Calcium Phosphate Prenucleation Complexes in Water by means of ab Initio Molecular Dynamics

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Calcium phosphates are the main inorganic components of bone and tooth tissues. The nucleation of calcium phosphates is thought to proceed by aggregation of so called prenucleation clusters (PNCs), which are already present in body fluids before nucleation. This nucleation pathway cannot be fitted in the frame of the Classical Nucleation Theory. We investigated the structure and verified the stability of the PNCs, recently identified as calcium triphosphate complexes $[Ca(HPO_4)_3]^{4-}$ [1], by means of *ab initio* Molecular Dynamics with Umbrella Sampling technique. We found the calcium to be seven coordinated by two water molecules, two bidentate phosphates and one monodentate phosphate. Free energy results obtained using umbrella sampling simulations showed that the complex with a Ca:P ratio of 1:3 is the most energetically favoured, and thermodynamically more stable than the free ions. At the moment we are studying the aggregation of Ca^{2+} and different ratios of PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ ions by means of classical molecular dynamics.
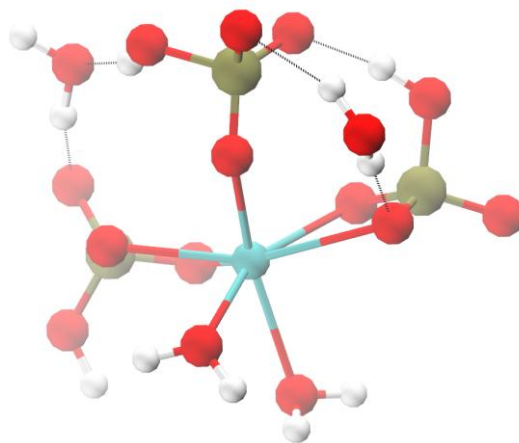

Fig. 1: Prenucleation cluster, structure obtained in water during MD.

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Computational Study of Enzymes Confined in Mesoporous Materials for Therapeutic Applications

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Confinement of biomolecules in ordered mesoporous materials is receiving particular attention, because of potential applications in drug delivery systems, as well as in bio-separations and bio-catalysis. Therefore, the interactions between proteins and the pore surface of mesoporous materials are systematically investigated to explain how surface curvature and pore size affect the orientation of an adsorbed protein. In this study, we perform all-atom molecular dynamics (MD) simulations for a single protein, namely lysozyme, placed at the center of a hexagonal prism of silica. Our preliminary results using a cylindrical pore model demonstrate that the protein adsorption mechanism on silica-like surfaces is driven by electrostatic interactions with positively charged residues helping to anchor the protein onto the surface. Because it is known from experimental studies using SBA-15 silica that the conformation of the adsorbed protein is strongly correlated with the local pore geometry, we model the roughness of the pore surface to extend the investigation of the protein contact with a more realistic pore surface of silica, more representative of SBA-15. We also investigate the fundamentals of the adsorption mechanism by analyzing the profile of the potential of mean force of the protein-silica system as a function of distance and orientation of the protein. The orientation of the ellipsoidal shape of the protein with respect to the pore surface is one of the significant parameters to consider.

Towards screening of Hypothetical Porous Organic Molecules: A computational study of Xe/Kr selectivity.

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Porous organic molecules (POMs) are an emerging class of porous materials with possible application in gas storage, chemical separations and catalysis.[1] Separation of noble gases, krypton and xenon in particular, is a complex and costly industrial process with prices for xenon reaching $5000 kg^{-1}. Much focus has been devoted to computational screening of potential materials for Xe/Kr separations. Sikora *et al.* have performed a high-throughput computational study of metal organic frameworks (MOFs), with over 137K hypothetical structures screened.[2] Such computational screening allows for relatively fast and cheap sampling of a vast chemical space unattainable experimentally. A previous study by Chen *et al.* focused on the POM known as **CC3**.[3] This organic cage-like molecule consists of a spherical void and four triangular "windows", with diameters close to Xe and Kr dimensions, making it a promising candidate for kinetic separation of Xe/Kr mixture. Herein, inspired by the performance of **CC3**, we present a computational study of Xe/Kr selectivity of previously reported POMs in search for other feasible candidates in this class of materials. As a result of the discrete character of POMs, we have developed in-house software for structural analysis of single molecules, in combination with atomistic and electronic structure calculations. For the database of previously reported POMs, Xe/Kr binding energies and the free energy barriers to their diffusion through the molecules have been calculated. Finally, preliminary results on the rational design of hypothetical POMs through the incorporation of the rapid on-the-fly window diameter assignment algorithm into an evolutionary genetic algorithm will be presented.

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Computational Design Strategies for Porous Organic Molecules

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Porous organic molecules are a class of materials that, by contrast with framework materials such as zeolites and MOFs, are constructed by the intermolecular packing of discrete organic molecules that contain void space in an internal cavity[1]. These porous materials show high mobility, a modular nature that allows for 'mix-and-match' strategies[2], and are typically solution processable. Many experimental and computational studies have been conducted on porous cages, however design and prediction of new molecular structures still represents a great theoretical challenge[3]. Even with only minor changes to reaction precursors, a given reaction can produce a collection of distinct molecular species, with different molar masses, which makes the prediction of the most likely reaction outcome challenging. Additionally, experimental conditions (solvent, temperature and concentration) can strongly influence the final product. The aim is to develop software that, starting from a library of possible precursors, is then able to produce a database of viable shape persistent structures, which will be automatically characterised (see Figure 1). Some of the structures which collapse after an initial screening, will be "inflated" with a technique[4] recently developed in the group, in order to simulate the scaffolding effect of solvent and locate higher energy metastable open conformers that can be observed when the molecule is in solution or the solvate solid state. Progress in the implementation of the software will eventually lead to the assembly of single molecules into periodic structures through Crystal Structure Prediction techniques, and finally to the synthesis of the most promising candidates (in collaboration with Prof Cooper's experimental group, University of Liverpool).
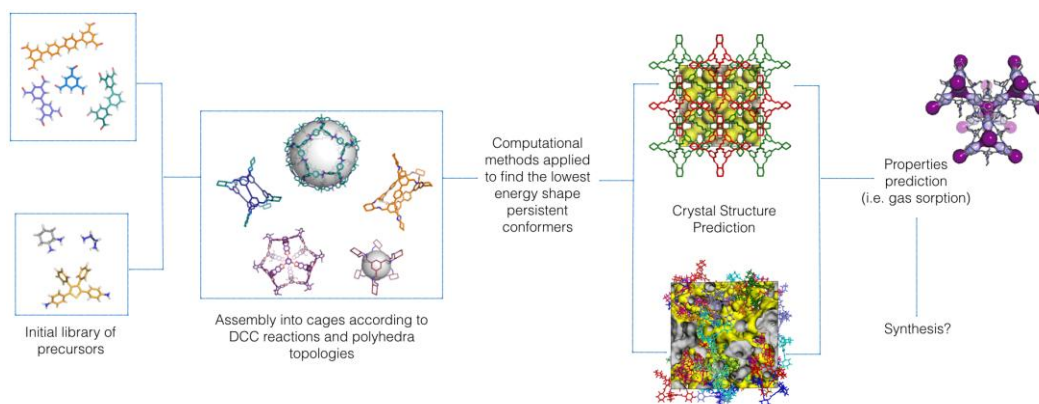

Figure 1: schematic representation of the poster.

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Electron Injection Facilitated Defect Creation in Amorphous SiO$_2$

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The mechanisms of electron interaction with amorphous (a)-SiO$_2$ and the nature of electron trapping sites are important for our understanding of radiation-induced damage and electrical breakdown, and for applications in fiber optics and microelectronics. Extra electrons are usually trapped at defect sites, such as oxygen vacancies and impurities. Our DFT calculations performed using CP2K show that precursor sites composed of wide O-Si-O bond angles in a-SiO$_2$ can act as intrinsic electron traps and accommodate up to two extra electrons. Trapped electrons are shown to weaken the corresponding Si-O bonds resulting in an efficient bond breaking pathway for producing neutral O vacancies and charged O interstitials characterized by low activation energies.

