

# Computational techniques and applications for materials modelling

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# INVITED TALKS

## **The first-principles statistical mechanics of materials**

M J Gillan

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Many problems in materials modelling require the calculation of free energies and other thermodynamic properties. Often, the quasi-harmonic approximation is inadequate or irrelevant. At the same time, one may wish to achieve good absolute accuracy for specific real materials, rather than a prediction of trends, so that quantum-based methods are essential. I will describe recent progress in the first-principles calculation of free energies and chemical potentials of liquids and solids, and hence phase boundaries. Current efforts to transfer these techniques to problems of surface chemistry, and strategies for achieving chemical accuracy in this area will be outlined.

## ***Ab initio* approach to hydrodynamic instability via molecular dynamics**

D C Rapaport

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Over the past decades, molecular dynamics simulation has been used in modelling two-dimensional hydrodynamic instabilities by allowing structured flow patterns to emerge spontaneously as a natural response of a system of interacting particles to the imposed driving forces. The approach has recently been extended to three dimensions. One example involves Taylor-Couette flow, in which toroidal vortices form in a fluid confined between rotating cylinders. Quantitative analysis of the vortex structure reveals excellent agreement with theory and experiment, despite the microscopic system size. A second example is Rayleigh-Benard convection, in which a variety of roll structures have been observed; in this case, multi-million particle simulations are essential to achieve sufficiently large systems. Some of the earlier work, as well as the parallel computational techniques employed, will also be discussed.

## Simulating nanoflows

N Quirke

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The way fluids flow into and fill regular nanopores is of wide interest, however there is little experimental data and few validated theoretical models. Nanoscale flow is dominated by surface properties and these can be studied directly using molecular simulation of model systems.

In previous work we have considered equilibrium, steady state and transient flow in nanopores<sup>1,2,5</sup> For example we have carried out molecular dynamics simulations of carbon nanotubes imbibing oil at an oil/vapour interface at 300K<sup>3,4</sup>. We found that the smallest (7,7) nanotubes imbibe extremely rapidly ( $\leq 800$  m/s with the penetration length  $L$  a linear function of time. We derived expressions for the penetration length  $L$  and the velocity of the imbibing oil and related both to the solid-fluid surface tensions and interfacial friction via the Maxwell coefficient. Density profiles (and the molecular structure) of the imbibing fluid in the pores have been analysed as a function of time and we have presented<sup>5</sup> analytical expressions for the density profiles (in  $x$  and  $t$ ) of the imbibing fluid as a function of the minimum decane-pore potential and the pore surface friction. We are therefore able to provide a complete description of imbibition of decane for a wide range of nanopores.

In this lecture we review what is known concerning flow in model nanopores from theory, simulation and experiment, and present new results for dynamical properties of filled and empty nanotubes<sup>6,7</sup>.

[1] V P Sokhan, D Nicholson and N Quirke, J Chem Phys **117**, 8531, (2002)

[2] V P Sokhan and N Quirke, Mol Sim, **30**, 217 (2004)

[3] S Supple and N Quirke, Phys Rev Letts, **90**, 14501, (2003)

[4] S Supple and N Quirke, J Chem Phys **121**, 8571 (2004)

[5] S Supple and N Quirke, J Chem Phys **122**, 104706 (2005)

[6] M Longhurst and N Quirke, Mol Sim **31**, 135 (2005)

[7] M Longhurst and N Quirke, to be published

## Hydrated Zeolites - modelling the effect of pressure and water Content

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Whilst simulations of zeolitic materials have a long and successful history in both reproducing and predicting physical properties, they have focussed, as have experiments, on high-silica materials and their catalytic activity. But, what of natural zeolites and applications in ion exchange? Here, the materials are predominantly low-silica and full of water! Can we model these materials?

Furthermore, can we provide similar insights into their properties: for example their thermal stability and the structural changes that occur on dehydration?

I will describe our recent attempts to model the structure of such materials, focussing on modelling of dehydration and the effect of extreme pressures. I will also describe our efforts at developing Grid-based database methods to allow the sampling of large phase spaces, such as those present in zeolites.

# Normal mode approach for predicting the mechanical properties of solids from first principles: application to compressibility and thermal expansion of zeolites

Scott M Auerbach, Roope Astala and Peter A Monson

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The discovery of new nanostructures with increasingly complex architectures challenges our understanding of the relationship between a material's atomic structure and its mechanical properties. An important example involves the crystalline polymorphs of silica,  $\text{SiO}_2$ . These include dense phases such as quartz and cristobalite, as well as nanoporous (zeolitic) polymorphs such as sodalite and silicalite. The mechanical properties of zeolites are particularly important because channel deformations can radically change a zeolite's capacity for adsorption, diffusion and reaction. These dense and nanoporous phases share common structural features, including Si-O bond lengths ( $\sim 1.6 \text{ \AA}$ ) and O-Si-O angles ( $\sim 109^\circ$ ). These phases differ in Si-O-Si angles ( $140\text{-}180^\circ$ ), densities, symmetries and bulk moduli. Despite progress in understanding the mechanical properties of networks, this variation in bulk modulus among silica phases remains poorly understood.

We present a method for analyzing the mechanical properties of solids, based on normal modes and their coupling to lattice strains.<sup>1</sup> This method was used to study elastic compression and thermal expansion of zeolites, with parameters calculated from density functional theory. We find in general that the bulk modulus can be divided into two contributions: a positive term arising from compression without internal relaxation, and a negative term from coupling between compression and internal vibrational modes. For silica polymorphs, the former term varies little among the phases studied, reflecting the intrinsic rigidity of  $\text{SiO}_4$  tetrahedra. In contrast, the latter term varies strongly from one polymorph to the next, because each polymorph exhibits different symmetry constraints on internal vibrations and their couplings to lattice strains. Typically only a few normal modes contribute to the bulk modulus. To facilitate parameterization of this normal mode model, we constructed a simplified classical spring-tetrahedron model for silica. After fitting to properties of silica sodalite, this model reproduces cell volumes and predicts bulk moduli of  $\alpha$ -cristobalite and silica zeolites CHA, LTA and MFI. We incorporated anharmonic effects into the theory, allowing the calculation of the thermal expansion coefficient. The resulting expression provides a generalization of classical Grüneisen theory, taking into account additional anharmonicities. This method was used to study thermal expansion of fcc aluminum and an aluminosilica sodalite, yielding good agreement with experiment.

[1] R Astala, S M Auerbach and P A Monson, *Phys. Rev. B* **71**, art. no. 014112 (2005)

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# CONTRIBUTED TALKS

## The electronic structure of surfaces and defects in ceria

Michael Nolan<sup>1</sup>, Dean C Sayle<sup>2</sup>, Stephen C Parker<sup>3</sup> and Graeme W Watson<sup>1</sup>

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Cerium dioxide, CeO<sub>2</sub>, is of great interest in automotive catalysis due to the relative ease with which it can be reduced in an exhaust gas environment [1]; loss or gain of oxygen atoms promotes reduction or oxidation of environmentally sensitive molecules. The properties of ceria surfaces, e.g. (111), (110) and (100), the effect of reduction and the interaction with small molecules all need to be better understood. We have studied pure and reduced (111), (110) and (100) surfaces with density functional theory (DFT) and DFT corrected for on-site correlations (DFT+U) [2, 3]. DFT gives a poor description of the electronic structure of reduced surfaces; the gap state observed experimentally between the valence band and the unoccupied Ce 4f states [4] is not reproduced and the electronic hole is incorrectly delocalised over the cerium ions of the surface. Application of the DFT+U approach corrects this: a gap state is found in the density of states as is localisation of charge and spin on the two Ce ions neighbouring the vacancy site, consistent with experiment.

