

Simulation of Materials - Techniques and Applications

CCP5 Annual Meeting 2003

University of Cardiff, UK

8 - 11 September 2003

ABSTRACTS

INDEX

- [INVITED TALKS](#)

The talk abstracts are in order of presentation.

- [Tom Darden \(National Institutes of Health\)](#)
Recent developments in long-ranged and short-ranged electrostatics
- [Florian Müller-Plathe \(International University Bremen\)](#)
Toward the real world - Hierarchical approaches in polymer simulation
- [Dr. Alastair N. Cormack \(New York State College of Ceramics\)](#)
Molecular dynamics simulations of silicate glasses
- [Prof. Gianfranco Pacchioni \(Università di Milano-Bicocca\)](#)
Ground and excited state properties of point defects in insulators from quantum chemical methods
- [Prof Sally Price \(University College London\)](#)
The Computer Prediction of Organic Crystal Structures - Progress, Problems and Polymorphism
- [P. Mark Rodger \(University of Warwick\)](#)
Simulations of crystal nucleation and inhibition
- [Dr. Paul Sherwood \(CCLRC Daresbury Laboratory\)](#)
A general purpose implementation of the QM/MM modelling approach with application to biological, zeolite and surface reactivity.
- [Professor Gerald Kneller \(CNRS - Orléans\)](#)
Multiscale relaxation phenomena in liquids and proteins studied by computer simulation and numerical signal processing
- [Robin W. Grimes \(Imperial College of Science, Technology and Medicine\)](#)
Atomic Scale Simulations for Compositional Optimization

- [Dr Graeme Watson \(Trinity College Dublin\)](#)
Density functional theory studies of surface structure and adsorption.

- CONTRIBUTED TALKS

The talk abstracts are in order of presentation.

- [Dr M. I. J. Probert \(University of York\)](#)
Constant Pressure Langevin Dynamics
- [Dr Mark R. Wilson \(University of Durham\)](#)
Atomistic Simulations of Liquid Crystals
- [Dr J. Ilnytskyi \(University of Durham\)](#)
Computer simulation study of the liquid crystalline dendrimers by various simulational techniques
- [Prof Yasuaki Hiwatari \(Kanazawa Univ. Japan\)](#)
Dynamical Significance in Alkali Metasilicate Glasses
- [Sanghamitra Mukhopadhyay \(University College London\)](#)
The Structure and Relative Concentrations of E' Centres in Amorphous SiO₂
- [J. L. Gavartin \(University College London\)](#)
Modelling of charged defects in oxides.
- [Dr Andreia Luisa da Rosa \(University of Sussex\)](#)
Density-functional theory calculations on H defects in Si
- [Mr P. G. Karamertzanis \(Imperial College London\)](#)
Ab initio crystal prediction using global optimisation
- [Dr Dorothy Duffy \(University College London\)](#)
The growth of polar crystals on ionised organic substrates
- [Dr Yu-Tsung Chiu \(Industrial Technology Research Institute, Taiwan\)](#)
Simulation of Silicon Melting and Crystallization by DL_POLY
- [Dr Ken-ichi Saitoh \(Osaka\)](#)
Strength of Nano-size Material Generated from Copper Clusters: Application of Interactive Molecular Dynamics Simulation
- [Dr James Elliott \(University of Cambridge\)](#)
Solvent interaction with carbon nanotube bundles under hydrostatic pressure
- [Ms Misbah Sarwar \(The Royal Institution of Great Britain\)](#)
Adsorption of chlorinated organic compounds in zeolites: A DFT study
- [Dr Ross Brown \(Université de Pau et des pays de l'Adour\)](#)
Molecular modelling of ALPO₄-5

- [Dr Philip Lindan \(University of Kent\)](#)
The first-principles picture of oxide-aqueous solution interfaces
- [Dr David J Cooke \(University of Bath\)](#)
Computer modeling of cation segregation to oxide and mineral surfaces in the presence of water
- [POSTER ABSTRACTS](#)

The poster abstracts are in alphabetical order.

- [S. M. Abrar \(University of Stellenbosch\)](#)
Development of an empirical force field for the molecular dynamics simulation of N,N'-dialkylimidazolium ionic liquids.
- [Dr. Hadi Arabshahi \(Tarbiat Moallem University, Iran\)](#)
Monte Carlo Simulation in Semiconductor Materials and Devices
- [Rudy Coquet \(Cardiff University\)](#)
Ab initio Study of Surface Point Defects on MoO₃(010) and adsorption of methyl
- [Joanne Fearon \(Trinity College Dublin\)](#)
Examination of the adsorption mode for methanal on the palladium {111} surface using Density Functional Theory.
- [J. H. Harding \(University College London\)](#)
Surface diffusion in rock-salt oxides
- [Tien-Jung Huang \(Industrial Technology Research Institute Taiwan\)](#)
Molecular Dynamics simulation of the Ionic Conductivity in Nafion Membranes

INVITED TALKS

Recent developments in long-ranged and short-ranged electrostatics

Tom Darden

Laboratory of Structural Biology, NIEHS, North Carolina 27709, USA

In this talk I will first summarize what I and others in the macromolecular simulation field have learned in the past decade about how to treat long-ranged electrostatics in the context of periodic boundary conditions. Strengths and weaknesses of various competing algorithms including cutoff methods, reaction field, fast multipole and other tree based methods, particle-mesh and multigrid techniques will be discussed. After this I will talk about recent work extending the particle mesh approach to efficient lattice summation of point dipoles and higher order point multipoles (up to hexadecapoles). Finally I will discuss recent efforts to implement this approach with a force field (Amoeba, from Jay Ponder) that includes atomic quadrupoles and inducible dipoles using the Thole' approach.

