Invited Talks

Exploring Battery Materials With Atomistic Simulations: Electrodes, Electrolytes, and Interfaces Thereof

René Windiks

Materials Design S.A.R.L.
42, Avenue Verdier, 92120 Montrouge, France

Invited Talk

The design of next generation batteries with high performance and long lifetimes requires a profound understanding of the constituent materials, essentially to predict their properties and interactions with each other. This talk shows how atomic-scale modeling with Materials Design's MedeA® environment [1,2] is complementary to experimental techniques to synthesize compounds and examine battery cells during cycling. Based on computational thermodynamics and molecular dynamics simulations we determined the structural stability, voltage profiles, electrical conductivity trends, and lithium transport mechanism of an anode material that is based on a Wadsley-Roth phase. Analogue computational techniques are used to predict the electrochemical stability window of solid electrolytes and the decomposition products that are formed in redox reactions with charge carriers. With density functional methods (VASP) and forcefield simulations (LAMMPS) we assessed the electrical conductivity and the ionic conductivity of the solid electrolyte interface. The phase-dependent open-current voltages of lithium nickel oxide are calculated with a cluster expansion technique (UNCLE) and post-density functional method.

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[1] M. Christensen et al. Software Platforms for Electronic/Atomistic/Mesoscopic Modeling: Status and Perspectives. Integrating Materials and Manufacturing Innovation (2017), DOI:10.1007/s40192-017-0087-2.

[2] MedeA®, Materials Design, Inc., San Diego, CA, USA, 2021, http://www.materialsdesign.com

Quantum Computing for Strongly Correlated Materials

Francois Jamet

National Physical Laboratory, Hampton Road, Teddington, Middlesex, UK, TW11 0LW

Invited Talk

Quantum embedding approaches for materials simulations, such as the dynamical mean-field theory (DMFT), provide corrections to first-principles calculations for strongly correlated electrons, which are poorly described at lower levels of theory. These embedding methods are computationally demanding on classical computing architectures, and hence remain restricted to small systems, limiting the scope of their applicability. Quantum computers have the potential to overcome this limitation.

In this talk, I will fist give an introduction to quantum computing and then I will give an example of a quantum algorithm for materials simulation: the Quantum subspace expansion algorithm for Green's functions (arxiv:2205.00094).

Computational Chemistry: An Industrial Perspective

Misbah Sarwar

Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, RG4 7QE

The talk will give an overview of how multi-scale modelling combined with advanced characterization techniques are being used in industry to understand the structure and activity of catalytic materials in industry. Examples of insight gained from modelling Pt nanoparticles for PEM Fuel cells combined with electron microscopy will be presented. A case study of how combining Molecular Dynamics and QENS provides insight into the diffusion mechanism of molecules in zeolites used as SCR catalysts will also be presented.

Predicting structure formation and transformation in low-dimensional systems via studying their energy landscapes

J. Christian Schön

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Invited Talk

New chemical materials and compounds serve as the foundation for the modern technology of our civilization, being environmentally friendly, with stable and controllable properties, and at the same time energy efficient in their synthesis. Such materials are nowadays often grown in a bottom-up approach on a substrate, and in the extreme we are dealing with and aiming for low-dimensional systems with bespoke properties, where the stability of such materials often becomes an issue of concern. Among these systems, we find monolayers on surfaces or inside layered compounds, ultrathin films, nanotubes and nanowires, just to name a few, which are becoming increasingly important from a technological point of view.

The ability to predict such kinetically stable and/or thermodynamically (meta)stable nanomaterials, followed by a computation of their properties and evaluation of their kinetic and thermodynamic stability and possible structural transformations, is clearly of great value in their design and synthesis.[1] For the past three decades, the prediction of feasible structures and transformations of three-dimensional bulk crystalline compounds[1,2] on the one hand, and of single atom clusters[3] and (bio)molecules[4] on the other hand, has shown great progress, and the computational approaches used are expected to be also applicable to low-dimensional systems.[5,6] In this presentation, we will discuss examples of predictions of structures and their transformations using global energy landscape explorations and molecular dynamics simulations, such as quasi-zero-dimensional (e.g., compact clusters),[7,8] one-dimensional (e.g., atom chains),[9] quasi-one-dimensional (e.g., nanotubes),[9] two-dimensional (e.g., monolayers),[5,10] quasi-two-dimensional (e.g., layer-like building blocks for layered compounds),[11] and composite (e.g., multi-molecule patterns on substrates)[12,13] systems.

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MCC Member Talks

Temperature Dependence of Charge Mobility in Rubrene from Fragment Orbital-Based Surface Hopping

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Charge transport in high-mobility organic semiconductors (OS) operates in a difficult regime between the limits of band transport and small polaron hopping. In previous work we developed fragment orbital-based surface hopping (FOB-SH), a non-adiabatic molecular dynamics technique for propagation of charge carriers coupled to lattice vibrations in nanoscale materials. Here we apply FOB-SH to calculate the temperature dependence of the hole mobility in the representative OS rubrene and obtain an inverse power law in excellent agreement with experiment. Our simulations show that this is a consequence of increasing non-local electron-phonon coupling with increasing temperature, resulting in a steady decrease in quantum delocalization of the hole and thus mobility. We also present first extensions of FOB-SH to study the non-equilibrium dynamics of charge carriers in response to a temperature gradient giving us access to the Seebeck coefficient and to a better understanding of the thermoelectric physics of OS.