Interaction of pure surfaces with CO leads to reduction of the surface and the formation of a carbonate adsorption structure, which is consistent with experimental observations. Interaction of reduced ceria surfaces with the NO<sub>2</sub> molecule leads to partial reoxidation of the surface and formation of (NO<sub>2</sub>)<sup>-</sup>. The partial reoxidation of the surface is consistent with experimental observations of a reduction in intensity of the Ce 4f gap state UPS peak [5]. Finally, we present initial results from a novel embedded cluster approach to the study of ceria surfaces, the hybrid quantum mechanical / molecular mechanics approach embodied in the ChemShell code [6]. We consider the cluster description of the surface structure using a number of quantum chemical approaches and present initial results on the electronic structure of vacancy defects in the (111) and (110) surfaces.

[1] A Trovarelli, editor, Catalysis by Ceria and Related Materials, Imperial College Press, UK, 2002

[2] M Nolan et al., Surf. Sci, 2005, 576, 217

[3] M Nolan et al., submitted to Surf. Sci.

[4] M A Henderson et al., Surf. Sci., 2003, 526, 1

[5] J A Rodriguez et al., J Chem Phys 2000, 112, 9929

[6] A H de Vries et al. THEOCHEM, 2003, 600, 1

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## Computer modelling of the structure and oxygen mobility at ceria surfaces

P Martin<sup>[1]</sup>, S C Parker<sup>[1]</sup>, D Sayle<sup>[2]</sup> and G Watson<sup>[3]</sup>

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The basis of these atomistic 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 the surfaces.

The aim of this presentation is to describe the recent progress in using atomistic simulation techniques to model the structure and oxygen ion transport at ceria surfaces.

We will review our attempts at studying the introduction of vacancy clusters to ceria surfaces, together with a constrained molecular dynamics simulation study of oxygen atom migration at the low index ceria surfaces, and in bulk.

We have found that our computer simulations predict that, for the stable {111} ceria surface, defect clusters that include sub-surface oxygen vacancies are energetically most stable.

Additionally, using MD coupled with Potential of Mean Force (PMF), we have studied the pathways and actual free energy of migration of oxygen vacancies. We have found for example that oxygen atom migration at the {111} ceria surface occurs via a burrowing mechanism involving the surface oxygen layer and the layer of oxygen atoms just underneath the surface, rather than a hopping mechanism involving just the surface oxygen atoms.

In summary, atomistic simulation represents a useful complementary technique to experiment for both vacancy clustering and oxygen atom migration, which are important for catalytic applications of ceria.

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## Molecular dynamics simulation of self-diffusion in 2/1-mullite and sillimanite

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In this study, we conduct NVT-molecular dynamics simulation of 2/1-mullite and sillimanite supercells at 1,273K and 1,923K using DL\_POLY. The crystal structure of sillimanite is obtained from inorganic crystal structure database (ICSD). The structure of 2/1-mullite is generated based on defect formula where we randomly replace Al at tetrahedral Si sites and remove the oxygen atom at O<sub>c</sub> sites in a sillimanite supercell. The inter-atomic potential models include Buckingham potential, three-body potential and the long-range electrostatic force. The potential parameters are obtained from the literatures and have been verified. We calculate the self-diffusivity of each species, radial distribution functions, van Hove self-correlation function and the trajectory plot of a specific O<sub>c</sub> site to analyze the diffusion process in 2/1-mullite. The issues related to thermic phase transformation from sillimanite to average mullite are also studied. The oxygen self-diffusivity of 2/1-mullite is compared with tracer diffusion experiments and possible diffusion mechanisms of 2/1-mullite are discussed.

H Schneider, K Okada and J Pask, *Mullite and Mullite Ceramics*, John Wiley & Sons, Chichester, p. 6. (1994)

R J Angel and C T Prewitt, *Am. Mineral.*, 71, 1476 (1986)

L Wondraczek *et al.*, *Phys. Chem. Minerals*, 29, 341 (2002)

R A Jackson, J E Huntington and R G J Ball, *J. Mat. Chem.*, 1, 1079 (1991)

R A Jackson and C R A Catlow, *Mol. Sim.*, 1, 207 (1988)

B Winkler, M T Dove and M Leslie, *Am. Mineral.*, 76, 313 (1991)

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# **Simulating bulk and surface processes in ceramics using temperature accelerated dynamics.**

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Simulating diffusion in ceramics presents a major problem for traditional molecular dynamics because the activation barriers are often so high the timescale is unreasonably long, particularly at temperatures of experimental interest. A combination of the hyperdynamics developed by Voter and coworkers [1] together with kinetic Monte Carlo methods can simulate these processes without the necessity of guessing (often wrongly) which are the dominant processes.

We give a number of examples from surface and bulk simulations of traditional ceramics to show that the complex, correlated processes are much more common than has often been thought and can dominate the behaviour of the system. Such processes make strong demands on the adequacy of potentials (particularly when they involve close oxygen-oxygen distances). We illustrate the problems with some recent calculations on MgO [2].

[1] A F Voter, F Montalenti and T C Germann, *Adv Rev Mater Res* 32, 321 (2002)

[2] G Henkelman, B P Uberuaga, D J Harris, J H Harding and N L Allan; *Phys Rev B* (in press)

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## Soft particle liquids

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Molecular simulation is a much broader discipline today than in 1979 when CCP5 started. In those days, there were essentially only two techniques you could use: Molecular Dynamics and Monte Carlo. The focus was therefore firmly on atomic scale detail and interactions. Today there are more techniques available. These can model liquids on a much wider range of length and time scales ('scales of scrutiny'). Mesoscale modelling has been one of the biggest growth areas in recent years, in which the focus of attention is typically on the micron and millisecond scale, and even larger. Dissipative Particle Dynamics (DPD) and Smooth Particle Hydrodynamics (SPH) are two of the most popular techniques used. The constituent particles are extremely soft by atomic standards (i.e., the potential varies only by a few kT over a substantial fraction of the nominal particle diameter). A generic feature of liquids, powders and solids is that the more coarse-grained the representation, the softer becomes the effective interaction between the relevant interacting 'units'. Also truly 'mesoscale' particles, such as colloids and polymers have an inherently greater variability in softness than is the case for liquids composed of small molecules. The softness of such particles can be adjusted during synthesis or formulation, and this can have a significant effect on the flow behaviour and material properties.

Attention has therefore naturally turned to understanding the effects of particle softness (or stiffness) on the physical properties of fluid or fluidised systems. We need to know how better to specify the form of the soft potential for a given application — as an essential component of any modelling tool or fine-tuning of a real application. This is an area we have been investigating in recent years [1-7]. In an attempt to understand some of the general principles governing the effects of particle stiffness/softness on static and dynamical properties, we have carried out a combined Molecular Dynamics and Statistical Mechanics study of the static and dynamical properties of a model soft particle fluid in which the particles interact through the soft-sphere potential  $\varphi(r)=\epsilon(\sigma/r)^n$ , where the exponent,  $n$  is a variable. We have investigated a range of model liquids with  $n$  ranging from 6 to 1152 to cover the transition from very soft (i.e. polymer-like) to very stiff (i.e., large colloid) particles. The talk will summarise these results and cover the various types of soft particle found experimentally. Current challenges will be highlighted.

