MM 19: Computational Materials Modelling IV - Finite Temperature

Time: Tuesday 10:15–12:00 Location: TC 006

MM 19.1 Tue 10:15 TC 006

Interfacial free energy calculations via direct thermodynamic integration across phase boundaries — •Paul Erhart[1,2] and Babak Sadigh[2] — [1]Applied Physics, Chalmers University of Technology, Gothenburg, Sweden — [2]Lawrence Livermore National Laboratory, Livermore, California, USA

We present a general technique for constraining macroscopic fluctuations in thermodynamic variables well-suited for Monte Carlo simulations of multiphase equilibria. In particular for multicomponent systems this amounts to an extension of the semi-grand canonical ensemble (SGC), the so-called variance-constrained (VC) SGC ensemble. It allows for Monte Carlo simulations of multiphase equilibria and thermodynamic integration across phase boundaries, from which equilibrium free energies of multiphase systems can be obtained. We apply this method to calculate alpha/alpha' interface free energies in Fe-Cr alloys as a function of orientation and temperature.

MM 19.2 Tue 10:30 TC 006

Fully ab initio determination of anharmonic contributions by efficient sampling strategies — •Albert Glensk[1], Blazej Grabowski[2], Tilmann Hickel[1], and Joerg Neugebauer[1] — [1]Max-Planck Institut für Eisenforschung — [2]Lawrence Livermore National Lab

Using ab initio approaches, temperature dependent thermodynamic free energies are nowadays typically calculated within the quasiharmonic approximation. Numerically highly accurate ab initio calculations for Al including anharmonic contributions on the other hand showed a significant change in the heat capacity and a dramatic effect on the entropy of vacancy formation in Al compared to quasiharmonic results [1]. By developing and implementing highly efficient sampling methods, we are now able to routinely determine anharmonic contributions for metals. Using these methods we were able to systematically improve the ab initio based thermodynamic description of Al-Mg-Si-Cu alloys. Particularly, the influence of anharmonicities on the unary subsystems of these alloys, consequences for the phase diagrams and deviations from quasiharmonic results will be discussed.

[1] B. Grabowski et al, PRB 79, 134106 (2009)

MM 19.3 Tue 10:45 TC 006

Analysing reaction coordinates and free energies for phase transformations within the reweighted path ensemble — •Jutta Rogal and Ralf Drautz — ICAMS, Ruhr-Universität Bochum, 44780 Bochum, Germany

Sampling rare events in complex, high dimensional systems, such as crystal nucleation and growth, remains a challenge for computational studies. Employing e.g. classical molecular dynamics simulations to model phase transformations with a sizeable nucleation barrier becomes quickly unfeasible as the system tends to spend most of the time within the stable states while it hardly samples the transition barrier regions of the phase space.

Among other approaches, transition path sampling (TPS) provides a possibility to explore transitions between stable states in rare event systems. One of the key advantages in TPS is that an a priori definition of a reaction coordinate is not required. And by using the underlying physical dynamics the true kinetics of the transition is sampled.

Here we introduce a reweighting scheme for the path ensembles and apply it to a solid-liquid phase transformation in a Lennard-Jones model system. Once the sampling has been performed, the reweighting allows for the analysis of free energy surfaces and committor projections in an arbitrary order parameter space. The reweighted path ensemble can then be used to optimise non-linear reaction coordinates and extract parameters such as the solid-liquid interface free energy, which is one of the key quantities governing nucleation and growth during solidification.

MM 19.4 Tue 11:00 TC 006

***Ab initio* study of elasticity and phase transformations in Fe above the Curie temperature** — Martin Friák[1], •Alexander Udyansky[1], David Holec[2], and Jörg Neugebauer[1] — [1]Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany — [2]Montanuniversität Leoben, Leoben, Austria

Understanding and tailoring the thermodynamic and elastic properties of paramagnetic body-centered cubic iron (β-Fe) is fundamental for developing Fe-based materials operating at elevated temperatures. We have therefore studied β-Fe, modeled by an antiferromagnetic supercell, with the internal distribution of local magnetic moments having the special quasirandom structure (SQS). In contrast to previously suggested antiferromagnetic models that were found to be mechanically unstable with respect to tetragonal deformations, the proposed SQS supercell is stable. Using this approach the thermodynamic stability of β-Fe with respect to tetragonal and trigonal deformations has been studied. The corresponding total energies have been determined for a broad range of deformations and are compared with those calculated for other magnetic states. The calculated single-crystalline elastic constants are found to closely reproduce experimental data detected within the temperature range of β-Fe.