Our calculations rule out simple vacancy diffusion and spontaneous Si-O bond breaking as the source of Frenkel defects in pristine, neutral a-SiO$_2$ as the activation energies required for these processes are very high (3-4 eV). We then studied Frenkel defect generation mechanisms under electron injection conditions by simulating charged periodic unit cells of a-SiO$_2$. Due to the varying local geometry in a-SiO$_2$, intrinsic sites composed of wide O-Si-O bond angles (>132°) act as deep electron traps and can accommodate up to two electrons, which further increases the O-Si-O bond angle to nearly 180° and stretches the corresponding Si-O bonds to the breaking point. These weakened bonds result in greatly reduced average activation energy of 0.7 eV and an efficient bond breaking pathway for producing O vacancies and interstitial O ions. Newly generated O ions are shown to migrate rapidly through the oxide with a barrier of 0.3 eV to the positive electrode while O vacancies remain behind. Finally, we show that this formation mechanism is only weakly correlated when the concentration of pre-existing vacancies in the system. Combining these findings we proposed a mechanism for electron injection facilitated defect formation in a-SiO$_2$. These results are discussed in the context of experimental data on time dependent dielectric breakdown and memory devices.

Spectroscopic Properties of Oxygen Vacancies in LaAlO$_3$

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Oxygen vacancies in LaAlO$_3$ (LAO) play an important role in the formation of the 2-dimensional electron gas observed at the LaAlO$_3$/SrTiO$_3$ interface and affect the performance of MOSFETs using LAO as a gate dielectric. However, their spectroscopic properties are still poorly understood, which hampers their experimental identification. We present[1] predicted absorption spectra and electron spin resonance (ESR) parameters of oxygen vacancies in LAO, calculated using periodic and embedded cluster models and Density Functional Theory (DFT) and time-dependent DFT (TDDFT). The structure, charge distribution, and spectroscopic properties of the neutral (V_O^0) and charged (V_O^+ and V_O^{2+}) oxygen vacancies in cubic and rhombohedral LaAlO$_3$ have all been investigated.

The absorption spectra calculated using TDDFT, as implemented in the Gaussian09[2] code, show that the highest intensity optical transitions have onsets at 3.5 and 4.2 eV for V_O^0 and 3.6 eV for V_O^+ in rhombohedral LAO and 3.3 and 4.0 eV for V_O^0 and 3.4 eV for V_O^+ in cubic LAO, respectively. These transitions are from the vacancy state to perturbed states in the conduction band, and from studying the molecular orbitals involved in the transitions, due to the D_{4h} point symmetry of the vacancy, all transitions are from A_{1g} to E_u states.

The calculations of ESR parameters we present can also be directly compared to experimental studies of the V_O^+ defect. We calculated an isotropic g-value of 2.004026, and due to the hyperfine splitting of the Al ions, we predict a signal broadening of 3mT. These results may further facilitate the experimental identification of oxygen vacancies in LAO and help to establish their role at the LAO/STO interfaces and in nanodevices using LAO.

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Hydrogen Defects and Diffusion in UO$_2$

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Uranium dioxide is generally an effective passivating layer over uranium metal, which protects the uranium metal and reduces the rate at which hydriding occurs. However, hydriding of the underlying metal still occurs. Therefore understanding how hydrogen interacts and is transported through UO$_2$ is of importance.

The UO$_2$ layer is generally a non-stoichiometric phase, such as U$_4$O$_9$ and U$_3$O$_7$, as UO$_2$ prefers hyperstoichiometry. These non-stoichiometric phases contain a range of oxygen defects clusters. Possible defect clusters include the split di-interstitial and the cuboctahedron. Therefore knowledge of the behaviour of hydrogen in UO$_2$, not least the interaction of hydrogen with oxygen defect clusters, is important.

The aim of the project is to explore the structure, stability and transport of hydrogen species in uranium based matrixes. As there is a lack of experimental data, in part due the difficulty of determining how hydrogen behaves, and the dangers associated with the handling of uranium materials, computational methodology provides a safe and efficient route to investigate these properties.

DFT has been used to investigate a range of hydrogen species in UO$_2$ and UO$_{2+x}$. Interstitial hydrogen can exist as a proton (as part of a hydroxyl group) and hydride. This suggests that the energy landscape of hydrogen in UO$_2$ is complex and the possibility that the diffusion pathway of hydrogen is also non-trivial.

Can holes trap in amorphous HfO_2?

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HfO_2 is a high dielectric constant material, which is used as a gate insulator in field effect transistors as a substitute for SiO_2 as the common gate oxide material in such devices. Control over oxide charging is of paramount importance to semiconductor device performance and the study of polaron states and trapped charge has significant implications. Charge traps within gate dielectrics may have undesired impacts on device performance, and holes are known to exist as shallow traps on 3 coordinated oxygen sites in monoclinic HfO_2.

In this work hole trapping in amorphous HfO_2 is investigated using 25 96-atom cells which were generated by a melt and quench procedure. The trapping has been simulated using hybrid density functional theory approximated within the auxiliary density matrix method (ADMM) implemented within the CP2K ab-initio software package. The process is repeated for a set of 324-atom cells to check for effects, such as charge-image interaction and to converge the relaxation of the structure upon hole trapping.

We found that holes trap spontaneously at precursor sites in amorphous HfO_2 with a range of associated trapping energies, as expected for an amorphous material. The majority of the spin density is localized on one oxygen atom in a p-state. Some of these holes trap more deeply than they do in their monoclinic hafnia. The one-electron defect levels are found to be, on average, 3.3 eV above the valence band maximum and are associated with a hole trapping energy of 0.61 eV. It is observed that holes trap on oxygen ions 2-coordinated by hafnium ions, or alternatively on 3-coordinated oxygen ions having longer O-Hf bonds. The structural relaxation due to the hole localization results in an elongation of the O-Hf bonds by approximately 0.1 Å.

Structure Prediction of Barium Oxide Nanoclusters using Global Optimisation Techniques

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Progress in the generation of new materials may rely on optimised properties that are tuned by changing the chemical composition or the atomic structure of the material. However, commercial and environmental concerns have recently reduced the range of acceptable compounds to the more abundant and safe elements. As a consequence, the focus has turned to the modification of the atomic structure, which in turn modifies the properties and electronic structure of the material. The size of the material is one key variable; the atomic structure can change incrementally or dramatically as the size of the material is reduced to and below the nanoscale, in one or more dimensions. Within the realm of computational simulations this is a rich area to investigate. The key experimental challenges are being able to: control the size of the nanoparticles; isolate particular sizes; and synthesise large quantities of a target nanoparticle of a given size.
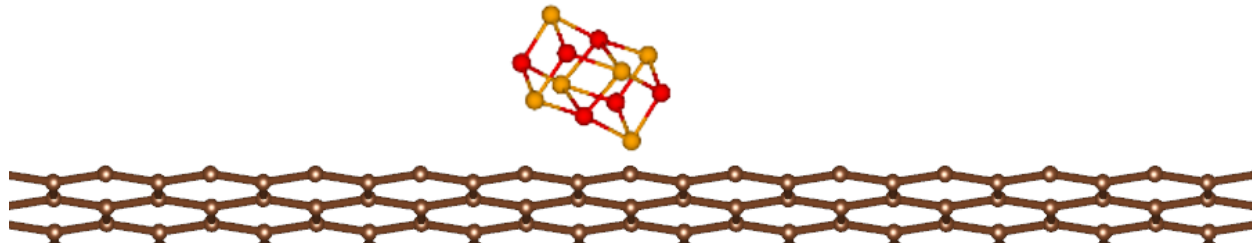
The computational part of this project exploits the employs the in-house KLMC code (http://www.ucl.ac.uk/klmc/Software/), which calls FHI-AIMS and NWChem to compute energies, forces and to refine LM atomic structures found (a) on the energy landscapes defined by interatomic potentials or (b) from a searchable web-database of atomic structures of inorganic nanoparticles (http://www.ucl.ac.uk/klmc/Hive/). Currently, the focus has been on testing our approach on barium oxide clusters in a vacuum, as (a) there are plenty of LM atomic configurations to data-mine from and (b) barium is a strong scatterer.

Computer Simulations of Borosilicate Glass

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Borosilicate glasses have an application in heat-resistive products due to their unique properties. In the pharmaceutical industry, it is used to create a variety of equipment from chemically resilient glassware to optical lenses/photonics.[1] A component in borosilicate glass is Boron Trioxide (B_2O_3), one of the three oxides of Boron. B2O3 is primarily found in two forms; a glassy, hygroscopic, white solid and the second being a more commonly found amorphous, vitreous form. This material possesses much difficulty when attempting to crystallise it. In fact it is commonly known as one of the hardest known compounds to crystallise.[2] The structure of glassy B_2O_3 is debated amongst researchers. The fundamental building block has been recognised as a $BO_{3/2}$ group, a trigonal planar molecule which then is connected to create the full structure. The links between these $BO_{3/2}$ groups is then not fully understood but several models have been proposed. A widely accepted understanding is that glassy boron trioxide (g-B_2O_3) is constructed with boroxol rings, a 6 membered ring with alternating coordination on the atoms. It is thought that these rings play a vital part in creating difficulties when attempting crystallisation. The Boron-Oxygen bond is partially covalent but interestingly the bond allows for the coordination of Boron to change depending on the environment it is in. It is thought that the Boron and Oxygen alternate from 3 to 2 coordination numbers, respectively.