[1] D M Heyes and H Sigurgeirsson, *The Newtonian viscosity of concentrated stabilized dispersions: Comparisons with the hard sphere fluid.*, Journal of Rheology, 48, 223-248, (2004)

[2] J G Powles and D M Heyes, *Viscoelastic Behaviour of Fluids with Steeply Repulsive Potentials*, Molecular Physics, 98, 917-928, (2000)

[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 Brańka and D M Heyes, *Time Correlation Functions of Hard Sphere and Soft Sphere Fluids*, Physical Review E, 69, 021202 (2004)

[5] A C Brańka and D M Heyes, *Elastic Properties of Inverse Power Fluids*, Computational Methods in Science and Technology, 10, 127-136 (2004).

[6] D M Heyes and A C Brańka, *The influence of Potential Softness on Transport Coefficients of Simple Fluids*, Journal of Chemical Physics (in press)

[7] G Rickayzen and D M Heyes, *The memory function for a fluid of molecules interacting through steeply repulsive potentials*, Physical Review E (in press).

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## **Computer simulations of free self-assembling amphiphilic systems**

David Michel, Doug Cleaver  
MERI Sheffield Hallam University

We describe the development of a coarse-grained molecular model for amphiphilic behaviour, and examine its ability to exhibit free self-assembly of complex structures at moderate computational cost. The model is based on mixtures of (rod-like) Gay-Berne and (spherical) Lennard-Jones particles, the rods being taken to be single-site model amphiphilic molecules immersed in a solvent of spheres.

The hydrophobic effect, believed to be the main driver of amphiphilic self-assembly, is incorporated by giving the rod-sphere interaction a dipolar symmetry. Results obtained indicate that free self-assembly of micellar (A), lamellar (B) and inverse micelle (C) arrangements can be readily achieved.

Consequently, the role played by key molecular interaction parameters in self-assembly processes can be studied methodically; examining the effects of modifying characteristics such as the hydrophobic strength and the hydrophilic-to-lipophilic balance, provides insight into the relation between molecular properties and the self-assembling mesoscopic structures to which they lead.

Following on from these preliminary simulations, amphiphilic mixtures are studied in the micellar and bilayer regions so as to examine the dependence of these phases on mixture composition. Finally, the transport properties of the model amphiphiles are examined.

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## Partial thermostating of coarse-grained molecular dynamics

Ben Leimkuhler

Centre for Mathematical Modelling, University of Leicester, UK

Thermalisation issues are studied for a multiscale molecular model based on successive coarse-graining. It is found that high frequency thermal energy can be trapped for long periods in regions with the smallest length scale. As these are precisely the regions where accurate dynamical modelling is generally required, a hybrid strategy is proposed to avoid introduction of artificial thermostating effects, based on the combination of two novel computational algorithms: Partial Thermostating Molecular Dynamics (PTMD) [Z. Jia and B. Leimkuhler, *Multi. Mod. Simul.*, 2005] is used to thermostat the coarse-grained region while preserving the dynamics of the atomistic region, and Recursive Multiple Thermostats (RMT) [C. Sweet and B. Leimkuhler, *SIAM J. Appl. Dyn. Sys.*, 2005] provides an effective multiscale dynamic-stochastic heat bath. The combined method is applied to a 1D quasicontinuum model, in which a molecular dynamics simulation is embedded within a dynamic finite element model.

This talk represents joint work with Alan Cocks and Simon Gill of the University of Leicester and Zhidong Jia of the Chinese Academy of Sciences.

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# Robust and accurate method for free energy calculation of charged molecular systems

Jamshed Anwar<sup>1</sup> and David M Heyes<sup>2</sup>

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The thermodynamic quantity, *free energy*, is key to characterising many equilibrium properties of chemical systems, including molecular binding and partitioning, and also has a strong influence on the chemical kinetics of processes. Whilst the free energy can now be routinely calculated by molecular simulation, such calculations are generally restricted to relatively simple systems. An important technical challenge that limits wider application is the problem associated with the creation and/or annihilation of atoms on going from one molecular state to another. The significant development of the ‘soft-core’ potential<sup>1-2</sup> has essentially solved this problem for van der Waals interactions, but its current implementation for electrostatic interactions is restricted to the reaction field method, which is not an exact solution of the electrostatics of a periodic system. We resolve this issue by extending the soft-core approach to include the formally exact Ewald summation method. Inter alia the proposed method<sup>3</sup> enables entire molecules to be mutated from a non-interacting (ideal) state in an efficient and robust way, thus providing a means by which accurate absolute free energies of structurally complex molecules (e.g. drugs) can be determined.

1. Beutler, T C, Mark, A E, van Schaik, R C, Gerber, P R & van Gunsteren, W F Avoiding singularities and numerical instabilities in free-energy calculations based on molecular simulations *Chem. Phys. Lett.* **222**, 529 (1994).
  2. Zacharias, M, Straatsma, T P & McCammon, J A Separation-shifted scaling, a scaling method for Lennard-Jones interactions in thermodynamic integration. *J. Chem. Phys.* **100**, 9025-9031 (1994).
  3. Anwar, J & Heyes, D M Robust and accurate method for free energy calculation of charged molecular systems, *J. Chem. Phys.* **122**, 224117 (2005).
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## A self-referential Monte-Carlo method for calculating the free energy of crystalline solids

M B Sweatman

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Free energy calculations for crystalline solids are important in studies of phase behaviour and systems in confinement, yet they are not yet entirely satisfactory. All Monte Carlo methods for the free energy of classical crystalline solids calculate the free energy difference between a state whose free energy can be determined relatively easily and the state of interest. They employ either a simple model crystal, such as the Einstein crystal, or a fluid as reference states. Here I describe a new, alternative 'self-referential' approach. The self-referential method employs a radically different reference state; it is the crystalline solid of interest but with a different number of unit cells. So it calculates the free-energy difference between two crystals, differing only in their size. Application of this approach to some simple systems, namely the face centred cubic hard sphere and Lennard-Jones crystals, is described. I expect this approach to be robust and straightforward for a wide range of crystals, and, although it is currently very inefficient, I will highlight schemes that could potentially result in a very efficient method indeed.

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## Determining crystal-melt interfacial free energy via computer simulation

Ruslan L Davidchack

Department of Mathematics, University of Leicester

Over the past few years, there has been much progress in the development of methods for computing the free energy of crystal-melt interfaces in molecular simulations. Currently, two qualitatively different approaches are being employed. The *thermodynamic integration* approach<sup>1,2,3</sup> stems from the definition of the interfacial free energy as the reversible work required to form a unit area of the interface. Within this approach, separate bulk crystal and melt systems prepared at the crystal-melt coexistence conditions are transformed along a continuous path that brings them in contact with each other creating an interface. Thermodynamic integration is performed along the path in order to determine the reversible work involved in the transformation process. The *capillary fluctuation method*<sup>4,5</sup> measures the magnitude of capillary fluctuations in the profile of a thin strip of the interface. For a macroscopically rough interface, the capillary fluctuation theory provides a simple relationship between the magnitudes of the capillary fluctuation modes and the interfacial stiffness, which can be used to determine the interfacial free energy and its anisotropy. I will describe both approaches and review the results obtained to date.