Effect of polymer topology on the self-assembly of micelles

Raquel Lopez-Rios De Castro, Robert M. Ziolek, and Christian D. Lorenz*

*Department of Physics, KCL   e05-biosoft-lor

The structure of molecules has often been shown to play an important role in the function and properties of the materials that they form at various lengths and time scales. In polymer science, the choice of macromolecular structures historically has been linear and randomly branched. More recently, more controlled polymer topologies have been formulated because of the development of increasingly advanced synthetic techniques. As a result, there has been an increased interest in the role that topology plays in a variety of systems, ranging from thin films [1] to elastomers [2,3] to micelles [4,5]. While in all these investigations there are differences observed as a result of the changing topologies, very little is known as to how the molecular scale interactions of these polymers which have the same composition but just different topology result in these differences.

In this presentation, I will show our latest results of large-scale molecular dynamics simulations in which we investigate the self-assembly of a range of different polymer topologies (linear diblock, linear triblock, branched and cyclic) of poly(methyl acrylate)-poly(ethylene oxide) block polymers. In doing so, we combine graph theory and machine learning (dimension reduction and clustering) techniques to gain a unique insight into the self-assembly process of these different topology polymer molecules. Also, we provide a detailed description of how the conformations of each of these different topologies vary within the self-assembled micellar structures. With this detailed description of the structure of these micelles, one can better assess how drugs could be incorporated into nanoparticles formed by the different polymers. Additionally, with the detailed description provided by our study, we have the foundations for topology-based rational design of self-assembled polymeric nanoparticles.

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Thermodynamics up to the melting point in a TaVCrW high entropy alloy: Systematic *ab initio* study aided by machine learning potentials

Ying Zhou[*], Prashanth Srinivasan, Fritz Körmann, Blazej Grabowski, Roger Smith, Pooja Goddard, Andrew Ian Duff

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Multi-principal-component alloys have attracted great interest as a novel paradigm in alloy design, with often unique properties and a vast compositional space auspicious for materials discovery. High entropy alloys (HEAs) belong to this class and are being investigated for prospective nuclear applications with reported superior mechanical properties including high temperature strength and stability compared to conventional alloys.

Here we calculate high temperature properties of the multicomponent body-centered low-activation HEA TaVCrW with DFT accuracy using a modified version of the two-stage up-sampled thermodynamic integration using Langevin dynamics (TU-TILD) approach. The proposed approach is based on density-functional theory (DFT) and thermodynamic integration combined with machine-learning based interatomic models, and in the present work improves the computational efficiency of the standard TU-TILD method by a factor of 4. The described methodology is also relevant to potential applications of HEAs in nuclear energy, and our modified formalism is well positioned for thermodynamic property prediction and high-throughput screening of multi-principal component alloys more generally. The machine learning potentials that were fitted using ab initio MD are now being tested for their applicability in radiation damage studies of HEAs. The outcome of this research will be reported at the meeting.

Thermal conductivity of radiation damaged tritium breeder materials

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*e05-power-***mur**

In a fusion reactor, the breeder blanket is the means by which the tritium fuel required for the fusion reaction is bred. Breeder materials are subjected to irradiation by high-energy neutrons leading to the formation of defects, such as vacancies and interstitials. The presence of these defects changes the efficiency of heat transfer through the breeder blanket to the coolant, directly affecting the overall efficiency of electricity generation of the reactor. The effect of these defects on overall heat transfer depends on how they modify the underlying thermal conductivity of the materials themselves. Measuring the impact of specific types of defects on the thermal conductivity of materials is experimentally difficult to achieve. Therefore, in this study we employ atomistic simulation, principally non-equilibrium molecular dynamics (NEMD), to study the evolution of the thermal conductivity in a leading ceramic breeder blanket candidate, Li_2TiO_3.

In the first instance, we examine the perfect crystal, where the simulations indicate a high degree of anisotropy in the thermal conductivity of in the different Cartesian directions, which is attributed to the material's complex layered structure. Following this, we examine point defects that may arise due to lithium burn-up and radiation damage. We show the relationship between the stoichiometry of Li_2TiO_3 and the thermal conductivity by examining both Li-rich and Li-poor cases, which respectively represent the expected beginning and end states of the ceramic breeder material. We also investigate larger defects such as voids and helium bubbles, the effects of which are studied as a function of porosity and bubble size. By examining how these defects in the material affect the thermal conductivity, we can discuss how this may impact reactor efficiency as the blanket material ages.

An ab initio investigation of the impact of intrinsic defects on the thermal properties of CeO$_2$

Thomas Smith[*], Samuel Moxon, Joshua S. Tse, Jonathan Skelton, David J. Cooke, Lisa J. Gillie and Marco Molinari

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Cerium dioxide is commonly used as a simulant material for PuO$_2$. This is beneficial not only experimentally as PuO$_2$ is toxic, radioactive and has high costs of post-processing, but also computationally as ceria does not require spin-orbit coupling and non-collinear magnetism, thus requiring significantly less resources. Ceria's use as a proxy is supported by both systems crystallising in the fluorite (Fm-3m) structure across a wide temperature range, and Ce and Pu both having oxidations states of 3+ and 4+. The thermal conductivity of the materials is an important property as it is associated with the performance of the nuclear fuel. Only a small difference of less than ~1 - 2 W m^{-1} K^{-1} is present across a wide temperature range of 300 - 2000 K between ceria and plutonia. As the harsh conditions imposed on nuclear fuels result in the formation of defects such as point defects and more complex Frenkel and Schottky defects, here we focus on the latter two as they will have an impact on the thermal conductivity of the material. We employ a DFT+U approach to investigate the thermophysical properties of defective ceria systems, to evaluate their phonon dispersions using a band unfolding methodology, and finally to calculate the thermal properties using the constant relaxation time approximation.