In this research project, the aim is to observe the relationship between structure, dynamics and properties of borosilicate glasses through computational MD techniques - Subsequently developing a model that accommodates the particular features. In the current phase of this project, Boron Trioxide has been studied. A structural model of B_2O_3 was constructed using the DL POLY program to observe the conformation of the previous research carried out by the Takada research group.[3] This research involved the use of the low-pressure crystalline phase of B_2O_3-I where under normal conditions this phase exists. Through molecular dynamics (MD) studies, phase one has seen the successful simulation of crystal to glass transition of Boron trioxide. The system has also been expanded and tested with both two and three body potentials with melt and quench steps separated for further analysis. Modelling B_2O_3 using both a two and three body potential has outlined the importance of both the B-O-B and O-B-O terms which is seen to be essential for the quench stage.

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Molecular Dynamic Study of the Gadolinium-Doped Ceria and Yttria-Stabilized Zirconia interface for Solid Oxide Fuel Cell Applications

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Gadolinium-doped ceria (GDC) and yttria-stabilized zirconia (YSZ) are very well known electrolyte materials, vastly used in solid oxide fuel cell (SOFC). They are responsible for the oxide anion conduction from the cathode to the anode, and this conduction undergoes via a vacancy hopping mechanism. The O^{2-} mobility in both depends on several aspects, like the association energy of the vacancies with respect to the dopants, the dopants concentration, or the temperature among others. Interestingly, one of the main differences between them is that GDC shows higher oxygen conductivity than YSZ but at lower temperatures, allowing developing SOFC that are able to work at intermediate temperatures.

Despite showing different oxygen conductivities at different temperatures, we can find GDC and YSZ used in bi-layered electrolyte systems. In them, YSZ thin layers are introduced in a GDC matrix to prevent electronic conductivity whilst maintaining the oxygen conduction. The fact that ionic conductivity remains almost unaltered is partly explained by the presence of grain boundaries (GBs. These GBs are believed to provide fast migration pathways, although little is known about the mechanism involved.

Therefore, to understand the mechanisms involved in the oxygen migration, we used molecular dynamic techniques to study these interfaces. We firstly used the amorphisation and recrystallisation strategy in order to obtain realistic models of the grain boundaries. Basically, that strategy consist in melting the material to then recrystallizing it at high pressures, allowing the inclusion of translocations and dislocations. Then, we performed a series of molecular dynamic simulations to evaluate the effect of the temperature in the ionic mobility and consequently the ionic conductivity. Our results seem to indicate that, as a consequence of the lattice misfit between both materials, the stress introduced in the system affects differently GDC and YSZ, and that has an unexpected impact in the oxygen mobility along the GDC/YSZ interface.

Computational Modelling of the SOFC Cathode $SmCoO_3$ (100) Surface

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Solid oxide fuel cells (SOFC) are an alternative to traditional power sources. Despite being very efficient, good performances are obtained at high operating temperatures, which affects the SOFC material's stability. Therefore, in order to reduce material costs and to improve SOFC lifetime, we need to develop new materials that are able to operate at lower temperatures.

This research involves the three different parts of the SOFC; anode, electrolyte, and cathode. Focusing on the cathode, this material should have a small thermal expansion coefficient compatible with its coupled electrolyte, high oxygen reduction reaction (ORR) catalytic activity at the operating temperature, and high surface area. Traditionally, perovskites like $La_{1-x}Sr_xMnO_{3-d}$ (LSM) are used for that purpose. However, recent studies have shown that doped $SmCoO_3$ is as effective as LSM, but at lower temperatures. By doping the Sm-site with Ba^{2+}, Ca^{2+}, or Sr^{2+}, oxygen vacancies (V_o) are generated, enhancing oxygen diffusion. On the other hand, doping the Co-site with Fe^{3+}, Ni^{3+}, or Mn^{3+}, alters the electronic properties and increases the electronic conductivity. The challenge, however, lies in the atomistic understanding of $SmCoO_3$ properties when doped, as well as its impact on the ORR, the oxygen diffusion or the vacancy migration.

To that end, we have used density functional theory calculations for a systematic study of doped $SmCoO_3$. Specifically, we have investigated the influence of the aforementioned dopants in the generation of oxygen vacancies and in the electronic structure for both bulk and the (100) surface. We have also investigated their influence in the ORR, in order to obtain a clearer picture of the system.

Self-consistent Hybrid Functional Calculations: Implications for Structural and Electronic Properties of Oxide Semiconductors

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Density functional theory has proven hugely successful in the calculation of structural properties of condensed matter systems and the electronic properties of simple metals. Band gaps of semiconductors and insulators, however, are often severely underestimated due to the limitations of existing approximate exchange-correlation functionals. Considerable improvements are possible by including a fraction of Hartree-Fock exchange, constructing a so-called ``hybrid'' functional. The precise proportion of Hartree-Fock exchange is typically treated as an empirical parameter chosen by intuition and experimental calibration.

This empiricism can be avoided with a *self-consistent* hybrid functional approach for condensed systems [1], which allows parameter-free hybrid functional investigations. Using this approach, we report on the implications for structural and electronic properties of oxide semiconductors, with ZnO, SnO_2, and MgO as specific examples. Structural and electronic properties will be compared to theoretical and experimental data, showing considerable improvement with respect to previous approaches.

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Entropy Loss on Adsorption of Organic Molecules at Insulating Surfaces

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Although it is recognized that the dynamic behavior of adsorbing molecules strongly affects the entropic contribution to adsorption free energy, detailed studies of the adsorption entropy of large organic molecules at insulating surfaces are still rare. In this study we compared the adsorption and mobility of two different functionalized organic molecules, 1,3,5-tri(4-cyano-4,4-biphenyl)benzene (TCB) and 1,4-bis(cyanophenyl)-2,5-bis(decyloxy)benzene (CDB), on the KCl(001) surface using density functional theory (DFT) and molecular dynamics (MD) simulations. These two examples were taken as prototypical rigid (TCB) and flexible (CDB) functional molecules.

In order to ensure an accurate representation of the system, van der Waals corrected DFT-D3 was benchmarked using Møller–Plesset perturbation theory calculations. The validated DFT data was then used to parametrize classical force fields for both the TCB and CDB molecules on the KCl(001) surface which were then used to perform molecular dynamics calculations. These simulations included potential of mean force (PMF) calculations of the adsorption of individual molecules which were used to extract information on the entropic contributions to adsorption energy at clean terraces and step edges. Our results demonstrate that entropy loss upon adsorption is significant for flexible molecules and that these effects can match the enthalpic contribution to adsorption energy at relatively low temperatures (e.g., 400 K).

