All-Electron Path to Energy-Related Inorganic and Organic-Inorganic Hybrid Materials

Volker Blum[*]

[*]*University of Duke*

Invited Talk

This talk highlights work in our group regarding energy-related materials, as well as recent developments in the FHI-aims all-electron electronic structure code that extend the reach of computational predictions in this area. Two application areas of specific interest are (i) graphitic carbon-nitride materials for light-induced hydrogen evolution, and (ii) the computational tuning of electronic levels in crystalline organic-inorganic hybrid perovskite materials with complex organic functionalities. Methodologically, FHI-aims combines the ability to achieve benchmark-accuracy calculations with scalability to large and/or complex periodic or non-periodic system geometries in a single code framework. We touch upon large-scale hybrid-functional calculations, spin-orbit coupling, and basis-set extrapolation for G0W0 energy levels in organic molecules, all of which are critical ingredients to predict ground state properties and electronic excitations in the materials of interest above. The short range information provided by the solid state NMR technique augmented with additional multiscale GIPAW DFT computation has provided sufficient information to initiate the unravelling of the complexities of the vaterite structure. By this combined approach we offer the first experimental evidence that the complex nature of the vaterite system can be described by a dynamic monoclinic carbonate-layered stacking.

Energy Landscapes and Nanomaterials

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Invited Talk

The drive to develop new materials with well-specified properties lies behind the creation of a new class of materials, the so-called nanomaterials. They bridge the gap between classical multi-crystalline, crystalline and amorphous materials, and individual molecules and clusters of various sizes. The combination of small size with (partly) regular extended structure and a relatively large surface-to-volume ratio leads to the existence of many modifications of a nano-object for the same overall composition. This structural plethora allows us to tune the physical and chemical properties of the nanomaterial to a much larger degree than possible in macroscopic materials. On the other hand, it is considerably more difficult to analyze the atomic arrangements of these nano-particles, and thus theoretical tools are needed to determine or even predict the (possible) structures present in the chemical system. Both the investigation of the wide range of possible structures in the system and the analysis of their stability require the study of the energy landscape of the system: the determination of the minima on the landscape and the generalized barriers separating them. Furthermore, the possible design of nanomaterials, e.g. via atom by atom or atom cluster by atom cluster assembly, or via the controlled deposition of molecules on surfaces, relies on information about the properties of the corresponding energy landscape.

In this presentation, we introduce the basic concepts of energy landscapes, and show applications of energy landscapes to nanomaterials[1], ranging from the study of clusters[2] over molecules on surfaces[3] to periodic two-dimensional systems such as C/Si compounds[1,4].

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From Building Blocks to Bulk: Design and Understanding of Nanostructured Materials from the Bottom-up

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Invited Talk

The computational design of new materials employing nanoscale building blocks is described taking examples from both inorganic and organic systems. In the former case we focus on globally optimised nanoclusters and how these can provide inspiration for a wide range of novel nanoporous materials with tailorable properties [1]. This approach strongly suggests that the apparent scarcity of inorganic polymorphs may be simply due to current synthesis limitations and not fundamental chemical/physical constraints [2]. We contrast this situation with that encountered for organic and organometallic materials where the number of experimentally realised covalent organic frameworks (COFs) and metal-organic frameworks (MOFs) appears to be increasing without limit. In this case the bottom-up building block approach closely mirrors the synthetic approach and our predictions can be made with more confidence that they will be experimentally validated. Here we highlight a new 2D COF built from radical building blocks; a synthetic challenge still yet to be accomplished. We show that an appropriately designed material of this type could open the door to multi-functional 2D open-shell organic networks with mechanically controllable properties [3].

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A Multinuclear Solid State NMR and GIPAW DFT Approach Towards the Evaluation of the Proposed Structural Motifs of Vaterite

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The nature of the disorder characterising the metastable vaterite polymorph of the $CaCO_3$ family has been debated in the literature for many years. This phase is extremely important as it is naturally produced on the surface of many living organisms to form a 'semi-amorphous' nanoparticle interface between the exterior of the organism and specific active biomolecules. Furthermore, recent computational and synthetic studies have suggested that $CaCO_3$ polymorphs can grow under both biogenic and abiotic conditions, and this has challenged the models of classical nucleation theory that have underpinned the conventional understanding of the formation of $CaCO_3$.[1-4]

The biggest problem confronting our understanding of vaterite structure is the clear lack of agreement between the structures proposed by characterisation techniques (such as X-ray diffraction, transmission electron microscopy and Raman spectroscopy) and those which have been demomstrated to be energetically favoured by *ab initio* computational methods. This stark lack of agreement has pushed research into considering more complex models for vaterite that extend beyond the notion of vaterite as a unique crystallographic structure. These motifs largely revolve around whether vaterite involves the co-existence of at least two different crystallographic forms in domains that co-exist within a pseudo-single crystal[5] or whether there is some level of higher order superstructure involving energetically favourable stacking of the carbonate layers. Such stacking models comprise of isolated vaterite structures that fall within any one of three approximately isoenergetic basins respectively.[6]

The short range information provided by the solid state NMR technique agumented with additional multiscale GIPAW DFT computation has provided sufficient information to initiate the unravelling of the complexities of the vaterite structure. By this combined approach we offer the first experimental evidence that the complex nature of the vaterite system can be described by a dynamic monoclinic carbonate-layered stacking.

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Identification of Preferential Sites for Intra-molecular Advanced Glycation End Products Formation in Fibrillar Type I Collagen And Their Effect on the Function of Collagenous Tissues: An All Atom Molecular Dynamics Approach

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The functionality of the musculoskeletal system is believed to be jeopardised by glycation and the accumulation of advanced glycation end products (AGEs). Some AGEs are generated by the non-enzymatic reaction of oligosaccharides with proteins in physiological systems. In collagen rich tissues, such as tendons and ligaments, AGEs are believed to form covalent cross-links within and between collagen molecules, thereby changing the properties of the tissue. Detrimental collagen stiffening properties are believed to play a significant role in several age-related diseases such as osteoporosis and cardiovascular disease. This study aims to identify specific sites involved in the formation of AGE cross-links within the collagen molecule, based on a relative energetics model using a proven fully atomistic MD approach. The results of this study will help to determine to what extent the position of these sites will affect the biological function and the mechanical properties of the tissue.

A distance-based criterion search was used to identify lysine and arginine residues within 5 Å of each other within a collagen molecule. Fully atomistic MD simulations, exploiting the D-band periodicity to replicate the dense fibrillar environment, were then conducted under pseudo physiological conditions in AMBER12. A site is a likely candidate for AGEs formation if the total energy of the collagen molecule is lower in the presence of a cross-link compared to an unbound glucose. Using a candidate cell and matrix interaction domains map of the collagen fibril, we then transpose our cross-link positions to determine their biological impact. Constant velocity steered MD simulations were conducted to calculate changes in the stiffness of the collagen molecule.

