

## MM 41: Methods in Computational Materials Modelling I: Ab initio thermodynamics

Time: Wednesday 15:45–18:00

Location: H52

MM 41.1 Wed 15:45 H52

**High-pressure phases of Li-S binaries** — •LILIA BOERI, CHRISTIAN KOKAIL, and CHRISTOPH HEIL — Institute for Theoretical and Computational Physics, Graz University of Technology, Graz (Austria)

Together with hydrides, high-pressure phases of Li-rich solids are natural candidates to for high- $T_c$  conventional superconductivity [1] and other quantum effects. [2] In this study we use methods for ab-initio crystal structure prediction [3] to study the phase diagram of the binary system Li-S, i.e. the lithium analog of the record conventional superconductor H3S.[4]

We show that several compositions which are not stable at ambient pressures are stabilized at high pressures; similarly to other Li binaries, some of these phases display semiconducting-to-metal and semiconducting-to-superconductor phase transitions. [5]

[1] N. W. Ashcroft, Phys. Rev. Lett. **92**, 187002 (2004). [2] J. B. Neaton and N.W. Ashcroft, Nature **400**, 141 (1999). [3] A. P. Drozdov, et al Nature **525**, 73 (2015); D. Duan, et al, Sci. Rep. **4** 6968 (2014). [3] A. R. Oganov and C.W. Glass, J. Chem. Phys. **124**, 244704 (2006). [5] Y. Xie et al., Phys. Rev. Lett. **104**, 177005 (2010); Y. Shen et al., arXiv 1504.06677 (2015).

MM 41.2 Wed 16:00 H52

**Ab initio description of phase transitions in pure Ti at finite temperatures** — •DOMINIQUE KORBMACHER, ALBERT GLENSK, BLAZEJ GRABOWSKI, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Ti and its alloys play an important role in many industrial applications, for example in medicine or aircrafts. In this project we investigate pure Ti within a fully *ab initio* based methodology using density-functional theory and including anharmonicity. Because bcc Ti is dynamically unstable at lower temperatures standard approaches cannot be applied. We have therefore developed a new method (referred to as TU-TILD [1]) which allows to capture the anharmonic contribution also for unstable systems. This method is based on optimized interatomic potentials which can be used as a highly efficient reference for thermodynamic integration. Applying the TU-TILD methodology, we have accurately investigated the phase stabilities of the three relevant phases in Ti ( $\omega$ , hcp and bcc). In particular we calculated the free energies and derived thermodynamic properties for the whole temperature regime up to the melting point, using two different exchange-correlation functionals. We show that the  $\omega$  to hcp as well as the hcp to bcc phase transition are correctly predicted by our methods. Furthermore we discuss the second order bcc to  $\omega$  phase transition.

[1] A. I. Duff, et al., PRB **91**, 214311 (2015).

MM 41.3 Wed 16:15 H52

**Including DFT data in phase diagram calculations for zirconium carbide** — •THERESA DAVEY<sup>1</sup>, ANDREW DUFF<sup>1</sup>, SUZANA FRIES<sup>2</sup>, and MICHAEL FINNIS<sup>1,3</sup> — <sup>1</sup>Department of Materials, Imperial College London, London SW7 2AZ, UK — <sup>2</sup>ICAMS, Ruhr-Universität Bochum, 44801 Bochum, Germany — <sup>3</sup>Department of Physics, The Thomas Young Centre, Imperial College London, London SW7 2AZ, UK

The CALPHAD approach takes experimental data and parameterises Gibbs energy curves with an optimal fit to this data, which can be phase boundary measurements or thermodynamic data. Thermo-Calc, and other phase diagram assessment codes, make no reference to the vacancy formation energy explicitly, leaving it only to be referred to implicitly within the Gibbs energy formulation [1]. Nevertheless, vacancy formation energies must significantly affect the phase stability when compounds are not strictly stoichiometric.

In recent years, theoretical calculations of the vacancy formation energy (or other point defect formation energies), which are difficult or impossible to measure experimentally, have been produced. This data could be used to increase the physical information encoded within a thermodynamic database.

For the zirconium-carbon phase diagram, I show how data from DFT calculations of the vacancy formation energy in the zirconium carbide phase can be introduced as a constraint on the parameterisation of the Gibbs energy, and how this changes the resulting phase diagram.

[1] J. Rogal et al. (2014), Phys. Status Solidi B, 251(1) 97-129.

