

MM 3: Development of Computational Methods: Evaporation, Growth and Oxidation – Density Functional, Tight Binding

Time: Monday 10:15–13:00

Location: SCH A 251

MM 3.1 Mon 10:15 SCH A 251

Towards machine learning potentials for field evaporation — ●SHYAM KATNAGALLU, JOERG NEUGEBAUER, and CHRISTOPH FREYSOLDT — Department of computational materials design, Max Planck Institut für Eisenforschung GmbH, Düsseldorf, Germany.

Field evaporation, an electrostatic field-induced ionization and subsequent evaporation of surface atoms, is the underlying principle of atom probe tomography. Ab initio simulations including 1-10 V/Å fields on metallic slabs have recently shed light [1] on the intricacies of the field evaporation process. These simulations underscore the importance of knowing the path of the evaporating atom prior to complete ionization to improve the spatial resolution of the technique. However, to properly sample the extremely shallow potential energy surface due to the electrostatic field extensive simulations with computationally expensive ab initio accuracy are needed. We, therefore, combine machine learning interatomic potentials with a charge equilibration scheme. To demonstrate the performance and accuracy of our scheme, we validate the Rappe et al charge equilibration model [2] using Hirshfeld decomposed DFT reference charges acquired from (13,5,7) Pt slab under electric fields ranging from (1-4.5 V/Å) and develop potentials for field evaporation in Al. [1]*M. Ashton, A. Mishra, J. Neugebauer, and C. Freysoldt, Ab Initio Description of Bond Breaking in Large Electric Fields, Phys. Rev. Lett. 124, (2020). [2]*A. K. Rappe and W. A. G. III, Charge Equilibration for Molecular Dynamics Simulations, J. Phys. Chem 95, 3358 (1991).

MM 3.2 Mon 10:30 SCH A 251

High temperature chlorine corrosion in waste-to-energy-plants: sulphation of chloride particles as source of released chlorine — ●SEBASTIAN PENTZ, MATTHIAS KROH, and FERDINAND HAIDER — University of Augsburg, Chair for Experimental Physics I, Universitätsstr. 1, 86159 Augsburg

Chlorine induced high temperature corrosion leads to massive problems especially in waste-to-energy-plants. During the combustion process chloride containing particles are released and deposited on heat exchanger surfaces. These chlorides get converted into sulphates with a release of chlorine species which then lead to severe corrosion. For chloride particle sampling from a plant a tempered probe was developed, allowing time series of deposit built-up at defined temperatures. From this online particle sampling during plant operation we collect information about sticking probability, size distribution of deposited particles and the chemical composition of the deposit built up. Especially the relation between detected chlorine to sulphur is of high interest, leading to the degree of conversion of deposited chlorides, which equals the amount of released chlorine. In further laboratory experiments the sulphation process of synthetic chloride particles can be systematically studied. From this we get the sulphation kinetics under various conditions like temperature, particle size or gas composition, which lead to an estimation of the time required for full chloride conversion. By combining the results gained from laboratory experiments, online particle sampling and offline deposit analysis, we try to model the ongoing sulphation process.

MM 3.3 Mon 10:45 SCH A 251

How to teach my deep generative model to create new RuO₂ surface structures? — ●PATRICIA KÖNIG, HANNA TÜRK, YONGHYUK LEE, CHIARA PANOSSETTI, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber Institute, Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany

Data-driven approaches to inversely design novel materials with desired properties constitute an emerging pillar in the exploration of energy conversion materials. In recent works, artificial neural networks were successfully used to create crystalline porous materials. Here, we present a related approach to tackle the problem of structure generation for nano-porous to partially amorphous surfaces. As a model system, we use the well-studied RuO₂ catalyst for oxidative conversion of CO to CO₂. To explore the chemical space of RuO₂ surface structures, we trained a Generative Adversarial Network (GAN) that is capable of cheaply generating diverse structural guesses for novel surface structures. For the training set, 28,903 RuO₂ surface terminations were created with a grand-canonical basin hopping method using

ML potential energetics. The atomic positions of these structures were mapped to Gaussian densities on a three-dimensional grid to generate the GAN input. We demonstrate how realistic three-dimensional surface models with inferred lattice lengths and energy conditioning can be created and how these generated densities can be mapped back to atomistic structures as a basis for property calculations.