Of the 24 positions identified based on the distance criteria, 6 sites were found to be energetically favourable compared to the unbound glucose collagen model, for glucosepane and 6 for DOGDIC with only 1 duplicate site. The local environment around the site has a significant effect on the energetics, with the sites within the gap region being more likely to have exothermic formation enthalpies. A number of favourable sites have potential for huge implications on the biological function of collagen, as they are within sites where key collagen-biomolecule and collagen-cell interactions occur. For example, the formation of glucosepane was found to be energetically favourable within close proximity of the Matrix Metalloproteinase-1 binding site, which could potentially disrupt collagen degradation. Our 3-dimensional collagen fibril model has identified likely sites for AGEs formation within collagen. The positioning of these sites is likely to have a significant effect on tissue function and integrity.

The Effect of Surface Chemistry on Protein Adsorption

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One of the most important aspects for biomaterial design is its interaction with living tissue, which can cause a foreign body reaction and ultimately rejection of a medical implant. Proteins play a key role in this process because they can adsorb on the biomaterial surface and act as anchors for subsequent cell binding. A main factor that governs protein adsorption, and thus cell binding, is the chemistry of the biomaterial surface.

In this project we use a fibronectin fragment to investigate its adsorption on a variety of surfaces. The fragment consists of the modules 8 to 10 of the type III fibronectin (8-10FNIII) and contains the cell-binding and synergy sites that mediate the protein-cell interaction through integrins on the surface of the cell. The biomaterial surfaces that we study cover a range of different properties regarding their charge and hydrophilicity, and include silica and self-assembled monolayers. Besides experimental techniques, we perform fully atomistic Molecular Dynamics simulations using NAMD   with an explicit solvent model for a more realistic representation of the protein-surface interactions. The combination of both computational and experimental techniques, and the way they complement and guide each other during this project, provides us with a better understanding of the protein adsorption process.

Modelling structural transformations in guest-adaptable MOFs

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Metal-organic frameworks (MOFs) are crystalline porous materials composed of inorganic nodes, either single ions or clusters of ions, bridged by organic linkers through metal-ligand coordination bonds. Recently, several biomolecules, such as amino acids, nucleobases, saccharides and peptides, were used as organic linkers in MOF synthesis, mainly because of the diversity of their metal binding sites. The incorporation of biomolecules in MOFs also attracts particular attention because they can improve the biocompatibility of the final products, enhance the structural and chemical diversity of the internal surfaces of MOFs, and afford chiral frameworks that may have unique separation and catalytic properties.

We present a new peptide-based MOF, [ZnCar]·DMF, which is assembled from Zn^{2+} and carnosine (Car), a natural dipeptide with the molecular structure β-alanyl-L-histidine. The structure displays 1D permanent porosity upon removal of DMF and is shown to undergo controlled structural transformations in response to the guest molecules present in the pores.

We use a combination of DFT and classical force-field calculations to study the role of the solvent in the structure control and to predict adsorption properties for gaseous and liquid guests. In particular, we identify the molecular mechanisms responsible for an unusually high adsorption energy for CO_2 and explore the capability of the material for separation of butanol enantiomers.

To identify new targets for materials design we use DFT to assess thermodynamic stability of hypothetical structures with the topology of [ZnCar] but built using linkers that are shorter or longer than carnosine. In particular, we show that the presence of an extra CH_2 group in the peptidic chain of carnosine, compared to classic dipeptide α-glycyl-L-histidine, is responsible for the formation of the observed 3D periodic structure, while an equivalent hypothetical structure for the shorter classic α-dipeptide is unstable.

The Role of Solvent in the Self-Assembly of m-aminobenzoic acid: a Density Functional Theory and Molecular Dynamics Study

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Solvent can have significant effects on the solution thermodynamics and crystallisation kinetics of organic compounds from solution. In the present work, the early stages of aggregation of the organic molecule m-aminobenzoic (mABA) in two different solvents, dimethyl sulfoxide (DMSO) and water were studied using a combination of quantum chemistry, molecular dynamics and metadynamics simulations. Density functional theory (B97-D and M06-2X) calculations with the continuum solvation SMD model were used to probe the potential energy surface of molecular clusters of m-aminobenzoic acid $(mABA)_n$ (n = 2-6), locate the low-lying energy structures, and compute the Gibbs free energies of $(mABA)_n$ in solution. In DMSO, the formation of the classic carboxylic $(mABA)_2$ dimer is exergonic and thermodynamically more favorable than in water. On the other hand, the self-association of dimers to form tetramers $(mABA)_4$ is thermodynamically possible in water but not in DMSO. The structure of the most stable dimer and tetramer in solution correspond to classic carboxylic dimer π−π stacking synthon found in the crystalline form-II of mABA. Molecular dynamics simulations of mABA solutions at different concentrations show a significant solvent-dependent aggregation behaviour of mABA: in water, even at low concentrations, mABA molecules spontaneously form H-bonded π-π stacking molecular clusters whereas in organosulfur solutions the molecules of mABA are in a much more solvated state. Metadynamics simulations and microsolvation density functional theory calculations are used to rationalize the low level of mABA aggregation in DMSO compared with water by revealing that in DMSO the energetic barrier associated to the desolvation of mABA molecules to form dimers and the strength of the mABA-solvent interactions are significantly larger than in water. This work shows how the solvent and its specific interaction with the organic solute molecules influence both the thermodynamics and kinetics of molecular self-assembly.

The Identification and Passivation of Performance Limiting Defects in 4H-SiC Devices: From the Bulk to the Interface and Beyond. An EDMR and *ab initio* Study

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Silicon Carbide (SiC) based devices have been an emergent device technology for the last 20 years. Huge leaps forward have been made during this time, taking devices from the lab bench to commercially available diodes, MOSFET, and integrated power modules. For the full potential of SiC to be realized, a number of challenges remain to be overcome. Key amongst these is the high defect concentration inherent in SiC devices, to tackle this, defect identification and passivation is critical.

Combining the single defect selectivity of electrically detected magnetic resonance measurement (EDMR) with theoretical modelling gives the potential to unambiguously identify performance limiting defects within fully processed devices. Comparing the EPR parameters, defect symmetry, charge state, multiplicity, and elemental composition allows defect identification with a high degree of confidence. Through this combination of techniques a systematic approach has been formulated to facilitate defect identification. Once a defect is identified the interaction of the defect with various atomic and molecular species are considered. This allows a systematic approach to passivation, moving away from the current bottom-up approach.

This approach was initially used to study defects within N-implanted pn-junctions, allowing the $N_C V_{Si}$ to be identified as the main source of N-dopant deactivation and poor mobility. The work of Kimoto *et al.* and Miyake *et al.* showed an improvement in device characteristics after a high temperature C-anneal. This was suggested to be due to the 'healing' of V_C present within the lattice. With the $N_C V_{Si}$ identified a competing mechanism has been identified resulting in the conversion of the $N_C V_{Si}$ defect into the $N_C C_{Si}$ which shows excellent agreement with the available experiment data.

From the simple case this approach was extended to the interface defects, which after an exhaustive study allowed the P_{bc} defect to be positively identified as the defect observed with EDMR. This has given a valuable insight into the nature of the SiC / SiO_2 interface and tantalising hints as to how these defects may be efficiently passivated.