BN doped PAHs – Towards 2D molecular recognition

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*e05-nano-***rol**

Boron-nitride is isoelectronic to sp^2 bonded carbon, as a BN and CC bonds contain the same number of electrons; furthermore, monolayer hexagonal BN (h-BN) is isostructural to graphene, both consisting of a uniform hexagonal lattice. h-BN is a wide-gap semiconductor, with an electronic bandgap in the UV region of 4.0-5.8 eV[1] with applications as a dielectric substrate material, an insulator, or as a thermal conductor[2]. Introducing BN sub-units to polyaromatic carbon molecules and extended graphene sheets is thus relatively accessible and can change the band gap and creates an electron poor hole in the surface of the graphene that could be complimentary for the adsorption of electronegative aromatic moieties.

2-8-14-trixylyl-hexaphenyl borazinocoronene was synthesized by our collaborators and was found to crystalise in the presence of aromatic species such as halogenated benzenes. The halo-benzene molecules within these crystals were found by x-ray crystallography to possess multiple common orientations. Should these orientations be separated by a suitable energy barrier then these crystals could be the foundation of a data storage device. Additionally, should a change in orientation change the bandgap of the coronene then perhaps these materials could also be used as molecular sensors.

In this study, we explore the interactions occurring in the co-crystal of 2-8-14-trixylyl-hexaphenyl borazinocoronene + C_6H_5X to determine the viability of BN-doped PAHs to be used for 2-D molecular recognition. We study the analogous non-doped coronene to determine the properties introduced by the borazine and then model the interactions occurring in both crystal systems. We also model the rotations of the halogenated benzenes to study the PES inside the crystal and evaluate the barriers of rotation. We find potential energy minima in our system that corresponds to the different occupancies in the crystal structures and evaluate the thermodynamic stability of those orientations. With this knowledge we will gain critical insight into the suitability of these materials as possible data storage material.

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Chlorine Activated Stacking Fault Removal Mechanism in thin Film CdTe Solar Cells: the missing Piece

Pooja Goddard[*], Peter Hatton, Michael J. Watts, John M. Walls, Ali Abbas, Roger Smith

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The conversion efficiency of as-deposited, CdTe solar cells is poor and typically less than 5%. A $CdCl_2$ activation treatment increases this to up to 22%. Studies have shown that stacking faults (SFs) are removed and the grain boundaries (GBs) are decorated with chlorine. Thus, SF removal and device efficiency are strongly correlated but whether this is direct or indirect has not been established. Here we explain[1] the passivation responsible for the increase in efficiency but also crucially elucidate the associated SF removal mechanism. The effect of chlorine on a model system containing a SF and two GBs is investigated using density functional theory. The proposed SF removal mechanisms are feasible at the 400°C treatment temperature. It is concluded that the efficiency increase is due to electronic effects in the GBs while SF removal is a by-product of the saturation of the GB with chlorine but is a key signal that sufficient chlorine is present for passivation to occur.

[1] Hatton et al, *Nature Communications*, 2021, 12(1), 4938

Understanding nucleation of Co and Mn nanoclusters on anatase (101) surface

Pavel V. Stishenko[*], Andrew J. Logsdail

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Cobalt-base catalysts on anatase support are widely used for Fischer-Tropsch synthesis. Knowing and controlling the size of Co nanoparticles is crucial for selectivity of the synthesis process. Recently, the addition of Mn as a promoter has been demonstrated to change the catalyst's selectivity, although the mechanism of this effect is still unclear. Characterisation studies have revealed that the presence of Mn during catalyst production significantly reduces the average size of metal nanoparticles, drawing a conclusion that the particle nucleation process is probably affected by Mn.

To examine the interactions of Co and Mn adatoms on the TiO_2 anatase surface, we have explored energy landscape of single-atom and two-atom clusters on the prominent (101) facet. The meta-GGA approximation of the density functional theory was employed, as implemented in the FHI-aims software. Comprehensive enumeration of probable adsorption sites was performed with subsequent geometry and spin optimisation. Pairs of adatoms placed in adjacent adsorption sites were enumerated with the SuSMoST code, and subsequently energetic quantities studied with FHI-aims. The calculations revealed that Co and Mn adatoms energetically prefer to form heterogeneous two-atom clusters., and that Mn adatoms seem to be less mobile than Co ones. Therefore, we conclude that the introduction of Mn adatoms results in reduced diffusion of Co adatoms, which hinders ripening and coalescence of catalyst's nanoparticles; the reduced coalescence results in smaller nanoparticle size and higher dispersion.