Toward the real world - Hierarchical approaches in polymer simulation

Florian Müller-Plathe

International University Bremen, PO Box 750, 561 Bremen D28725, Germany

Systematic coarse-graining combines accurate atomistic models with longer-ranged mesoscopic models. The combination of the two allows to study polymer properties, which depend on long length and time scales, starting from low level descriptions. The automatic mapping technique will be discussed together with a few applications to polymer melts and solutions.

Molecular dynamics simulations of silicate glasses

Dr. Alastair N. Cormack

New York State College of Ceramics, Alfred University, NY 14802, USA

In this presentation, we will discuss the application of molecular dynamics to the characterization of silicate glass structures and related properties.

Firstly, we will present the basic structural features of silicate glasses, which will serve as a foundation for a discussion of the issues surrounding agreement between experiment and simulation. We then venture into the realm of glass surfaces, where experimental data are somewhat scarce and will describe the results of calculations on the hydroxylation of silica surfaces. A hierarchy of active sites, based on the energetics of hydroxylation, can be established.

Finally, we will describe some studies on alkali ion diffusion mechanisms in alkali silicates, including the mixed alkali effect.

Our illustrations will largely be taken from 'simple' alkali silicate glasses, but will also encompass some bioactive glass compositions, which are considerably chemically more complex.

Ground and excited state properties of point defects in insulators from quantum chemical methods

Prof. Gianfranco Pacchioni

Dipartimento di Scienza dei Materiali Università, di Milano-Bicocca, via R. cozzi, 53, Milano, 20125, Italy

In this lecture we will review recent applications of quantum chemical studies to the problem of point defects in insulators. Through the comparison of the ground and excited state properties of oxygen vacancies in three oxides, SiO_2 , MgO , and SrTiO_3 , it will be possible to make some general consideration about the electronic structure of these materials. The results will be put in the context of experimental results and will provide an example of combined theory-experiment approach to the study of materials.

The Computer Prediction of Organic Crystal Structures - Progress, Problems and Polymorphism

Prof Sally Price

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

Can we predict the crystal structure of an organic molecule prior even to its synthesis? This problem is made more challenging, and worthwhile, by the phenomenon of polymorphism, when a molecule can adopt more than one crystal structure. The unexpected appearance of a new polymorphic form of a pharmaceutical can be an industrial disaster, and hence there is considerable practical interest in forming a computational model for predicting possible polymorphs. A simple thermodynamic approach of searching for the global minimum in the lattice energy can be successful, but it is far from reliable and often predicts far more energetically feasible structures than known polymorphs. Some examples of preliminary attempts to consider kinetic effects on crystallisation will be discussed.

A general purpose implementation of the QM/MM modelling approach with application to biological, zeolite and surface reactivity.

Dr. Paul Sherwood

CCLRC Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, UK

I will present the implementation of a general purpose QM/MM approach [1], with particular emphasis on the specific features needed to tackle a range of different classes of chemical systems including solid state, zeolite and biological systems.

The talk will include:

- a comparative review of the available QM/MM methods
- some remarks on the implementational details appropriate for the use of different classes of forcefields including those of shell model and valence type
- generation of finite cluster models for the QM/MM study of zeolite and oxide materials
- approaches to geometry optimisation and transition state location for systems with many degrees of freedom

The talk will be illustrated with results of a number of collaborative applications from the QUASI project [1,2].

References

[1] A General Purpose Implementation of the QM/MM Approach and its Application to Problems in Catalysis. Paul Sherwood, Alex H. de Vries, Martyn F. Guest, Georg Schreckenbach, C. Richard A. Catlow, Samuel A. French, Alexey A. Sokol, Stefan T. Bromley, Walter Thiel, Alex J. Turner, Salomon Billeter, Frank Terstegen, Stephan Thiel, John Kendrick, Stephen C. Rogers, John Casci, Mike Watson, Frank King, Elly Karlsen, Merethe Sjøvoll, Adil Fahmi, Ansgar Schäfer, Christian Lennartz. *J Mol Struct (Theochem)* In press.

[2] www.cse.clrc.ac.uk/qcg/quasi

Multiscale relaxation phenomena in liquids and proteins studied by computer simulation and numerical signal processing

Professor Gerald Kneller

Centre de Biophysique Moléculaire, CNRS, Rue Charles Sadron, Orleans, 45071, France

The lecture gives an introduction into the simulation-based modeling of relaxation processes in simple and complex liquids. Starting from the classical Langevin equation, the lecture presents briefly the Mori-Zwanzig description of dynamical correlations in liquids. A key point is the discussion of memory effects described by the generalized Langevin equation. It will then be shown how numerical methods known in the field of signal processing can be used to compute numerical estimates for time correlation functions, their Fourier spectra and the corresponding memory functions. Applications are shown for simple liquids, molecular liquids, and proteins. It will be demonstrated that slow internal protein dynamics exhibits long time memory effects which are compatible with a model of fractal Brownian dynamics.

Atomic Scale Simulations for Compositional Optimization

Robin W. Grimes

Dept. of Materials, Imperial College, Prince Consort Road, London SW7 2BP UK

It is now routine to carry out atomic scale computer simulations of defects in oxides. Consequently it is possible to generate data over a wide compositional range and thereby develop an understanding of how defect processes evolve as a function of composition. This should lead to an enhanced ability to tailor compositions to functional requirements.

Here we will review data for two systems, ABO_3 perovskites and $A_2B_2O_7$ pyrochlores. In the case of the pyrochlores there is a structural transformation from pyrochlore to fluorite as a function of composition and defect process energies evolve towards that boundary. For perovskites structures change from rhomboherdal to orthorhombic to hexagonal to cubic as a function of composition. For some processes we see an abrupt change in defect process energy as boundaries are crossed but sometimes we do not.