Water Gas Shift Reaction Mechanism on Pd (100) Surface

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The water gas shift reaction (WGSR) has been of great interests to scientists in industries and academia for a very long time. In the redox mechanism of WGSR the oxidation of CO takes place by atomic O obtained from H_2O by two successive H abstraction steps or by one H abstraction followed by disproportionation of two OH species. However, the carboxyl mechanism involves the oxidation of CO by OH to form carboxyl or the COOH species. Carboxyl so formed may then yield CO_2. The reaction occurs on a number of surfaces and catalysis and in this study we focus on a model Pd (100) surface. In the current study we have taken into account of both of these reaction mechanisms to understand the WGSR in Pd(100) surface.
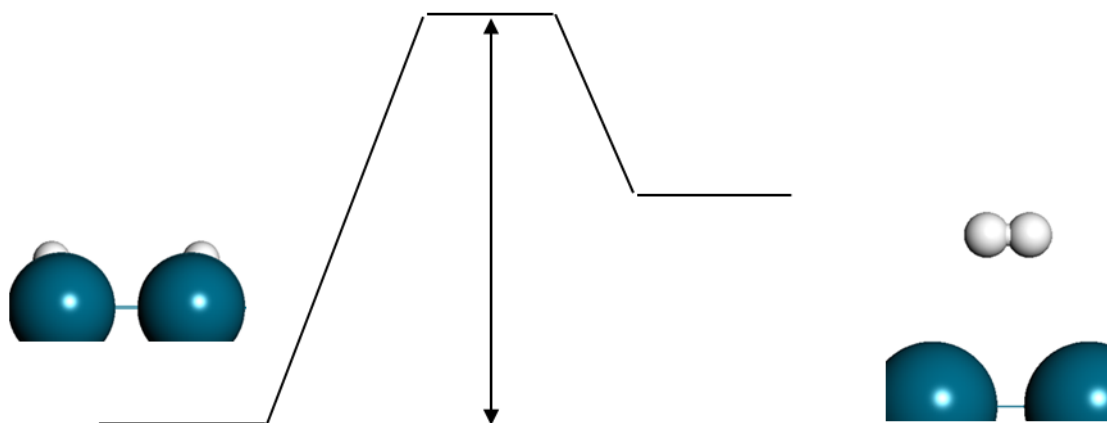
We have shown the mechanism for WGSR involving both direct CO oxidation and decomposition of carboxyl to produce CO_2 along with the interaction of water with the Pd(100) surface to form hydroxyl groups and surface hydrogen and oxygen. H_2 can be evolved from the surface with a barrier of 1.67 eV.

Adsorption of methyl acetoacetate on Ni (111) Surface: Theory and Experiment

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One of the most studied examples of enantioselective heterogeneous catalysis is the hydrogenation of β-ketoesters over Ni catalysts. In the case of the simplest β-ketoester, methyl acetoacetate (MAA), such reaction results in a product mixture of the R and S enantiomers of methyl-3-hydroxybutyrate (MHB) when performed over bare catalysts. However, co-adsorption of α-amino or α-hydroxy acids onto Ni catalysts from solution influences the hydrogenation reaction such that one enantiomer is produced in excess over the other. Hence, understanding the mechanism of adsorption of MAA is a key step in achieving enantioselective behavior of Ni-based catalyst. We present here a combined theoretical and experimental study of MAA adsorption on Ni(111).

MAA is a β–dicarbonyl that contains CH_3 and OCH_3 functionals groups, leading to two tautomeric forms: the diketo (favored by OCH_3) and enol (favored by CH_3). Our DFT-D3 calculations predict that the enol tautomer is more stable than the diketo form in the gas phase. A gas electron diffraction (GED) analysis showed a mixture of 80% enol tautomer and 20% diketo form at 309K.

We find that in the non-defective (111) surface the adsorption of MAA should occur only in the enol form. MAA is absorbed with the molecular plane tilted with respect to the surface, via both carbonyl groups, and with deprotonation of the hydroxyl group. In a defective surface, the diketo and enol tautomer interact with the Ni adatom via the carboxylic groups with the plane of both molecules in parallel. In the case of enol MAA the deprotonation also takes place. This latter configuration is the most stable found in the present study.

We obtained XPS spectra of C1s and O1s from DFT to compare with experiment. O1s XPS spectra show two clear peaks separated by 2 eV, the lower BE peak being more intense. We obtained same trend in all cases of the MAA adsorption via deprotonation: two oxygen atoms, from the carboxylic groups, are in lower BE than the oxygen corresponding to the OCH3 group. Such differences are estimated between 1.8-2.5 eV. Therefore, our calculations allow us to understand the origin of the experimental peaks.

Ice, Ice, Maybe: A Brute-Force Study of Heterogeneous Ice Nucleation

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Despite its importance to science (e.g. cryopreservation [1] or climate [2]) and technology (e.g. food [3] or aviation [4]), many aspects of heterogeneous ice nucleation are still poorly understood. Because of the small length and time scales involved, this phenomenon provides a tough challenge for experiments. Therefore, atomistic simulations are a promising tool in the quest to unravel the molecular details of waters ubiquitous phase transition.

We performed a systematic trend study in which we explore the structure and dynamics of supercooled liquid water and ice on several generic model substrates by molecular dynamics simulations [5]. We consider the (111), (100), (110) and (211) surfaces of an fcc crystal, varying the strength of the water-surface interaction and the lattice parameter. Water is represented by a coarse-grained model [6] which in some cases allows for the observation of nucleation with unbiased simulations.

We find a complex interplay between hydrophobicity and morphology that can promote the formation of different faces of ice on the very same surface. Furthermore, we propose three circumstances where heterogeneous ice nucleation can be promoted by the crystalline surface: (i) the formation of a water overlayer that acts as an in-plane template; (ii) the emergence of a contact layer buckled in an ice-like manner; and (iii) nucleation on compact surfaces with very high interaction strength. These findings provide insight into the microscopic details of water-solid interfaces and into the effects of morphology and hydrophobicity on ice formation.

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Modeling Hydrated and Carbonated Magnesium Minerals

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A combination of quantum and potential based methods have been used to model hydrated magnesium carbonate minerals. Brucite and hydromagnesite are phases of particular interest, specifically their interaction with water and carbon dioxide. This is important as magnesium rich phases are the main components of Magnox nuclear sludge. Therefore before studying the sorption of radionuclides on mineral surfaces, one has to characterize the composition of the sludge. Experimental techniques have been found useful, but the nature of the samples has hindered the characterization of the sludge due to safety concerns.

Computational techniques are a safe and powerful way of studying nuclear sludge. For magnesium rich minerals containing H_2O and CO_2, the inclusion of van der Waals dispersion forces in DFT calculations have been shown to improve the comparison with experimental data. Therefore, we have compared the Grimme D3 and vdW-DF methods as implemented in the VASP code and found that both methods give good agreement with experimental structural parameters. However, vdW-DF has shown an improvement when comparing order of stability of different phases. We have reproduced the phase diagrams of magnesium rich minerals varying the chemical potentials of CO_2 and H_2O, and found that at 350ppm CO_2 and 32mbar H_2O at 0K, Lansfordite is the most thermodynamically stable phase. This agrees well with the work of Chaka et al. The identification of the phase diagram for magnesium rich minerals gives useful insights into the compositions, which will be more likely to interact with radionuclides in the Magnox nuclear sludge.

Calculating the electronic band edges at TiO$_2$/water interfaces

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A major challenge within the energy transformation towards sustainable and renewable energy sources is the energy storage. One potential solution is to store chemical energy in the form of H$_2$ obtained by photoelectrolytic water splitting[1]. Current photoelectrolytic water splitting cells are not working efficiently enough to be industrially feasible yet. Their efficiencies largely depend on the electronic structure of the photoelectrodes, in particular on the alignment of electrodes' electronic band edges with respect to the redox potentials of water. In this project, many-body perturbation theory within the *GW* approximation was used to accurately calculate the electronic structure of bulk titanium dioxide which is the prototype of all photoelectrodes[2]. Joint density-functional theory[3,4] (JDFT) rather than ab initio molecular dynamics will be employed to reference the obtained energy levels with respect to the redox potentials associated with the hydrogen and oxygen evolution reactions in water.

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The interaction of a carbon monoxide molecule with an adsorbed porphyrin molecule on a metal surface.

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Tetraphenylporphyrin molecules (TPP) with a metal centre belong to a class of molecules that play important roles in biological systems, for example, in oxygen transport and light-harvesting [1]. This class of molecules could also have possible applications in the development of molecular devices such as colorimetric gas sensors, photonic wires, field-effect transistors, and light emitting diodes.

Recent sum frequency generation (SFG) experiments of the internal CO stretch mode have shown that the anharmonicity parameter is anomalous for CO adsorbed on a dense overlayer of Ru-TPP on Cu(110), indicating an unusual interaction [2]. In order to elucidate the interactions that can give rise to such an anomalous anharmonicity parameter, we are carrying out density functional theory calculations of this parameter for CO in various chemical bonding situations including Ru-TPP/Cu(110). In the case of an isolated CO molecule and CO adsorbed on Cu(110), the calculated values are normal and in good agreement with experiments. In the case of Ru TPP/Cu(110), we are currently investigating different adsorption geometries of CO molecule as done for similar systems [3]. The structure of the Ru-TPP overlayer is found to be similar to the Co-TPP overlayer on Cu(110) with an unusual conformation [4].