Early Stages of Epitaxial Graphene Growth: Hydrocarbon Decomposition and Nucleation of Carbon Clusters

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One method of growing epitaxial graphene is temperature programmed growth (TPG). In this method hydrocarbon molecules are deposited onto a transition metal surface at room temperature and then the temperature is increased in order to facilitate the thermal decomposition of the hydrocarbons and lead to the formation of graphene flakes.

The thermal decomposition mechanism of ethylene was investigated with a combined approach of experimental and theoretical techniques. X-ray photoelectron spectroscopy (XPS) experiments were used along with core level binding energy calculations to identify the evolution of species on the Ir(111) surface as the temperature is increased. A complete reaction scheme incorporating all possible reactions between the various C_nH_m species, from ethylene to C monomers and dimers, was also developed. The energy barriers for each reaction were calculated using the DFT based nudged elastic band method. Using these energy barriers the kinetics of the thermal decomposition were determined by both solving rate equations for the reactions, and by developing a kinetic Monte Carlo (KMC) code to include spatial effects. In the latter case the resulting temperature evolution shows an excellent agreement with the experimentally determined reaction pathway. The molecular dissociation mechanism begins with the dehydrogenation of ethylene to vinylidene (CH_2C), which is then converted to acetylene (CHCH) by the removal and addition of an H atom. The C-C bond is then broken to form methylidyne (CH), which finally dehydrogenates to produce C monomers that are available for the early stage nucleation of the graphene islands.

Following from this nucleation of carbon clusters prior to the formation of graphene islands was also investigated. The number of carbon atoms in the critical cluster, which is equally likely to grow or to shrink in the prevailing conditions, was determined by the considering appropriate nucleation free energy. Using ab initio density functional theory calculations, the free energies of carbon clusters (containing up 16 C atoms) on the Ir(111) surface were calculated based on the configurational and vibrational contributions. The results are strongly dependent on temperature, showing its importance to cluster growth. Furthermore, we find that different types of cluster (linear, compact, dome etc.) are more stable over different size ranges. Based on this mechanism, which allow the clusters to reconstruct, their structure are investigated.

Physical Properties of MgSiN$_2$

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Ultraviolet light-emitting diodes (UV-LEDs) based on wurtzite structure III-nitrides currently have low efficiencies and lifetimes. The light-emitting quantum well (QW) regions of most UV-LEDs are based on AlGaN alloys, but unfortunately it is not possible to achieve lattice-matched and polarisation-matched QW heterostructures with appropriate band gaps and band offsets using this alloy system. It is therefore motivated to search for alternative wide band gap nitride materials that could introduce additional degrees of freedom for UV-LED device design, either to assist in the lattice-matching or in the polarisation-matching within the active light-emitting region.

The Group II-IV nitride semiconductors are emerging as promising alternatives for these applications. These materials have wurtzite-derived orthorhombic crystal structures and can be obtained by substituting pairs of Group III (e.g. Al, Ga or In) atoms in a III-nitride for a single Group II (Be, Mg, Ca or Zn) atom and a single Group IV (C, Si, Ge or Sn) atom. We have recently focused on the II-IV nitride MgSiN$_2$ from both theory and experiment. On the theoretical side, density functional theory has been used to obtain accurate structural properties, elastic constants and piezoelectric properties of MgSiN$_2$. As an example, we have shown that MgSiN$_2$ has a large indirect band gap of similar size to the direct band gap of AlN [1], while having a crystal size which is intermediate between AlN and GaN. MgSiN$_2$ should therefore facilitate better lattice matching during film growth and in the creation of heterostructures compared to III-nitrides, and therefore constitutes a good candidate material to be used in novel high efficiency UV-LEDs. We have also studied the effects of adding Al to MgSiN$_2$, thereby creating a $(MgSi)_{2-2x}Al_{2x}N_2$ alloy and found that the band gap varies slightly with increasing amount of Al and, furthermore, for relatively small Al concentrations the band gap becomes direct as in the case of wurtzite AlN.

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Defect and Band Engineering in Sn-based Oxides

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The most commercially successful TCO so far is tin doped indium oxide (Indium Tin Oxide – ITO), which has become the industrial standard TCO for many optoelectronics applications; the ITO market share was 93% in 2013. Its widespread use stems from the fact that lower resistivities have been achieved in ITO than in any other TCO; resistivities in ITO have reached as low as $7.2 \times 10^{-5} \Omega$ cm, while retaining >90% visible transparency. In recent years, the demand for ITO has increased considerably, mainly due to the continuing replacement of cathode ray tube technology with flat screen displays. However, indium is quite a rare metal, having an abundance in the Earth's crust of only 160 ppb by weight, compared with abundances for Zn and Sn of 79000 ppb and 2200 ppb respectively, and is often found in unstable geopolitical areas. The overwhelming demand for ITO has led to large fluctuations in the cost of indium over the past decade. There has thus been a drive in recent years to develop reduced-indium and indium-free materials which can replace ITO as the dominant industrial TCO. Recent research has therefore focused both on developing alternative TCOs, such as SnO_2, ZnO, and $BaSnO_3$, which are all more abundant and less expensive. In this presentation I will focus on the electronic structure and defect chemistry of Sn-based TCOs, critically analysing them as viable alternatives to ITO.

Enhancing the Reducibility of CeO$_2$: The Role of Divalent Dopants

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CeO2 (ceria) has gained widespread recognition for its utility in heterogeneous catalysis, with notable applications including three way catalysts[1] and the water-gas shift reaction.[2] The catalytic utility of ceria, which stems partially from the ease with which Ce(IV) ions are reduced to Ce(III) thus facilitating the removal of oxygen ions, has led to the material's use not just as a support for metal catalysis but also as a catalyst itself. Incorporation of divalent dopant ions such as Pd and Pt to form noble metal ionic catalysts has been shown to be highly effective in catalysing reactions such as NO and NO$_2$ reduction, CO oxidation, methane oxidation, and the Heck reaction.[3-6]

To determine the fundamental causes of the observed catalytic enhancement upon Pd and Pt doping, density functional theory calculations with a +*U* to account for on-site Coloumbic interactions have been performed on Pd- and Pt-doped low index surfaces ({100}, {110}, {111}) of ceria. Structural optimisation predicts that while Ce ions adopt cubic coordination in the fluorite lattice, the d^8 divalent dopant ions are preferentially present in a square planar environment. Upon substitution of Pd(II) and Pt(II) for Ce(IV), structural distortion in the coordination sphere of the dopant to achieve square planar configuration results in some neighbouring oxygen ions being under-coordinated and weakly bound. Oxygen vacancies are thus more easily created, lowering the reduction energy and enhancing the catalytic efficacy of ceria.

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Surface Composition of Magnesium and Calcium Rich Minerals

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Modelling of minerals and their interfaces in contact with water and CO_2 is of key importance for understanding the interfacial processes in environmental conditions and relevant to many industrial applications.

In our research, we have applied density functional theory to predict the surface composition of magnesium (Mg) and calcium (Ca) rich minerals. We focused on two applications where these minerals are of interest.