Simulations of crystal nucleation and inhibition

P. Mark Rodger

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

Direct investigation of phase nucleation processes with techniques such as molecular dynamics is a desirable goal that is now beginning to be achievable. In recent years there have been successful attempts to simulate both condensation and crystal nucleation in atomic systems. Very recently, crystal nucleation in molecular systems has also been shown to be accessible through molecular dynamics simulations. This talk will focus on the use of molecular dynamics to study crystal nucleation - and inhibition - of methane hydrate at a liquid water / fluid methane interface.

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 involve 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. This talk will show that simulated nucleation is possible even in such a complex system, and that considerable new insight into a challenging scientific problem can be obtained from such simulations. Further, the successful simulation of hydrate nucleation has made it possible for the first time to simulate the activity of "low dosage" hydrate inhibitors-akin to anti-freeze peptides-an yielding some surprises for our understanding of how such inhibitors work.

Density functional theory studies of surface structure and adsorption.

Dr Graeme Watson
Dept. of Chemistry, Trinity College, Dublin 2, Ireland

Density functional theory is widely applied to problems of surface structure and adsorption. We will examine these aspects with reference to recent work performed at Trinity College Dublin.

We will discuss the use of DFT for predicting oxide surface structure and relaxation by comparison with experiment and force field methods. We will examine the basal plane of Cr_2O_3 and the effect of the anti-ferro magnetic structure. We will also examine the low index surfaces of CeO_2 with particular emphasis on comparison with previous force field predictions.

One key industrial reaction is hydrogenation for which the group 10 metals are extensively used. We will discuss the adsorption of hydrogen onto the $\{111\}$ surfaces of the group 10 metals showing that the energetics on Pt are quite different to Ni and Pd with Pt showing an almost site independent adsorption energy implying very fast surface diffusion. We will extend this to Sn Pt surface alloys which are used to reduce the reactivity and increase the selectivity of Pt catalysts. These calculations indicate that adsorption close to the Sn is unfavourable and therefore blocks potential diffusion pathways.

Finally we will discuss the adsorption of ethene onto the group 10 metals and in this case show that Pd gives rise to different adsorption characteristics. However, in this case we will show that much of the experimental data, which has been used to identify a pi adsorbed mode, fits our di-sigma adsorbed ethene significantly better and we suggest that the experimental data should be reanalysed.

CONTRIBUTED TALKS

Constant Pressure Langevin Dynamics

M. I. J. Probert and D. Quigley
Department of Physics, University of York

Constant pressure/temperature molecular dynamics is a familiar and powerful tool for the simulation of materials. The most common method combines the Nose-Hoover thermostat with an Andersen-Hoover barostat. However, this deterministic dynamics approach is not always best suited to all problems and hence there is sometimes a need for stochastic dynamics based upon the Langevin equation. In this talk, various Langevin algorithms will be presented for performing constant pressure dynamics. Examples of when this approach is superior to the conventional deterministic approach will also be given.

Atomistic Simulations of Liquid Crystals

Mark R. Wilson¹, David L. Cheung², and Stewart J. Clark²

1. Department of Chemistry, University of Durham, South Road, Durham DH1 3LE
2. Department of Physics, University of Durham, South Rd., Durham DH1

With recent rapid advances in computing power, atomistic simulation of liquid crystals is set to become a major tool in the design of new liquid crystalline materials. Atomistic simulations provide a “*picture*” of what is happening at the molecular level in terms of both the molecular structure within a liquid crystal phase, and individual interactions between neighbouring molecules. They also provide a route to predicting key material properties within a bulk liquid crystal phase. As such, they offer the tantalising possibility of using input from simulation to design new materials with the desired physical properties (molecular engineering). While this goal is not yet within reach, the progress towards it looks exciting.

This paper describes the recent advances we have made in Durham in three key areas, which have a major impact on the use of atomistic simulation in future “molecular engineering applications”.

1. **Force field development** - we have developed an *ab initio force field* for the simulation of LC molecules derived from high accuracy *density functional theory* quantum calculations.
2. **Atomistic simulations of the nematic phase and the pretransitional region of the isotropic liquid phase** for system sizes as large as 1000 molecules. These are the most detailed simulations of a liquid crystal ever to be carried out, and provide new insights into what is happening in a liquid crystal in terms of individual molecular interactions.
3. **Development of methods to calculate material properties.** Here we have been able to use atomistic simulation to provide predictions for densities, order parameters, rotational viscosities and flexoelectric properties in the nematic phase; and dipole correlation factors in the liquid phase.

References

Cheung D. L., Clark S. J., Wilson M. R. Parametrization and validation of a force field for liquid-crystal forming molecules. *Phys. Rev. E* 65: 051709, 2002.

Cheung D. L., Clark S. J., Wilson M. R. Calculation of the rotational viscosity of a nematic liquid crystal *Chem. Phys. Lett.* 356: 140, 2002.

Cook M. J., Wilson M. R. The first thousand-molecule simulation of a mesogen at the fully atomistic level. *Mol. Cryst. Liq. Cryst.* 363: 181, 2001.

Cook M. J., Wilson M. R. A molecular dynamics simulation study of dipole correlation in the isotropic phase of the mesogens me5NF and GGP5CI. *Mol. Cryst. Liq. Cryst.* 357: 127, 2001.

Cook M. J., Wilson M. R. Development of an all-atom force field for the simulation of liquid crystal molecules in condensed phases (LCFF). *Mol. Cryst. Liq. Cryst.* 357: 149-165, 2001.