References:

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Chiral valley phonons and flat phonon bands in moiré materials

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A chiral object is not the same as its mirror image. The chirality of quasiparticles is a critical concept behind many modern developments in condensed matter physics. Some recent examples include Klein tunnelling and the chiral magnetic effect due to chiral Fermions. Using detailed atomistic simulations, we show that multiple phonon modes in twisted bilayers of WSe2 can be chiral [1]. We demonstrate distinct chiral behavior of the K/K' valley phonons for twist angles near 0 and 60 degrees. Furthermore, we observe the flattening of bands near the phononic bandgap edges in this system. We find that a finite phonon angular momentum can be generated by applying a temperature gradient in this system [2]. We discuss the possibility of using different optical spectroscopy techniques to probe these chiral phonons. Our findings, which are more generally applicable to moiré systems created from 2D materials that break inversion symmetry, have important implications for understanding electron-phonon and exciton-phonon scattering and for designing phononic crystals.

[1] I. Maity, Arash A. Mostofi, J. Lischner, Phys. Rev. B Letters, 105 L04140 (2022).
[2] S. Mandal, Arash A. Mostofi, J. Lischner, M. Jain, I. Maity, under preparation.

Phosphate adsorption on {111}, {110}, and {100} surfaces of ceria: A DFT study

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*e05-surfin-**mol***

Ceria nanoparticles (CeNPs) are nanozyme that exhibit enzyme mimetic activities (e.g. superoxide dismutase, catalase, phosphatase). Such activities are hindered by the adsorption of bodily electrolytes at the surfaces of CeNPs when in contact with biological media. A strong bodily electrolyte is the phosphate ion and here we study its interaction with the three most stable {111}, {110}, and {100} surfaces of ceria using Density functional theory (DFT) calculations. We found that the preferential facet for phosphate adsorption follows {100} > {110} > {111}. An adsorbed 5-fold coordinated P species is also seen and calculated as a stable intermediate, suggesting that this species could be responsible for the early stages of the scavenging of ceria surfaces, a process known experimentally that sees the transformation of ceria into cerium phosphate. The IR and Raman spectra are evaluated for all the most stable adsorption configurations showing that the main vibrational fingerprint for the ceria-phosphate interaction is between 500 and 1100 cm^{-1}.

The thermoelectric properties of Polyaniline-SrTiO$_3$ composites

Nathan D. Wood[*,1], Joshua S. Tse[1], Jonathan M. Skelton[2], David J. Cooke[1], Lisa J. Gillie[1] and Marco Molinari[1]

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Oxides are well-explored materials for thermoelectric (TE) applications. However, they are currently limited to higher temperature applications (> 700 K) in part due to their high thermal conductivity ($\sim$ 1 - 10 W m^{-1} K^{-1}) at lower temperatures. TE devices allow the direct conversion of heat into electricity and as such will play a critical role in the sustainable and green energy generation. The performance of a TE materials is gauged using the figure of merit, ZT = S$^2\sigma$T/κ, which includes the Seebeck coefficient S, the electrical conductivity σ, and the thermal conductivity κ. An oxide of great promise is SrTiO$_3$ but its applicability as low temperate hinders its applications (κ = 9–12 W m^{-1} K^{-1} at room temperature). Decreasing κ can be achieved through several methods: doping, nanostructuring and nanocompositing. Doping SrTiO$_3$ has been shown to lead to improvements in both σ and κ, whilst nanostructuring has been shown to be a less effective strategy for reducing κ compared to other oxides. Therefore, recent work has moved towards nanocompositing, i.e. generating composites of SrTiO$_3$ using conductive polymers or graphene. The introduction of these materials creates an interface that can scatter phonons and/or induce quantum effects, which lead to an enhancement of the thermal and electrical TE properties. Our research explores the structural and TE properties of the interface between the most stable surface {100} of SrTiO$_3$ and polyaniline in its various oxidation states using a DFT+U methodology and energy minimisation techniques.

Obtaining Interfacial Free Energies from Atomistic Simulations using an Einstein Crystal Reference State

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We present a general method for computing interfacial free energies from atomistic simulations which is particularly useful for solid/liquid interfaces. Our method uses an Einstein crystal as a universal reference state and is more flexible than previous approaches [1]. Surfaces with dipoles, complex reconstructions, and partially dissolved species are all easily accommodated within the framework. It may also be extended to calculating the relative free energy of different phases and other types of defect. We tested our method by calculating the interfacial free energy of NaCl with water and obtained a value of 0.13 J/m2, in line with previous work. We have applied our method to interfaces of bassanite and gypsum with water and predicted equilibrium morphologies for bassanite and gypsum that compare well with experiments and previous calculations. Results for calcium carbonate and potassium nitrate will also be presented.

[1] Stephen Yeandel, Colin Freeman and John Harding; J. Chem. Phys. (in press) (2022); https://doi.org/10.1063/5.0095130

Towards Modelling Realistic WS$_2$/H$_2$O/SiO$_2$ Interfaces

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Transition Metal Dichalcogenides (TMDs) are widely studied 2D materials with applications in photovoltaics and transistors [1]. These thin materials are transferred onto insulating substrates such as SiO$_2$ for use in electronic devices. However, the transfer method is known to affect the optical properties of TMDs, with mechanical exfoliation methods increasing the band offsets between the TMD and SiO$_2$ substrate [2]. Mechanical exfoliation occurs in ambient conditions thus, the SiO$_2$ substrate will have water adsorbed to the surface. Therefore, we explore the effect of confined water trapped between the SiO$_2$ substrate and WS$_2$. Three interfaces were built and optimized explicitly with 1, 2, and 3 water layers present using molecular dynamics (MD), density functional theory (DFT), and ab-initio MD (AIMD). AIMD allowed us to sample more configurations at 400 K to avoid over-structuring water. The electronic properties of the interface, such as band gaps and band alignment, were investigated using DFT. Overall, we show there is a change in band offset depending on the amount of water present. Understanding the effect of water will be critical in understanding the functioning of 2D materials in electronic devices and understanding experimental results.

