. We use energy minimisation to relax the different mineral habits but one of the primary problems to overcome is generating uncharged nanocrystals with non-defective surfaces. Various strategies were explored to solve this problem. Once minimised the nanocrystals were increased in size and surface energies calculated in order to test convergence. Once the nanocrystals have been formed we have begun to explore the reactivity of these mineral surfaces. This is achieved by comparing the defect and segregation energies of impurities at different locations on the nanocrystal. Finally we describe its possible application in colloid chemistry. We describe how molecular dynamics can be used investigate whether or not different sized nanocrystals will coagulate or repel each other, initially in vacuum but later considering the effects of solvents, particularly water.

---

## Nano and microscale simulation of exotic structures in zeolites

Ben Slater

Royal Institution of London, 21 Albemarle Street, London W1S 4BS, UK

The internal crystal structure of a wide range of zeolites have been studied extensively using simulation methods, to probe transport properties, the role of the nanoporous host in catalysis and a wide range of other properties. The external surfaces of zeolites are now perceived to have a much more important role in numerous applications than previously thought, which has prompted experimental investigation and rather more limited computational study. We have developed simulation approaches to investigate the surface structures which has prompted more detailed and demanding work into growth mechanism of zeolites. We have recently applied a newly developed simulation scheme to propose an atomic model of a screw dislocations in zeolite A [1]. These play an important role in growth but it turns out they have profound and novel physicochemical properties. The simulation scheme is based on static lattice approximation using adapted short range potentials in conjunction with a 1D Wolf summation algorithm, and domain decomposition to handle ~200,000 distinct sites within the dislocation model. Time permitting, results of an investigation of surface mediated dissolution and growth will be discussed (again based on static lattice calculations). In the latter work, a semi-infinite approach is used to model the surface using a 2D Ewald scheme and driver software was developed to generate possible surface structure configurations and to explore the relative stability of the myriad apolar terminating structures possible during growth [2]. The results of this work suggest that monomeric growth units are potentially key to growth, in contrast to the widely held view that zeolites are formed from polyatomic units known as oligomers.

### References

[1] A.M. Walker, J. D. Gale, B.Slater, K. V. Wright, *Nature Materials* (in review), 2004

[2] M. Chiu, B. Slater, J. D. Gale, submitted to *Angew. Chem.*, 2004

---

## Chiral Discrimination by Chemical Force Microscopy: Simulations

Esther Haines, Trevor Rayment, Chris Abell and Jonathan Goodman

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

Molecular dynamics simulations of the interaction between a surface coated with an alkanethiol terminated with either the R or S form of 3,5-Dinitrobenzoyl phenylglycine (Pirkle's resin) and a surface coated with an alkanethiol terminated with the R form of mandelic acid show that the SR interaction is stronger than the RR interaction, in agreement with experiment. Both surfaces relax considerably as they are brought together so that the dinitro groups of the Pirkle resin molecules occupy pockets in the mandelic acid surface. The chiral discrimination arises from the interaction of the surfaces as a whole rather than from binding between individual molecules.

---

## Atomistic modelling of the structure and reactivity of Ionic Nanoparticles - Ceria.

Paul Martin <sup>1</sup>, S.C. Parker <sup>1</sup>, D. Sayle <sup>2</sup>, and G. Watson <sup>3</sup>

1. Department of Chemistry, University of Bath, Bath, BA2 7AY, U.K.
2. Cranfield University, Royal Military College of Science, Shrivenham, Swindon, U.K., SN6 8LA.
3. Department of Chemistry, Trinity College, Dublin, Ireland

Atomistic modelling of the structure and reactivity of Ionic Nanoparticles - Ceria. Atomistic simulation techniques represent a powerful complementary tool for studying mineral surfaces. The aim of this presentation is to describe the recent progress in modelling the structure of cerium oxide and in particular to review our attempts at studying the introduction of single and multiple vacancy sites, which are important for catalytic applications of ceria. The basis of these techniques is to use the Born Model of Solids where simple parameterised analytical equations are employed to describe the interactions between atoms. Once these interatomic forces are specified energy minimisation and molecular dynamics techniques can now be applied to model ionic nanoparticle surfaces. In agreement with previous work our results show the following order of low index surface energies,  $\{111\} < \{110\} < \{100\}$ . Further investigation of the  $\{111\}$  surface has highlighted more stable potential single oxygen vacancy sites, and vacancy pairs. Other oxygen vacancy clustering is also being investigated. In summary, atomistic simulation is a useful tool for relating surface structure and reactivity and provides a good complement to experiment. Keywords: Atomistic simulation, Mineral surfaces simulation, Cerium Oxide

---

## Osmotic pressure calculation for dilute solutions of rod-like polyelectrolytes

Dmytro Antypov and Christian Holm

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, Germany

A number of experimental studies finds the osmotic coefficient of strongly charged rod-like polyelectrolytes to be lower than that predicted by the Poisson-Boltzmann (PB) theory even in the case of univalent counterions in a dilute regime. We performed a systematic analysis of a number of effects neglected in the PB treatment to assess their effect on the resultant osmotic coefficient. These include both electrostatic and excluded volume counterion correlations, the finite rod size effect, the effect of charge distribution on the rod and ion-counterion interactions, rod flexibility and rod-rod correlations in the solution. When all the improvements had been incorporated into the model, the calculated pressure was found to be significantly higher than expected. This suggests that the underlying physics of osmometric experiments goes far beyond the PB formalism.

