

MM 23: Methods in Computational Materials Modelling (methodological aspects, numerics)

Sessions: APT and Diffusion; Method and Code Development

Time: Wednesday 10:15–13:15

Location: H44

MM 23.1 Wed 10:15 H44

Understanding field evaporation in atom probe tomography from a first-principles perspective — ●CHRISTOPH FREYSOLDT, MICHAEL ASHTON, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40273 Düsseldorf

Field evaporation is the elementary process at the heart of atom probe tomography (APT): single atoms or molecules evaporate from the sample under the influence of a very high electric field. Despite 50 years of APT experiments, a comprehensive predictive theory is still lacking.

We approach the problem in the framework of density-functional theory. From the minimum-energy path for desorption as a function of applied field, we compute critical fields and transition barriers for a variety of surface sites in good agreement with available experimental data. Our results show that atoms evaporating from within the surface at steps or kinks stay in close bonding contact at the transition state. The surface bonding characteristics of the evaporating atom is thus much more important than the electron transfer process, which was assumed to be the dominant mechanism in previous models.

From our insights, we propose a simple analytic theory. The critical zero-barrier field results from the balance between the maximum intrinsic force along the reaction coordinate and the field-induced force. The latter can be obtained directly from the change of the surface dipole along the reaction coordinate, while the former is not very sensitive to the applied field. The theory also provides barrier heights for subcritical fields.

MM 23.2 Wed 10:30 H44

Evaporation Mechanisms for Field-Ionized Surface Atoms — ●MICHAEL ASHTON, CHRISTOPH FREYSOLDT, and JOERG NEUGEBAUER — Max Planck Institut für Eisenforschung GmbH, Max-Planck-Str. 1 40273 Düsseldorf

Detailed information regarding the atomic-scale mechanisms of field evaporation has long eluded the theoretical community, in part due to the challenge of applying finite electric fields in density functional theory (DFT) models that require periodic boundary conditions. We explain how our recent advances in the treatment of electric fields in DFT have enabled fundamental insights into the near-surface mechanisms of field evaporation for atoms on Tungsten surfaces. These insights are obtained from static calculations of the energy landscapes for low-coordinated atoms departing from a charged surface. They show that even for very strong fields a two-stage rollover mechanism - in which an evaporating kink atom rolls into the hollow site above the neighboring step and then proceeds to evaporate - is the minimum energy path. We find that this two-stage rollover mechanism is circumvented at fields very close to the critical evaporation field, resulting in a much simpler single barrier trajectory. The origin of this change in mechanism will be discussed along with some of its implications for experimental evaporation procedures. Finally, we discuss the similarities and differences between our DFT results and those obtained using classical models to describe field evaporation.

MM 23.3 Wed 10:45 H44

Atomistic description of self-diffusion in molybdenum — DARIA SMIRNOVA¹, YANYAN LIANG¹, GRISELL DIAZ LEINES¹, SERGEI STARIKOV¹, NING WANG¹, ●MATOUS MROVEC¹, RALF DRAUTZ¹, DAVIDE SANGIOVANNI², IGOR ABRIKOSOV², and MAXIM POPOV³ — ¹The Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-Universität Bochum, Germany — ²Linköping University, Linköping, Sweden — ³Materials Center Leoben Forschung GmbH, Leoben, Austria

According to the experimental data, self-diffusion coefficient in molybdenum shows non-Arrhenius behavior, however, its origin is controversial. In this work, we apply first-principle calculations and classical molecular dynamics to study the nature of self-diffusion in bcc molybdenum. We consider vacancy diffusivities, formation and migration energies depending on temperature in a wide temperature range: from zero temperature up to the melting point. We also carried out molecular dynamics simulations that allow to observe directly the process of self-diffusion at the atomic scale. Summarizing the results obtained by different calculation methods, we can conclude that the peculiarity

observed for self-diffusion can be caused by strong temperature dependence of the vacancy formation energy. The methodology reported here is universal and can be applied to analyze self-diffusion in another metals.

MM 23.4 Wed 11:00 H44

The Anharmonicity of Al self-diffusion — RAYNOL DSOUZA, ●LIAM HUBER, BLAZEJ GRABOWSKI, and JOERG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

To study kinetic properties, e.g. diffusion, at the atomistic scale with molecular dynamics (MD) it is usually necessary to operate at very high temperatures where processes occur at high rates, or to use some approximation or acceleration scheme. At low temperatures it is common to use the quasi-harmonic approximation (QHA), where finite-T effects are represented using phonon calculations. However, even for the relatively simple thermodynamic property of vacancy formation in aluminum, anharmonic effects not captured by QHA appear well below room temperature [1].