[1] Choi, W. et al. Materials Today 20, 116–130 (2017)

[2][Afanas'ev, V. v. et al. Nanotechnology 30, (2019)

Approximating Many-Electron Wave Functions using Neural Networks

Matthew Foulkes[*], Gino Cassella, Wan Tong Lou, Halvard Sutterud, David Pfau, James Spencer

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Given access to accurate solutions of the many-electron Schrödinger equation, most of condensed matter physics, chemistry and materials physics could be derived from first principles. Exact wave functions of systems with more than a few electrons are out of reach because they are NP-hard to compute in general, but approximations can be found using polynomially scaling algorithms. The key challenge for many of these algorithms is the choice of an approximate parameterized wave function, which must trade accuracy for efficiency. Neural networks have shown impressive power as practical function approximators and promise as a way of representing wave functions for spin systems, but electronic wave functions have to obey Fermi-Dirac statistics. This talk introduces a deep learning architecture, the Fermionic neural network, which is capable of approximating many-electron wavefunctions and greatly outperforms conventional approximations. The use of FermiNet wave functions boosts the accuracy of the simple and appealing variational quantum Monte Carlo method until it rivals the very best conventional quantum chemical approaches.

Anharmonicity and entropic stabilisation in zirconia from first principles

Kasper Tolborg[*], Aron Walsh[*]

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Stability of high temperature phases is of continuous importance in solid state chemistry with many materials exhibiting exciting properties in their high temperature polymorphs. However, their discovery is largely serendipitous due to a lack of computational methods to predict high temperature stabilities.

Here, we investigate the high temperature stability and properties of zirconia, which is one of the most studied oxide ceramics, using anharmonic phonon theory and ab initio molecular dynamics simulations.

Applying self-consistent phonon theory including quasi-particle corrections, we show how the soft-mode cubic-to-tetragonal phase transition develops. However, anharmonic free energies at the current level of theory are unable to predict the reverse transition upon heating.

Based on molecular dynamics simulations, we show that the cubic polymorph is likely to be stabilised due to spontaneous defect formation, which is also the driving force for the well-known ionic conductivity at high temperatures.

Exploring the Nanoparticle Exsolution Process in Perovskite Oxide

Ji Wu[*], Steve Parker

[*]*Department of Chemistry, University of Bath*   *e05-bulk-**par***

The creation of socketed metal nano-particle through dopant exsolution from complex perovskite oxides has attracted significant interests over the past few years in the field of solid state ionics. Compared to deposited metal nano-particles, these exsoluted nano-particles retain good catalysis performances but are more resilient towards coking and delamination/agglomeration during cycling. Thus, these durable exsoluted nano-particles have many promising applications, like in chemical looping devices and anodes of solid oxide fuel/electrolyser cells (SOCs).

Despite its great application potential, the mechanism behind the nano-particle exsolution process is not yet clear. Earlier theoretical efforts have shown that the migration of the transition metal dopants towards the perovskite surface are thermodynamically favourable. However, these findings cannot explain the highly reducing condition (5% H_2/Ar mixed gas) and high temperature (above 950°C) required to activate the exsolution process in experiments. In this work, atomistic simulation methods were applied to two typical perovskite systems, $(La, Sr)_{1-x}(Ni, Ti)O_{3-d}$ and $(La, Ca)_{1-x}(Ni, Ti)O_{3-d}$, to study the kinetics of the metal cation migration during exsolution. We have shown that the introduction of A-site deficiency greatly reduces this barrier and makes cation migration viable under reported experimental conditions. Furthermore, we have evaluated a number of factors possible to affect the diffusion kinetic and identified what might be effective to ease the exsolution condition, and provide insights for future optimisation to utilize this exsolution process better.

The Impact of E Field on Defect Generation and Migration Processes in Dielectrics

J Strand, J Cottom, A Shluger

[*] *Department Of Physics and Astronomy, UCL*   *e05-bulk-**shl***

The interaction between electric fields and metal oxides is of fundamental importance to develop accurate models of dielectric breakdown. In this talk, we demonstrate the use of hybrid density functional theory, implemented in CP2K[1], to calculate how an applied electric field[2] affects the generation of oxygen Frenkel pairs in monoclinic (m-) HfO_2. We find that, within a linear regime, the electric field modulates the barrier height by a simple dot product between the electric field intensity and the zero-field electric dipole at the transition state, similar to previous results for MgO[3]. Even at breakdown fields, barriers for Frenkel pairs generation exceed 6 eV in the perfect m-HfO_2 lattice. Injection of extra electrons from electrodes significantly lowers the barriers for creation of defect pairs (DPs), which are further reduced by the field to around 2 eV. We find the existence of electrons in a trap state not only reduces the activate energy of the generation process, but also opens up new reaction pathways which have even lower (1.5 eV, 0.8 eV) activation energies, making vacancy generation at room temperature physically feasible. Our calculation therefore show that electron injection is a vital part of the oxygen vacancy generation mechanism in m-HfO_2. While bias application facilitates the injection of electrons into the oxide, these extra electrons facilitate the creation of O vacancies and the energy barrier for this process is, in turn, also lowered by the field. The field also affects the rates of electron transfer through O vacancies and diffusion of O vacancies and interstitial ions. The investigation of the diffusion of O interstitial ions through multiple migration pathways demonstrates that the rapid diffusion of O ions in pristine m-HfO_2 is only possible within the 3C oxygen lattice.