---

## **Ab-Initio Simulations of Ionic Liquids**

Mario Del Popolo, Jorge Kohanoff and Ruth Lynden Bell

Atomistic Simulation Centre School of Mathematics and Physics, Queen's University Belfast, Belfast, UK

Room Temperature Ionic Liquids (RTIL) have recently come into focus as a green alternative to traditional organic solvents for chemical synthesis. Amongst the various green properties of RTIL, probably the most relevant one is their negligible volatility. In addition, RTIL are being used in other areas such as electrochemistry, where their electrostatic properties such as screening or conductivity are exploited. Ionic Liquids are complex fluids formed by highly asymmetric organic cations paired with bulky inorganic anions. Their structure results from a balance between molecular packing and screening which in turn depends sensibly on the intermolecular interactions. In the past years some research has been performed on the structure of RTIL using polarisable and non-polarisable force fields. Good general agreement with neutron scattering experiments has been observed, although some discrepancies still remains unsolved. In this work we present results based on ab-initio Molecular Dynamics simulations of the model ionic liquid dimethylimidazolium chloride. Excellent agreement with the experimental structure is found. We discuss our results on the light of site-site and three-dimensional distribution functions, electronic structure features and the nature of the interactions between cation hydrogens and anions.

---

## **Langevin Dynamics in non-Hamiltonian Systems : The NPT Ensemble**

Mr David Quigley and Dr Matt Probert

Department of Physics, University of York, Heslington York YO10 5DD

The method of constant pressure Langevin dynamics is reviewed, and extended to the Parrinello-Rahman system. We present a theoretical justification that these methods correctly sample the appropriate ensembles. Example results will be presented, with emphasis on ab-initio applications. Finally, the scheme will be compared to traditional deterministic methods.

---

## Molecular Dynamics Simulations of Fluids composed of Particles with Variable Softness

D.M. Heyes<sup>1</sup>, J.G. Powles<sup>2</sup>, and G. Rickayzen<sup>3</sup>

1. University of Surrey, Division of Chemistry, School of Biomedical and Molecular Sciences, Guildford, Surrey, GU2 7XH, UK
2. The Physics Laboratory, The University, Canterbury, Kent CT2 7NZ, UK
3. A.C. Brañka, Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznań, Poland.

Many complex liquids (e.g., colloids and globular proteins) can be represented approximately on a coarse-grained level, by a central force interaction that is purely repulsive. The properties of these systems depend on the level of steepness of the interparticle potential. There is still much to learn about the effects of particle softness on the dynamical and material properties of such systems - which is the subject of this talk. We have explored the static and dynamical properties of so-called soft-sphere fluids, where the particles interact with a potential of the inverse power form, with exponent,  $n$ . We have investigated a wide range of  $n$  values between (6 and 1152) to cover the transition from very soft to very stiff particles. In the latter case, the hard sphere fluid is shown to be a useful reference fluid. These near-hard sphere systems pose a challenge for Molecular Dynamics simulation as they are characterised by a wide range of key timescales, from the very short, that of the collision itself, to the mean collision time and longer. All of these scales should be taken into account to make full use of the simulation's potential. Because of the short range of the potential, these systems undergo essentially binary collisions at short times, even at high packing fractions. I will summarise some of the key dynamical and mechanical features of these systems, determined recently [1-4].

### References

- [1] J.G. Powles and D.M. Heyes, "Viscoelastic Behaviour of Fluids with Steeply Repulsive Potentials", *Molecular Physics*, **98**, 917-928, (2000)
- [2] D.M. Heyes, J.G. Powles and G. Rickayzen, "The velocity autocorrelation function and self-diffusion coefficient of fluids with steeply repulsive potentials", *Molecular Physics*, **100**, 595-610, (2002)
- [3] G. Rickayzen, J.G. Powles and D.M. Heyes, "Viscoelasticity of fluids with steeply repulsive potentials", *Journal of Chemical Physics*, **118**, 11048-11056, (2003)
- [4] A.C. Brañka and D.M. Heyes, "Time Correlation Functions of Hard Sphere and Soft Sphere Fluids", *Physical Review E*, **69**, 021202 (2004)
-

## **Combination of Molecular Dynamics and SPH Methods in Simulation of Bi-Material Interface**

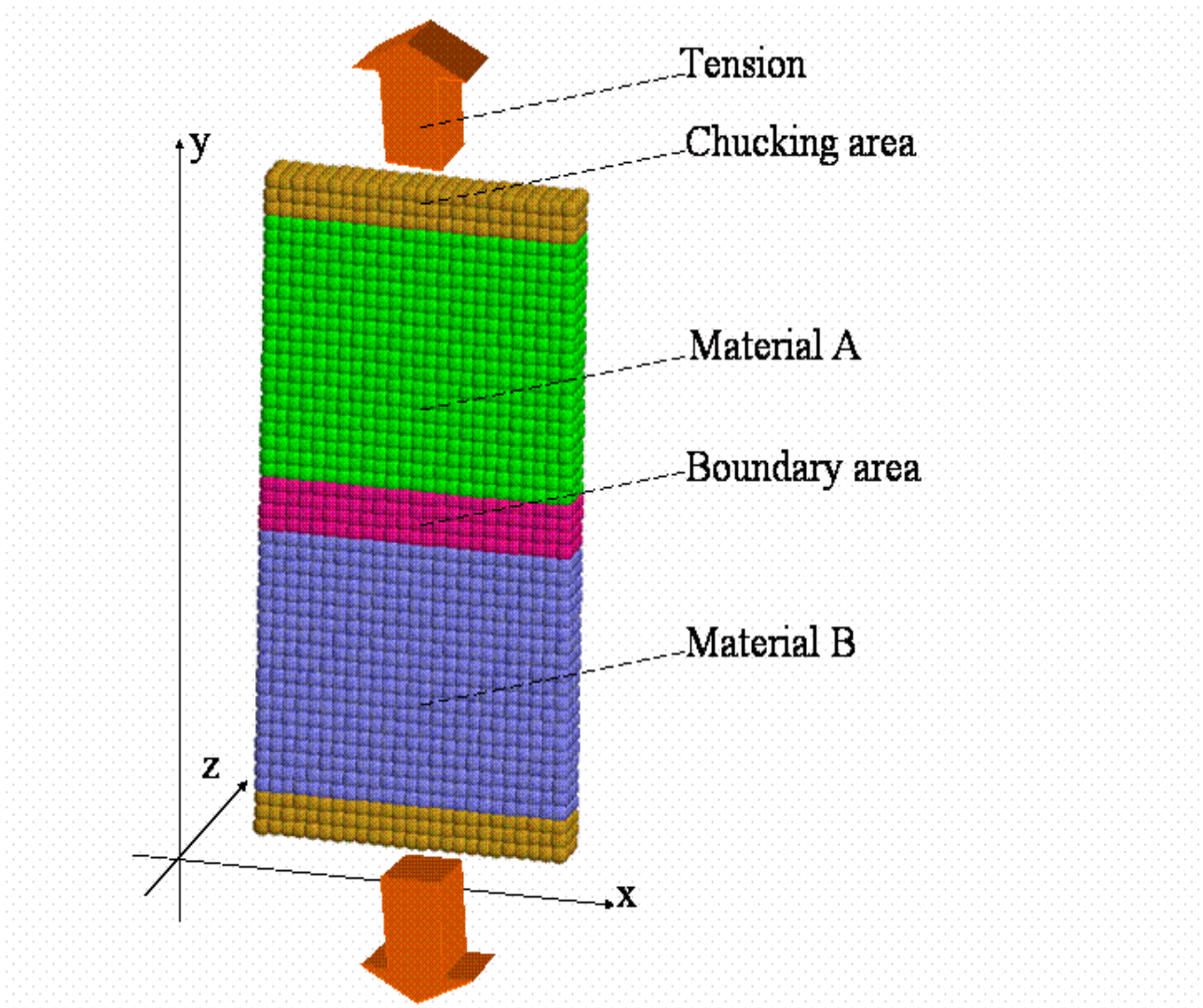
Ken-ichi Saitoh, Noboru Shinke and Yuki Tateoka