MM 3.4 Mon 11:00 SCH A 251

Liquid-Diffusion-Limited Growth of Vanadium Dioxide Single-Crystals — ●NICO SPRINKART, DANIEL KAZENWADEL, ROMAN HARTMANN, and PETER BAUM — Department of Physics, University of Konstanz

Vanadium dioxide (VO₂) is a strongly correlated material with an ultrafast first-order phase transition between rutile/insulator and monoclinic/metallic close to room temperature. The unusual and complex properties of this transition make VO₂ one of the most heavily investigated materials in modern condensed matter physics. Consequently, high-quality single-crystals are in large demand.

Here we present a method for the growth of mm-sized stoichiometric VO₂ crystals by thermal decomposition of liquid V₂O₅. Time-resolved measurements of the oxygen release reveal that the crystal growth rate is limited by liquid-phase diffusion; the properties of the gaseous environment, which were previously assumed to be decisive, are almost insignificant.

Our results signify the role of gas-liquid diffusion in crystal growth and will simplify future research on VO₂ and its subsequent application in ultrafast electronics and thermal energy management.

MM 3.5 Mon 11:15 SCH A 251

Dynamic restructuring of oxidation states in magnetite — ●EMRE GÜRSOY¹, GREGOR B. VONBUN-FELDBAUER², and ROBERT H. MEISSNER^{1,3} — ¹Institute of Polymer and Composites, Hamburg University of Technology, Hamburg, Germany — ²Institute of Advanced Ceramics, Hamburg University of Technology, Hamburg, Germany — ³Institute of Surface Science, Helmholtz-Zentrum Hereon, Geesthacht, Germany

Magnetite is a mineral that undergoes a metal-insulator transition called the Verwey transition at 125 K (T_V). Its conducting behaviour above T_V is linked to electron hops between Fe²⁺ and Fe³⁺ on octahedral sites and complex oxidation state patterns emerge as a direct consequence. Oxidation states are frequently assessed using quantum mechanical methods, but these computationally expensive methods are not scalable to relevant systems with several thousand atoms. Therefore, a computationally inexpensive method that provides a detailed atomistic description of magnetite would be beneficial. We present a hybrid Monte Carlo/Molecular Dynamics (MC/MD) approach for atomistic modeling of magnetite, magnetite surfaces, and nanoparticles that can capture many aspects of this oxidation state patterning. It is based on swapping the oxidation states of Fe ions using MC either in simulated annealing, or in a hybrid combination with MD. We confirmed the accuracy of our model by comparison with oxidation states determined from density functional theory. This simple yet efficient approach paves the way to elucidate aspects of oxidation state ordering and electron hopping in inverse spinel structures in general.

15 min. break

MM 3.6 Mon 11:45 SCH A 251

Role of an adsorbed gas layer in field ion microscopy contrast — ●SHALINI BHATT, FELIPE F.MORGADO, SHYAM KATNAGALLU, CHRISTOPH FREYSOLDT, and JÖRG NEUGEBAUER — Max Planck Institut für Eisenforschung GmbH Düsseldorf Germany

The imaging contrast in field ion microscopy (FIM) is associated with the ionization probability of gas atoms near a surface under 10-100 V/nm electric fields. To better understand contrast variations among atoms observed in FIM, we employ density functional theory (DFT) in combination with the Tersoff-Hamann approximation that links electron tunneling from the gas atom to the surface with the surface's local density of states at the position of the gas atom 3-6 Å away from the surface. Based on our new EXTRA approach (extrapolated tail via reverse algorithm) that eliminates numerical noise in the tails of

the wavefunctions, we demonstrate a chemical brightness contrast for Ta in Ni (012) surface. However, we find that the simulated imaging contrast for Ni alone is much lower than in experiment. We therefore explore the role of an adsorbed gas layer as an essential ingredient to explain FIM's unexpectedly large spatial resolution.

MM 3.7 Mon 12:00 SCH A 251

A Workflow for Obtaining Robust Density Functional Tight Binding Parameters Across the Periodic Table — ●MENGHAN CUI, JOHANNES T. MARGRAF, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany

The Density Functional Tight Binding (DFTB) approach allows electronic structure based simulations at length and time scales far beyond what is possible with first-principles methods. This is achieved by using minimal basis-sets and empirical approximations. Unfortunately, the sparse availability of parameters across the periodic table is a significant barrier to the use of DFTB in many cases.

In this contribution, we therefore propose a workflow which allows the robust and consistent parameterization of DFTB across the periodic table. Importantly, the approach requires no element-pairwise parameters and can thus easily be extended to new elements. Specifically, the parameters defining the band energy and repulsive potential are obtained via Bayesian Optimization on a set of elemental solids. In this way, robust baseline parameters can be obtained for arbitrary element combinations. The transferability of the parameters and applications in hybrid DFTB/Machine Learning models will be discussed.