Computer simulation study of the liquid crystalline dendrimers by various simulational techniques

J. Ilnytskyi and M. R. Wilson

Dept. of Chemistry, University of Durham, South Road, Durham, DH1 3LE

We present the results of computer simulation studies of the liquid crystalline dendrimers both in the nematic and smectic solvent and in a bulk phase. The united atom level of modelling is used to represent both the carbo-silane internal core and flexible tails of the dendrimers. The mesogenic groups are represented via rigid Gay-Berne pseudo-atoms. The advantages and disadvantages of molecular dynamics and configurational biased Monte Carlo method applied to the dendritic molecules are discussed.

Dynamical Significance in Alkali Metasilicate Glasses

Y. Hiwatari¹ J. Habasaki²

1. Kanazawa University, Kakuma, Kanazawa 920-1192, Japan
2. Tokyo Institute of Technology, 4259 Nagatsuta-cho, Yokohama, Kanagawa, 226-8502, Japan

The relaxation dynamics of a complex interacting system can be drastically changed by mixing with another component having different dynamics. In this work, we elucidate the effect of the less mobile ions on the dynamics of the more mobile ions by molecular dynamics simulations of lithium ions motion in lithium metasilicate glass by freezing some randomly chosen lithium ions (5 %, 10 % and 25 %) at their locations in the initial time for 700 K. A remarkable slowing down of the dynamics of the majority mobile Li ions was observed both in the self-part of the density-density correlation function, $F_s(k, t)$, and in the mean squared displacements, MSD. On the other hand, there is no significant change in the structure. The plot of squared displacement against the number of jumps of each Li ion within the time period T (≈ 920 ps) reveals that the ions, which shows faster dynamics (Levy flight) facilitated by cooperative jumps, decreases considerably. This behavior is quite similar to that observed in molecular dynamics simulations of the mixed alkali system, LiKSIO_3 , where the suppression of the cooperative jumps occurs due to the jump paths being intercepted by other kind of alkali metal ions^[1,2]. We also use molecular dynamics simulation to study "cooperativity blockage" by confining the Li metasilicate glass by parallel walls made of the same glass except all Li ions therein are frozen. Both slowing down and stretching are observed and the effect is largest near the wall and decreases monotonically with distance from the wall. Scheidler et al.^[3] have observed similar slowing down of a similar system of binary Lennard-Jones particles confined by walls made of frozen particles. The length scale of the blockage effect could be related with the size of the cooperative rearranging region (CRR) and the magnitude of the coupling with surrounding particles. Large finite size effect is expected only when the characteristic length becomes comparable order of magnitude to the cell, because the motion of particles is affected by their ghost particles due to periodic boundaries. There are a number of common properties between the dynamics of conducting ions and other glass forming liquids. Thus the dynamics observed in our systems may be also useful to understand the glass transition of the glass forming materials and dynamics in the confined systems.

References

- [1] J. Habasaki, I. Okada and Y. Hiwatari, *J. Non-Cryst. Solids*, **183** 12 (1995) *J. Non-Cryst. Solids*, **208**, 181 (1996)
- [2] J. Habasaki and Y. Hiwatari, *J. Non. Cryst. Solids*, **307**, 930 (2002).
- [3] P. Scheidler, W. Kob, K. Binder and G. Parisi, *Philos. Mag.* **B82**, 283 (2002).
-

The Structure and Relative Concentrations of E' Centres in Amorphous SiO₂

Sanghamitra Mukhopadhyay, Peter V. Sushko, Alexander L. Shluger
Department of Physics & Astronomy, University College London, Gower Street, London WC1E
6BT, United Kingdom

We study how disorder in amorphous materials affects the structure, properties and relative concentrations of basic defects, such as vacancies, interstitial atoms and impurities. In this presentation we discuss the influence of the local and medium range order in amorphous silica, $a - SiO_2$ on the structure of positively charged oxygen vacancies, known as E' centres. We have used two different ideal continuous random network structures to model $a - SiO_2$ and the *ab-initio* embedded cluster method to study the structure and relative concentrations of E' type centres in this material, assuming that they can be formed at any site of the amorphous structure. We find that, contrary to crystalline silica, where only two types of E' centres can be formed, there are more than ten structural types of E' centres in $a - SiO_2$. We developed structural criteria, which allow us to predict a type of centre from analysis of a local environment of a site in the perfect amorphous structure it is formed. This allowed us to predict relative concentrations of different structural types of E' centres. We calculated the electronic structure of these centres and predicted the hyperfine interaction of the unpaired electron with the surrounding nuclei in good agreement with the experimental data. Our results demonstrate that these defects induce a very long-range distortion in the flexible amorphous network of $a - SiO_2$.

Modelling of charged defects in oxides.

J. L. Gavartin and A. L. Shluger
Department of Physics and Astronomy, University College London, Gower Street, London WC1E
6BT, UK

The remarkable property of dielectric materials is that the intrinsic and extrinsic lattice imperfections (defects) there may co-exist in different charge states in a wide range of values for the electron chemical potential. Owing to the usually high electron-phonon coupling strength and to a high mobility of some of the defect species, the change of the charge state is usually accompanied by the large local lattice relaxation or even the chemical reactions involving the defects and the host lattice. Such phenomena greatly affect optical, dielectric and even mechanical properties of the dielectric materials. Depending on the applications, the charged defects may play either constructive or adverse rôle. For example, depending on their type, certain charged defects alter (enhance or degrade) relative stability of crystalline polymorphs of zirconia giving rise to the massively exploited transformation toughening phenomena. At the same time, potential application of the same material as a gate stack dielectric in the CMOS devices, is problematic due in part to the naturally high charge accumulation in the films with a high dielectric constant. The fluorescence efficiency and wavelength of the II-VI and III-V quantum dots also radically depends on their charge state.