In this work, we apply the finite temperature string method [2] to study the effect of these anharmonicities on Al self-diffusion. This technique allows us to probe the temperature range above the threshold at which QHA begins to lose validity, but still well below the temperature at which calculation by direct MD becomes feasible. Finally, we consider the combination of thermodynamic integration [3] with FTS in order to capture anharmonic behaviour with the full power and accuracy of quantum mechanics.

[1] Glensk et al. Phys Rev X 4 (2014)

[2] Vanden-Eijnden and Venturoli, J Chem Phys 130 (2009)

[3] Duff et al. Phys Rev B 91 (2015)

MM 23.5 Wed 11:15 H44

Kinetic Monte Carlo simulations of vacancy diffusion in non-dilute Ni-X (X=Re,W,Ta) alloys — ●MAXIMILIAN GRABOWSKI, JUTTA ROGAL, and RALF DRAUTZ — ICAMS, Ruhr-Universität Bochum, 44801 Bochum, Deutschland

The mobility of vacancies in alloys may limit dislocation climb which is important for high performance Ni-based superalloys. Using a combined density functional theory and kinetic Monte Carlo approach we investigate vacancy diffusion in Ni-Re, Ni-W, and Ni-Ta binary alloys up to 10 at.% solute concentration. We introduce an interaction model that takes into account the chemical environment close to the diffusing atom to capture the effect of solute-host and solute-solute interactions on the diffusion barriers. In contrast to an ideal solid solution it is not only the diffusion barrier of the solute atom that influences the vacancy mobility, but primarily the change in the host diffusion barriers due to the presence of solute atoms. This is evidenced by the fact that the observed vacancy slowdown as a function of solute concentration is larger in Ni-W than in Ni-Re, even though Re is a slower diffuser than W. To model diffusion in complex, non-dilute alloys an explicit treatment of interaction energies is thus unavoidable. In the context of Ni-based superalloys two conclusions can be drawn from our kinetic Monte Carlo simulations: the observed slowdown in vacancy mobility is not sufficient to be the sole cause for the so-called Re-effect; and assuming a direct correlation between vacancy mobility, dislocation climb, and creep strength the experimentally observed similar effect of W and Re in enhancing creep strength can be confirmed.

15 min. break

MM 23.6 Wed 11:45 H44

Density-gradient-free variable in exchange-correlation functionals for detecting inhomogeneities in the electron density — ●FABIEN TRAN and PETER BLAHA — Vienna University of Technology, Vienna, Austria

A new type of approximation for the exchange and correlation functional in density functional theory is proposed. This approximation depends on a variable, u , that is able to detect inhomogeneities in the electron density ρ without using derivatives of ρ . Instead, u depends on the orbital energies which can also be used to measure how a system differs from the homogeneous electron gas. Starting from the

functional of Perdew, Burke, and Ernzerhof (PBE) [Phys. Rev. Lett. **77**, 3865 (1996)], a functional depending on u is constructed. Tests on the lattice constant, bulk modulus, and cohesive energy of solids show that this new u -dependent PBE-like functional is on average as accurate as the original PBE or its solid-state version PBEsol. Since u carries more nonlocality than the reduced density gradient s used in functionals of the generalized gradient approximation (GGA) like PBE and α used in meta-GGAs, it will be certainly useful for the future development of more accurate exchange-correlation functionals.

MM 23.7 Wed 12:00 H44

Advanced Path Integral Methods - Beyond the Benchmarks — ●VENKAT KAPIL and MICHELE CERIOTTI — Institute of Materials, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

The precise description of quantum nuclear fluctuations in atomistic simulations is possible by employing path integral techniques. However, many challenges such as the high computational cost of running path integral simulations and the overhead of implementation of path integral methods in electronic structure packages, have prevented their widespread use. In this talk, I will present molecular dynamics (MD) methods based on advanced MD integrators and high order factorizations of the Boltzmann operator that reduce the computational cost of path integral simulations, and their implementation in i-PI. Going beyond benchmarks, I will demonstrate their improved convergence in obtaining accurate estimates of the heat capacity of metal organic frameworks, and proton momentum distribution for various phases of water at a fraction of the computational cost that would be required if using conventional techniques.