Department of Mechanical Engineering, Faculty of Engineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka, 564-8680, Japan

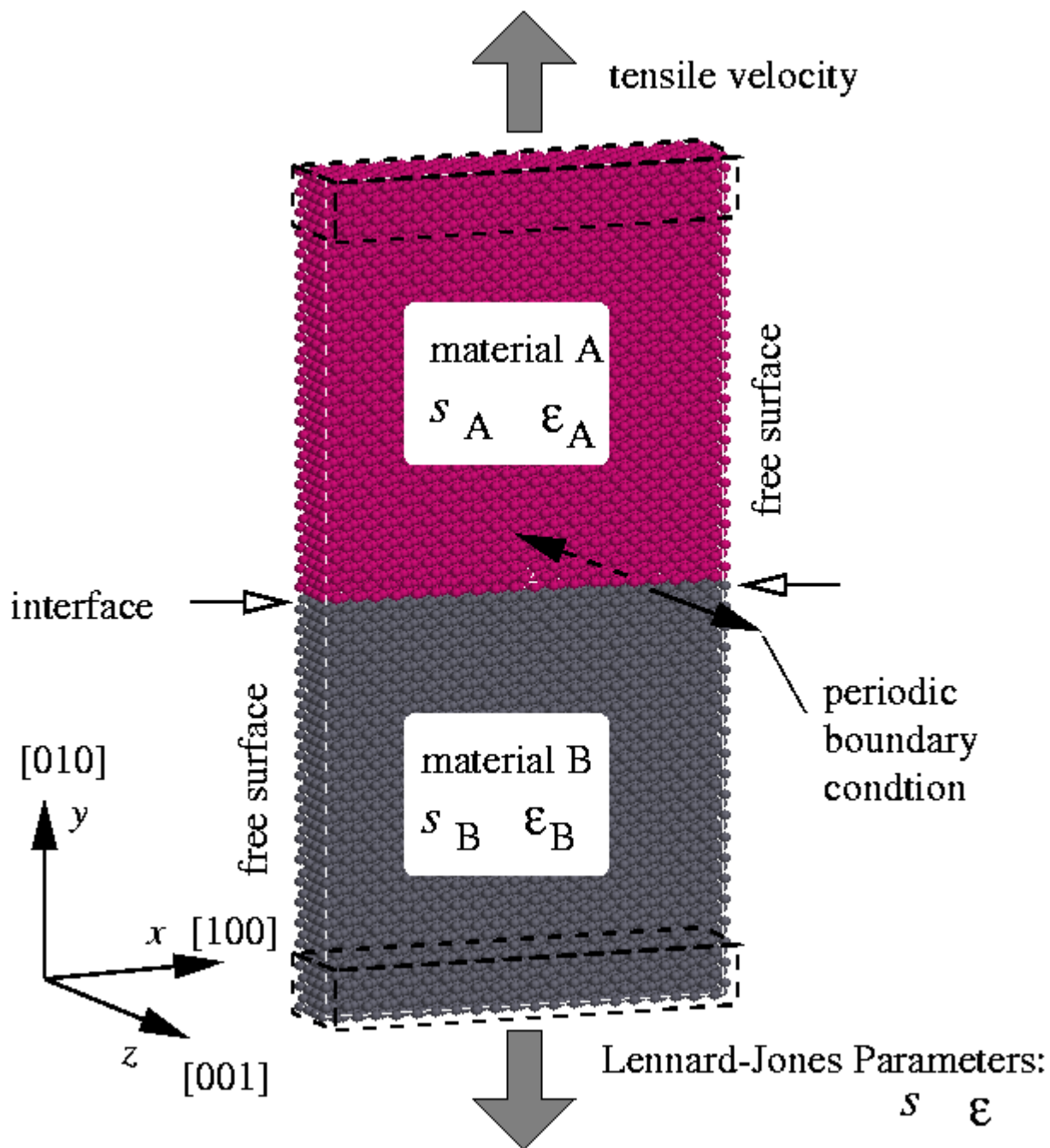
email: [saitou@ipcku.kansai-u.ac.jp](mailto:saitou@ipcku.kansai-u.ac.jp)