1. R L Davidchack and B B Laird, *Phys. Rev. Lett.* **85**, 4751 (2000)
  2. R L Davidchack and B B Laird, *J. Chem. Phys.* **118**, 7651 (2003)
  3. R L Davidchack and B B Laird, *Phys. Rev. Lett.* **94**, 086102 (2005)
  4. J J Hoyt, M Asta, and A Karma, *Phys. Rev. Lett.* **86**, 5530 (2001)
  5. J Morris, *Phys. Rev. B* **66**, 144104 (2002)
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## A computational study on the role of fluoride in the synthesis of SSZ-23 zeolite

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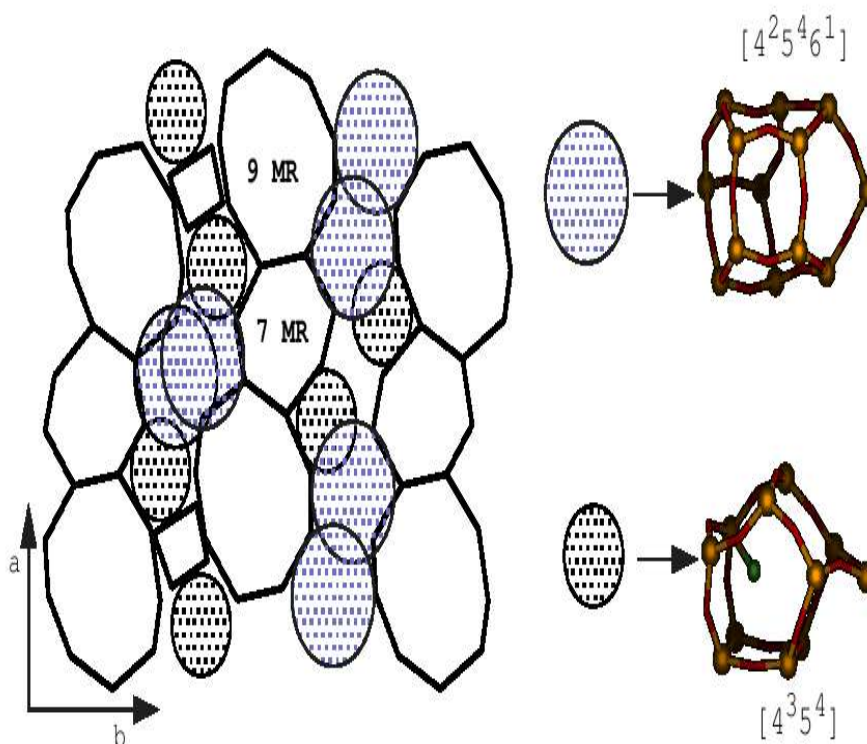
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Zeolites are microporous crystalline aluminosilicates formed by corner sharing TO<sub>4</sub> tetrahedra (T=Si,Al). The shape of the micropores are not only straight channels but also sinusoidal and circular, and they may cross each other forming cages, all together giving a large variety of molecular sieves whose sizes, in the range 3-20 Å, allow physico-chemical phenomena to take place under interesting constraints and special conditions of catalytic interest.

The fluoride route has been used for the synthesis of defect-free pure silica zeolites with an enormous success due to the role played by the F<sup>-</sup> anion in stabilising certain small cages that form structural units of the zeolite framework. Two of such small cages, found in SSZ-23 [1] are shown in the figure below.

Some key questions whose answers will provide a better understanding of the synthesis are: why F<sup>-</sup> in SSZ-23 are only found in the [425461] cages and not in the [4354]?, why F<sup>-</sup> form covalent bonds with only three specific Si atoms of the cage?, does the organic template influence any of the two previous questions?.

A recently parameterised force field for zeotypes and F<sup>-</sup> anions [2] is used to calculate the stability of the framework in different configurations of F<sup>-</sup> and organic cations. This will be used to explain the F<sup>-</sup> stable location and role.



Scheme of SSZ-23. Rings are labelled as number of Si membered rings (MR)

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## **The DFT study of propane and oxygen individual and co-adsorption by alkaline-earth zeolites**

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Alkaline earth exchanged Y zeolites promote selective oxidation of alkenes and alkanes at room temperature [1]. Originally the mechanism of this process was suggested for photo-oxidation of branched alkenes and it involved charge transfer complex  $[(C_nH_{2n})^+ \cdot O_2^-]$ . The role of the zeolitic matrix was reduced to providing the electrostatic field which stabilizes the charge transfer. Later this mechanism was also accepted for the thermal and photo-oxidation of light alkanes. Reaction activity of gas phase propane oxidation was found to increase in order  $BaY < SrY < CaY$  attributed to the increasing electrostatic field [2]. However, it was recently shown that the activity of MgY is much lower compared to SrY and CaY, against the expectations.

The theoretical studies help clarify the mechanism of this reaction and the role of the cations in it. To our knowledge no theoretical study of the interaction of light alkanes or  $O_2$  molecules with alkaline-earth cations stabilized in the zeolite has been performed before.

In the present work propane and oxygen interaction with exchanged  $Mg^{2+}$  and  $Ca^{2+}$  cations was studied using the cluster DFT modelling. It was shown, that due to different size and Lewis acidity of these cations the interaction of the hydrocarbon molecule with them strongly differs in nature. Where in case of the  $Ca^{2+}$  cation the ion-dipole interaction is a predominating, in case of  $Mg^{2+}$  rather strong charge donation from propane to the cation was detected. Also it was shown that interaction of the  $O_2$  molecule with the electrostatic field of the cation strongly increases the electron affinity of the adsorbed molecule.

Thus, the obtained results clearly shows that the unexpectedly lower activity of MgY zeolite compared to CaY could be explained with differences in interaction of the adsorbed molecules with the cations. Therefore, the role of the exchanged cations can not be reduced only to providing the electrostatic field stabilizing the charge-transfer complex.

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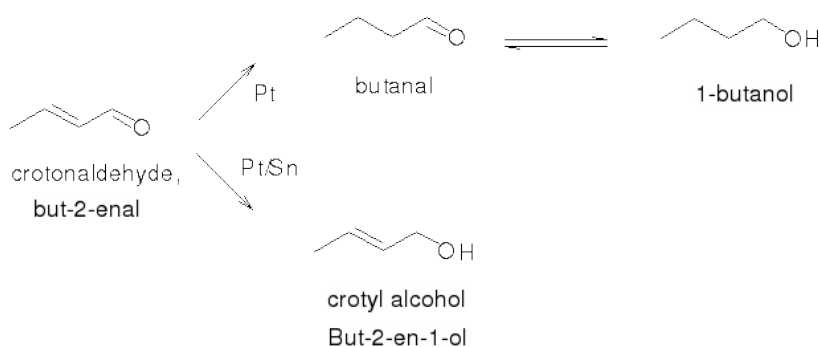
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# Understanding catalytic selectivity from first principles: C=O and C=C moieties on Pt and PtSn {111} surfaces

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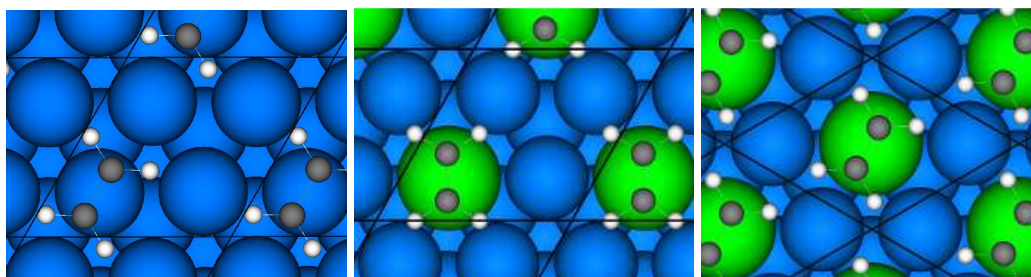
Density functional theory is routinely applied to surface adsorption. In this work adsorption calculations are used as a starting point in describing observed catalytic selectivity. Controlling the product proportions is a major goal in modern catalytic chemistry. An important example is the selective hydrogenation of  $\alpha$ - $\beta$  unsaturated aldehydes over platinum catalysts. Hydrogenation of the carbonyl double bond results in unsaturated alcohols, which are valuable intermediates in pharmaceutical, flavouring and fragrance industries. Over the pure metal the hydrogenation is hard to control and the product yield is made up of the saturated alcohol and saturated aldehyde. When the catalyst is modified with other metals, such as tin, the yield of the unsaturated alcohol, the more desirable product is improved (figure 1).