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Modelling the Interaction of Corroded Magnox Surfaces with Fission Generated Strontium

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The spent uranium fuel rods and associated cladding from the first generation British civil nuclear reactors are stored in water filled storage ponds at reactor sites and reprocessing facilities prior to reprocessing or final disposal. The cladding material of the herein stored used fuel rods was a magnesium-aluminium alloy (known as Magnox), which corroded during the a storage period and formed a brucite sludge.[1] In the meantime, a variety of radioactive elements; primarily uranium and two of its nuclear decay products, strontium and caesium (^{238}U, ^{90}Sr and ^{137}Cs), leached out from the fuel into the sludge and now exist in aquo or hydroxide complexes. Brucite, alias $Mg(OH)_2$, has a highly reactive hydroxide-terminated surface (0001) and it was proven experimentally that it can easily adsorb some of the above mentioned ions.[2] Investigating the interaction between the newly formed surfaces and the presented ions is crucial to understand the real time conditions of the storage ponds and to create successful treatment strategies for the waste. In this project, we embarked to develop a successful model which is able to describe the aquo and hydroxide complexes of the strontium and their interactions with a hydrated brucite surface, aiming to create an approach which can be generally used later on for the investigation of other radioactive ions too. Initially, we have focussed on the identification of possible candidate Sr^{2+} complexes for interaction with the hydrated brucite surface.[3,4] After the solvation studies, we moved on to develop a sufficient surface model for the adsorption reactions. Using the periodic embedded cluster method, implemented in the TURBOMOLE code, we created a quantum chemically treated cluster in an infinite array of point charges and used this model to explore the adsorption of Sr^{2+} and s block cations such as Ba^{2+} or Cs^+ on bare and hydrated surfaces. These results are going to be presented along with two comparison studies of our simplified model with periodic DFT calculations which were carried out with the CRYSTAL code using ARCHER. The overall aim of this presentation to introduce a simple and efficient model which can be used to energetically investigate the ion adsorption on brucite surfaces.

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Electronic Structure of Pd Multi-Layers on Re(0001): the Role of Charge Transfer

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Understanding the origin of the properties of metal-supported metal thin films is important for the rational design of bimetallic catalysts and other applications, but it is generally difficult to separate effects related to strain from those arising from interface interactions. Here we use density functional (DFT) theory to examine the structure and electronic behavior of few-layer palladium films on the rhenium (0001) surface, where there is negligible interfacial strain and therefore other effects can be isolated. Our DFT calculations predict stacking sequences and interlayer separations in excellent agreement with quantitative low-energy electron diffraction experiments. By theoretically simulating the Pd core-level X-ray photoemission spectra (XPS) of the films, we are able to interpret and assign the basic features of both low-resolution and high-resolution XPS measurements. The core levels at the interface shift to more negative energies, rigidly following the shifts in the same direction of the valence *d*-band center. We demonstrate that the valence band shift at the interface is caused by charge transfer from Re to Pd, which occurs mainly to valence states of hybridized *s-p* character rather than to the Pd *d*-band. Since the *d*-band filling is roughly constant, there is a correlation between the *d*-band center shift and its bandwidth. The resulting effect of this charge transfer on the valence *d*-band is thus analogous to the application of a lateral compressive strain on the adlayers. Our analysis suggests that charge transfer should be considered when describing the origin of core and valence band shifts in other metal/metal adlayer systems.

Simulation of Gas Solubility and Transport in Plasticised Polymers

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Background
Nitrocellulose is a complex energetic polymer with explosive properties once the nitrogen content is above 12.6%. It is widely used throughout the propellants industry. During the storage of nitrocellulose degradation occurs by a series of complex steps. As a result a number of gases are produced including NO_2 which is thought to lead to autocatalysis of nitrocellulose decomposition. Stabilisers are often added to nitrocellulose propellant formulations which absorb these decomposition products and plasticisers are added to satisfy mechanical properties and safety requirements.

Nitroglycerine is widely used as a plasticiser for nitrocellulose, however nitroglycerine exudes from the nitrocellulose propellant formulation during storage. Research has therefore focused on replacement plasticisers for nitrocellulose.

Research Objectives
One approach to prevent exudation of the plasticiser from the polymer matrix is to use a compound which has similar structural elements to the polymer to aid miscibility. 2,4,6 - trinitroethylbenzene (TNEB) and 2,4 - dinitroethylbenzene (DNEB) have some structural similarity to nitrocellulose and contain energetic nitro groups which increase the overall energy output of an energy formulation.

Research will focus on the mixture of TNEB and DNEB, K-10, as a plasticiser of nitrocellulose. Specifically the solubility and transport of gases that are linked to autocatalytic decomposition of nitrocellulose within the plasticiser will be investigated.

Methods
Current work involves parameterisation and testing of a force field. Molecular Dynamics simulations will be conducted to observe the miscibility and mechanical properties of the plasticised nitrocellulose. Solubility and transport of gases will be investigated using Grand Canonical Monte Carlo simulations.

DFT study of the Perceived Acidity of Zeolites using trimethylphosphine oxide as Probe Molecule

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Trimethylphosphine oxide (TMPO) has been experimentally used to probe the concentration and strength of Brønsted acid (BA) sites within zeolites employing NMR. When the acid proton is transferred to the O_{TMPO} atom the P^{31} chemical shift displaces from 39 ppm to the range 60 - 90 ppm. Several peaks appear within this interval which are classified as very strong, strong, and weak depending on the effectiveness of the proton transfer [1,2]. In the present work the internal and external acidity of MFI zeolites were computationally studied using TMPO as probe molecule in order to have a better understanding of the experimental results at the atomic scale. The analysis of the simulations was based on the consequences that confinement and molecular agglomeration have in the perceived acidity of zeolites. Our work may explain why very strong and weak acidities are detected at the external surface but not that classified as strong, even when the three varieties are observed at the internal surface [2]. Also, the present results may give an answer to the increment of the relative concentration of the very strong acidity with the increment of the Si/Al ratio [1].

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Novel Stoichiometries of Mercury Halides

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This poster will illustrate methods of crystal structure prediction devised and used in the discovery of novel mercury chlorides with highly unusual stoichiometry. The methods used to determine their stability with respect to temperature and pressure will also be detailed.

Recent investigations into ionic systems under non-ambient conditions have revealed exotic compounds such as $NaCl_3$, which exhibit more covalent bonding character[1]. This project aims to further study changes in the nature of chemical bonding in high pressure systems[2], initially by determining the pressure stability range of predicted structures with exotic stoichiometries. Several methods of generating structures with unique geometries and stoichiometries have been developed for this purpose, and standard techniques such as molecular dynamics and phonon dispersion calculations are used to assess stability. Electronic band structure and DOS calculations are also employed in the study of the electronic nature of the systems of interest with respect to pressure. Enhanced sampling methods such as metadynamics are utilised as another tool to fully characterise the free energy surface of a system of specified stoichiometry.

The class of compounds of interest to this work are the mercury halides. The reason for this is that mercury is "softer" than sodium, and exists in 2 oxidation states in natural minerals. In fact, the calomel crystal structure, a molecular crystal of Hg_2Cl_2, is common to all mercury halides, alongside a crystal structure which is unique to each halide. It is hoped that each of the remaining structures may be adopted by the other mercury halides under non-ambient conditions.

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The Quantum Nature of DNA Base Pairs

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Despite the inherently quantum mechanical nature of hydrogen bonding it is unclear how nuclear quantum effects (NQEs) alter the strengths of hydrogen bonds. With this in mind we use ab initio path integral molecular dynamics to determine the absolute contribution of NQEs to the binding in DNA base pair complexes; arguably the most important hydrogen bonded systems of all. We find that depending on temperature NQEs can either strengthen or weaken the binding within the hydrogen bonded complexes. As a somewhat counterintuitive consequence, NQEs can have a smaller impact on hydrogen bond strengths at cryogenic temperatures than at room temperature. We rationalize this in terms of a competition of NQEs between low frequency and high frequency vibrational modes. Extending this idea, we also propose a simple model to predict the temperature dependence of NQEs on hydrogen bond strengths in general. Overall this work shows that the now established concept of competing quantum effects can be used to predict how NQEs alter hydrogen bond strengths but that the influence of NQEs on hydrogen bonds is more complex and significant than anticipated.

Modeling the reactivity of CO2 at trapped electron sites on Mn-MgO and MnO [001] surfaces

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We have performed embedded-cluster QM/MM calculations for the adsorption of CO_2 on to the pristine and defective (100) surface of Mn-doped MgO and MnO. For Mn-MgO, the interactions of CO_2 with the surface sites considered are broadly in agreement with those seen previously for MgO, both in terms of the calculated adsorption energies and the observed structures. However, the formation energy for each of the oxygen vacancy defects is reduced by the presence of a Mn-dopant when compared to undoped MgO. This lower formation energy, coupled with the consistent transfer of electrons onto the CO_2 adsorbate, leads us to believe that catalytic activity observed for MgO would be enhanced by the presence of transition metal dopants such as Mn.