Interfaces appearing in composite materials or grain boundaries in polycrystalline metal play an important role in evaluating their strength in solid state. The behavior of atoms in the vicinity of interface revealed by molecular dynamics (MD) shows microscopic mechanism of stress concentration, plasticity, and critical process such as crack propagation or grooving from the junction between interface and outer edge. On the other hand, multi-scale point of view concerning dynamics should be taken into account in the numerical simulation of interface. By hand-shaking between macroscopic view and microscopic one, deep understanding of interface strength will be brought about. In this study, how MD simulation can be concurrently linked with macroscopic particle method such as SPH (smoothed particle hydrodynamics) is discussed. The present model (Fig.1) is a metal-metal (e.g. aluminum-copper) joint surrounded by free surfaces, subjected to tensile loading. For simplification, constitutive relation used in SPH is restricted just to the elastic regime. Development for plasticity in SPH is discussed based on MD results of the similar model configuration in which simple Lennard-Jones potential function is used. In both particle methods, behavior of stress concentration is adequately predicted. The mechanism causing concentration is identical for two methods. Since difficulty in SPH is found in defining position of interface due to its continuous nature, some particle arrangements are compared. A model for hybrid simulation between microscopic and macroscopic methods is conceptually proposed and discussed by comparing SPH and MD results before actual computational implementation is conducted.

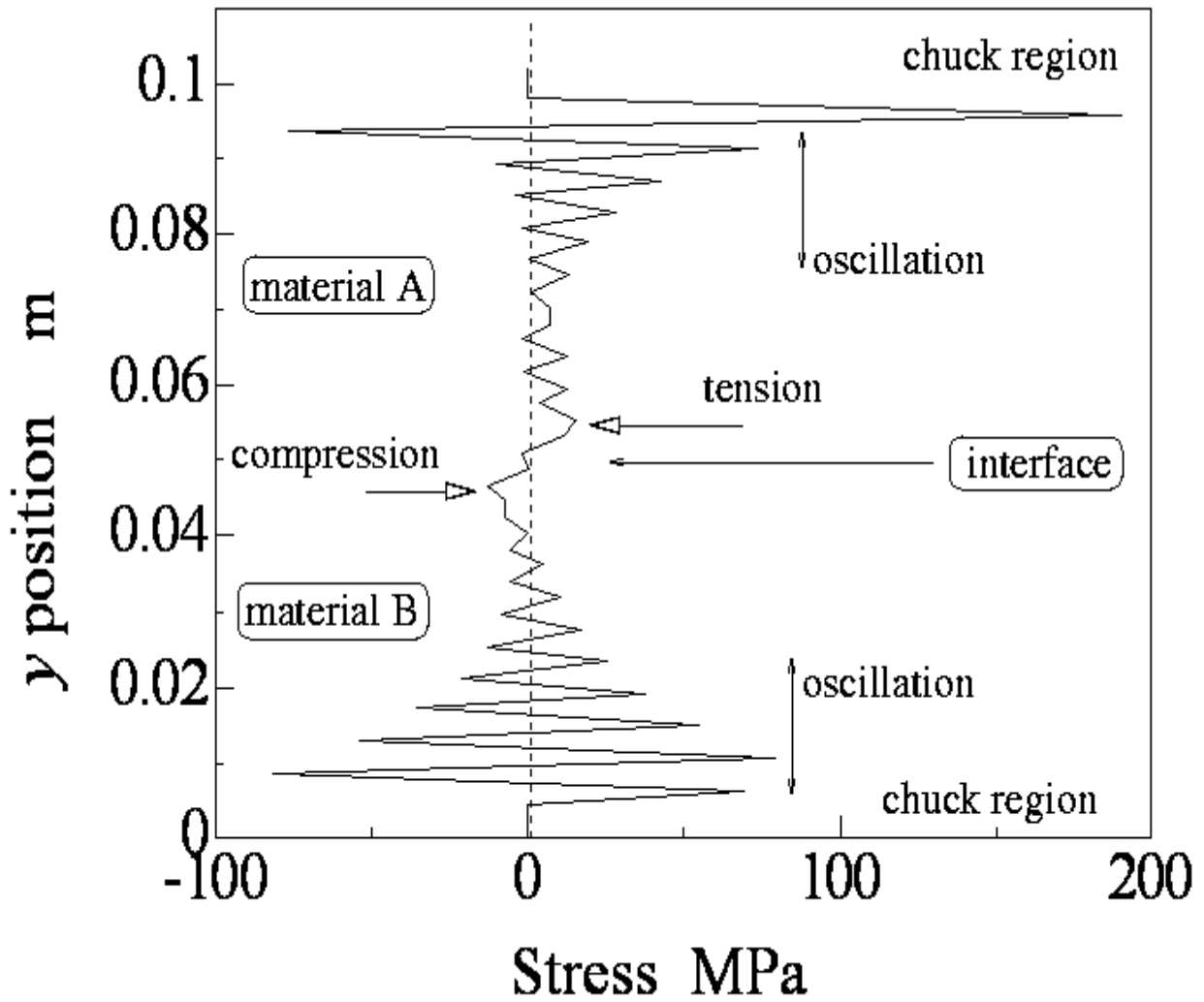
**Fig.1 Bi-material interface models and results**



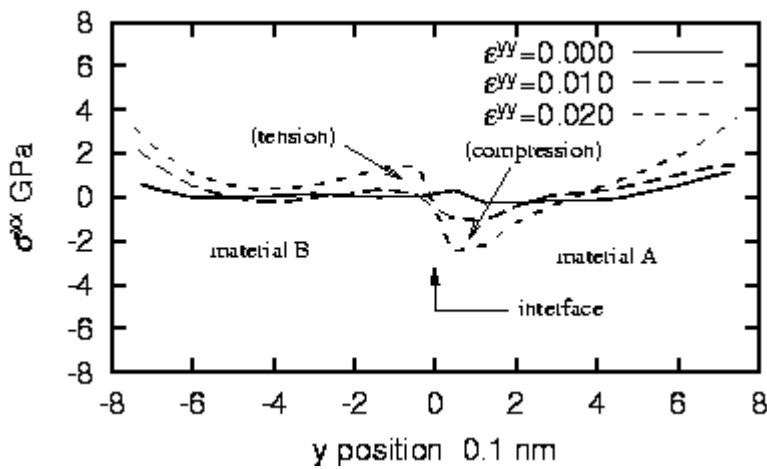
(A) SPH model



(B) MD model



(C) Stress distribution (SPH)



(D) Stress distribution (MD)

## Potential of Mean Force Between Colloidal Particles: Effect of Ion Polarizability

Frederico Tavares<sup>1</sup>, and Mathias Bostrom<sup>2</sup>

1. Escola de Quimica, Universidade Federal do Rio de Janeiro, Ilha do Fundao, Rio de Janeiro, RJ 21949-900, Brazil
2. Department of Physics and Measurement Technology, Linköping University SE-581 83 Linköping, Sweden.