Despite a remarkable progress in quantum theory of condensed matter, the accurate studies of charged systems present a substantial challenge. The prime difficulties appear on both the fundamental and methodological level.

First, the probability for a defect to have a certain charge state depends on the number of available

carriers, that is, on the value of a chemical potential, μ . Most practical variational electronic structure methods essentially rely on the fixed number of particles, so a direct evaluation of μ is not possible. Further difficulties arise when using quasi infinite models, that is the periodic or antiperiodic boundary conditions, or embedded cluster techniques, where the energies of the systems with different number of electrons cannot be directly compared.

Second, even using the chemical potential as an external parameter may not give an adequate physical picture, since the characteristic times for reaching thermodynamic equilibrium may be extremely long due to a low charge mobility in the dielectrics. Therefore, relevant experimental measurements or device characteristics may represent a system at metastable rather than thermodynamic equilibrium.

Third, a multitude of possibilities to accommodate charge in the lattice requires very accurate calculations of energy differences between various possible defects. These energy differences are often reduced to a delicate balance between the energy of an electron on a defect level and the valence and conduction band edges (shallow centres). This balance leads to a so-called charge localization problem, which is known to be ill-represented in both Hartree-Fock and Kohn-Sham based approaches

In this paper we give a brief overview of a problem of charged defects as it arises in transformation toughening in ceramics and in dielectric properties of high-k oxides.

We present density functional static and molecular dynamics simulations of the martensitic phase transformations in zirconia and discuss the role of water and hydrogen in these transformations. Next we consider the problem of trapped charge in high-k dielectrics and how it can be passivated by nitridation.

Density-functional theory calculations on H defects in Si

Andreia Luisa da Rosa¹, N. Martsinovich¹, C. P. Ewels², M. I. Heggie¹ and P. Briddon²

1. University of Sussex CPES, Falmer, Brighton, BN1 9QJ United Kingdom
2. Physics Centre, School of Natural Science, Newcastle, NE1 7RU, United Kingdom

Hydrogen is a very common impurity in Si. In high concentrations H generates extended planar defects (H-induced platelets), which develop into microcracks and lead to surface blistering of Si samples. This phenomenon is the basis of the SmartCut process of obtaining high quality Si on insulator layers. In this work we employ first-principles calculations and elasticity theory to study H aggregates in Si and its interactions with dislocations and impurities. Among several structures, we find that the hydrogenated glide dislocation dipole is the preferred structure for small number of H atoms and it expands by dislocation glide with H condensing in the shuffle plane between the dislocations. In addition to the study of H aggregates, we also investigate the possible effect O/H complexes might have on the O diffusion. We find that a dislocation dipole structure with two H atoms and one O atom at the cores of the dislocations to be stable and compare it with the stabilities of other O/H complexes.

Ab initio crystal prediction using global optimisation

P. G. Karamertzanis and C. C. Pantelides

Centre for Process Systems Engineering, Department of Chemical Engineering, Imperial College London SW7 2BY, UK.

The determination of the crystal structure is of major importance because it influences the properties of the materials, including density, colour, taste, solubility, rate of dissolution, melting point, chemical stability, optical properties and crystal morphology. This paper considers techniques for the ab initio determination of the crystal structure, based solely on the atomic connectivity of the molecule under consideration. This is useful when powder diffraction techniques cannot be used, or when it is necessary to predict the crystal structure of an organic molecule prior to its synthesis. Even if one crystal structure for a specific compound is known, the ability to explore the polymorphic landscape is of major importance for the pharmaceutical and pigment industries, where the discovery of unpredicted crystal forms in a late stage of the design of the production line can have disastrous consequences (the case of the antiHIV drug Norvir™ where the appearance of the most stable polymorphic form II changed significantly the dissolution rate and thus the bioavailability of the product).

The method developed is based on the global minimisation of the molar enthalpy of the crystal with respect to the lattice lengths, lattice angles and atomic positions. The repulsion dispersion interactions are modelled with widely accepted potential models, while the optimum molecular geometry and the molecular electric potential (MEP) are calculated at the Hartree-Fock / 6-31G** level. The modelling of the electrostatic interactions is accomplished through the use of a set of distributed charges, whose magnitudes and positions are found such that the relative root mean square (RRMS) accuracy of the MEP is globally minimised. No constraints are imposed on the space group symmetry, treating the positions and orientations of all molecules in the unit cell as decision variables. A forced convergence technique is used to ensure accurate calculation of the electrostatic contributions. Moreover, significant effort has been invested in the analytical computation of all derivatives, which is essential for the efficient and reliable operation of local minimisation methods and their convergence to true local minima.

In order to identify all the local minima, a two-phase stochastic/deterministic global optimisation method has been developed. The method uses low discrepancy (quasi-Monte Carlo) sequences to generate a number of initial guesses in the space of the optimisation variables. It then initiates local optimisation calculations with a sequential quadratic programming algorithm. The algorithm is parallelized on a Beowulf cluster, allowing minimisations from many thousands of initial guesses to be carried out in reasonable time.

A number of test cases to illustrate the applicability of the algorithm are presented.