In the first case, the construction industry is investigating the usage of low-carbon/energy lime materials to reduce the reliance on cement-based material, although the cost effective fast setting time of cements hinders the large scale application of lime. Therefore, the mechanisms of dissolution and carbonation of the mineral phases involved have to be understood in order to improve the setting time of the putty.

In the second case, Mg and Ca rich minerals are the main constituents of the nuclear sludge formed by the corrosion of radioactive Magnox fuel, which is stored underwater at high pH (>10) and high $p(CO_2)$. The goal here is to understand how radionuclides are adsorbed or incorporated into the sludge. However, as there is a limited knowledge of the composition of the sludge, the design of a successful treatment strategy is hindered.

In each case, we discuss how simulations can give useful insights into the surface composition and processes.

Explaining the Stability of the Polar Surfaces of ZnO Using Interatomic Potentials

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Zinc oxide is an important wide-gap *n*-type semiconductor with uses ranging from electronics to catalysis. One of the most puzzling features of this material is the stability of its polar surfaces –the Zn-terminated (0001) and the O-terminated (000-1), which is not evidenced in other oxides. Understanding the stability of ZnO polar surfaces will help to improve its performance, e.g. identifying the active sites of the Cu/ZnO catalyst used in the synthesis of methanol.

We investigate the origin of the stability of the ZnO polar surface using global search techniques coupled with methods of interatomic potentials and density functional theory. Morphology and mechanisms of the stabilisation of the polar surfaces are related to thermodynamic and optical properties of ZnO.

To model a ZnO polar surface it is essential to remove the inherent dipole, which is typically achieved in simulations by altering the number of atoms in the terminating layers. We employ one-sided 2D-periodic slab surface models, with the reconstruction done by removing Zn or/and O atoms from the surface and spreading compensating charge uniformly over the slab bottom. According to our calculations, the optimum ratio of Zn (or O) vacancies is very close to $|VZn - VO| = 6$ (the remaining dipole is compensated by the use of point charges). A cell size of (5x5) was chosen because of both: findings in STM images and our dipole calculations with respect of the cell size.

The global search using Monte Carlo routines, as implemented in our in-house Knowledge-Led Master Code, probed more than 500, 000 different reconstructions using different Zn/O stoichiometries at the top layers, in both polar surfaces. The lowest energy configurations reveal definitively triangular patterns on the Zn-terminated surface in excellent agreement with experiment and DFT. We calculated big surface energy differences among different stoichiometries in the Zn side, which might be an explanation of the well-defined patterns observed in STM images. The variation in the surface energy among the different stoichiometries at the O-terminated side is smaller when compared to the Zn-terminated side, which explains the difficulty to attribute one single reconstruction pattern to the (000-1) surface.

Numerical Analysis of Pickering Emulsion Stability: Insights from ABMD Simulations

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Particles and nanoparticles (NPs) can be used to stabilize the so-called Pickering emulsions. Indeed, Pickering emulsions have attracted enormous attention because of a variety of applications including cosmetics, food-stuffs, and waste-water treatment. Qualitative analysis is thus needed to improve the stability of Pickering emulsions and understand the fundamentals of the phenomena that contribute to this stability.

Because NPs are used as emulsifiers, their characteristics have critical effects on the emulsions properties. The density of nanoparticles on the droplet surface is known to be the most important parameter for this stability. Indeed, the interfacial tension of the droplet depends strongly on the NPs coverage, which also depends on the NPs affinity to the interface. Furthermore, when the density is large enough, the three-phase contact angle discriminates between nanoparticles that are effective at stabilizing emulsion and those that are not. To be effective in preventing droplet coalescence, the solid particles should be able to prevent fluid molecules to transfer from one droplet to the other when the droplets are not at contact. Moreover, particles, once adsorbed, are rather difficult to displace from the interfaces. Janus nanoparticles play a specific role in the stability as they are believed to be more effective than other type of nanoparticles (like homogeneous NPs) when Droplets are forced to coalesce. Indeed, Janus NPs typically have high adsorption energies, and therefore are expected to pack densely at an interface, achieving large interfacial tension reduction.

To understand the fundamentals of the behavior of NPs adsorbed at oil/water interfaces at a mesoscopic level, Dissipative Particle Dynamics simulations are implemented. We show that, for a sufficiently dense layer of particles around the emulsion droplets, the stabilization mechanism can strongly depend on the collision speed achieved numerically during the merging process. This is specific to a coalescence mechanism governed by the rheology of the interfacial region. Considering Adiabatic Biased Molecular Dynamics simulations where the system is forced to coalesce *adiabatically*, we highlight that, for pulling velocities sufficiently slow compared to the rate of drainage of the thin liquid films trapped between the coalescing emulsion droplets, the ability of the NPs to stabilize Pickering emulsions is not discrimated by the shape deformation of the droplet, but by NP mobility and the associated caging effect threshold

Local Electronic Properties of Cu and its Oxide Clusters on CeO$_2$ Surface

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*e05-surfin-**cat***

Introduction

Cu/CeO$_2$ based catalysts have attracted great interest recently for heterogeneous catalysis because of their high catalytic activities towards NO reduction and CO hydrocarbon oxidation.[1] Similarly, the CuO/CeO$_2$ mixed-oxide catalyst has been experimentally shown to have high activity and selectivity CO oxidation in hydrogen-rich mixtures for CO clean-up in hydrogen mixtures for proton-exchange membrane fuel cells.[2] Therefore, in the current study we have investigated the local electronic properties of Cu and CuO clusters supported on CeO$_2$ surfaces. In catalytic applications the ability of ceria to release oxygen by forming oxygen vacancies under oxygen-poor (reducing) conditions and conversely, to store oxygen by filling oxygen vacancies under oxygen-rich (oxidizing) conditions is employed to stabilize the air-to-fuel ratio at the desired level. This property is related to the quantum process of electron localization and delocalization. In CeO$_2$, oxygen has a formal valence of -2 (O^{2-}) and when an oxygen atom is released, in the form of (half) an oxygen molecule, i.e. 2Ce(IV)O$_2$ → Ce$_2$(III)O$_3$+0.5O$_2$ two electrons are left behind. These electrons localize on the *f*-level of two Ce atoms, which change their formal valence from +4 to +3. The theoretical description of Ce (III) and Ce(IV) oxide materials is of primary importance for understanding their functioning and advancement of their practical applications. This is not a simple task since the additional electron, which is introduced on the Ce centre upon reduction of Ce(IV) to Ce(III) is a strongly correlated *f* electron. Hence, from a computational point of view, a balanced theoretical description of CeO$_2$ and Ce$_2$O$_3$ oxides is not straightforward. In this work we address these issues using Density Functional Theory (DFT) to clarify the local electronic properties of Cu and (CuO)$_n$ clusters on CeO$_2$ surfaces.
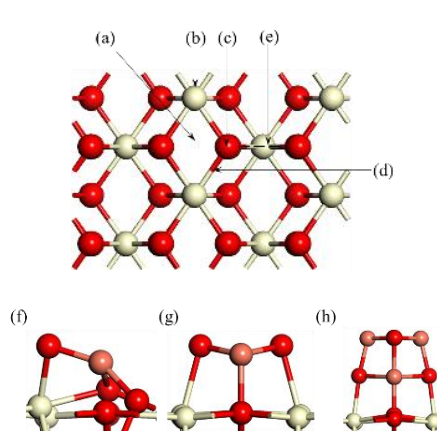
Computational Details