In an aqueous electrolyte solution, the potential of mean force for two macroions is affected not only by the size and charge of each electrolyte ion but also by the ion's polarizability. The mean force between two colloidal particles in a saline solution can be calculated by augmenting electrostatic interactions with salt-specific dispersion (van der Waals) interactions between small ions and between small ions and macroions. Results of Monte Carlo simulations are qualitatively consistent with specific-salt effects observed experimentally by numerous investigators. We have also obtained good agreement of our simulations with those from numerical integration of the non-linear Poisson-Boltzmann equation.

---

## Computations of activated processes in biomolecules

Chandra Verma

Bioinformatics Institute, 30 Biopolis way, #07-01 MATRIX, 138671 Singapore

Current state of the art computer simulations of biomolecules probe timescales that are generally very short compared to those that characterize most interesting biochemical and biological processes. New developments in simulation methods extend the reach of simulation in a trend that reflects the increasing time-resolution of experimental spectroscopic techniques. One methodology that is used to compute reaction paths of conformational changes, is shown to be successfully applied to a range of phenomena that encompasses a large range of timescales and holds immense promise.

---

## Modelling Liquid Crystal Display Cells Using Parametric Hard Gaussian Overlaps

F. Barmes

Centre Européen de Calcul Atomique et Moléculaire, 46, Allée d'Italie, 69007 Lyon, France

We present the development of the Parametric Hard Gaussian Overlap model (PHGO) and its application to liquid crystal display (LCD) cells modelling. The PHGO model is a pairwise steric potential whose contact distance extends that of the generalised Gay-Berne potential towards representing non centro-symmetric particles. It is fitted so as to represent pear-shaped particles whose target shape is designed using Bezier curves; close agreement between the target and modelled shapes can be achieved.

The potential is tested by computing the phase behaviour of pears with elongation  $k=3$  and  $5$  as well as a tentative phase diagram for  $k=3$  and varying pear angles  $\theta$  in the range  $[44^\circ - 17^\circ]$ .

One particle shape ( $k=5$ ,  $\theta=17^\circ$ ) is applied towards modelling two-way switching in a novel bistable LCD cell in which surface bistability and molecular flexoelectricity are believed to be of critical importance.

---

## **Order from disorder: crystal growth and inhibition in hydrocarbon/water mixtures**

P.M. Rodger, C. Moon and R.W. Hawtin

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

In this paper we describe some of the molecular modelling studies we have performed to provide a mechanistic understanding of some of the crystallisation processes that can occur in oil pipelines. The focus will be on studies of clathrate hydrate nucleation and growth, showing an analysis of the nucleation processes, the development of spatial order in the water network, and the extent to which this is tolerant of defects in the initial clusters formed. Some studies with potential inhibitors, and with other crystallisation processes will also be discussed.

---

## **Computer simulation and perturbation theory for the solid-liquid-vapour phase behaviour of chain molecules: rigid and flexible models**

A. Galindo <sup>1</sup>, C. Vega <sup>1</sup>, E. Sanz <sup>1</sup>, F. J. Blas <sup>2</sup>, and E. de Miguel <sup>2</sup>

1. Dept. de Química Física, Fac. Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain
2. Dept. de Física Aplicada, Fac. Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain

Although it is generally assumed that flexibility is not crucial in determining the fundamental phase behavior of many chain-like fluids, observing in more detail it can be seen that the vapor-liquid critical points of chain-like molecules of differing flexibility are different. Similarly, in the solid phase, the stable solid structure of a molecular system is crucially determined by the intramolecular geometric restrictions. In this contribution we compare the global (solid-liquid-gas) phase behavior of fully flexible and rigid chain molecules. We consider chains formed by tangent spherical segments, and examine two systems: one in which the segments are modelled as hard-spheres and attractive interactions are taken into account at the mean field level of van der Waals, and one in which Lennard-Jones chain molecules are considered. The phase behavior of the flexible systems is obtained using the thermodynamic perturbation theory (TPT1) of Wertheim, and its implementation within SAFT for the case of molecules formed by Lennard-Jones segments. A recent extension allows the description of the solid phase in these systems within the same framework. In the case of the rigid systems, both scaling arguments and computer simulations are used to determine the global phase diagram of the systems. We find that the difference in chain flexibility has a dramatic effect in the phase behavior. In both models considered a stabilisation of the solid phase, and an increase in the triple temperature is observed for increased chain stiffness, together with a widening of the transition in terms of density. The triple temperature is also seen to increase with increasing chain stiffness. In terms of the global phase behavior, the results obtained suggest that the fluid-vapour transition will become metastable with respect to the fluid-solid transition as the chain length increases.

---

## **The Role of Random Numbers in Computer Simulation, and Development of a Newly Combined Method Generating Random Numbers**

Abdollah Aghaie

Department of Industrial Engineering K N Toosi University of Technology, POBox 16315-979, Theran-Iran. AAghaie@kntu.ac.ir

Computer simulation models of real world systems have become extremely important as a means of testing theories, predicting future events and understanding different aspects of systems. In many cases, understanding and disclosing the extreme situations of systems is more critical and essential. One of the major applications of simulation is to predict the hazards and extreme situation more efficiently. This ability and strength of simulation depends mostly on use of random numbers so that researchers believe random numbers are in fact the nuts and bolts of simulation. Therefore, the impact of randomness on reliability of simulation results is inevitable. However, the effectiveness of random numbers in simulation modeling depends mostly on the degree of randomness. On the other hand to generate real random numbers for computer simulation is clearly impractical. So the best practical method widely use in all computer simulation models is pseudo random number generators, such as congruential generators. This paper describes the importance of random numbers in computer simulation, and then reviews different random number generators. We developed a newly simple algorithm for generating random numbers based on combing two traditional methods that are not individually enough reliable. The result of different tests on newly developed algorithm was very successful.