**Figure 1:** reaction scheme for hydrogenation of but-2-enal with Pt and Pt/Sn catalysts

It appears that the tin modifies the relative activation of the two functional groups so allowing the preferential hydrogenation of the carbonyl group. To completely understand the process a detailed understanding of the interactions between each of the functional groups of the unsaturated aldehyde and the surface is required.

We present DFT calculations for the adsorption of model carbonyl (methanal) and alkene (ethene) molecules on pure Pt and two ordered Pt/Sn {111} surfaces namely a  $2\times 2$  and  $\sqrt{3}\times\sqrt{3}R\ 30^\circ$  (figure 2). The structural and electronic properties are compared to those for adsorption of methanal and ethene on the Pt {111} surface to investigate the effect of tin doping.



**Figure 2:** ( $2\times 2$ ) Pt {111} and the two possible ordered surface alloys of Sn on Pt{111}:  $2\times 2$  and  $\sqrt{3}\times\sqrt{3}R\ 30^\circ$

Combining this data with related work, where we studied the hydrogen diffusion profiles on the pure and doped surfaces helps us to build up an explanation for the observed selectivity.

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## **Multi-scale modelling of minimally hydrated short-side chain perfluorosulphonic acid membranes for fuel cell applications**

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Polymer electrolyte membranes based on perfluorosulphonic acid materials, such as Nafion (DuPont), are a very important component of redox fuel cells for power generation and energy storage applications. Although their properties are now reasonably well characterised, the morphology of these membranes at the molecular and mesoscopic levels is still poorly understood, and it is highly desirable to develop new membranes that are easier and cheaper to synthesise chemically, and that can work at higher operating temperatures. In order to do this, the connection between membrane morphology and ion transport (in particular protons) must be fully understood. In this talk, I will present results from a combined first principles and classical force field based molecular modelling investigation of the possible role of the side chain in effecting proton transfer in the short-side-chain perfluorosulphonic acid fuel cell membrane [with chemical formula:  $\text{CF}_3\text{CF}(\text{---O}(\text{CF}_2)_2\text{SO}_3\text{H})\text{---}(\text{CF}_2)_n\text{---CF}(\text{---O}(\text{CF}_2)_2\text{SO}_3\text{H})\text{CF}_3$ , where  $n = 5, 7$  and  $9$ ] under minimal hydration conditions. Specifically, we have found that fully optimized structures at the B3LYP/6-311G\*\* level revealed that the number of water molecules needed to connect the sulphonic acid groups scaled as a function of the number of fluoromethylene groups in the backbone, with one, two, and three water molecules required to connect the sulfonic acid groups in fragments with  $n = 5, 7$  and  $9$ , respectively. With the addition of explicit water molecules to each of the oligomeric fragments, we found that the minimum number of water molecules required to effect proton transfer also increases as the number of separating tetrafluoroethylene units in the backbone is increased. Furthermore, calculation of water binding energies on CP-corrected potential energy surfaces showed that the water molecules bound more strongly after proton dissociation had occurred from the terminal sulfonic acid groups independent of the degree of separation of the side chains. Finally, we will show how the backbone conformations found in bulk membrane systems computed using classical molecular dynamics simulations using the PCFF force field affect the results obtained from isolated oligomeric fragments.

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## Derivation of an ‘accurate’ forcefield for ionic liquid simulation

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Ionic liquids (ILs) are currently receiving a great deal of attention owing to their prospective use as replacements for common solvents used in industrial organic synthesis. However, like many molecular liquids they are not easily investigated by experimental techniques. Since the pioneering work of Lynden-Bell, [1] simulation of ILs has become a rapidly expanding area allowing previously unobserved structural and electronic properties to be quantified. The simplest imidazolium-based ionic liquid, dimethylimidazolium chloride (dmimcl), has been the focus of several molecular dynamics (MD) studies. [1–4] Since parameters specific to ILs do not exist in the current stock of available forcefields, each proposes a different parameterisation of the system. Nevertheless, observed densities and ion-ion radial distribution functions (RDFs) are broadly similar, despite variation in the descriptions of the dmimcl ions.

In this work, three semi-rigid forcefields based on OPLS-AA were proposed for dmimcl, employing different schemes for the atomic point charges. Again, ion-ion RDFs and densities agree with the results in [1–4]. Recently, however, the first *ab-initio* MD simulation of an IL was published, [5] focusing on dmimcl for which the structure has also been determined experimentally through neutron diffraction. [6] Good agreement between [5] and [6] was found on the basis of ion-ion RDFs, 3D liquid structures, electronic structure features and the nature of the H...Cl<sup>-</sup> interaction. Importantly, the *ab initio* study allows scrutiny of individual atom-atom RDFs, which show some disparity with those of the classical studies. So, while classical forcefields can reproduce the general structural features of both experiment and *ab initio* simulation, for the fine structure there is the potential for some improvement.

The availability of an *ab initio* simulation of dmimcl opens up the possibility to perform a force-matching procedure [7] in order to refine a classical forcefield. Previously such methods have been applied to the generation of atomic potentials [7,8] and small molecular systems. [9,10] However, the execution of force-matching on targets of greater complexity such as dmimcl has been limited both by the complexity of the parameter space of larger systems and the lack of suitable *ab initio* data, for which the computational demands are somewhat prohibitive. Results from initial simulations using a new forcefield derived from a simulated annealing force-matching technique are presented and compared with the other available data.

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## **Interactions of polarisable media in water solutions: a molecular dynamics study**

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We have undertaken classical molecular dynamics studies of the interactions between ions and/or polarisable media in solution in support of a project concerning forces between hydrated DNA molecules, specifically with regard to DNA recognition and aggregation. Present analytic theories of DNA-DNA interactions [A. A. Kornyshev and S. Leikin, *J. Chem. Phys.* 107, 3656 (1997)] suggest that electrostatic forces between molecules, which dominate the interaction, not only result from the distribution of the charge groups along the DNA surfaces but also consist of image charge effects arising from the finite polarisability of the DNA cores. And so to supplement and test these theories, we have developed a model to incorporate generic polarisable media into classical molecular dynamics simulations. As a precursor to the more complicated analysis of DNA systems, we have carried out a fundamental study of interactions, in an explicit water solution, between single ions and macroscopic polarisable media as well as between the polarisable media themselves. Results will be presented which cannot be predicted using continuum theories for water, e.g. Poisson-Boltzmann, for solute-solute interactions at close separations where solvation and geometrical effects of explicit water must be considered.

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## **Direct molecular simulations of hydrate nucleation**

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Methane hydrate is a crystalline mixture of methane in water which is frequently found in both industrial and geological settings. There are many technological and environmental applications for methane hydrate that require the ability to control the crystallisation process, either to promote or inhibit it. The nucleation process involves the formation of a tetrahedral hydrogen bonding network (as occurs with ice), but is complicated by mass transport limitations due to the poor mixing of the methane and the water.

In this paper we show how we have used classical molecular dynamics simulations to provide a direct simulation of the nucleation process for methane hydrate. These simulations have enabled us to characterise the molecular processes involved in nucleation and have thereby provided new insight into the validity of existing theories for nucleation, such as the labile cluster and local order models. These simulations also provide the foundation for a fundamental investigation the activity of low dosage inhibitors, as discussed in a companion paper.

