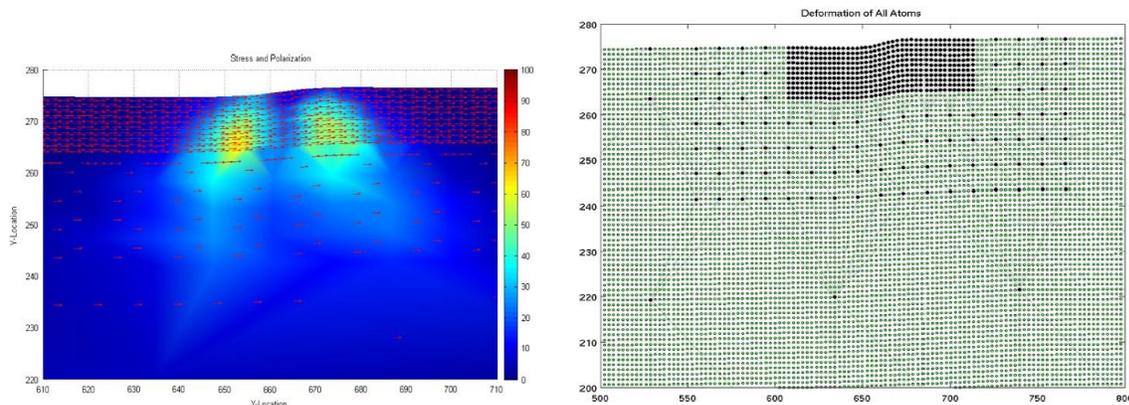


A Multiscale Atomistic Method for Defects in Ionic Materials

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Ionic solids are important for electronic and energy storage/conversion devices. Examples include ferroelectrics and solid oxides. Defects in these materials play a central role in enabling their properties: for example, the electromechanics of ferroelectrics occurs by the nucleation and growth of domain wall defects, and solid oxide ionic conduction is through the motion of point defects. I will talk about our efforts to develop multiscale atomistic methods to understand the structure of defects in these materials. These materials have long-range electrostatic interactions between charges, as well as electric fields that exist over all space outside the specimen. I will describe a multiscale methodology aimed at accurately and efficiently modeling defects in such materials in complex geometries. Our approach is based on a combination of Dirichlet-to-Neumann maps to consistently transform the problem from all-space to a finite domain; the quasicontinuum method to deal with short-range atomic interactions, and rigorous thermodynamic limits of dipole lattices from the literature.



The first figure shows an atomic-level stress measure and polarization vector field when a ferroelectric with a free surface is subject to a localized electric field just above the free surface, and the second figure shows the corresponding ionic displacements.

We thank ARO and AFOSR for support, and Richard D. James, Saurabh Puri, and Yu Xiao for useful discussions.

[1] Atomistic-to-Continuum Multiscale Modeling with Long-Range Electrostatic Interactions in Ionic Solids. Jason Marshall and Kaushik Dayal. *J. Mech. Phys. Solids*, 62:137, 2014.

Defect and surface properties of Multinary Alloys for Solar Energy Absorber

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Multinary alloys, such as $\text{Cu}_2\text{ZnSnS}_4$ and recently discovered ABX_3 , are the most promising absorber materials for thin-film solar cells, since it is a low-cost material with the optimal band gap 1.5 eV for single-junction solar cells and a high adsorption coefficient. Although the synthesise of such compound could be long time ago, due to the complicity of these multinary compound, the properties are not well understood, which are crucial for improving the solar cell performance.

In this talk, I will focus on the defect properties of $\text{Cu}_2\text{ZnSnS}_4$ and ABX_3 , the intrinsic point defects and also complex defects. The dominant defect in CZTS will be p -type Cu_{Zn} antisite, which has an acceptor level deeper than the Cu vacancy. We proposed that $\text{Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}$ and $2\text{Cu}_{\text{Zn}}+\text{Sn}_{\text{Zn}}$ defect complex could be detrimental to efficiency, with a small Voc. We predicted the possible reconstruction configurations of the frequently observed cation-terminated (112) and anion-terminated ($\bar{1}\bar{1}\bar{2}$) surfaces, and found that the polar surfaces are stabilized by the charge-compensating defects, such as vacancies (V_{Cu} , V_{Zn}), antisites (Zn_{Cu} , Zn_{Sn} , Sn_{Zn}) and defect clusters ($\text{Cu}_{\text{Zn}}+\text{Cu}_{\text{Sn}}$, $V_{\text{Zn}}+2V_{\text{Cu}}$). I will also show the defect properties of the ABX_3 , which is important to understand its high efficiency.