---

## Applications of computer modelling in the development of solid state materials for optical devices

Robert A Jackson<sup>1</sup>, Mario E G Valerio<sup>2</sup>, Marcos A Coutos dos Santos<sup>2</sup>, and Jomar B Amaral<sup>2</sup>

1. School of Chemistry and Physics, Keele University, Keele, Staffordshire ST5 5BG, UK
2. Department of Physics, Federal University of Sergipe, 49 100-000 São Cristóvão-SE, Brazil

There is considerable interest in the development of solid state materials for use as photonic devices in a range of technological applications. Among the materials that have been identified as being suitable are the mixed metal fluorides (e.g.  $\text{BaLiF}_3$ ,  $\text{BaY}_2\text{F}_8$ ,  $\text{YLiF}_4$ ,  $\text{LiCaAlF}_6$  and  $\text{LiSrAlF}_6$ ), doped with rare-earth ions. For example, the  $\text{Ce}^{3+}$ -doped forms of both  $\text{LiCaAlF}_6$  and  $\text{LiSrAlF}_6$  can be used as lasers in the UV region [1], while  $\text{Nd}^{3+}$ -doped  $\text{LiCaAlF}_6$  is used in photolithography [2].

The development of such materials is a time-intensive process, involving the screening of a wide range of host materials and dopants for the desired optical behaviour. There is therefore motivation to use computer modelling methods to help with this process, by identifying host-dopant ion combinations having the desired properties.

The use of computer modelling in the study these materials is carried out in two distinct stages. First, there is the question of the site in the material where the dopant ion substitutes, as its environment will affect its optical properties, particularly if charge compensation is involved. This can be determined by calculation of solution energies for the rare-earth ions of interest at all the possible sites in the material; this process has been carried out for  $\text{LiCaAlF}_6$  and  $\text{LiSrAlF}_6$  [3]. From these calculations, the optimal substitution site and form of charge compensation (if needed) can be predicted.

Secondly, prediction of the optical properties of the host-dopant ion combinations is considered. Here, crystal field calculations have been combined with the results of the solution energy calculations. On their own, crystal field calculations can be used to predict the optical properties of the dopant ion, but it has usually been assumed that when the substitution takes place, the dopant ion adopts the same symmetry and environment as the ion it has replaced, and the surrounding host ions are unaffected. This is clearly not the case for rare-earth substitution into mixed metal fluorides; not only may there be differences in ionic radius, but if there is a charge imbalance, the charge compensating ions (or vacancies) will affect the local environment of the ion [4]. The crystal field calculations have therefore been modified to take this into account, making it possible to predict the optical behaviour of the substituted ion in its new environment. Results will be presented for rare-earth dopant ions in  $\text{LiCaAlF}_6$ ,  $\text{LiSrAlF}_6$  and  $\text{BaY}_2\text{F}_8$  and the suitability for use in optical devices will be assessed for a range of host-dopant ion combinations.

### References

- [1] Dubinskii MA, Semashko VV, Naumov AK, Abdulsabirov RY, Korableva SL, *Laser Phys.* **3** 216 (1993)
  - [2] Sarantopolou E, Kollia Z, Cefalas AC, *Microel. Eng.* **53** 105 (2000)
  - [3] Amaral JB, Plant DF, Valerio MEG, Jackson, RA, *J. Phys. Condensed Matter* **15** 2523 (2003)
  - [4] Couto dos Santos MA, Valerio MEG, Jackson RA, de Lima JF, *Chem. Phys. Letters* **369** 90 (2003)
-

## POSTER ABSTRACTS

### **Modelling of Glassy State Relaxations in Polymers: The Rotation of the Methoxy Group in PVME**

J.C. Berthet, Geoff R. Davies

The IRC in Polymer Science and Technology, Department of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, UK

Glassy state relaxations in polymers occur too slowly to be modelled by conventional molecular dynamics. We are therefore investigating alternative ways of obtaining information about such processes in solid, amorphous polymers. Saelee and Davies previously showed that the distribution of energy barriers for the rotation of the CH<sub>3</sub> group in amorphous PVME could be obtained by the quasi-static method. In this method, the dihedral angle of each CH<sub>3</sub> group in an amorphous cell of PVME was forced to a series of different values while all other co-ordinates were minimised. Good agreement was obtained with experimental energy barrier data from quasi-elastic neutron scattering. We have now investigated the application of this method to the rotation of the larger and asymmetric OCH<sub>3</sub> group to predict dielectric relaxation data. We find that the relaxation strength is dominated by those few groups which have two energy minima of similar energy with 4% of the groups contributing more than 90% of the relaxation strength. Prediction of the relaxation times required the effective moment of inertia of the group. This was obtained from an analysis of the librations in a short dynamics run at 50 K. The complete frequency and temperature dependence of the dielectric permittivity could then be predicted. Good agreement with experiment is found.

---

## **Determining the structure of zeolite catalysts through a distributed computing strategy**

Rosemary Coates

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

A knowledge of the precise distribution of atoms within both the framework and pores of microporous solids such as zeolites, is paramount, in both understanding their chemical activity (as catalysts or ion exchange materials) and in understanding their formation (how do interactions between the framework and extra-framework species direct the formation of specific structures?).

However, when attempting to determine such distributions, one of the major hurdles to overcome is the sheer number of configurations that need to be considered; a typical zeolite has 10<sup>5</sup>-10<sup>8</sup> unique distributions of Al and Si in the framework alone. The aim of this study has therefore been to develop a methodology that allows a large number of calculations of zeolite structures to be performed, in an automated fashion utilizing a distributed computing strategy: that is, using unused clock cycles on desktop PCs. We have also developed analysis tools that allow the ready construction of relational databases, so that the vast amount of structural and energetic information from these calculations can be processed and structure-property relationships extracted. Our analysis codes have been designed to allow flexible user control of the precise analysis performed enabling new correlations to be extracted and added to the database and to allow facile comparison with experimental data.