The plane-wave based VASP code is used, employing the PBE exchange-correlation functional with an energy cut off of 550 eV. A 4×4×1 Monkhorst-Pack k-point mesh is used for sampling the surface Brillouin zone. Quasi-Newton technique is used to relax the atomic positions till the forces on atoms are less than 0.01 eV/Å. Conventional density functional schemes that apply different flavors of the density approximation underestimates the strong on-site Coulomb repulsion of the Ce 4*f* electrons and consequently fail to capture the localization. Therefore, in this study we have employed the DFT+U approach and for all the calculations we used a U value of 5.0 for Ce and Cu atoms.[4,5]

Figure 1. (a) Hollow (b) On top of Ce, (c) on top of oxygen atom, (d) on bridge site of O – Ce (110) surface and (e) long-bridge-site and (f) CuO, (g) (CuO)$_2$ and (h) (CuO)$_4$ clusters on pristine CeO$_2$(110) surface.

Figure 2. Partial density of states of 4*f* orbitals (a) before and (b) after adsorption of Cu atom on CeO$_2$(110) surface.
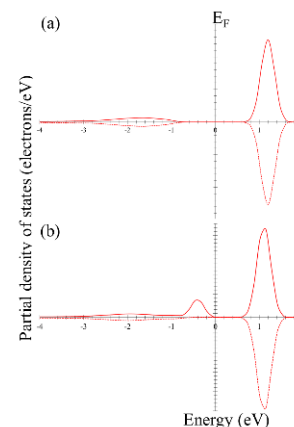
Results and Discussion

First, the stable sites for the adsorption of a Cu adatom on different sites on CeO$_2$(110) [as shown in Figure 1 (a–d)], is calculated. From our analysis we find that the Cu adtom on the top-long-bridge site is most stable i.e., on fully relaxing the Cu adatom on top of O-atom [Figure 1(c)] move to the long-bridge-site between two oxygen atoms, [Shown by a black dashed line in Figure 1(e)]. The Cu–O distance is measured as 1.753 Å. We then compare the partial density of states (PDOS) for pristine and Cu adsorbed CeO$_2$(110) surface for understanding the nature of interaction between adsorbed Cu and the CeO$_2$(110) surface. It is seen that after the Cu adsorption signatures due to the *f*-orbitals appeared near the Fermi energy, which otherwise is absent for pristine CeO$_2$ surface [Figure 2 (a–b)]. This confirms electron transfer from Cu 4*s* orbitals to Ce 4*f* orbitals.[6] This also show that there is more than just a physical interaction between Cu and CeO$_2$ surface. We then extend our studies to understand the detailed local geometrical and electronic properties of Cu on surface and in the bulk of CeO$_2$ with an oxygen defect and on (CuO)$_n$ clusters, where n=1, 2 and 4 [Figure 1 (f – h)] interactions on CeO$_2$(110) and CeO$_2$(111) surfaces. This study is further extended to investigate structure-property relationship using hybrid QM/MM methods as implemented in ChemShell.

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Density Functional Theory Study of the Greigite (Fe$_3$S$_4$) Surface to Bulk Oxidation

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e05-react-**lee**

Greigite (Fe$_3$S$_4$), the sulfide counterpart of the spinel-structured magnetite (Fe$_3$O$_4$), is attracting considerable interest for the catalytic conversion of CO$_2$ into precursors of fine chemicals under sustainable conditions. The enhancement of the catalytic activity of Fe$_3$S$_4$ surfaces due to a passivating oxidation, where sulfur is replaced by oxygen, and the mechanism of oxygen ion migration towards the bulk of the partially oxidised catalyst are not fully understood on the atomic scale.

Here, the early oxidation processes on the Fe$_3$S$_4$(001) surface by water and the surface to bulk oxygen ion migration in the partially oxidised material are investigated computationally using density functional calculations. We have proposed three pathways for the oxidation of the (001) surface. Low levels of H$_2$O coverage and basic conditions seem to be essential, leading to the most favourable energetic landscape for the oxidation of the Fe$_3$S$_4$(001) surface. Some pathways are followed by a solid-state diffusion of the O atom towards its most stable position. We have derived the thermodynamic and kinetic profile for each mechanism and plotted the concentration of H$_2$S and protons in aqueous solution and thermodynamic equilibrium with the stoichiometric and partially oxidized Fe$_3$S$_4$(001) surface as a function of the temperature. Changes of the simulated vibrational frequencies of the adsorbed intermediates are used as a means to characterise their transformation.

We also estimated the substitution energies and found that replacing a surface sulfur atom is more exothermic in the top layer of the (001) and (111) surfaces than in the bulk. However, by explicit calculation of the substitution energies at different depths, we found that oxygen atoms are stabilised by a further 0.27 eV when they are located in the first sub-surface layer along the [001] direction. This suggests that oxygen atoms tend to accumulate near the surfaces of the material, passivating the surfaces and ensuring good catalytic performance over relatively long periods of time. The insight provided in this study is valuable for the future optimization of Fe$_3$S$_4$ nanoparticles for the catalytic reduction of CO$_2$ in realistic working conditions.

Formaldehyde Oxidation on Ytrria-Stabilized Zirconia

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*e05-react-**cat***

Yttria-stabilizied zirconia (YSZ), commonly used as a support for metal particle catalysts, has been shown to be active for catalytic partial oxidation of methane (CPOM) in its own right[1]. CPOM on YSZ has been shown to proceed via a Mars-van Krevelen mechanism, with surface vacancies providing sites for oxygen activation, with exclusively lattice oxygen contained in oxidation products. Furthermore, formaldehyde is proposed to be a major reaction intermediate and it has been shown that formaldehyde oxidizes to surface formate on pre-activated YSZ surfaces[2].

We have investigated the surface reduction of YSZ in order to provide active sites for molecular oxygen activation. We find that molecular oxygen (O_2) is activated by the reduced YSZ surface, strongly adsorbing to the oxygen vacancy and resulting in a partially reduced surface oxygen species (Figure 1), This activated oxygen species provides a pathway for hydrogen abstraction from formaldehyde, resulting in oxidation to surface formate, as observed experimentally.
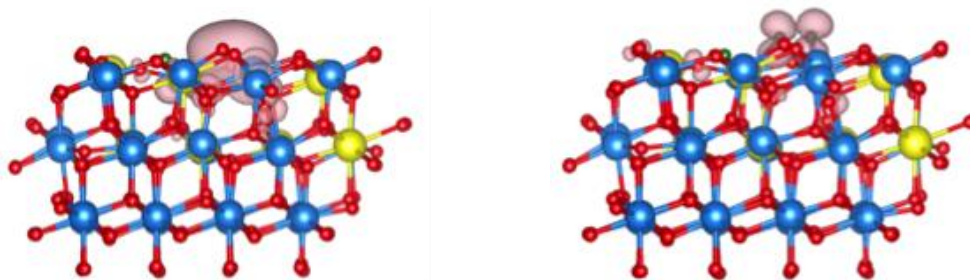
Figure 1. Reduced YSZ surface (left) and reduced surface with molecular oxygen adsorbed into the surface vacancy (right).