First-principles molecular dynamics of Li transport in Li_3InBr_6 : Tools for high-throughput screening

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All-solid-state batteries have the potential to dramatically improve the capacity and safety of high-density energy storage. Inorganic electrolytes with sufficiently high conductivity and mechanical and thermal stability are needed to develop these batteries.

Understanding the effect of ion correlation, lattice properties and disorder on Li conductivity will provide design rules to accelerate high-throughput screening of potential electrolytes.

Using a recently synthesized highly conductive electrolyte candidate [1], Li_3InBr_6 , we explore the role of phonon modes, 3D channels and lattice strain on Li diffusivity using first-principles molecular dynamics simulations. Molecular dynamics simulations allow us to discover new Li conduction pathways and mechanisms. Figure 1 shows the mean squared displacement of Li, projected along different directions in the lattice, which predicts a strong anisotropy of the diffusivity. In this work we will present some uncommon, though not entirely new[2], techniques for analyzing structural and electronic

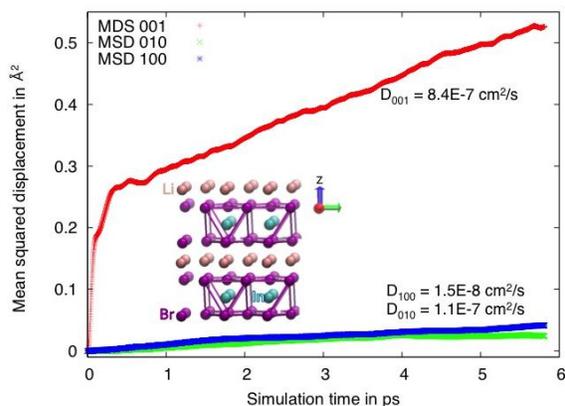


Figure 1: The mean squared displacement of Li in Li_3InBr_6 is projected into the three axes.

Discovery of new solid Li-ion electrolytes”, to discover new battery materials using high-throughput screening. In-depth density functional theory simulations of a variety of Li-conducting electrolytes are an integral component of the project’s Automated Infrastructure and Database for *Ab-Initio* design (AIDA).

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

[1] K. Yamada, *et al.*, Solid State Ionics. **117**, 87 (2006).

[2] B. Wood, *et al.*, Physical Review Letters, **97**, 166401 (2006).

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properties that could be predictors of high ionic conducting materials.

The insights gained from our in-depth character of the Li transport mechanisms in this promising material will aid the search for better inorganic solid-state batteries. Computer resources on Oak Ridge National Laboratory’s TITAN supercomputer enable many different constraints to be placed on the system and run simultaneously using Quantum Espresso’s Car-Parinello code. Our computer time is granted from an INCITE project, “Safety in numbers:

Conductivity of doped ceria from non-equilibrium molecular dynamics

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The color-diffusion algorithm is implemented in an *ab initio* molecular dynamics simulation of doped cerium oxide for calculating oxygen ion diffusion. The time scales needed to capture rare events such as ionic diffusion are typically too long to be simulated with conventional molecular dynamics. By assigning fictitious “color charges” to the oxygen ions and acting on them with a fictitious “color field”, it is possible to accelerate these rare events. In the limit of zero field this non-equilibrium algorithm gives the oxygen diffusion coefficient for the undisturbed system. We discuss some technical details of this approach and our results for ceria doped with rare-earth elements.

First-principles and molecular dynamics simulation for diffusion problem of YSZ and Ni/YSZ in solid oxide fuel cells

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The solid oxide fuel cell (SOFC) is one of the most promising energy sources due to its high efficiency in energy conversion and variety of fuel types. To achieve high performance and durability, diffusion problems must be addressed. For example, the mechanism of oxygen diffusion in electrolyte has to be revealed because lower diffusivity leads to lower electric current density. As sintering in anode materials, which can cause change in microstructures, has to be reduced for better reliability, the diffusion mechanism in anode cermet should be examined to find ways to suppress sintering.

In this study, we first develop a potential for yttria-stabilized zirconia (YSZ) and Ni/YSZ interface, which are typical electrolyte and anode materials in SOFCs. For better reliability and transferability, we adopt the Tangney-Scandolo (TS) dipole model [1], where electric polarization around each atom is represented by electric dipole. Potential parameters are fitted to first-principles density functional calculation results via the real-coded genetic algorithm and the force-matching method, so that the optimized potential can be applied to the cubic phase of YSZ for a reasonable range of yttria concentration. The optimized potential can reproduce YSZ surface energies, Ni/YSZ interface energies and energy barriers of oxygen vacancy migration.