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## **Molecular dynamics simulation of homogeneous nucleation from the vapour phase**

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Homogeneous nucleation of argon from supersaturated vapour phases is investigated by molecular dynamics simulation. In such simulations the heat of condensation has to be removed from the system. There are different ways of how to couple the simulation system with a thermostat. A method mimicking the experimental situation is an inert gas thermostat. A gas is added to the nucleating system which does not condense under given conditions and which removes the heat from the nucleating system by collisions. Such method has been applied, for example, for metal vapour nucleation and particle growth [1,2].

Here, simulations of argon nucleation are performed without employing a thermostat during the nucleation. The initial state of the system is obtained by NVE simulations of saturated vapour phases of argon. After equilibration kinetic energy is removed from the system by rescaling the atomic velocities in very few time steps in order to reach a target temperature. After this energy removal the simulation is continued in the NVE ensemble. During this simulation the system nucleates and forms clusters which grow by surface growth and coalescence. During nucleation and growth the temperature increases until it reaches a level below the initial state. The nucleation rates are calculated from the cluster size statistics and correlated by simple functions. From these correlations properties of the critical clusters are estimated using the nucleation theorems.

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## **Towards modelling the biological - mineral interface**

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Over the past thirty years it has become possible to study ever more complex minerals, their surfaces, morphologies, dislocations and interfaces using computer simulation. More recently it has also been able to study directly the interaction of minerals with an aqueous phase.

Similarly in the biological and biochemical community it has become possible to study more complex systems and increasingly calculations, once only possible in the gas phase are being considered in the presence of water. However like work has been undertaken in combining the two. Since many aspects in geo-chemistry, medical chemistry and beyond are governed by the interaction of biological systems with minerals we, with others, as part of a consortium have begun to consider such systems.

In this talk we will discuss some of the key challenges which need to be overcome and illustrate with some preliminary results how we have begun to meet tackle some of these issues.

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# POSTER ABSTRACTS

## **Anchoring of liquid crystals on self-assembled monolayers**

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This study relates to the anchoring of liquid crystals (LCs) on substrates coated with self-assembled monolayers. We are investigating, by Monte-Carlo simulation, the effect of novel substrate chemical patterning on liquid crystals anchoring. For this, the well-established Gay-Berne model is used to simulate the liquid crystal molecules and exploring their behaviour when confined between various patterned substrates.

The aim is to relate these observations to the behaviour of real LCs on patterned SAM systems being studied by our collaborator in Leeds.

Some information on the substrate-molecules models used and a range of types of patterning to be looked at (e.g. Sharp boundaries, gradual boundaries controlled by explicit surface parameters) are exposed.

Some initial results on some of these are discussed.

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## **Development of a lattice model for mesoscopic simulations of polymer-nanoparticle assemblies**

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Lattice representation of a polymer is an efficient and relatively simple way of exploring conformational space of a polymeric molecule. It also allows us to coarse-grain molecular interactions into the model and study both static and dynamic properties of polymers by means of the dynamic Monte Carlo technique. In this poster we demonstrate advantages of using an FCC lattice model over an ordinary cubic lattice to study polymer solutions. The effect of the solvent and changes of polymer properties upon mixing with different model objects are studied. An entropy driven contraction and reduction of diffusivity of a polymer chain are illustrated by several examples. This work aims to create a basis for future mesoscale simulations within an inter-university consortium on bio-inorganic interface modelling. One of the final targets is the mapping and reverse mapping of real-life systems onto a computationally efficient lattice model.

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# Molecular simulation of gas adsorption and transport in nanoporous carbons

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Nanoporous carbons are widely used in industry for separation, purification and catalytic reaction processes, and also in new applications such as capacitors, gas storage and biomedical engineering applications. Understanding the porous structure and its correlation to the performance of the porous materials is a scientifically and technologically important problem as this will allow us to better design these materials and increase the range of their applications. Despite the fact that considerable experimental studies, theoretical work and computer simulations have been devoted to this class of problem, our understanding remains incomplete [1]. In this work, we are carrying out molecular simulations to investigate the effect of pore structure on adsorption and transport in nanoporous carbons. We aim to develop a validated pore-level model which can be applied in the design of these materials.

Extensive grand canonical Monte Carlo simulation of gas ( $\text{CH}_4$ ,  $\text{CF}_4$  and  $\text{SF}_6$ ) adsorption [2] is carried out in a series of slit-shaped pores of a “pore network model” (PNM), which is a tractable approach to the modelling of real carbons. These results are then used to analyze a “virtual porous carbon” (VPC) [3], which is a highly realistic (but much less tractable) representation of a real carbon. Based on this analysis, the pore size distribution (PSD) and the pore network connectivity (defined as the mean number of pores meeting at a junction) of the VPC are obtained and used to generate a PNM with the same effective structure (from the point of view of diffusion) as the VPC [4].

The equilibrium Molecular Dynamics simulation (EMD) method, which has been successfully used by several authors [5] for computing non-equilibrium transport coefficients of confined fluids, is used to study the transport of these three species in each pore of the PNM.

The effective transport coefficients for each species in the PNM as a whole are determined using an approximate solution method: the Monte Carlo renormalized effective medium approximation (MC-REMA) [6]. The PNM parameters, i.e. the PSD and the network connectivity, and the transport coefficients in individual pores (calculated by EMD) are the inputs to the MC-REMA calculation. In this way, we can evaluate the performance of the PNM in describing diffusion in real carbons, represented here by the realistic VPC model.

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## Molecular dynamics of misogynic, pear-shaped particles

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This project is concerned with molecular dynamics simulations of bulk systems of liquid crystal molecules represented by tapered or pear-shaped particles (pears). The model used consists of a parameterised contact function inserted into a soft repulsive potential. The same contact function has previously been used in hard particle Monte Carlo simulations [1].

The purpose of these studies is to investigate the effect that changes in particle shape, specifically the overall aspect ratio and the degree of tapering along the major axis, have on the bulk behaviour of the system. Compression sequences of pears with an aspect ratio of 3 have revealed isotropic-smecticA-crystal, isotropic-domain ordered and isotropic-nematic-smectic A phase sequences depending on the degree of tapering. Thus, the phase behaviour is extremely sensitive to small changes in particle shape.

We are also currently working in collaboration with the Department of Physical Chemistry of Materials, Bologna University to measure the splay and bend flexoelectric coefficients for these systems. Flexoelectricity is a physical phenomenon that plays an important role in the operation of certain liquid crystal devices such as the ZBD [2] but the relationship between the flexoelectric coefficients and molecular shape is not well understood. The model being used here allows long runs to be performed on large systems (up to 10,000 particles) and so has the potential to make an important step towards addressing this issue.

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## **Investigation of micromechanism of tool spreading–wear by molecular dynamics method**

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In the case of metal cutting process, the tool works under worse condition such as high temperature, large cutting force and intensive friction between chip and tool rake face etc., which can disable cutting tool. With the development of ultraprecision manufacturing technology (nanometric manufacturing technology), the depth of cut is in the level of nanometers or sub nanometers, there may be some new discipline dominants in this regime and there should be new definition of tool wear. Molecular dynamics (MD) method, which is different from continuous mechanics, has already played an important role in describing the microscopic world. Taking the example of single crystal aluminium, this paper carried out MD simulation research of spreading–wear mechanism by varying work material property and technique parameters. From the simulation results we found that increasing depth of cut may result in more active spreading–wear process while crystal anisotropy have little effect about spreading!

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## **Structural analysis of titania nanoparticulates and their interface with organic materials**

Yue Han and James Elliott

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Nanoscale tubular structures have received much attention because of their exceptional properties which differ from those of their bulk materials. Following the first recognition of carbon nanotube structure in 1991 by S.Iijima, extensive research work on the synthesis and characterization of non–carbon nanotubular materials has been carried out. Among these materials, titanium dioxide (TiO<sub>2</sub>) has drawn particular attention due to their potentially wide range of interesting applications. But both the structure and composition of the prepared nanotube are still under debate.