The growth of polar crystals on ionised organic substrates

Dorothy Duffy and John Harding

Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, UK

Organic substrates have been used in experiments to modify the nucleation and growth of inorganic crystals in an attempt to mimic biomineralization processes. Such crystals often nucleate on polar surfaces that are generally unstable in the absence of the substrate. A particular example is the polar (01.2) face of calcite, which nucleates on a diverse range of substrates, including self-assembled monolayers, hydrogen-bonded ribbons and polymer arrays. We have used molecular dynamics to model interfaces between polar calcite surfaces and ionised organic substrates. We found that a particular type of surface defect will not only accommodate the lattice mismatch between the substrate and the crystal but it will also quench the dipole moment of the polar surface. We show how such defects can be used explain the morphology of calcite crystal grown on self-assembled monolayers.

Simulation of Silicon Melting and Crystallization by DL_POLY

Yu-Tsung Chiu and J. -T. Yeh

Industrial Technology Research Institute (ITRI) Materials Research Labs Rm. 222, Bldg. 77, 195, sec. 4, Chung Hsing Rd. Chutung, Hsinchu, 31040 Taiwan

In this research, we adapt the parallel molecular dynamics program DL_POLY to simulate silicon melting and crystallization by adopting Stillinger-Weber's three-body potential. The accuracy of the modified program is verified by calculating material characteristics from the numerical output and comparing these values with the ones from related literature. These material properties are the bulk modulus, coefficient of thermal expansion, melting, and crystallization speeds. Finally, the revised DL_POLY is used to study the temperature dependency of the critical size of the silicon crystal embedded in the corresponding amorphous matrix. As a result, it is found that the critical size decreases when the temperature is reduced, which is consistent with existing thermodynamics models.

Strength of Nano-size Material Generated from Copper Clusters: Application of Interactive Molecular Dynamics Simulation

Ken-ichi Saitoh

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

Strength of nano-size materials is still in puzzle, though nowadays such miniature substance could be experimentally tested by using highly advanced nanotechnology. In this study, a novel type of nano-size materials built up from clusters of copper atoms are computationally investigated concerning the mechanical behavior and strength. Isolating metallic clusters, e.g. copper clusters, which are only with nanometer-size dimension, have been known as ultra fine particles. However, their assembled form as well as their mechanical behavior is not well understood. Molecular dynamics (MD) simulation is adopted to examining and predicting their possible assembled structure and their strength. With various arbitrary arrangements of copper clusters composed of 683 atoms, a lot of computational specimens are constructed and tested. They can be aligned in regular array with 1-D, 2-D, or 3-D arrangement. It is found that this type of structure often shows brittle fracture when some voids are included inside. Rotation of clusters promoted by generation and annihilation of stacking faults is responsible for increase of the brittleness. An another approach using "interactive molecular dynamics", which is a variant of the MD software and particularly enhances real-time visualization and interactive touching, is attempted to be utilized for setting up initial clusters' array required in the present MD application.

Solvent interaction with carbon nanotube bundles under hydrostatic pressure

James Elliott and Kristin Rule

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

The high theoretical modulus and strength of single-wall carbon nanotubes (SWNTs) makes them an ideal candidate for use as a filler material in polymer composites. More recently, the response of carbon nanotubes to molecular pressure produced by the cohesive energy density (CED) of a solvent has opened up the possibility of using carbon nanotubes as molecular sensors. Aspects of both of these potential applications of carbon nanotubes are explored by computer simulation via the application of hydrostatic pressure. In this paper, we apply constant stress (NST) Molecular Dynamics simulations, carried out using DL_POLY with classical macromolecular force field, to two-dimensional hexagonal bundles of SWNTs surrounded by a solvent bath. The aim of these simulations was (i) to elucidate the effect of bundle size on SWNT collapse pressure, and its relation to the collapse mechanism postulated for tubes in infinitely periodic bundles (Elliott et al., in press), and (ii) to gain a better understanding of solvent-nanotube interactions under hydrostatic pressure, specifically with relation to solvent polarity and CED of the solvent. In particular, the effect of solvent CED on the pressure at which the nanotubes inside the bundle collapse is investigated. The effects of solvent crystallisation both inside and outside the nanotube under pressure were also considered.

Adsorption of chlorinated organic compounds in zeolites: A DFT study

Misbah Sarwar, Dr Robert G Bell and Dr Alexandra Simperler
The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS

Chlorinated Volatile Organic Compounds (CVOCs) are the by-products of many industrial processes. This class of compound are causing concerns due to the dangers they pose to human health and to the destruction of the ozone layer in the stratosphere. Currently the most common destruction method is catalytic oxidation using transition metal catalysts. These however are not very effective as they are deactivated by halide poisoning. As a result alternative methods to removing or breaking down these compounds are currently being sought and zeolites are one such alternative. They have two very useful properties that can be utilised: they act as adsorbents and catalysts.

We are currently investigating the adsorption of 3 CVOCs; dichloromethane, 1,2 dichloroethane and trichloroethylene in the MFI (Si/Al=27), FAU (Si/Al=2) and MOR (Si/Al=5) frameworks. The aim is to model the catalytic reactions of these compounds in zeolites and thus studying adsorption is particularly important, as it is a pre-step to catalysis. Theoretical studies provide an insight into the locations and orientations of the molecule at the active site and the start of the reaction mechanism, something difficult to obtain experimentally. We have performed Monte Carlo docking calculations to probe the adsorption of these molecules in the various zeolite frameworks. From the periodic frameworks we have extracted framework fragments surrounding the adsorption site. We have performed Density Functional Theory calculations (PW91, dnp) on both purely siliceous and Bronsted acidic aluminosilicate clusters. In the aluminosilicate clusters we have modelled the interaction of the sorbate with the most thermodynamically stable acid site. The clusters vary in size ranging from 120 — 220 atoms and have been selected to represent as much of the framework surrounding the active site as possible. We present the trends in the binding energies for the CVOCs, rationalised in terms of the locations and orientations of the molecules at the adsorption site.