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Adsorption and Diffusion of Aromatics on Metal Surfaces

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Predicting the structure and the arrangement of supramolecular materials is a long-standing scientific challenge for computational material chemistry. By studying the self-assembly of 2D materials on solid surfaces one can greatly simplify the problem by reducing the available degrees of freedom. Furthermore, atomic-scale resolved STM measurements allow to compare and benchmark the results of the density functional theory calculations with real-space experimental data. The potential energy landscapes determined by DFT calculations can also be rigorously tested by comparing the calculated diffusion barriers with the results obtained by surface-sensitive scattering probes, such as He diffraction spectroscopies. Finally, first-principles calculations on adsorbed aromatics molecules constitute a test for the robustness and transferability of dispersion-corrected DFT.

In the last several years we have studied the adsorption and diffusion of a series of aromatics molecules on metal surfaces: cyclopentadienyl[1], pyrrole[2], thiophene[3] and benzene; and demonstrated the capability of DFT to predict the structures, energetics and dynamics of these prototypical organic precursors. We discuss the effect of charge-transfer[1], zero point energies[2] and rotational degrees of freedom[3] on the adsorbate mobility. Ongoing computational and experimental work on sulphonic macrocycles allow us test the predictive power of DFT calculations for larger and more realistic functional materials that could find real-world applications as nanoporous materials for sensor technology.

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A DFT Study of Free and Supported Au-Rh Nanoalloys

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Density functional theory calculations were performed on both free and $TiO_2(110)$-supported 38- and 79-atom truncated octahedron Au-Rh nanoalloy clusters at various compositions to investigate Au-Rh alloying properties at the nanoscale and the influence of the support. Furthermore, H_2, O_2, and CO adsorption properties were also investigated with a view to estimating and optimizing the catalytic performance of Au-Rh nanoalloys. Among the structures studied, the $Rh_{core}Au_{shell}$ morphology was found to be the lowest energy structure for bare clusters, while molecular adsorption energies are greatest on surface Rh atoms. It is shown that multiple CO and O_2 adsorption can change the stability order of nanoalloy clusters selectively. For example upon adsorption of 6 molecules of CO (or O_2) the centroid (or hex) structure, which has 6 surface Rh atoms, becomes the lowest energy structure for the $Au_{32}Rh_6$ composition. It is also shown that Janus type clusters become more competitive to the $Rh_{core}Au_{shell}$ on the $TiO_2(110)$ support due to surface-induced stabilisation.
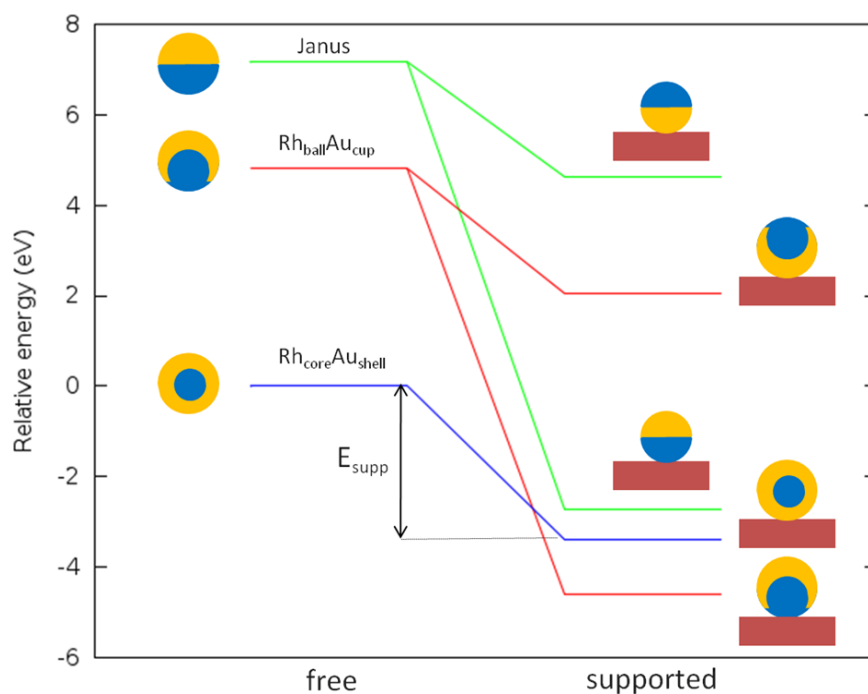
Software for Structure Prediction at the Nanoscale

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We have developed a software package KLMC (Knowledge Led Master Code)[1] that utilises massively parallel computer platforms and third-party computational chemistry software to perform stochastic sampling and systematic searches for local and global minima on energy landscapes. Our software enables us to investigate diverse physical and chemical phenomena including prediction of atomic structure of nanoparticles, surface reconstructions of polar surfaces, and defect complexes. Automation within KLMC[1] alleviates repetitive or mundane computational tasks or processes typically required in simple task farming, global optimisation routines such as basin hopping and genetic algorithms, and statistical sampling. KLMC has recently been successfully exploited to predict plausible structures of nanoparticles of binary compounds[1,2] (e.g., ZnO, CdSe, MgO, KF, LaF_3); mechanisms of polar surfaces reconstruction[3] (including $KTaO_3$ and ZnO); nucleation and growth of nanoparticles on metal supports[4] (e.g., ZnO on Ag).

Complementary to KLMC, we are now developing a novel nanocluster database WASP@N (Web Assisted Structure Prediction at the Nanoscale)[5], in which we intend to link the web-interfaced database and compute nodes dedicated to help scientific community to search, discover and disseminate nanoclusters. The web-interfaced database is designed to calculate physical properties of the uploaded nanoclusters (e.g. symmetry, moments of inertia, and electrical dipoles), to find similar structures which were previously uploaded and to perform on-demand calculations.

Combining KLMC and WASP@N provides a powerful solution to the problem of structure prediction at the nanoscale for materials scientists from data mining to visualisation.

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Simulations of CO$_2$ Capture by Porous Metal-Organic Framework Materials

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One option to permit the continued use of fossil fuels without releasing CO$_2$ into the atmosphere is to capture the gas at source within the combustion process and then store it within geophysical reservoirs. In response to the need to find materials for the gas capture process we have used molecular dynamics simulations to study the absorption of CO$_2$ by a range of zinc imidazolate metal-organic framework structures. These materials are promising because they form porous network structures that are direct analogies of silicate zeolites, but with larger internal pores and channels. The talk will describe the approach used to develop the force field (parameterized from *ab initio* energy surfaces with charges developed using the distributed multipole analysis method) together with the approach taken to simulate the absorption process (compressing a gas above a slab of material). These models were used to assess the stability and flexibility of the structures, and we identified a number of phase transitions on changing temperature and pressure. The results from the simulations show clearly the mechanism of absorption of the gas stream, and we were able to compare the behavior seen in different materials. In some cases the absorption of gas caused a reversible structural phase transition. We also demonstrated that it is possible to use heat to recover the gas from the material for subsequent storage. There are few experimental results with which to compare our results, but where there are results the comparison is good.