As a test case for our methodology, we have extended our previous studies on Mordenite [1]. Even through the use of constrained Monte Carlo minimization methods, computational cost limited our study to ca 20000 configurations, which took approximately 6 months of CPU on a dedicated workstation. Using distributed computing we have been able to collect over 40000 configurations over a matter of a few weeks. We will present an analysis of the distribution of Al in the framework, correlating to experimental X-ray diffraction and NMR studies. We will also consider the distribution of cations and the correlation between cation site and the location of Al in the framework.

### **References**

[1] Gray, A.; O'Brien, A.; Lewis, D. W. *Stud. Surf. Sci. Catal.* **135**, 16, 11 (2001)

---

## **Preparation and Characterization of Porous matrices by computer Simulations**

Hector Dominguez <sup>1</sup>, Margarita Rivera <sup>2</sup>, and Edgar Nunez <sup>1</sup>

1. Instituto de Investigaciones en Materiales, Universidad Nacional Autonoma de Mexico, UNAM Ciudad universitaria, circuito exterior s/n Mexico D.F. Mexico
2. Instituto de Fisica, Universidad Nacional Autonoma de Mexico, UNAM Mexico, D. F. 01000

Series of Molecular Dynamics simulations to study the porosity on different matrix configurations are studied. The matrices were prepared in two different processes. In the first method we used direct simulations of a fluid at constant density and the matrix was taken from the last configuration of its particles. In the second method we simulated a binary mixture where one of the components served as a template material and the final porous matrix configuration was obtained by removing template particles from the mixture. Matrices were prepared at different densities and at different matrix particle interactions. The results showed that the matrix structure and the matrix porosity were affected by the way the porous matrices were prepared. The volume distribution, the cluster formation and the connectivity between the particles in the pore matrix were also investigated. Finally, we also investigated the diffusion of a fluid inside the matrices. It was observed that this quantity is also affected by the kind of porous matrix employed. The calculations were performed for several fluids at different densities in the different porous matrices. From these studies we observed that the highest porosity and diffusion coefficient were found in matrices prepared with attractive particle interactions and without any template.

---

## **Temperature-accelerated dynamics of alumina**

J.H. Harding <sup>1</sup>, and D.J. Harris <sup>2</sup>

1. Dept. Engineering Materials, Sir Robert Hadfield Building, Mappin St, Sheffield, S1 3JD, UK
2. Dept. Physics & Astronomy, University College London, Gower St LONDON WC1E 6BT, UK

The mechanisms of diffusion in alumina are a long-standing problem, particularly when the alumina contains impurities and the diffusion is therefore extrinsic. We show how new methods of accelerated dynamics, first developed by Voter and co-workers, can help us understand the complex diffusion behaviour in this material. In particular, the simulations show the importance of correlated mechanisms in diffusion processes in oxides of the corundum structure and the importance of oxygen interstitial diffusion in alumina doped by aliovalent metals such as titanium.

---

## **Multi-scale modelling of membrane materials for fuel cell applications**

Dr J. A. Elliott and Dr S. J. Paddison

Department of Materials Science & Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK

A detailed physical understanding of the mechanisms of proton conduction in polymer electrolyte membranes is crucial in designing novel materials that will function efficiently in primary fuel cells involving direct oxidation of hydrogen or hydrocarbons. In particular, the production of membranes that will function at elevated temperatures, above the boiling point of bulk water, whilst still maintaining acceptably high levels of conductivity is extremely desirable. This poster describes an EPSRC-funded project (GR/S80455/01) at Cambridge, which seeks to understand the fundamental mechanisms of such ion transport using quantum mechanical computer simulations of ion transport, embedded within a classical molecular mechanics model of the polymer membrane. The molecular mechanisms of proton transport are complex, but two main possibilities are recognised. The first of those possibilities is that excess protons use water molecules as ‘vehicles’ (convection-like) and the second possibility is structural diffusion or “Grotthuss” mechanisms, in which protons hop through a network of water molecules (conduction-like). We will describe preliminary simulation work using a combination of DL\_POLY and Gaussion03 (the ONIOM method) to model both the membrane morphology and proton transport in the most commonly used types of perfluorinated ionomers (those chemically similar to Nafion®), and try to draw some tentative conclusions as to the most important structural features that influence proton conductivity.

---

## **Modelling of Glassy State Relaxations in Polymers: The Linear Polymer Problem**

Taining Liang and Geoff R. Davies

The IRC in Polymer Science and Technology, Department of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, UK

Glassy state relaxations in polymers occur too slowly to be modelled by conventional molecular dynamics. We are therefore investigating alternative ways of obtaining information about such processes in solid, amorphous polymers. While the quasi-static technique readily deals with the rotation of small side groups (see presentation by Jean-Claude Berthet and G.R. Davies), it is not clear how to deal with simple linear polymers where there is no simple transition co-ordinate. We have attempted to map a representative portion of the potential energy surface in terms of local minima and the transition states connecting them and to use these data to generate the relaxation time spectrum. We have found that the quasi-static technique applied to all backbone torsions is the most effective method of locating transition states in the neighbourhood of a given minimum. Steepest descent minimisation from these transition states then yields new minima from which the transition state search is re-initiated, thus building up the connected grid of minima and transition states. For small systems such as short alkane chains, the relaxation time spectrum can be directly calculated from the grid data by diagonalisation of the inter-site transition rate matrix. For large systems with many minima, such as an amorphous cell of polyethylene, the diagonalisation becomes prohibitive and we therefore adopt a Monte-Carlo method to generate a typical trajectory from which the auto-correlation function is calculated. The relaxation time spectrum is then obtained from the correlation function.