In view of these aspects, the current study focuses on understanding and analyzing the possible titanium oxide nanotubular structures using computing simulations. The Cerius2 and METADISE packages were used to conduct the simulation work. X–ray powder diffraction (XRD) simulation pattern was mainly employed to analyse the structural properties of materials. Titanium oxide bulk (rutile and anatase), surface (stable surfaces of rutile and anatase, trititanate and lepidocrocite surfaces) and corresponding tubular structures were studied respectively. After comparison with experimental XRD results, the assumption is made that the titanium oxide nanotube produced by softchemical method (hydrothermal treatment of TiO<sub>2</sub> particles with NaOH aqueous solution) is likely to be composed of a mixture of nanotubes of anatase and trititanate phase.

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## A new scaling relation for the inverse–power fluid

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Of all the different models for a many–body classical system of particles, those interacting through an inverse–power pair potential,  $u(r)=\epsilon(\sigma/r)^n$ , possess particularly attractive and useful features. These include, for example, the fact that the thermodynamic properties depend upon a temperature–scaled density and that a number of the key physical properties are (unusually) directly related to the compressibility factor. In addition, systems from soft to extremely hard can be represented with this interaction potential by changing only one parameter, the interaction ‘softness’ (*i.e.*,  $n^{-1}$ ). It is also a natural reference system for liquid perturbation theory and a good model system for some naturally occurring and synthetic soft particles (*e.g.*, microgel, granular, and colloidal particles). Its usefulness in these areas of application relies to a large extent on having analytic formulae for the physical properties for different softnesses.

In the poster a new feature of the inverse–power fluid is demonstrated – that of local scaling of structural properties, which in turn yields a relatively simple analytic general equation of state or compressibility factor,  $Z$  [1,2]. This allows us to make a detailed and clearer assessment of the role of the softness than hitherto. The thermodynamic properties of the entire fluid phase has been mapped out for  $n>12$ . This involves the determination of an accurate compressibility surface,  $Z$  (density, softness), which also gives us the possibility to analyse some aspects of the dynamic properties of these systems [3]. It also allows us to derive an effective hard sphere diameter applicable across the phase diagram.

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## Modelling of Hydrogen Bonding in Urea and Dimethylurea

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*Ab Initio* calculations are used to investigate the nature of the bifurcated hydrogen bond in urea and dimethyl urea. The predicted carbonyl stretching frequency of monomer and dimer is compared with the experimental value, but cluster calculations do not capture the large frequency shifts that occur experimentally. A variety of computational methods are compared and it is shown that a density functional method using the EDF1 functional is particularly cost effective for predicting vibrational frequencies.

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## Evaluation of the Amoebapro polarisable force field

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Our goal is ultimately to conduct atomistic simulations of the interaction of biomolecules with inorganic substrates. Our current target application is aimed at complementing existing experimental data of Sano and Shiba [1], who recently reported a hexapeptide motif that preferentially binds to the TiO<sub>2</sub> surface.

The interface between TiO<sub>2</sub> and liquid water at ambient pH should give rise to a nanoscale variation of charge on the TiO<sub>2</sub> surface. Similarly, the peptide side groups may also carry charge. Because of this charged environment, and because we wish to use multipoles to describe the electrostatics of flexible biomolecules, we seek to model the non-bonded interactions of the peptide and water with the titania surface using a recently introduced polarisable force field, amoebapro [2].

Amoebapro is as yet untested, and in this work we evaluate this forcefield in the description of peptide – water interactions and water – water interactions, and have compared this with simulation data for conventional forcefields such as Amber and CHARMM. For comparison in the case of the water – peptide system, we have generated *ab initio* data of several dipeptide – water interactions as a benchmark. We also examine the computational costs associated with using amoebapro in simulations, as compared with conventional forcefields.

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## Investigation of Defect States in Reduced $\text{TiO}_2$ using DFT+U

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Titanium dioxide is of great importance in several technological applications including photocatalysis, sensors, solar cells, and memory devices<sup>1</sup>. The behaviour of  $\text{TiO}_2$  in many of these applications depends upon its surface properties which have consequently been the subject of considerable experimental and theoretical interest<sup>2</sup>.

In the case of the rutile phase of  $\text{TiO}_2$  the (110) surface has been extensively studied as it is this surface which is most stable. Thermal annealing to high temperatures produces oxygen vacancies<sup>3</sup>. These defects, which have been assigned as  $\text{Ti}^{3+}$  species neighbouring the oxygen vacancies, appear in ultraviolet photoelectron spectroscopy as band gap states at 0.7 eV below the conduction band edge.

We have performed DFT studies of the (110) (100) and (001) surfaces of both stoichiometric and reduced rutile. Calculations performed on an oxygen vacancy on the (110) rutile surface show the problems DFT can have with the description of strongly localised systems, wrongly predicting electron delocalisation over all the titanium atoms in the simulation cell. By employing the DFT+U methodology we demonstrate an improvement in the description of these partially occupied titanium 3d states in partly reduced  $\text{TiO}_2$ . This leads to the appearance in the DOS of a new gap state between the valence and conduction bands. Analysis of the partial charge density shows that the states associated with this band are localised on Ti atoms neighbouring the vacancies.

The effects of the choices of both the thickness of the slabs and the surface expansion have been investigated. The same value of U as used for the (110) surfaces was taken for the calculations performed on the reduced (100) and (001) surfaces. In general these display the same characteristics: gap states are found to be present with associated charges which are localised on surface Ti atoms. The geometries of both the stoichiometric and reduced surfaces obtained using DFT+U have been compared with those from GGA calculations.

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# **Grand Canonical Monte Carlo analysis of the evolution of the pore size distribution and the pore network connectivity of porous carbons**

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Activated carbons, highly porous carbon materials, can be produced from a variety of carbonaceous source materials such as coals, lignite, agricultural waste or waste synthetic polymers [1]. Applications of these materials include processes of separation, purification, concentration and catalysed reaction. To produce these porous solids with optimum properties for each different process it is necessary to understand the mechanisms involved in the formation of the solids. We have applied molecular simulation to characterise these solids, to obtain a more accurate description of the micropores present in the solids and to have a deeper knowledge of the processes of porosity development.

The aim of this work is to study the development of the pore network connectivity applying Grand Canonical Monte Carlo simulations to obtain the Pore Size Distribution (PSD) of the solid. This connectivity is usually quantified in terms of the mean coordination number,  $Z$ , which represents the number of pores meeting at a node or intersection in the network [3]. The PSDs obtained from ethane at 264K and nitrogen at 77K, for a set of samples produced at a sequence of times, were used as inputs to a method based in percolation theory [4] to study the changing accessibility of the pores during reaction.

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## **Molecular simulation of metal-organic coordination networks**

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Metal-organic coordination networks are a very interesting kind of materials. They can exert enantioselective and catalytic activity. The problem with these materials is that they are unstable and difficult to make. This paper will deal with a study of the stability of Metal-Organic coordination networks.

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## Structure and dynamics of a confined room temperature ionic liquid

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Room temperature ionic liquids (ILs) have recently emerged as alternative solvents for dye sensitised solar cells (DSSC) (1). Unlike usual electrolytic solutions, their high viscosity and vanishing vapour pressure imply an improvement over undesirable properties like evaporation and leakage.