MM 23.8 Wed 12:15 H44

Performance of van der Waals Methods at Non-Equilibrium Molecular Geometries — ●DENNIS BARTON, YASMINE AL-HAMDANI, and ALEXANDRE TKATCHENKO — Université de Luxembourg, Luxembourg, Luxembourg

An accurate description of van der Waals (vdW) dispersion interactions is a fundamental problem in electronic-structure calculations. These interactions are subtle, but of highest importance for the description of the structure, stability, and dynamics of biomolecules, chemical compounds, and materials.

Usually, approximate models for vdW interactions are used in combination with semi-local density functionals [1,2]. Common vdW methods are parametrized by one or more parameters, optimized for systems at equilibrium distances. Hence, their accuracy can only be granted at the energetic minimum.

We investigate vdW methods in terms of interatomic distances in small and weakly bound bimolecular complexes. We find a systematic increase of accuracy for the Many-Body Dispersion (MBD) method with respect to the intramolecular distance. In contrast, pairwise approaches (e.g. TS, D3) and non-local functionals show a non-systematic behavior.

Our analysis of the performance of vdW methods away from equilibrium geometries will greatly help to develop new methods with high accuracy everywhere on the potential-energy surface.

[1] Grimme *et al.*, Chem. Rev. **116**, 5105 (2016)

[2] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)

MM 23.9 Wed 12:30 H44

Limitations of the DFT-1/2 method for covalent semiconductors and transition-metal oxides — ●JAN DOUMONT, FABIEN TRAN, and PETER BLAHA — Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna,

Austria

The DFT-1/2 method in density functional theory [L. G. Ferreira *et al.*, Phys. Rev. B **78**, 125116 (2008)] aims to provide accurate band gaps at the computational cost of semilocal calculations. The method has shown promise in a large number of cases, however some of its limitations or ambiguities on how to apply it to covalently bonded semiconductors have been pointed out recently [K.-H. Xue *et al.*, Comput. Mater. Science **153**, 493 (2018)]. In this work, we investigate in detail some of the problems of the DFT-1/2 method with a focus on two classes of materials: covalently bonded semiconductors and transition-metal oxides. We argue for caution in the application of DFT-1/2 to these materials. Specifically, two conditions must be met for a reliable application: the electron density close to the valence band maximum must be sufficiently similar to the atomic orbital used to calculate the DFT-1/2 correction potential and the orbitals at the valence band maximum and conduction band minimum must be well separated in real space.

MM 23.10 Wed 12:45 H44

Implementation of stress tensor in LAPW method with emphasis on WIEN2k — ●KAMAL BELBASE, ANDREAS TRÖSTER, and PETER BLAHA — Institute for Materials Chemistry, Vienna University of Technology, Vienna, Austria

The theoretical derivation and practical implementation of the stress tensor in all electron density functional theory (DFT) codes of the linearized augmented plane wave (LAPW) type is a long standing and demanding problem. Here we present some theoretical calculations and results for hydrostatic pressure as implemented in the WIEN2k code. Similar to the structure of force formulas, we derive the Hellmann-Feynman and Pulay contributions to the full stress tensor. Hydrostatic pressure is obtained by taking the trace of these terms. Comparison for our thereby calculated pressure to that computed from fits of the total energy using the Birch-Murnaghan's equation of state is presented for some cubic crystals.

MM 23.11 Wed 13:00 H44

Parallelization and Acceleration of the FLEUR Code: New Possibilities for All-electron Density Functional Theory — ●ULIANA ALEKSEEVA, DANIEL WORTMANN, and STEFAN BLÜGEL — Institute for Advanced Simulation and Peter Grünberg Institut, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The perpetual evolution of the high performance computing (HPC) hardware is a considerable challenge for scientific software, which has often been developed over decades. In particular, the need to adapt for new hardware can require substantial changes in the data layout, the parallelization strategy and the fundamental algorithms. The interplay of different functionalities amplifies the redesign challenge.

An example of such a scientific software package is the all-electron DFT code FLEUR developed at the Forschungszentrum Jülich (<http://www.flapw.de>). While its main field of application is the simulation of complex magnetic structures, the employed full-potential linearized augmented plane wave (FLAPW) scheme ensures a general applicability for all bulk and film setups. We will present our experiences with implementing the hybrid MPI+OpenMP parallelization, the challenges arising from finding an efficient algorithm and from optimizing the performance. In addition, we will report on porting of the code to NVIDIA GPUs. Finally, we demonstrate that the improved scalability of the code allows calculations for unit cells with over 1000 atoms.

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