Molecular modelling of ALPO_4-5

Ross Brown¹, M. Merawa¹, P. Labéguerie¹, J. Kirstein²

1. Laboratoire de chimie théorique et de physico-chimie moléculaire, umr 5624 du CNRS et de l'Université de Pau et des pays de l'Adour, IFR, rue J Ferry, 64000 PAU France
2. Lehrstuhl für Physikalische Chemie, Ludwig-Maximilian Universität München, Butenandstr. 11, 81377 MÜNCHEN, Germany.

Although ALPO_4-5 was among the first of the aluminophosphate molecular sieves to be synthesized in the early 80's, its crystal structure still continues to pose interesting questions, notably the large displacement parameters of some oxygens and the precise space group among a number of candidates with hexagonal or orthorhombic symmetries. After summarising the data, we present the results of classical molecular dynamics and periodic ab initio calculations, in agreement with a number of observations on this material, showing a solid-solid phase transition which may account for some of the experimental difficulties.

The first-principles picture of oxide-aqueous solution interfaces

Philip Lindan and Changjun Zhang
School of Physical Sciences University of Kent

We report on the results of an array of first-principles calculations on oxide-water systems ranging from the vacuum surface science (VSS) regime to the interface involving an aqueous solution. These calculations help in interpreting vacuum experiments on well-characterised surfaces with a low coverage or adsorbates, they reveal mechanisms; and they provide insight and predictions in the absence of experimental data. The latter is crucial for oxide-solution interfaces where there is almost no secure understanding of at the molecular level.

We present highlights from five areas of study:

1. sub-monolayer water chemistry;
2. molecular processes on the ideal and the defective surface (H_2O , H_2 , H_2S and SO_2);
3. the formation and properties of the first three layers of water, a system still accessible to VSS;
4. the interface with liquid water, and
5. the behaviour of an excess proton in solution at the interface.

Among the new findings and ideas to be illustrated are that the adsorption state may depend on coverage because of complex substrate deformation, that the distinction between water physisorption and chemisorption is rather fuzzy and depends on the number of water layers adsorbed, that proton-conducting wires may be formed under certain circumstances, and that chemical intuition may be misleading when considering surface hydroxylation.

Computer modeling of cation segregation to oxide and mineral surfaces in the presence of water

David J Cooke, Sebastian Keresit and Steve C Parker
Department of Chemistry, University of Bath, Bath, BA2 7AY UK

Atomistic simulation is a valuable tool for predicting the structure of surfaces. This talk considers some of our recent work aimed at applying the approach to mineral surfaces in contact with water. In general we use energy minimisation and molecular dynamics which are coupled with inter-atomic potentials. The use of such potentials enables the surface properties to be calculated rapidly and enables the study of complex systems. Therefore it is essential that we can derive and verify suitable parameters to describe these systems. This is illustrated with in recent work where we combined techniques that use inter-atomic with electronic structure calculations using Density Functional Theory (DFT) to investigate the interactions of water with the surfaces of carbonate minerals. We first compared the two techniques for small model systems, namely the adsorption of a monolayer of water of the surface of calcite, dolomite and magnesite. We then re-considered the potential model for the water-mineral interactions to improve agreement with the DFT calculations and enabled us to model with confidence the adsorption of water on the most significant low index surfaces and on growth steps. Finally, we performed classical molecular dynamics simulations of calcite surfaces in contact with bulk water to investigate the effect of temperature and kinetics on the calcite-water interface. The need to simulate surfaces in contact with water is illustrated in recent work concerned with the surfaces of hematite (α - Fe_2O_3). It was found that the relative stability of the low index surfaces, and hence the morphology is highly dependent on whether water is present and to a lesser extent on whether the water layer consists of dissociated hydroxide ions or molecular water. This is further illustrated in work where the segregation of various iso-valent cations to the (00.1) and (0.12) surfaces of hematite where the presence of water significantly effects the segregation process. Finally we highlight a key challenge for the future, which is not only to simulate at the interface between a mineral surface and a water layer, but also consider the interaction when the water layer contains charged species.

POSTER ABSTRACTS

Development of an empirical force field for the molecular dynamics simulation of N,N'-dialkylimidazolium ionic liquids.

S. M. Abrar, Prof. J. Dillen and C. Esterhuysen
Dennesig 7601, P.O.Box : 2036 University of Stellenbosch, South Africa.

Monte Carlo Simulation in Semiconductor Materials and Devices

Dr. Hadi Arabshahi
P.O.Box 161, Physics Dept. Tarbiat Moallem University, Sabzevar, Iran

Self-consistent Monte Carlo simulation has been developed and used to model electron transport in bulk semiconductor materials and the devices made from the materials(for example, Heterojunctions field effect transistors HFETs, metal semiconductor field effect transistors MESFETs, HEMTs and so on).

Ab initio Study of Surface Point Defects on MoO₃(010) and adsorption of methyl

Rudy Coquet and Dr David Willock
Department of Chemistry, Cardiff University, PO Box 912, Cardiff CF10 3TB, UK

Density Functional Theory calculations on the (010) surface of MoO₃ are performed using VASP. The weak electrostatic interactions bonding the bi-layers parallel to the (010) plane require a specific approach because the density functional theory does not take it into account. Oxygen vacancies are created within a (2x2) ordered array and the surface is then optimized : the symmetric oxygen vacancy is found to be the less favourable, due to less important relaxation. While previous studies report no significant displacement parallel to the (010) plane, we find that the oxygen atoms surrounding the terminal and asymmetric vacancies move to compensate the defect. Finally, energetics of methyl radicals adsorption on different binding sites of the MoO₃(010) surface with a (2x2) array of terminal oxygen vacancies are calculated.