For MnO, the defect formation energies for each of the F-centres are approximately the same as seen for Mn-doped MgO, but the behaviour of adsorbed CO_2 suggests that electrons are less strongly localised within the vacancy. In particular, the surface-adsorbate complex seen for F^0-centres at the MnO (100) surface is interesting because it suggests that oxygen vacancies would be less likely to degrade in reactions as a result of CO_2 decomposition. Also, the rotation of the adsorbed CO_2^- species when adsorbed on MnO (Figure 1) brings the carbon atom closer to the surface than for MgO, making it more accessible for the initiation of onwards reactions.
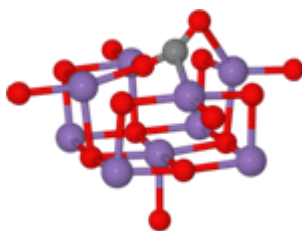

Figure 1. CO_2 adsorbed on the MnO(100) surface at an F0-centre. O atoms shown in red, Mn in purple and C in grey.

A NMR Crystallography Approach to Solve the Structure of a Disordered Mullite System

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Mullites are ceramic aluminosilicates which have diverse applications such as tableware, catalytic convertor substrates and heat shields on space re-entry vehicles.[1] There is a drive to produce synthetic mullite due to its excellent stability in challenging environmental conditions. Synthetic mullite has a nominal composition of:

$$Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x} \qquad 0:2 < x < 0:9$$
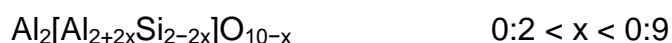
The structure of mullite is proposed to be closely related to the crystalline aluminosilicate sillimanite,[3] which consists of edge sharing AlO_6 octahedral chains running along the *c*-axis cross-linked with SiO_4 and AlO_4 motifs.[4] In mullite there is an excess of Al with respect to Si, which causes oxygen vacancies to form due to charge compensation:

$$2Si^{4+} + O^{2-} \rightarrow 2Al^{3+} + O_v$$
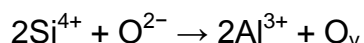
The oxygen vacancy (O_v) gives disordering of the cations in the tetrahedral units. The O_v causes the two-coordinate oxygen site (T_2O) in the moiety containing "bridging" tetrahedral motifs to be removed. The oxygen deficient tetrahedral motifs ($T_{2\square}$) then fold in on themselves to bond to nearby T_2O oxygens, creating a new three-coordinate oxygen site (T_3O).

This investigation uses an NMR crystallographic approach where modelling of a statistically relevant number of superstructures (containing defects and vacancies), molecular dynamic simulations and first principles GIPAW DFT calculations are corrolated with multinuclear [27]Al, ^{29}Si and ^{17}O solid state NMR methods to elucidate the structure of the disordered 3:2 mullite. Using this methodology, it is shown that a novel AlO_{4+1} site is formed in a significant proportion of the T_3O moieties. Moreover, this combined computational/solid state NMR approach has demonstrated the tricluster speciation becomes more diverse, increasing from 3 separate species in the ordered base sillimanite structure to 5 in the disordered 3:2 mullite structure.

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Molecular Dynamics Simulations of Ionic Liquids for CO_2 Capture

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Ionic Liquids (ILs) are salts, liquid at near-ambient (< 100 °C) temperatures and usually consist of bulky organic groups (either on the cation/anion/both). ILs have recently been reported to have high CO_2 capacities and are thus worthy of research as a medium for industrial CO_2 capture. Specific ILs will be chosen based on experimental collaborators' work at Queen's University Belfast, all for a larger project "A Comprehensive and Coordinate Approach to Carbon Capture and Utilisation" (4CU).

From a computational perspective, Molecular Dynamics plays an indispensable role in predicting and explaining the chemical and physical properties of these ILs and the CO_2 sorption capabilities. Primary objectives of this research is to explore and validate force fields for MD of ILs and to carry out MD simulations of IL $[P_{66614}][NTf_2]$ not widely published in literature, with the addition of CO_2.

The force field parameters used were CL&PFF (Canongia Lopez and Padua), [1] for the IL and TraPPE FF for CO_2, [2]. A system of 250 ion pairs of $[P_{66614}][NTf_2]$ was simulated at 298K in the NPT ensemble. An average density of 1.409 mol dm^{-3} (0.01% error) compares well with the experimental value of 1.394 mol dm^{-3}. Significant differences can be seen in IL structure and dynamics with and without CO_2, e.g. the reduction of diffusivity of cation and anion and a change in spacing between ions evidenced by radial distribution functions (RDFs).

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Atomistic Simulation of Oxide Interfaces in Materials for Energy Technologies

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Solid oxide interface materials are of a crucial importance with regards to energy applications due to the stability and versatility of such materials. Perovskite-fluorite nanocomposites, namely $CeO_2 \| SrTiO_3$ interfaces are the model system used in this research. Understanding the structure of these interfaces is of significant importance when considering electronic, thermal and transport properties. Energy minimization (EM) combined with a potential model techniques have been used in order to study heterogeneous ([111] $CeO_2 \|$ [111] CeO_2) and homogeneous ([111] $CeO_2 \|$ [111] $SrTiO_3$) interfaces where reliable structural models have been produced. The energy applications of this model are dependent on which material is used as the substrate. When CeO_2 is grown on $SrTiO_3$ (STO) it is used in three-way catalysts for oxygen storage when oxygen is unavailable in the airstream for the conversion of CO/NO_x and excess hydrocarbons as CeO_2 is an inexpensive alternative to platinum. High temperature superconductors such as $EuBa_2Cu_3O_{7-\delta}$ also benefit from the incorporation of this interface as an artificial barrier as when high temperatures are applied, structural deterioration is reduced thereby improving thermal stability. When STO is grown on CeO_2 this is used to study the ferroelectric properties of STO and when considering the high dielectric constant of STO, electrical energy is able to be stored resulting in this material being an excellent candidate for microwave devices such as in spectroscopy or communications. Perovskite-fluorite nanocomposites exhibit mixed-ionic electronic conductivity which results in the discussed materials being good candidates for the electrolyte and cathode in solid oxide fuel cells and oxygen separation membranes.

As EM techniques are limited to smaller systems, molecular dynamics (MD) models can be used to investigate larger systems and polar surfaces such as [001] $CeO_2 \|$ [001] $SrTiO_3$ and [111] $CeO_2 \|$ [111] $SrTiO_3$ and can be used to investigate transport properties of the interfaces such as oxygen transport and thermal conductivity. Through the use of a amorphization/recrystallization (A&R) reliable interface models can be generated which can be compared with the pristine interface structure. As the properties of each of these materials are enhanced under reducing conditions, oxygen vacancies will be incorporated using different incorporation techniques and different vacancy concentrations. Quantum mechanics methods will be further be used to measure the stability of interfacial oxygen vacancies which can therefore be compared to the results obtained for the potential model techniques.

Ab initio phonons for photovoltaic modelling: predicting stability and spectroscopy

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The lattice dynamics of solid-state materials play a key role in their phase stability, and are used as a routine diagnostic tool in the form of Raman and infrared spectroscopy, among other techniques. Interpretation of experimental data is much aided by accurate calculations of bulk vibrational properties. Actual samples are often formed in mixed phases, or have structures which cannot be unambiguously assigned by X-ray diffraction.

Hybrid organic-inorganic materials with the perovskite crystal structure are currently the subject of intense research effort, with some hybrid halide systems offering promising performance in photovoltaic devices. We have studied the phase transitions of methylammonium lead iodide (MAPI) between its orthorhombic, tetragonal and cubic polymorphs by computing the phonon spectra of in each phase. In addition to the spectra, we have obtained the intensities of the IR and Raman-active modes through computation of the Born effective charge tensors and mode-dependent macroscopic dielectric tensors, respectively.[1] The resulting spectra can be aligned with experimental data, and facilitate reliable assignment of spectroscopic signals to atomic movements.