Yttrium stabilised Cubic Zirconia

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Zirconia is an important industrial material. It has been used on oxygen pump, oxygen cells and fuel cells due to its high oxygen conductivity. However, pure Zirconia, which is monoclinic structure, does not appear high oxygen conductivity at room temperature and pressure. That property can only be achieved by doping high concentration of divalent or trivalent cation to form cubic structure. We used MD simulation to study this monoclinic to cubic transition, and observe significant microstructures transforming to cubic structure in domains with increasing Y. The whole structure transform to cubic phase after Y concentration reaches to 20%, which agree with the experiment result. We separate cubic phase in the structure by comparing the coordination with cubic phase. The concentration and correlation length of cubic structure has also been calculated to quantify this transition.

Accelerated Discovery of Two New Structure Types in a Complex Inorganic Phase Field

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In this work we present the use of computational "probe" structures to accelerate the exploration of the unreported Y-Sr-Ca-Ga-O phase field, with the results guiding subsequent synthesis. Probe structures are created using a Monte-Carlo implementation of the Extended Module Materials Assembly (EMMA) method, with density functional theory and force fields used to calculate energies. Once probe structures have been calculated, the convex hull (including known materials) of the phase field was then constructed and the energies of the probe structures compared to the hull.

These calculations indicate the presence of a low energy region, where the energies of probe structures were comparable to known binary and ternary oxides, indicating an area of the phase field where new compounds may be found. Synthesis was then focused around this region. Single crystal and powder crystallography reveal the existence of two new oxide materials: a 4 x 4 x 4 triclinic supercell of $A_{1-x}B_{1-y}O_{3-z}$ Perovskite and a layered $A_{2.5}B_3O_7$ Melilite material (fig 1), with both materials containing novel co-ordination environments.
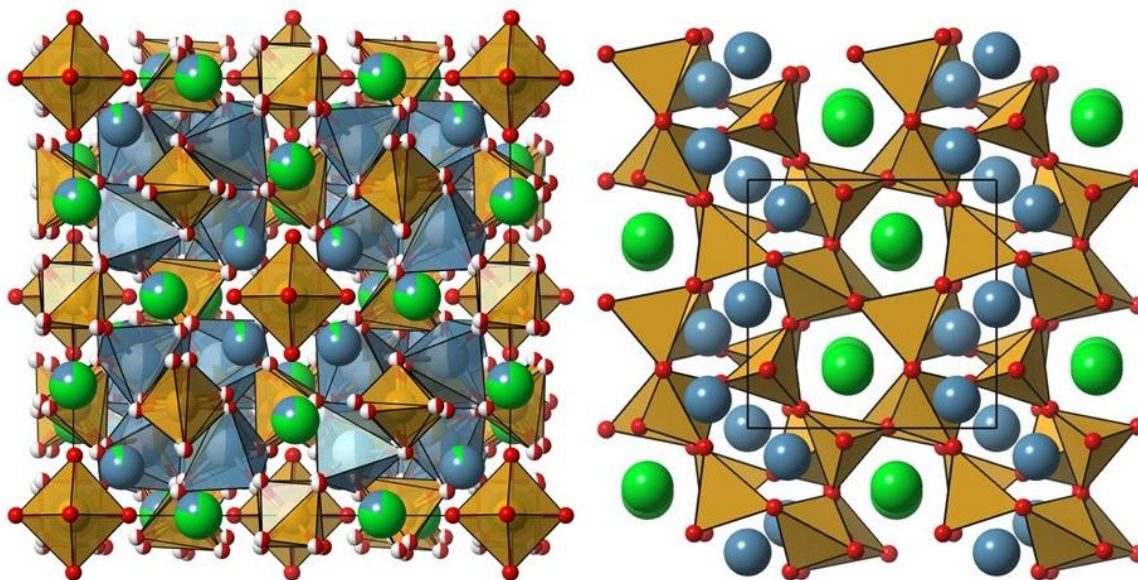

Fig1. The two new structures discovered within this work: Perovskite related (left) and Melilite related (right).

Accurate Exchange-correlation Energies for Warm Dense Matter

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*e05-gener-**fou***

Interest in warm dense matter has increased dramatically during the past few years because of its importance to many fields of active research including inertial confinement fusion, the constitution of planetary interiors and the laser irradiation of solids. Recent attempts to parameterize finite-temperature density functionals for the simulation of warm dense matter have relied on restricted path-integral Monte Carlo (RPIMC) results for the uniform electron gas [Phys. Rev. Lett. **110**, 146405 (2013)]. Subsequent configuration path-integral Monte Carlo (CPIMC) results [Phys. Rev. Lett. **55**, 136 (2015)] cast into doubt the validity of RPIMC in the warm dense regime, with significant differences found at low temperatures and high densities. This work uses the interaction-picture density matrix quantum Monte Carlo method recently introduced by our group [J. Chem. Phys. **143**, 044116 (2015)] to resolve this controversy. We verify the CPIMC findings and extend the CPIMC results to bridge the present gap between low and high densities.

Optical properties of point defects and defect complexes in GaN from Hybrid QM/MM

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GaN, which has gained much attention for applications in solid-state lighting and high power microelectronics, needs both n- and p-type conductivity for devices, e.g. blue LEDs. However, neither the mechanism of the native n- type nor the p-type conductivity is well understood. Whether the GaN native n-type conductivity originates from nitrogen vacancies or impurities, why the p-type conductivity succeeds only with magnesium doping and has such a low doping efficiency, which impurity or native defect state in GaN leads to which photoluminescence line, e.g. yellow luminescence, have been the subject of intense debate for the last fifty years. To cast some light on these issues, we have performed hybrid quantum mechanical/molecular mechanical (QM/MM) embedded cluster calculations to study the optical and electronic properties of defects and defect complexes in GaN. We have showed that the nitrogen vacancy is the source of native n-type conductivity and acts as compensating centres in p-type carriers [1]. We have studied a comprehensive range of magnesium-related defects and complexes and analysed their contribution to p-type conductivity and the associated spectroscopic features. We have also addressed the role of carbon in inducing yellow luminescence that is widely observed in GaN.

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Simple Rules for Solid-state Design: From Bulk to Interface

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High-throughput screening enterprises such as Materials Project and the OQMD are well suited to the application of density functional theory for assessing the merits of known bulk materials. The blind exploration of the new combinations and permutations of the periodic table is a daunting task, to paraphrase Samuel Beckett we *feel lost before the confusion of innumerable prospects*. Centuries of research have provided us with myriad rules for assessing the feasibility of a given stoichiometry and the likelihood of particular crystal arrangements. We explore the ways in which chemical knowledge and state-of-the-art computational physics can be combined to accelerate materials design. We present the SMACT (Semiconducting Materials by Analogy and Chemical Theory) package, which combines these rules with searching of chemical space to predict plausible and heretofore unknown compounds. Finally we provide some illustrative examples of materials' design focusing on several important issues: (i) designing new photovoltaic materials [1], (ii) the role of surfaces and polymorphism in controlling electronic properties [2,3], and (iii) the design of porous materials [4].