ILs are formed by asymmetric cations combined with mostly inorganic anions. The high concentration of ionic species implies a high level of charge carriers but, due to high viscosity, ions in the IL tend to diffuse slowly (2). Therefore, processes such as charge recombination or dark current that degrade the performance of DSSC, are sensitive to the charge transport in the IL. In DSSC a semiconducting (TiO<sub>2</sub>) layer that forms a nanoporous structure collects the excited electrons. A redox couple (I-/I<sup>3-</sup>) dissolved in the IL must penetrate the pores to regenerate the dye molecules that coat the TiO<sub>2</sub> particles. In this work we study, by molecular dynamic computer simulations the properties of the IL dimethylimidazolium chloride confined between two parallel planar walls. Confinement effects are analyzed in terms of the density profile of cations' centers and anions along the coordinate *z*, perpendicular to the walls, for different inter-walls separations. As a result, layering behaviour is observed for both cations and anions and the charge density shows charge ordering and oscillatory behaviour along *z*. We also observe a dipolar double-layer near the walls, which is relevant for processes such as charge regeneration and transport across the liquid. By decreasing the inter-wall separation we observe an accumulation of both cations and anions, near the walls. The diffusion coefficient of both species in the *xy*-plane, shows that cations diffuse faster than anions. Also, diffusion coefficients increase upon confinement, reaching a maximum at an inter-wall separation of 28Å. This behaviour appears to be related to the relative increase in the number of particles near the walls, where they diffuse faster than in the bulk.

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## Simulation of carbon dioxide adsorption on MCM-41

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MCM-41 is a mesoporous material that possesses advantageous properties for adsorption, such as high porosity, high surface area, and a narrow and controllable pore size distribution [1]. MCM-41 can be functionalised by incorporation a wide range of organic groups in the silica structure. Molecular modelling can help to identify suitable structures for a given gas separation task before they are synthesised.

We create atomistic models of MCM-41 based on a kinetic Monte Carlo (kMC) approach [2]. The polymerisation of the silicic acid in the presence of the templating micelles and the succeeding calcination step are simulated following the real synthesis path. The surface of the resulting porous silica structures may then be modified by substituting surface silanol groups by organic groups.

We predict the adsorption of carbon dioxide on the model structures with and without organic surface groups by use of Grand Canonical Monte Carlo (GCMC) simulations. Ewald summation is employed to handle the long-ranged electrostatic interactions. This allows us to investigate the influence of the pore size and the organic surface groups on adsorption, and to optimise the properties of the material for particular gas separations.

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# Molecular dynamics simulation of fission track formation and annealing in apatites

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Apatites, of which a typical example is calcium fluoride phosphate, are a widely distributed group of minerals that are used as geological thermochronometers by measuring fission tracks. Invisible tracks are formed in apatite by the fission products of radioactive impurities, principally uranium-238, which naturally exist in the crystals. These tracks, which initially have the same length, are shortened through the process of annealing resulting a distribution of track lengths. The degree by which tracks are shortened depends on the temperature, the pressure and the composition of the crystal. Apatite crystals in geological samples can be polished and etched to reveal the tracks under the microscope given that the tracks are more easily dissolved than the rest of the crystal. The distribution of track lengths is measured by eye and the uranium concentration is determined by counting the new tracks formed by the fission of uranium-235 after bombarding the samples with thermal neutrons. It is assumed that the uranium-238 concentration is in a fixed ratio with that of uranium-235. Samples are then heated at various temperatures with the length distribution being remeasured at several intervals to discover the rate at which tracks anneal with respect to the temperature. The track length distribution, experimental annealing rate data, and the measurement of the uranium concentration, can be used to derive a time-temperature profile.

This method is affected by the compositional diversity of apatite. Not only are apatites a solid solution of three main varieties (fluor-, chlor- and hydroxy apatite), but most natural samples contain large quantities of impurities such as the rare earth elements and carbonate. These impurities have a complex influence on the crystal structure and therefore on the annealing rate of fission tracks. There are also difficulties in extrapolating the laboratory measurements of the annealing rate, carried out over a period of weeks, to geological timescales of millions of years.

The aim of this project is to study, by means of computer modelling:

- how naturally occurring impurities are distributed in the apatite lattice;
- what effects these impurities have on the crystal structure of apatite;
- how the annealing rate of fission tracks in apatite depends on composition, temperature and pressure;

It is hoped that this study will result in a quantitative model of the factors affecting the use of apatite as a geological thermochronometer. The research may also yield broader insights into the field of materials chemistry, especially with respect to radiation damage and gas diffusion in apatite composites.

The initial phase of the research concerns the derivation of parameters for models of the interatomic forces in apatite. These parameters attempt to describe the size and compressibility of ions as short range forces that complement the electrostatic forces between these ions in the crystals. Our parameters extend previously-developed sets to include the main impurities in natural apatite. The interatomic potentials will then be applied in molecular dynamics simulations of the radioactive decay of impurities to model the formation and annealing of fission tracks. It is important to include temperature and pressure variations in the simulations, given that the aim is to model apatites under the geological conditions prevailing in the upper crust.

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## Computer simulations of nanoparticles in arrays and at interfaces

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For a metallic or semi-conducting nanoparticle its optical and electronic properties vary profoundly with its size. Thus, the properties of a two or three-dimensional superlattice of nanoparticles can be tuned according to its constituent particles. Self-assembly provides an inexpensive and relatively simple way of constructing ordered superstructures from colloidal nanoparticles. Typically, chemically stabilised nanoparticles are allowed to self-organise, often under compression, into ordered arrays at the air-water interface. These compact arrays can be transferred to a substrate using Langmuir-Blodgett techniques.

Despite the many recent successes of this method, a theoretical understanding of the structure and properties of these arrays is still lacking. We employ molecular dynamics simulations to investigate the structure and dynamics of butanethiol and dodecanethiol passivated gold nanocrystals isolated in vacuum, confined in arrays, and adsorbed at the air-water interface. We find that the geometry of the metallic core exerts almost no influence over the inter-nanoparticle forces, except at distances of close contact. The core geometry also has little influence in determining the structure of the nanoparticles arrays. The structure of the arrays is rich ranging from open structures, similar to those appearing in diffusion limited processes, to more compact structures in which the symmetry is dependent upon the chain length of the passivating surfactants. At the interface the particles are shown to be stable, exhibiting large contact angles dependent upon chain length. The length of the passivating chains are also shown to determine the shape of the adsorbed particles.

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## The structure and properties of ceramics with stereochemically active $ns^2$ lone pairs

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Ceramics of Sn, Pb, and Bi display a wide range of interesting optical and conduction properties. While numerous studies have dealt with these materials their detailed electronic structure has not been well documented and a number of questions remain to be answered. One key outstanding issue is that of the lone pair associated with the  $ns^2$  electronic configuration (Pb(II), Sn(II), Bi(III)). While considered to be a chemically inert orbital formed from the on-site hybridization of the cation  $s$  and  $p$  orbitals, the stereochemical activity of the lone pair is somewhat unpredictable with some materials adopting distorted structures (e.g. PbO, SnO) and others adopting symmetric structures (e.g. PbS, SnTe). We have performed density functional theory calculations on PbO, PbS, SnO and Bi<sub>2</sub>O<sub>3</sub>. Analysis of their electronic structure shows a strong anion dependence of this lone pair, with the cation  $s$  and  $p$  states too far apart to couple directly. The interaction of cation  $s$  states with anion states of appropriate energy results in a filled antibonding cation  $s$  -anion  $p$  combination just below the Fermi level. This creates the high energy cation  $s$  states needed to couple with the cation  $p$  thus producing the sterically active asymmetric density on the cation. The formation of these  $ns^2$  lone pairs thus relies on direct electronic interaction with the coordinated anions.

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