The accessibility of routine harmonic phonon calculations with density-functional theory (DFT) on modern HPC facilities allows for consistent studies of groups of materials to be performed, and the construction of temperature-dependent phase diagrams. This technique has been applied to the photovoltaic Cu-Zn-Sn-S (CZTS) system, building on previous work on a smaller subset of the system.[2]

Finally, the *ab initio* study of higher-order three-phonon interactions has recently become computationally tractable. We have applied this to the kesterite materials $Cu_2ZnSn(S,Se)_4$. This methodology offers insight into the phonon-phonon scattering processes which substantially impact thermal conductivity and electron-phonon interactions. Phonon linewidths from these anharmonic force constants, when combined with methods to predict intensities, provide improved agreement with Raman spectroscopy measurements.[3]

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Perovskite Oxides as Thermoelectric Materials

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Oxide materials based on the perovskite structure are promising thermoelectric material due to their chemical flexibility, abundance and stability at oxidation condition and at high temperature, and low toxicity compared to the conventional thermoelectric materials.

Our research focusses on the n-type thermoelectric material $CaMnO_3$. Its usage in thermoelectric devices is hindered by cracking. We have used density functional theory to investigate the oxygen sub-stoichiometry in $CaMnO_3$ and found that upon reduction the structure undergoes a large volume expansion which induces the formation of domains as seen experimentally and cause cracking in the samples. The impact of oxygen sub-stoichiometry on the thermoelectric properties was found to be favorable in terms of Seebeck coefficient for certain stoichiometries, which explains the large variation of measured values. We have also modelled ways of improving the material properties. For example, extrinsic doping using Sr helps prevent the cracking, and further doping with higher valence transition metals such as Mo and Nb injects electrons into the structure and improves the thermoelectric properties.

We also present our work on Tungsten Bronze Barium Neodymium Titanate ($Ba_{6-3n}Nd_{8+2n}Ti_{18}O_{54}$), which is a layered perovskite based structure. Here, we examined the distribution of Ba and Nd in the structure and their role in modifying the thermoelectric properties. We find that the energetically preferred defect distribution and the layered structure decrease the thermal conductivity. This is a major advantage for increasing the thermoelectric figure of merit, making it a potentially attractive thermoelectric material.

Formation of Methyl Ammonium Lead Iodide

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Methylammonium Lead Iodide (MALI) is one of the most actively investigated materials for use in photovoltaic devices. MALI is a promising material as it displays critical properties, notably a band gap makes it usable as a photoabsorber, and a significant light extinction coefficient that makes the material ideal for the fabrication of solid state thin film solar cells. Futhermore, MALI is an excellent charge carrier, and so unlike most organic dyes used in photovoltaics, it does not require a mesoporous charge conducting substrate.

While a great deal of computational effort has been directed at modelling the electronic structure of MALI, and determining how the band gap may be tuned to create an optimal photoabsorber, or to understand the influence of surface defects of the material and how that in turn influences the manner in which water and solvents penetrate the material, no effort has been directed towards understanding the mechanism of formation of MALI.

MALI is a perovskite, $MAPbI_3$, where the A site methylammonium cation sits in a dodecahedron, surrounded by corner sharing PbI_6 octahedra. MALI is readily made through simple grinding with a solvent, of PbI_2 and MAI. This means that the transition from the edge sharing PbI_6 octahedra to corner sharing is facile.

We present simulations that recreate the initial conditions that lead to the formation of MALI by investigating the interactions of MAI and PbI_2, using both Density Functional Theory and a newly parameterized force field to understand the mechanisms involved in the formation of MALI.

Ionic Transport in Hybrid Lead Iodide Perovskite Solar Cells

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Solar cells based on organic–inorganic halide perovskites have recently shown rapidly rising power conversion efficiencies, but exhibit unusual behaviour such as current–voltage hysteresis and a low-frequency giant dielectric response. Ionic transport has been suggested to be an important factor contributing to these effects; however, the chemical origin of this transport and the mobile species are unclear. Here, the activation energies for ionic migration in methylammonium lead iodide ($CH_3NH_3PbI_3$) are derived from first principles, and are compared with kinetic data extracted from the current–voltage response of a perovskite- based solar cell. We identify the microscopic transport mechanisms, and find facile vacancy- assisted migration of iodide ions, with an activation energy of 0.6eV, in good agreement with the kinetic measurements. The results of this combined computational and experimental study suggest that hybrid halide perovskites are mixed ionic–electronic conductors, a finding that has major implications for solar cell device architectures.

'Ionic transport in hybrid lead iodide perovskite solar cells', C. Eames, J. M. Frost, P. R.F. Barnes, B. C. O'Regan, A. Walsh, M. S. Islam, *Nature Comms.*, (2015)

Atomistic Analysis of Li$^+$/Na$^+$ Diffusion in Olivine-Structured Cathodes

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*e05-gener-**leo***

The production of a new high performance rechargeable cathode is currently attracting a lot of interest. Due to the recent commercialisation of LiFePO$_4$, the olivine-structured orthophosphate family (Li/Na)MPO$_4$ (M = Fe, Mn) has become of particular interest. Inherent to the performance of the cathode is the ability for Li$^+$ or Na$^+$ to reversibly intercalate and hence diffuse through the host structure (MPO$_4$). Due to the corrugated potential energy surfaces with distinct energy barriers associated with a typical diffusive process, the required simulation times for molecular dynamics are not plausible. When sampling a system the system will frequently occupy stable/metastable long lived configurations. The events of interest, Li$^+$/Na$^+$ particle jumps, are seldom realised. A novel 'Shooter' algorithm in association with molecular dynamics has been employed to generate the velocity distributions that are not typical for the ensemble average and hence realise the particle jumps. This method has been utilised at a range of temperatures for LiMnPO$_4$, NaMnPO$_4$ and NaFePO$_4$ and successfully simulated diffusion of Li$^+$/Na$^+$ during reasonble simulation times. It is hoped that this method can be employed to test the validity of a cathode material and even be used to discover new candidates.

Computationally Investigating and Identifying Stable Compositions of the layered 7ap Structure

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Identification of complex inorganic structures is becoming increasingly easier though the use of theoretical prediction methods, of which EMMA (Extended Module Materials Assembly) [1] is one. Made within our research group, this program identifies materials containing realistic atomic environments, by ranking structures containing multiple atom types in multiple geometries, to aid the discovery of new functional materials.

Following on previous work, we have returned to the perovskite Yttrium Barium Calcium Iron Oxide layered system, as possible cathode materials for solid oxide fuel cells. From the initial EMMA studies, $YBa_2Ca_4Fe_7O_{18}$ or 7ap (representing a 7 layered material, where ap is the dimension of an ABO_3 perovskite unit cell) was identified as a metastable compound, however all attempts made so far to experimentally isolate this system has been unsuccessful.

The original 16ap material determined with EMMA [1] was also identified as metastable, and initially required small amounts of Cu ions in the synthesis. Therefore, our studies focus on doping the postulated 7ap to help identify compositions with improved stability. The feasibility of the doped material will be calculated to better direct experimental synthesis of the 7ap structure, using the same approach that successfully led to prediction of Mn doping in $YBa_2Fe_3O_8$ [2].

[1] *Science*, 2013, **340**, 847-852, DOI: 10.1126/science.1226558

[2] *Chemical Science*, 2014, **5**, 1493-1505, DOI: 10.1039/c3sc52734d

Electronic and Crystal Structure of High Temperature Thermoelectric $La_{1/3}NbO_3$ Perovskite.

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A combination of experimental and computational techniques has been employed to study crystal structure and thermoelectric properties of A-site deficient perovskite $La_{1/3}NbO_3$ ceramics. $La_{1/3}NbO_3$ at room temperature has orthorhombic structure with a $\sim 2a_p$, $b \sim 2a_p \sim$ and $c \sim 2a_p$ where a_p is the unit cell length of the ideal cubic perovskite. Atomically-resolved imaging and analysis showed that there are two distinct A-sites: one is occupied randomly with La and vacancies and the second site is fully un-occupied. This material possess exceptionally high Seebeck coefficient and low temperature stable thermal conductivity as well as desirable band-structure for n-type thermoelectric material. The only drawback of this material for use in thermoelectric modules is its low electronic conductivity. Our first-principle electronic structure calculations couple the temperature dependence of the measured Seebeck coefficient to the evolution of the density of states with temperature and show a way for its further optimization through the doping. Whereas calculated lattice thermal conductivity with classical molecular dynamics gives an insight into dependence of the thermal conductivity with crystallographic directions of the material. In summary, our calculations show a way to increase working temperature of the material as well as to improve its electronic transport properties through band engineering by exploiting the temperature dependence of the effective band degeneracy trough the band convergence.