We then perform nudged elastic band (NEB) calculations and molecular dynamics simulations of oxygen vacancy diffusion in YSZ, and discuss the effect of surfaces on ionic conductivity. We also examine Ni diffusion on YSZ surfaces by first-principles and molecular dynamics calculations to evaluate the effect of impurity segregation on Ni diffusion.

[1] P. Tangney and S. Scandolo, *J. Chem. Phys.*, **117**, 19 (2002).

Atomistic Simulations of Thermal Transport in Nanostructured Semiconductors

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We present the results of atomistic simulations of heat transport in realistic models of ordered and disordered semiconductors. In particular we discuss the thermal properties of Si and SiGe at the nanoscale (with focus on nano-wires [1] and nanoporous materials [2,3]) as obtained from molecular dynamics simulations and Boltzmann transport equation calculations [4]. We also discuss recent ab initio results on Si based clathrates [5,6], e.g. the newly synthesized $K_8Al_8Si_{38}$.

These works were supported by the U.S. DOE/BES

[1] Yuping He and Giulia Galli, *Phys. Rev. Lett.* 108, 215901 (2012)

[2] Yuping He, Davide Donadio and Giulia Galli, *Nano Lett.* 11, 3608-3611 (2011)

[3] Yuping He, Davide Donadio, Joo-Hyoung Lee, Jeffrey C. Grossman and Giulia Galli, *ACS Nano* 5, 1839 (2011)

[4] Yuping He, Ivana Savic, Davide Donadio and Giulia Galli *Phys. Chem. Chem. Phys.* 14, 16209-16222 (2012)

[5] Yuping He, Fan Sui, Susan Kauzlarich and Giulia Galli (submitted). [6] Yuping He and Giulia Galli (submitted)

Stability and kinetics of Se overlayers on Mo(110) and the role of Na impurities: from ab initio data to thermodynamics and kinetics

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The selenization of molybdenum is nowadays technologically relevant for the production of thin film chalcopyrite solar cells based on $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) and might become an important step in the production of nanostructures based on the layered compound MoSe_2 . However, the control of the process is still very poor, due to the lack of basic knowledge of the surface thermodynamics of the system. The kinetics, moreover, can become crucial to obtain preferred textures and, thus, electronic properties.

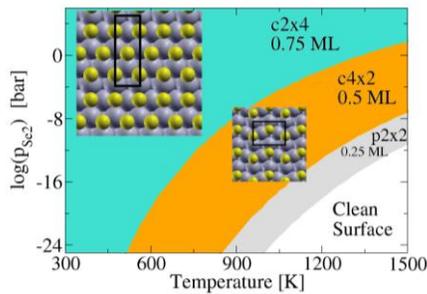


Figure 1: Surface phase diagram of Se adsorbed overlayer on the Mo(110) surface.

In the case of solar cells the role of sodium impurities, and maybe oxygen, has been invoked, claiming that it could help the formation of an Ohmic contact. Based on first principles calculations of adsorption energies [1,2] and migration energies of Se, Na, and O on the Mo(110) surface we predict stable patterns for adsorbed Selenium [3] -or surface selenides- for various ambient conditions. Our results show that the attainable Se coverages range from 1/4 to 3/4 of a monolayer, depending on the partial pressure and size of Se molecules composing the gas with which the surface is in equilibrium. We provide simulated scanning tunneling microscopy images to help the experimental characterization of adsorbed surface

patterns. We acknowledge financial support from the comCIGS II project of the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety of Germany.

[1] G. Roma and L. Chiodo, Phys. Rev. B 87, 245420 (2013).

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[3] G. Roma et al., Appl. Phys. Lett. 104, 061605 (2014).

A self-consistent first-principles approach model carrier mobility in organic materials

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Transport through thin organic amorphous films, such as those used in OLED and OPV devices, has been difficult to model on using first-principles methods. Nevertheless the carrier mobility depends strongly on the disorder strength and reorganization energy, both of which are significantly affected by the environment of each molecule. Here we present a multi-scale approach to model carrier mobility in which the morphology is generated using DEPOSIT, a Monte Carlo based

atomistic simulation approach. From this morphology we extract the sample specific hopping rates, as well as the on-site energies using a fully self-consistent embedding approach to compute the electronic structure parameters which are then used in an analytic expression for the carrier mobility. We apply this strategy to compute the carrier mobility for a set of widely studied molecules and obtain good agreement between experiment and theory for over ten orders of magnitude in the mobility without any adjustable parameters.