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Investigating the Structure and Stability of PdZn Bi-Metallic Alloys by Coupling Density Functional Theory and Cluster Expansions

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Metals alloys are known to improve the performance of heterogenous catalysts for many different reactions, such as CO2 hydrogenation [1,2]. Predicting an effective and novel catalyst, by computing combinations of elements and compositions using Density Functional Theory (DFT), is expensive and highly time-consuming. To accelerate the discovery process, one can couple DFT with cluster expansion (CE), which we demonstrate here in the identification of an effective and novel catalyst for CO_2 hydrogenation. We focus on the PdZn (101) and (110) facets, which are most stable for binary alloys, and CE models for both of facets were tested in the concentration range where the body-centred tetragonal (BCT) phase exists, which is from 40 to 50 % Zn concentration. Our results show that higher Pd concentrations are predicted for both facets in the sub-surface while the top layers remain chemically ordered in a 1:1 alloy; the behavior changes outside the stable BCT range, where segregation of Zn on the top surface is predicted for Zn concentrations above 50 %. The outcomes highlight the critical importance of CE approach for determining structure−property relationships and accelerating the discovery and design of surfaces and nanostructured materials.

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Computational design of *green* ternary semiconductors for optoelectronic applications

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Perovskites based on lead halide are one of the most promising contenders for different optoelectronic applications. Despite rapid progress, their inherent toxicity and stability issues still remaons to be resolved. To mitigate these problems, different approaches such as cation mixing, anion mixing, or doping have been investigated. These studies have generated a parallel interest in the design and discovery of green materials made of abundant, inexpensive and environmentally friendly chemical elements. We pursue this search by identifying recurrent structural templates other than perovskites.

Through combination of high-throughput methodology and DFT studies, we identified several new structural templates. A further analysis on few selected templates based on Cu and Zn led to several promising candidates. There has been a recent report on the synthesis of $RbCu_2Cl_3$ [1].

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Crystal structure predictions of organic halide salts

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The ability to predict the crystal structures of a given material from its chemical composition has been a long-standing goal of the computational community. With the help of the blind test studies hosted by the CCDC, significant developments in crystal structure prediction (CSP) methodologies of organic molecular materials have been made which typically involve a form of global search of the lattice energy surface. It is now possible to generate accurate crystal structure landscapes for quite complex and (often) polymorphic systems, including pharmaceutical molecules, multi-component crystals and even solvates. However, despite these achievements there is still significantly less progress in the prediction of salt structures.

As part of an on-going collaboration aimed at the discovery of porous molecular crystals, we will demonstrate a workflow that we have used in our research group for performing CSP studies on a series of organic halide salts. We will show that in many cases, we are able to predict the experimental crystal structure of different polymorphs and have been successful in elucidating the crystal structures of some salts for which only an experimental powder x-ray diffraction pattern could be obtained.
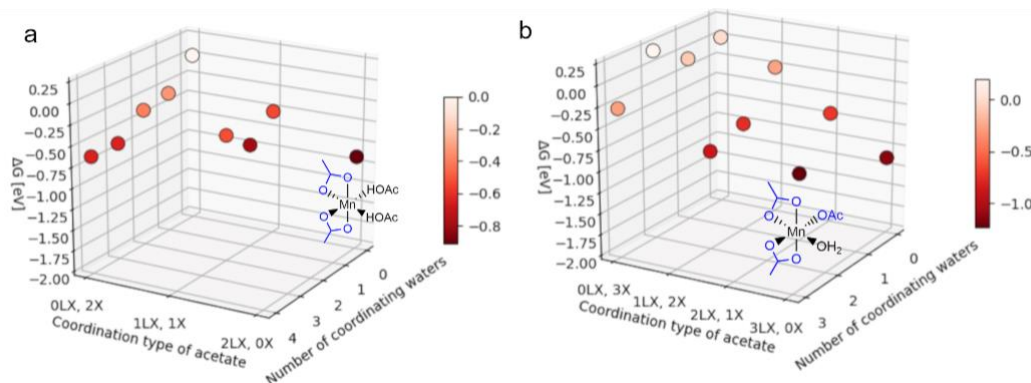
Ab initio study of the Para-xylene Oxidation Redox Cascade

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The industrial oxidation of para-xylene to terephthalic acid uses a homogenous Co/Mn/Br catalyst in aqueous acetic acid solvent under elevated temperatures and pressures. [1] The oxidation process is of significant commercial value as terephthalic acid is an intermediate used in the production of polyethylene terephthalate (PET), which meets 7% of the global plastic demand, including 62% of plastic bottles. [1] The process engineering and kinetics aspect of the para-xylene oxidation process is well understood, and there is a strong correlation between the structure of the catalyst and its activity; [2] however, there is little knowledge of the actual catalyst structure under operating conditions. To aid in elucidating the catalyst structure, computational modelling has been used here to assess the thermodynamic stability of possible manganese and cobalt complexes; redox potentials are also calculated, in an aim to relate the structure of the catalyst to its activity.