Generation Rates and Energy Distribution of Plasmon Induced Hot Carriers in Metallic Nanoparticles.

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*e05-gener-**lis***

Nanoplasmonic devices, capable of confining light into ultrasmall domains well below the operating wavelength, bear great promise for novel energy technology applications, such as plasmonic photovoltaics or plasmonic water splitting. A key physical process in these systems is the generation of energetic or "hot" electrons and holes, which can be transferred to a substrate or trigger chemical reactions, from the decay of plasmon excitations. The theoretical description of this process, however, is very challenging: it requires the combined modelling of the classical characteristics of the plasmon and its quantum nature.

We use accurate first principles approaches for the theoretical description of electronic excitations in materials to investigate fundamental processes in nanoplasmonic energy conversion. Specifically, we use time-dependent density functional theory (TDDFT) to describe plasmons in nanoparticles of various sizes and elemental compositions (jellium, aluminium and gold).

Quasiparticle properties are obtained from accurate many-body Green's function approaches, such as the GW method. In particular, we determine quasiparticle energies and quasiparticle-plasmon coupling constants in nanoparticles. This will enable us to calculate hot electron and hot hole generation rates and energy distributions.

Epitaxial Strain Effects on Lithium Conductivity in Li-Doped MgAl$_2$O$_4$ Spinel Electrolytes

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*e05-store-**bjm***

Lithium-ion batteries are well established in the portable electronics market as energy storage solutions. Conventional Li-batteries use liquid organic-polymer electrolytes, however, which are thermally unstable. Replacing these liquid organic electrolytes with electrochemically stable and non-flammable inorganic ceramic electrolytes would allow the construction of all-solid-state Li-ion batteries with improved safety and durability. While the commercial use of solid-state electrolytes is impeded by their typical low ionic conductivity, this is not simply due to their bulk electrolyte conductivity: Li-ion batteries have multiple components (anode | electrolyte | cathode), and device performance depends on the rate of lithium transport between the electrolyte and electrodes, which in turn depends on the interfacial resistance.

One strategy for minimising electrode–electrolyte interfacial resistance is to select electrode and electrolyte materials with a common crystal lattice structure and matched lattice parameters. This is expected to provide aligned diffusion pathways fast ionic transport through the device [1]. Spinel structured electrodes are already used in commercial batteries, e.g. LiMn$_2$O$_4$ (cathode) and Li$_4$Ti$_5$O$_{12}$ (anode), and recently a new class of spinel structured lithium-ion conductors based on (Li,Al)-doped (Mg,Zn)Al$_2$O$_4$ has been synthesized [2], raising the possibility of all-solid-state Li-ion batteries with a coherent fcc oxide lattice across anode, electrolyte, and cathode.

In practice, perfect lattice matching between the electrolyte and both electrodes is not possible, because the electrodes will have unequal lattice parameters. Constructing epitaxially matched interfaces at both electrodes therefore requires some residual strain. Local strain will modify the local potential energy landscape for lithium diffusion, and can be expected to affect diffusion barriers and net lithium conductivity.

We have used DFT-NEB calculations to explore the effect of residual epitaxial strain on Li transport in Li-doped MgAl$_2$O$_4$ spinel electrolytes. Under epitaxial strain to match typical electrode lattice parameters net Li diffusion is predicted to be enhanced, however, the effect on activation barriers for specific diffusion pathways varies depending on the local crystal structure.

[1] Thackeray et al., *US Pat.*, 4507371, 1985; [2] Rosciano *et al. PCCP,* **15**, 6107 2013.

A DFT Study of CO_2-H_2 Co-adsorption on Ni/YSZ(111) for Solid Oxide Fuel Cell applications

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e05-store-lee

Solid Oxide Fuel Cell (SOFC) devices convert chemical energy into electrical energy by oxidizing fuels such as hydrogen, natural gas, ethanol or hydrocarbon mixtures, which highlights the capability of SOFCs as candidates for applications in stationary power generation. The main species used as fuel in the SOFC are H_2 and CO which are oxidized at the anode [1]. Instead of pure H_2 or CO, H_2/CO mixtures can be used leading to more complicated mechanisms since other processes such as the water-gas shift reaction (CO + H_2O $\leftrightarrow$ CO_2 + H_2) are involved.

Robust materials are needed for SOFC since the working temperature is approximately equal to 800°C. For example, a suitable anode is Ni/YSZ (nickel – yttria stabilized zirconia) since it has a high catalytic activity, mechanical and chemical stability and compatibility with the electrolyte under working conditions [2]. It is well known that the performance of the Ni/YSZ cermet depends on the microstructure and the distribution of Ni and YSZ phases in the cermet [3]. Additionally, this performance depends on the key reactions occurring at the triple phase boundary where the gas phase, Ni particles and YSZ surface meet. Thus, it is relevant to understand, at the atomic scale, the structure of Ni/YSZ and its interaction with the gas phase, and in particular CO2 and H2.

To simulate the interaction of CO_2 and H_2 with Ni-YSZ, we have used electronic structure calculations based on the Density Functional Theory using the Vienna Ab-initio Simulation Package (VASP). We have studied the deposition of Nin (n=4-10) clusters on the YSZ(111) followed by the adsorption of molecules on the optimized Nin/YSZ(111) structures and calculated the geometric and electronic structure at the most stable adsorption site. We have also analyzed the reaction path of the reverse water-gas shift reaction (CO_2 + H_2 $\leftrightarrow$ CO + H2O) on three different Nin/YSZ(111) (n = 5, 6 and 10) interfaces, considering two possible pathways intermediates: hydrocarboxyl or formate.

Finally, we have observed that both CO2 and H2 prefer to adsorb on the Nin cluster rather than on the surface. On the metal cluster the CO2 molecule is activated and the H2 is dissociated upon adsorption, whereas charge is transferred from the cluster to the molecules. We have determined two intermediate states and three intermediate states for the carboxylic acid and formate intermediate pathway, respectively, on the three Nin/YSZ(111) (n = 5, 6 and 10) interfaces.

[1] J. Hanna, W. Y. Lee, Y. Shi and A. F. Ghoniem, Prog. Energy Combust. Sci., 2014, 40, 74–111.
[2] Kim, S. et al. Solid State Ionics, (2007), 178, 1304–1309.
[3] Kim, S. et al. Solid State Ionics, (2006), 177, 931–938.

Modelling Point Defects and Dopants in LaFeO$_3$ for Fuel Cell Applications

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Solid oxide fuel cells (SOFCs) are a strong candidate for zero-emission electricity generation. However, the high temperatures necessary for operation lead to long start up times and short lifetimes. Intermediate temperature SOFCs suffer from a decreased rate in the oxygen reduction reaction (ORR) at the cathode site, leading to an interest in mixed ionic electronic conductors (MIEC) as cathode materials which can increase the area within which the ORR can take place, increasing the reaction rate. In this work we discuss intrinsic point defects, substitutional defects and oxide ion migration in LaFeO$_3$, a promising MIEC cathode material, studied using molecular mechanical and density functional theory calculations. The majority of intrinsic defects investigated have high formation energies with the key exception being O^{2-} vacancies. A range of divalent substitutional defects have been investigated for both the A- and B-site and the most appropriate for each will be discussed, along with their affect on the electronic properties of the material. Oxide ion conduction calculations revealed small activation energies along the majority of paths between two oxygen vacancies, with values that agree well with experiment.
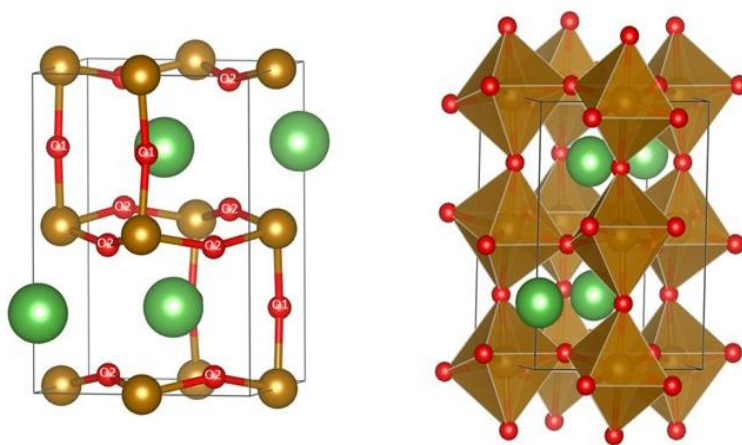
Figure 1. Orthorhombic LaFeO$_3$