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Band Gap Engineering of Iron Disulfide (FeS$_2$) for Photovoltaic Applications

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Iron disulfide (FeS$_2$) occurs naturally as two polymorphs. Pyrite crystallizes in the cubic space group, *Pa3* while marcasite belongs to orthorhombic *Pnnm*.[1] Pyrite has received a lot of attention as a promising photovoltaic material because of its high abundance, non-toxicity, and strong light absorption ($\sim 10^5$ cm^{-1} for hv > 1.4 eV).[2] The monocrystalline FeS$_2$ photoelectrodes and solid-state Schottky solar cells of FeS$_2$ have shown large short-circuit current densities (30–42 mA cm^{-2}) and quantum efficiencies (up to 90%).[3] However, the energy conversion efficiency of pyrite solar cells is still limited by its low open-circuit voltage (OCV) which is less than 0.2 eV.[3] The band gap of pyrite is 0.95 eV, which is however too narrow for optimal photovoltaic applications although it is small enough for FeS$_2$ to absorb a wide range of solar spectra. In order to develop the pyrite-based photovoltaics, modulating the band gap of FeS$_2$ is greatly necessary to solve the long-standing problem of its low OCV.

In semiconductor production, doping is one of the most feasible methods to modulate the electronic properties of the semiconductor. Here, we have used density functional theory calculations, corrected for long-range dispersion interactions (DFT-D2), to explore various doping candidates that have the potential to improve the electronic band gap of pyrite for photovoltaics applications. Our results show that the band gap of FeS$_2$ can be increased by alloying with ruthenium, osmium, zinc and oxygen. We have also investigated the electronic properties of marcasite and showed that contrast to the widely reported small gap of 0.34 eV, marcasite should have an energy gap quite similar to pyrite. This result suggests that marcasite which co-exists with pyrite, but was usually seen as a useless impurity, might actually be a useful semi-conductor and photocatalyst in its own right.

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Path Sampling Adventures - Using High Performance Computing to Determine the Pathway, Mechanism and Energy Landscape of a Solid-Solid Phase Transition

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*e05-gener-**leo***

Zinc oxide (ZnO) is a cheap, abundant and useful material with a plethora of potential uses in the electronics and optics industries. However, its wurtzite (WZ) ground state structure leads to a number of undesirable properties which have made exploitation of this versatile compound prohibitive. As a result, knowledge of how to access and stabilise more useful ZnO metastable phases is desirable. To that end, the talk will focus on recent work to deduce the mechanism of the pressure-induced phase transition between the zincblende (ZB) and rocksalt (RS) polymorphs of zinc oxide using an advanced Molecular Dynamics technique known as Transition Path Sampling (TPS). Starting from an initial model trajectory, the simulation converges upon the 'true' pathway, providing sensible mechanistic data for the transition. This particular transformation shows differing forward and backward pathways, and features a number of competing intermediates. In addition, a novel and innovative technique to construct a free energy profile for the solid-solid transition will be discussed, which utilises a combination of metadynamics and TPS. This technique clearly shows the route of the pathway of the transformation (as well as the intermediates generated) in exquisite detail, which would not be possible from analysis of enthalpy or potential energy alone. Due to the demanding nature of these calculations, high performance computing has been required and the use of super-computing services such as ARCHER have been central to the success of this project.

Mechanisms of Li Extraction from Li-rich Layered Manganese Oxide Cathode Li_2MnO_3

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*e05-store-**isl***

Li-rich layered oxides $Li_{1+x}M_{1-x}O_2$ (0<x<0.33), where M=Co, Mn, Ni, have emerged as promising cathode materials, because they can deliver much higher capacities (> 250 mAh/g) than the conventional $LiCoO_2$ cathode. Important issues relate to what is the origin of the electrochemical activity and high capacity? In this work, possible charge compensation mechanisms upon lithium extraction from Li_2MnO_3 are studied by ab-initio density functional theory calculations: (a) Reversible oxidation of bulk O^{2-} to other anion species such as superoxide or peroxide; (b) Loss of lattice oxygen (oxygen evolution). Both thermodynamic (reaction enthalpies and electrochemical potentials) and kinetic (ion migration) aspects are investigated.

Dynamic Excitations in the Solid Lithium-Ion Electrolyte LLZO

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Lithium-stuffed garnets, $Li_xA_3B_2O_{12}$ are a promising family of solid lithium-ion electrolytes, and have been proposed as replacements for conventional liquid polymer electrolytes in next-generation lithium-ion batteries. Within this material family, the lattice cation identities {A,B} and lithium content can both be varied, and differences in lithium-ion conductivity of $\times 10^3$ have been achieved by changing the chemical composition. The most studied member of this family, $Li_7La_3Zr_2O_{12}$ (LLZO), exhibits two phases with strikingly different ionic conductivities: a cubic phase, favoured at high temperature, or stabilized by doping, with $\sigma \approx 10^{-4}$ S cm^{-1}, and a tetragonal phase formed at low temperatures in stoichiometric samples, with $\sigma \approx 10^{-6}$ S cm^{-1}. This large difference in ionic conductivities is somewhat surprising, because the pathways available for lithium-ion conduction are topologically identical in both phases, and is not understood.

We have performed long-timescale molecular dynamics using an atomistic potential developed from first-principles calculations on the cubic and tetragonal phases of LLZO. This method allows much longer simulations than previous *ab initio* molecular dynamics studies, and provides much better statistical sampling of the lithium transport, while avoiding empirical parameterisation.

Applying two techniques from the supercooled liquid community, we identify displacive excitations of groups of ions, which have quantitatively different behavior between the two phases. In tetragonal LLZO, these excitations are temporally and spatially sparse, with lithium moving preferentially around closed loops. This qualitative difference is explained as a consequence of lithium ordering in the tetragonal phase, and provides a mechanistic basis for the much lower ionic conductivity of tetragonal versus cubic LLZO.

Modelling Defect Microstructure in the Cathode Layer Material LaCoO$_3$

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e05-store-**cat**

The search for suitable mixed ion-electron conducting cathode materials for intermediate temperature solid oxide fuel cells has led to the study of complex oxide perovskite materials such as LaCoO$_3$ doped with Sr and Fe. Understanding the role of defects, both intrinsic and extrinsic, is key to understanding the transport properties of this system. We present results of first principles calculations on the formation of intrinsic point defects, substitutional defects, and defect complexes in LaCoO3. From our results we derive the most favourable charge compensation mechanisms for the defects studied, whether via point defect or polaron formation, having implications for the ionic and electronic transport mechanisms that dominate in the system. Our results agree well with available experiment and provide design strategies for fuel cell cathode applications.