To derive the thermodynamic stability of the catalysts, changes in Gibbs' Free Energy (ΔG) for substituting inner-sphere ligands were evaluated using density functional theory (DFT). [3] The Mn(II) and Mn(III) species with the lowest ΔG coordinate zero and one waters, respectively, as shown in Figure 1. The low number of waters coordinating to Mn(III) facilitates inner-sphere bromide coordination, allowing for efficient electron transfer. [2] The analogous results for the Co(II) and Co(III) species suggest both coordinate zero water ligands, which implies reduced thermodynamic driving force for ligand rearrangement when compared to the Mn complexes. Coupling the results with calculated Mn(II/III) reduction potentials aids in understanding the active form of bromide involved in the catalysis. Figure 1: ΔG landscape for the speciation of the (a.) Mn(II) and (b.) Mn(III) catalysts, with the schematics of the most thermodynamically stable structures shown. ΔG are calculated assuming a solvent environment of 34.6 mol% water in acetic acid and industrial operating conditions of T= 473 K and P = 2.25 MPa. ΔG are normalized against the values for the neutral acetates, giving ΔG =0 for these species.

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Interatomic-potential-based Computational Approaches for Modelling Defect Chemistry and Surface Oxidation of Solid Materials

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Atomistic simulations using interatomic potentials (IPs) have long been playing an active role in disentangling the mysteries in materials science, especially for understanding complex materials and interfaces that are computationally too demanding for electronic-structure calculations. We presented several recent advances in modelling defects and surface oxidation dynamics using IP-based approaches. Polarisable shell-model IPs are widely used for modelling charged defects at the dilute limit in solids using the Mott-Littleton approach and hybrid QM/MM embedded-cluster techniques. Recently, we proposed a novel IP development scheme assisted by the QM/MM approach that, for the first time, unifies the predictions of different charged states of intrinsic defects in CeO_2 between the Mott-Littleton approach and QM/MM calculations using hybrid DFT functionals. The new IP accurately reproduces a wide range of physical, chemical, and thermodynamical properties of CeO_2, showing excellent agreement with experimental and DFT references. These findings offer opportunities for accurate large-scale modelling of the partial reduction behaviour and nonstoichiometry in CeO_2, as well as a prototype for developing robust shell-model IPs for other imperfect crystals.[1] Besides, the reactive force-field (ReaxFF) provides a cost-effective framework for modelling the dynamics of chemical reactions in a wide range of systems. Using ReaxFF-based molecular dynamics (MD) simulations, we elucidated the distinct oxidation mechanisms of nanomaterials, including nanoparticles, nanowires, and two-dimensional materials, which can be significantly different from their bulk counterparts and result in various novel oxide nanostructures with unique properties.[2-4] These results demonstrate the critical role of IP-based techniques in extending the modelling time- and length-scales towards a more realistic description of defect chemistry and surface reactions.

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A mechanism for the CO_2-to-CO conversion catalysed by carbon monoxide dehydrogenase

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*e05-react-**ter***

The carbon monoxide dehydrogenase enzyme efficiently converts CO_2 to CO and, therefore, could enable an affordable CO_2 recycling strategy. The reduction of CO_2 occurs at a peculiar nickel-iron-sulfur cluster, following a mechanism that remains little understood. In this study, we have used ab initio molecular dynamics simulations to explore the free energy landscape of the reaction. We predict the existence of a COOH ligand that strongly interacts with the surrounding protein residues and favours a mechanism where a H_2O molecule is eliminated before CO. We have taken advantages of the insights offered by our simulations to revisit the catalytic mechanism and, in particular, the role of the residues surrounding the active centre, thus assisting in the design of inorganic catalysts that mimic the enzyme.

Localised thermal levering events drive spontaneous kinetic oscillations in catalysis

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A combination of computational and experimental techniques have been used to rationatise the origins of oscillations is CO oxidation products over Rh/Al_2O_3 catalysts, under *in-operando* conditions. *State-of-the-art* spectroscopy techniques have allowed for temporal and spatial fine scale resolution of CO oxidation, with both DRIFTS and XANES analysis pinpointing the relative changes in absorbed species during time "on-line". When combined with *in-situ* mass spectrometry a highly resolved picture of coupled oscillations in CO oxidation and CO_2 production emerged. Periodic DFT techniques were then applied to rationalize these experimental observations, with the use of both the PBE and SCAN functionals in combination with plane-wave basis sets. Surface mediated reaction profiles were calculated for each of the low-index surfaces of Rh for the following reactions: (1) carbon oxidation, (2) CO oxidation and (3) Boudouard reaction. It was found that with a high barrier of >2.5 eV, the Boudouard reaction was kinetically inaccessible under reaction conditions; however, the CO oxidation barriers of between 0.63-1.35 eV could be accessed at around 300K. Additionally, the localised release of ~2.9 eV for CO oxidation may enable a coupled subsequent Boudouard reaction step that would regenerated surface binding sites for CO through a highly exothermic carbon oxidation step. Therefore, our combined experimental/computational results are consistent with our proposed localised leveling phenomenon, whereby CO oxidation is a precursor to coupled Boudouard and carbon oxidation steps. This work offers an important proof of concept, where turning of thermally coupled reaction mechanisms at the nanoscale is possible and may be harnessed toward novel chemical routes.