MM 19.5 Tue 11:15 TC 006

Wall-liquid and wall-crystal interfacial excess free energies via thermodynamic integration: A molecular dynamics simulation study — •Ronald Benjamin and Juergen Horbach — Institut für Theoretische Physik II, Heinrich-Heine-Universität, D-40225 Düsseldorf, Germany

A method is proposed to compute the wall-liquid and wall-crystal interfacial excess free energy by molecular dynamics simulation. Our approach is based on a thermodynamic integration scheme, where the wall-liquid (or wall-crystal) interaction potential is gradually modified so that we move from a reference state of known interfacial energy to the state of interest and then computing the difference in the Gibbs excess free energy. We test our method by applying it to a Lennard Jones (LJ) system in contact with a wall, which is either flat or structured. The flat wall is modeled by a WCA potential and the structured wall consists of a few layers of particles rigidly fixed at the sites of an ideal fcc crystal lattice and interacting with the liquid (crystal) via the LJ potential. The interfacial excess energy is also determined from the stress anisotropy and we find good agreement between the two approaches.

MM 19.6 Tue 11:30 TC 006

The solubility of oxygen in HCP-Ti revisited on the basis of first-principles calculations — •Paul Erhart[1] and Mark Asta[2] — [1]Department of Applied Physics, Chalmers University of Technology, Gothenburg, Sweden — [2]Department of Materials Science and Engineering, University of California, Berkeley

Most experimental and computed phase diagrams for the Ti–O system indicate a very large solubility of O of up to 30% in hexagonal closed packed (HCP) Ti at low temperatures. Yet already much smaller amounts of oxygen on the order of just fractions of a percent are known to cause rather dramatic changes of the mechanical properties, most notably the ductility. Using a combination of first-principles calculations and Monte Carlo simulations based on lattice Hamiltonians, we have systematically investigated the Ti-rich end of the Ti–O phase diagram. The simulations predict three distinct Ti–O phases that are based on the HCP lattice: Ti_6O, Ti_3O, and Ti_2O. The structures of these phases are in exact agreement with the results of neutron diffraction experiments that hitherto have been integrated incompletely or not at all into available phase diagrams. Using our approach we obtain a revised equilibrium phase diagram in the concentration range up to 33% oxygen. Our results show that the effectice equilibrium solubility of O in Ti is fact less than 1% at room temperature. Beyond this concentration excess oxygen precipitates in the form of Ti_6O. We suggest that the Ti_6O regions effectively lead to a form of precipitation hardening (as opposed to solution hardening) and thus have an important effect on dislocation motion and plasticity.

MM 19.7 Tue 11:45 TC 006

Point defect interactions of boron in α-Fe — •Arthur Bialon, Thomas Hammerschmidt, and Ralf Drautz — ICAMS, Ruhr Universität Bochum, Bochum, Germany

Modern steels are multicomponent systems that combine iron and carbon with further elements in order to achieve specific properties. The effect of boron additions depends on their spatial distribution that are affected not only by the fabrication process but also by interactions with other constituents. The latter may result in boron redistribution or the formation of boron-containing precipitates. In order to gain insight into the interaction of boron with point defects and impurities within the host matrix, we performed ab-initio calculations based on density functional theory for the case of α-Fe. We determined the distance-dependent interaction energies for different point defects, in particular a second boron atom, a vacancy and borons' nearest neighbours in the periodic table: carbon, nitrogen and oxygen atoms. We observe that the interaction tendency is primarily determined by the position of boron, and virtually independent of the second point defect: substitutional boron binds the second point defect, while interstitial boron repels it.