Examination of the adsorption mode for methanal on the palladium {111} surface using Density Functional Theory.

Joanne Fearon and Graeme W. Watson
Chemistry Department, Trinity College, Dublin, Ireland.

Palladium is an important hydrogenation catalyst.^[1] Methanal is an important product in the decomposition of methanol a reaction which has been observed on supported palladium catalysts.^[2] In another important reaction oxygen can be added selectively to adsorbed CH_2 and CH_3 fragments on palladium surfaces to give methanal (and other products).^[3] In industrial processes hydrogenation of larger carbonyl compounds in particular α,β -unsaturated ketones over palladium catalysts is potentially very useful as high enantioselectivity can be achieved.^[4] However the adsorption mode for the ketone with the surface is not clear.^[5,6] In previous work we have looked at the interaction of a C=C species, ethene with the Pd{111} surface. Here we consider the carbonyl functional group, C=O in the methanal molecule on this surface.

Density functional theory calculations have been carried out as implemented in the code VASP.^[7,8] Four adsorption modes have been considered as shown in the figure.

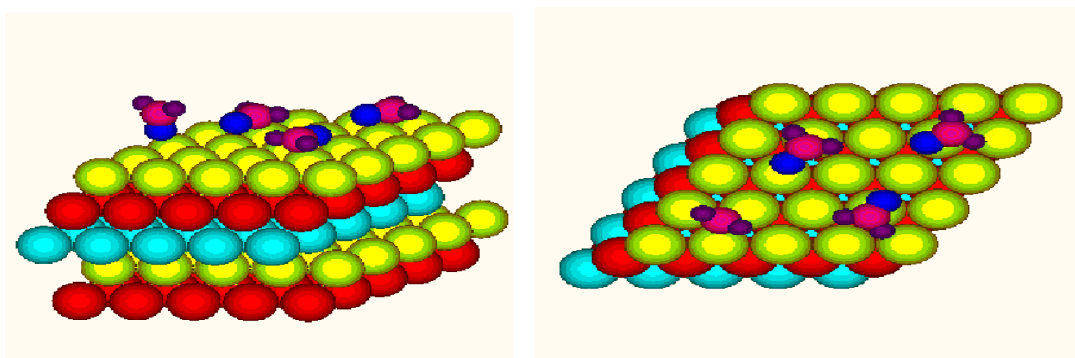


figure 1: adsorption modes for methanal on Pd{111}.

The bridge mode is found to be the mode stable by a significant amount. The higher adsorption energy is accompanied by an elongation of the C=O bond. The molecule lies approximately parallel to the surface though the Pd-O distance is slightly shorter than the C-Pd length.

The structural parameters, electronic density of states and vibrational frequencies of each of the adsorption modes will be presented.

References.

- [1] R. L. Augustine in *Heterogeneous Catalysis for the Synthetic chemist*, Marcel Decker, New York, 1995.
- [2] S. M. Francis, J. Corneille, D. W. Goodman and M Bowker, *Surface Science*, **364** (1996), 30-38.
- [3] F. Solymosi, I Kovacs and Kévész, *Surface Science* **356** (1996) 121-129

- [4] G. Webb and P. B. Wells, *Catalysis Today*, 1992, **12**, 319
- [5] N. R. Avery *Surf. Sci.*, 1983, **125**, 771.
- [6] W. S. Simm, T. C. Li, P. X. Yang and B. S. Yeo, *J. Am. Chem. Soc.*, 2002, **124**, 4970.
- [7] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [8] G. Kresse, and J. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
-

Surface diffusion in rock-salt oxides

J. H. Harding ¹, D. J. Harris ¹, T. S. Farrow ¹, M. Lavrentiev ², N. L. Allan ² and J. A. Purton ³

1. Dept. Physics & Astronomy, University College London, Gower St. London WC1E 6BT
2. School of Chemistry, University of Bristol
3. CCLRC Daresbury Laboratory

Our computer simulations using the Temperature-Assisted Methods developed by Voter and coworkers show that exchange processes dominate ionic surface diffusion on terraces in ceramics. Unlike exchange diffusion in metals, the Coulombic bonding between ions ensures that the ions must diffuse in pairs. Such a molecule moves across the surface by alternate exchanges of the cation and anion with the corresponding ions in the surface while the counterion remains close by, bound by Coulombic attraction. We present results for BaO, SrO and some mixed oxide cases. Step edge processes have also been considered and Kinetic Monte Carlo methods have been used to simulate island growth.

Molecular Dynamics simulation of the Ionic Conductivity in Nafion Membranes

Tien-Jung Huang, J. -T. Yeh and Yu-Tsung Chiu

Industrial Technology Research Institute, Materials Research Laboratories, Rm. 222, Bldg. 77, 195 Sec. 4, Chung Hsing Rd. Chutung, Hsinchu, Taiwan 310, R.O.C

In this research, the parallel molecular dynamics program DL_POLY, is adopted to study the diffusion and ionic conductivity of hydronium ions in polymer membranes, Nafion 117. Simulations were conducted at 373K and six relative humidity swelling values to mimic the experiment of G. Alberti et al. The effect of the swelling of the system on the diffusion of hydronium ion is examined by diffusion theory. Furthermore, the hydronium ion conductivity at different swelling values of Nafion is calculated. The simulated diffusion coefficient of hydronium ions and Nafion molecules is calculated from the Einstein equation. Then the ion conductivities were computed from the Nernst Einstein equation. Finally, the diffusion coefficients and ion conductivity of hydronium ion obtained in this research are consistence with experimental data from the literature.