The Wadsley-Roth Materials Family as Functional Energy Materials

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The Wadsley-Roth (W-R) family of materials is made up of transition metal oxides mainly composed of Tungsten, Titanium and Niobium and are thought to be highly disordered. Members of the W-R family are defined by their structure based on ReO_3 – type blocks, which stack to form blocks of corner-sharing octahedra of size (m x n) delimited by crystallographic shear planes (CS) and are connected to each other via edge-sharing. Block units connect infinitely in directions perpendicular to the (m x n) plane. Tetrahedral sites can also be present in the same plane as the blocks to fill voids. An index was created to classify these materials depending on their type of block structure.

Over recent years, these materials have gained much interest from the scientific community. However, publications almost systematically study these materials individually (i.e. interest in a particular composition) rather than as a family of materials. This has led to the properties of the W-R family remaining unknown, for the most part, especially in terms of how the block structure can influence electronic and insertion properties, for example. Typically, one would dope such materials in an aliovalent fashion to bolster their electronic properties such as electronic conduction and charge carrier migration, for example. However, with the difference in Oxygen to Metal (O/M) ratio between structures of the W-R family being quite small, it proves to be an arduous task to identify which compound is synthesised. Furthermore, it is not clear whether doping through traditional methods for these materials (annealing to include oxygen vacancies etc.) would be effective here as a phase transition from a doped compound to a defect-free block structure is possible thanks to the proximity in O/M ratio values between different W-R members.

With no current or past studies on the relationship between structure and electronic properties in W-R compounds, it is impossible to predict which methods will be more effective than others to better these promising materials and thus leaves researchers to the time-consuming method of trial and error. For this reason, I have endeavoured throughout my PhD research to be able to present the first comprehensive computational prediction study on the W-R materials as energy materials and, more importantly, on the relationship between structure and electronic performance and how these are transferrable across the entire W-R family. This research was carried using HF-DFT methods and the GTO-based code CRYSTAL17, thus also rendering it a higher precision study than all the few computational studies concerning W-R materials in the materials' community literature.

Molecular Dynamics Simulations of Radiation Damage in High Temperature Superconductors

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The advent of high-temperature superconductors (HTS) with high field strengths offers the possibility of building smaller, cheaper magnetically confined fusion reactors. However, bombardment by high energy neutrons ejected from the fusion reaction may damage the HTS tapes and impair their operation. Recreating the conditions present in an operational fusion reactor is experimentally challenging, therefore, this work uses molecular dynamics simulations to understand how radiation modifies the underlying crystal structure of $YBa_2Cu_3O_7$. To facilitate the simulations a new potential was developed that allowed exchange of Cu ions between the two symmetrically distinct sites without modifying the structure. Radiation damage cascades predict the formation of amorphous regions surrounded by regions decorated with Cu and O defects found in the CuO-chains. The simulations suggest that the level of recombination that occurs is relatively low, resulting in a large number of remnant defects and that there is a no substantial temperature effect

Surprising improvement of SnS$_2$ properties through superlattice formation for battery applications

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*e05-power-**hep***

In order to address the ever-increasing demand for better battery materials, we present a study exploring the potential of multi-layered superlattice made from 2D materials to understand the benefits and drawbacks such layered materials could have as potential electrodes.

Layered materials have demonstrated promise as electrode materials due to their interlayer spacing allowing for easy lithium intercalation and diffusion, and SnS2 has in particular shown promise as an electrode material. Unfortunately, whilst this material has exhibited fast rates and high capacities, this results in the consumption of the layered SnS2 structure. However, recent techniques have allowed the development of novel materials formed by superlatticing with other layered materials.

Using first-principles density functional theory, we show the properties of SnS2 can be enhanced through combination with other layered materials in a superlattice structure. In particular, we explain how the properties vital to a successful working electrode (such as the open-circuit voltage, electrical conductivity and volumetric expansion) can be predicted from those of the components, offering improvements over those of SnS2 itself. Using thermodynamic arguments, we able to comment on the stability of these materials during cycling and ultimately predict the final lithium capacities, something that is vital for maximising the overaaa energy density of a battery. With these, we also identify a further improvement in the thermodynamic stability arising from superlattice formation, where the resultant lithium storage capacity is dramatically higher than that possible with either of the component materials.

Intrinsic Defect Study on High-voltage Spinel $LiMn_{1.5}Ni_{0.5}O_4$ as Cathode Material for Li-ion Batteries

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High-voltage spinel $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) is a promising cobalt-free cathode material which can deliver high energy density (650 W h kg^{-1}) due to its high operating voltage ~4.7 V (*vs* Li$^+$/Li) arising from the Ni^{2+}/Ni^{4+} couple. The material can be synthesized with varying degree of cation disorder, and they have different electrochemical performance. Cation disordering is usually accompanied by the formation of oxygen vacancies and Mn^{3+} species, making it challenging to rationalise the most significant factors towards designing LMNO with optimum electrochemical performance.

This presentation will share the latest scientific findings on the defect chemistry of the ordered phase *P4$_3$32* LMNO where we used density functional theory to predict the defect formation energy of all possible intrinsic defects under various synthesis conditions. We find that most defects are deep and small polarons are formed, generating Mn^{3+}, Mn^{2+} (*n*-type) and Ni^{3+} (*p*-type) species. The cation disordering behaviour can be explained by the low formation energy of antisite defects. Our work provides explanations for experimental observations and guidelines for defect-controlled synthesis.