MM 3.8 Mon 12:15 SCH A 251

Coupling Many Body Perturbation Theory (MBPT) with Polarizable Continuum Models (PCM) — ●PINO D'AMICO¹, DARIO A. LEON VALIDO², MARGHERITA MARSILI³, DANIELE VARSANO¹, STEFANO CORNI⁴, and ANDREA FERRETTI¹ — ¹S3 Center, Istituto Nanoscienze CNR, Modena, Italy — ²Dpt. REALTEK, Norw. Univ of Life Sci., Ås, Norway — ³Dpt. di Fisica e Astronomia, Univ. di Bologna, Italy — ⁴Dpt. di Scienze Chimiche, Univ. di Padova, Italy

The theoretical description of quantum systems embedded in external environments represents a challenge for the application of MBPT approaches to the study of the electronic excitations. Different level of accuracy can be used to treat the actual system, for which a quantum mechanical description is employed, and its surrounding environment, that can be approximated through a simplified quantum model, a molecular mechanical approach, or a continuum model. We will present a theoretical framework in which a MBPT treatment of the quantum system (eg at the level of GW and BSE) is coupled to a PCM description of its surrounding environment. The formalism has been implemented within the YAMBO code[1], based on plane-waves and pseudopotentials, by exploiting the ENVIRON package[2] coupled to the Quantum ESPRESSO suite[3]. Preliminary results of the newly developed methodology will be presented, focusing on selected molecules and two-dimensional materials in water. [1] D. Sangalli et al., *J. of*

Phys.:Cond.Mat. 31, 325902 (19).[2] O. Andreussi et al., *J.Chem.Phys.* 136, 064102 (12).[3] P. Giannozzi et al., *J.Phys.:Cond.Mat.* 29, 465901 (17).

MM 3.9 Mon 12:30 SCH A 251

A DFTB-based approach to calculating electron-phonon couplings — ●ALEXANDER CROY¹, ELIF UNSAL², GIANAURELIO CUNIBERTI², and ALESSANDRO PECCHIA³ — ¹Institute of Physical Chemistry, FSU Jena, Germany — ²Institute of Materials Science, TU Dresden, Germany — ³Institute of Nanostructured Materials, CNR, Italy

The calculation of electron-phonon couplings from first principles is computationally very challenging and remains mostly out of reach for systems with a large number of atoms. Resorting to semi-empirical methods, like density-functional based tight-binding (DFTB), has been shown to be a viable approach for obtaining quantitative results at moderate computational costs. In this contribution, we present a method for calculating the electron-phonon coupling matrix within the DFTB approach and demonstrate its implementation which is based on dftb+ and phonopy. It further allows the calculation of relaxation times and interfaces with BoltzTrap2 to compute transport properties. Exemplarily, we show results for γ -graphyne which was recently synthesized. Consistent with earlier predictions we obtain mobilities on the order of $10^4 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature.

MM 3.10 Mon 12:45 SCH A 251

Toward Coarse-Grained Elasticity of Single-Layer Covalent Organic Frameworks — ●DAVID BODESHEIM¹, ANTONIOS RAPTAKIS¹, AREZOO DIANAT¹, ALEXANDER CROY², and GIANAURELIO CUNIBERTI¹ — ¹TU Dresden, Dresden, Germany — ²FSU Jena, Jena, Germany

Covalent Organic Frameworks (COFs) are crystalline porous materials that are based on organic monomeric units, so called building blocks. As a multitude of different building blocks can be combined in reticular chemistry, manifold different porous structures with tailored properties have been synthesized in recent years. Through current experimental progress, monolayer COF materials have been synthesized, providing a new class of 2D materials.[1,2] However, these materials have defects and grain boundaries which make it challenging to describe properties of realistic materials computationally. To approach this issue, we show in this work how to use a surrogate model to calculate elastic properties of 2D COFs based on density functional based tight binding (DFTB) calculations.[3] This allows us to model defective systems at low computational cost and paves the way for multiscale modeling. Furthermore, this approach enables us to predict elastic properties from the properties of the monomeric building blocks.

[1] A. Ortega-Guerrero, et al. *ACS Appl. Mater. Interfaces*, 13, 22, 26411-26420 (2021).

[3] Z. Wang, et al., *Nat. Synth.*, 1, 69-76 (2022).

[3] A. Croy, et al. *J. Phys. Chem. C*, 126, 44, 18943-18951 (2022).