---

## Molecular Modelling of Self-Assembling Amphiphilic Systems

David Michel, Dr. Doug Cleaver and Prof. Chris Care

Materials Research Institute, Sheffield Hallam University, City Campus, Howard Street, Sheffield S1 1WB, UK

In this poster we study the self-assembly of biological structures using computer simulations methods, with a particular emphasis on the liquid crystalline phase of lipid bilayer membranes. The study involves the analysis of self-assembling amphiphilic structures via molecular modelling of the membrane components using Molecular Dynamics simulation techniques. This work uses coarse-grained models to study the relationship between intermolecular interactions and the mesoscopic structures to which they lead. In order to achieve this, a single particle model has been developed based on rod-sphere mixtures of Gay-Berne particles and Lennard-Jones particles [1]. By generalising this model, essentially by giving the rod dipolar symmetry, hydrophobic effects can also be introduced so that membrane-like self-assembling structures result. A further generalisation being considered is the effect of molecular shape on the macroscopic phase behaviour [2]. Results obtained thus far indicate that free self-assembly of micellar and bilayer arrangements can be readily achieved using the generic models employed here, raising the prospect that this approach may well be able to make a link between molecular interactions, molecular shape and self-assembling structures.

### References

[1] D. Antypov and D.J. Cleaver, "The role of attractive interactions in rod-sphere mixtures" *J. Chem. Phys.*, **120**, 10307 (2004).

[2] J. Israelachvili, "Intermolecular & surface forces", Academic Press, 1991.

---

## The Influence of Poly(ethylene oxide) Oligomer End-Groups on their Interface With a Silica Nanoparticle

S. Neyertz<sup>1</sup>, D. Barbier<sup>2</sup>, A.-C. Grillet<sup>1</sup>, and D. Brown<sup>1</sup>

1. LMOPS-UMR CNRS 5041, Université de Savoie Bât IUT, Campus Scientifique, 73376 Le Bourget-du-Lac, FRANCE
2. Lab. de Rhéologie des Matières Plastiques, Fac. des Sciences et Techniques, 23 rue du Dr Paul Michelon, 42023 Saint-Etienne, FRANCE

Fully atomistic molecular dynamics (MD) simulations have been carried out on a series of bulk melt pure PEO oligomers and PEO oligomer-silica systems. The PEO oligomers were terminated either by methyl or hydroxyl end groups. The silica nanoparticle was described by a hybrid model consisting of an ionic core linked to a molecular surface coating of silicon, oxygens and silanol hydrogen atoms. The model allowed for fine-tuning of the surface thickness and the number of OH groups per unit surface area. The PEO oligomers were decorrelated in all systems under study in order to prevent any artefacts related to the preparation procedure. Significant changes were found to occur in the immediate vicinity of the silica interface, due to the highly specific structure and dynamics adopted by the PEO backbone and different end-group atoms. Radial mass density profiles as well as chain alignments, conformations and configurations were clearly affected up to ~15 Å from the silica surface. In particular, hydroxyl end-groups displayed a very high affinity for the surface by positioning themselves perpendicular to the surface and forming dynamic hydrogen-bonding complexes between the hydroxyl oxygens and the silanol hydrogens. Interestingly, the range of influence of the nanoparticle was on the order of ~30 Å for translational and conformational dynamics.

---

### **High-temperature glass transition in model C60.**

Romina Ruberto, M.C.Abramo, C.Caccamo and D. Costa

Dipartimento di Fisica, Università degli Studi di Messina, Contrada Papardo, C.P. 50, 98166 Messina, Italy.

C60 exhibits a glass transition at 90K, associated with the quenching of the orientational disorder of the fullerene cages. We report evidence from molecular dynamics simulation that a central pair potential model of C60 undergoes a glass transition associated with the quenching of positional disorder from the liquid phase, at  $T=1100\text{K}$  for a pressure  $P=3.5\text{ MPa}$ , and at higher temperatures for higher pressure values. Two remarkable features turn out to be associated with such a basic prediction: the "effective" packing fraction of the system quantitatively reproduces that of hard spheres at their own glass transition; a strict analogy emerges between our findings and recent mode coupling theory determinations of structural arrest lines in short-range potential models of protein solutions. We argue on such a basis that the conclusions of the present study hold for a wide class of short-range potentials currently in use to model complex fluids, some of biological interest, this suggesting how to achieve at least qualitative predictions of vitrification in these systems.

---

### **Sensitivity of the Thermal Diffusion Factor of Diatomic-diatomc and Monoatomic-Diatomc Mixtures to the Details of the Intermolecular Potential by DNEMD Simulation**

Saeed Yeganegi and M. Tossi

Dept. Chem., Fac. Basic Sciences, University of Mazandaran, Babulsar, Iran, P.O. Box 47416-1467

The thermal diffusion Factor ( $\alpha_T$ ) was calculated by Non-Equilibrium Molecular Dynamics simulation (NEMD) for binary mixtures of diatomic-diatomc and diatomic-monoatomic fluids and its sensitivity dependence to the anisotropy of intermolecular potential, mass and momentum of inertia ratio of mixture components and L-J parameters was investigated. Result is shown that  $\alpha_T$  increases by increasing of the bond length of diatomic molecule and the anisotropy of intermolecular potential in diatomic-diatomc mixtures. The most change is in range of  $R^*=0.3$  to  $R^*=0.6$ . Increasing reduce bond length more than 0.6 does not effect on the  $\alpha_T$ . Analysis of energy flux shows that intermolecular energy flux increases and kinetic energy flux decrease as well as the anisotropic interactions increase. In diatomic-monoatomic mixture  $\alpha_T$  decreases when the bond length of diatomic component increases. Simulation's results shows that the effect of the mass ratio of diatomic mixtures on the thermal diffusion factor is similar to monoatomic mixtures that had been reported before. Increasing of the moment of inertia ratio decreases the  $\alpha_T$  but its effect is more less than mass ratio. Thermal diffusion factor has very sensitive to L-J parameters in diatomic mixtures. Result shows that the component having the biggest radius and the strongest potential, tends to increase in the hot area.

---