MM 41.4 Wed 16:30 H52

**Formation Energy of Ions in Water using ab-initio Molecular Dynamics** — •ANOOP KISHORE VATTI, MIRA TODOROVA, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

Understanding hydration of ions is key feature for chemical and biological processes occurring in water and the specific adsorption of ions at solid-liquid interfaces. Identification of theoretical concepts that allow to probe accurately and computationally efficiently reproduce the complex atomic and electronic structure of ions in liquid water at the microscopic level is crucial. We performed an extensive ab-initio molecular dynamics simulations to study the solvation of charged and neutral cations (Zn/Mg)/anions(Cl/Br/I) in water. Structural correlations and electronic properties of the studied ions are analyzed and compared to experimental observations. Method used here for the calculation of formation energies is inspired from the semiconductor defect chemistry approach. Aligning the water band edges on an absolute scale allows us to benchmark calculated formation energies and transition states, and compare them to experiment[1]. We find a good agreement with photo-emission experiments[2] for the calculated transition levels for the anions in water.

[1] M. Todorova and J. Neugebauer, Phys. Rev. Applied **1**, 014001 (2014).

[2] B. Winter et al., JACS **127**, 7203 (2005).

## 15 min. coffee break

MM 41.5 Wed 17:00 H52

**Intricacies of phonon line shapes in random alloys: A first-principles study** — •BISWANATH DUTTA<sup>1</sup>, DEBASHISH DAS<sup>2</sup>, SUBHRADIP GHOSH<sup>2</sup>, BIPLAB SANYAL<sup>3</sup>, TILMANN HICKEL<sup>1</sup>, and JÖRG NEUGEBAUER<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Eisenforschung GmbH, D-40237 Düsseldorf, Germany — <sup>2</sup>Department of Physics, IIT Guwahati, Guwahati 781039, India — <sup>3</sup>Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden

Lattice vibrations in random alloys are governed by the amount of mass and force-constant disorder present in the system. Disorder-induced scattering in these systems results in broadening of phonon peaks, which can be asymmetric and (for extreme disorder) can even split into two branches. To calculate phonon frequencies, lifetimes, as well as the complex phonon line shapes, sophisticated modeling approaches are required. We use the itinerant coherent potential approximation (ICPA), a Green's function based formalism to account for local fluctuations in random alloys. The interatomic force-constants are calculated using density functional theory and are fed into ICPA to perform the configuration averaging. Our computed results for Cu-Au and Ni-Pt alloys show that a single Lorentzian function cannot describe the phonon line shapes for several wave-vectors. The comparison between theory and experiment also depends on the choice of the Lorentzian function. We discuss the results in the framework of phonon line shape convolution and conclude that multiple Lorentzian fitting for certain wave-vectors in random alloys gives new insights on phonon frequencies and their line widths which can be relevant for their functional properties.

MM 41.6 Wed 17:15 H52

**The effects of lattice vibrations on electronic and magnetic properties of paramagnetic Fe: A disordered local moments molecular dynamics study** — •BJÖRN ALLING — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf — Linköping University, Sweden

High temperature lattice vibrations in the paramagnetic states of Fe is studied employing the disordered local moments molecular dynamics (DLM-MD) method. In particular its impact on the magnetic and electronic structure is investigated. It is found that lattice vibrations strongly affect the local magnetic moment distribution which correlates with the local atomic volumes. Without explicit vibrations, the mean local magnetic moment and mean field derived magnetic entropy in paramagnetic bcc Fe are larger in comparison to paramagnetic fcc Fe which would indicate that magnetic degree of freedom contribute to stabilize the bcc phase at high temperatures. However, when explicit lattice vibrations are taken into consideration, the picture is changing

at high temperature and very similar local magnetic moment distributions and mean-field magnetic entropies of bcc and fcc Fe are found close to the  $\gamma$  to  $\delta$  transition. This qualitative change, due to vibrations, is consistently observed in the electronic density of states which are found to become equally similar with increasing temperature. Our findings illustrate the need for an explicit consideration of vibrational disorder and its impact on electronic and magnetic properties to understand paramagnetic Fe.

MM 41.7 Wed 17:30 H52

**Electron-phonon interactions in 2D materials: going beyond the limitations of plane-wave density-functional theory** — •THIBAUT SOHIER<sup>1,2</sup>, MATTEO CALANDRA<sup>2</sup>, and FRANCESCO MAURI<sup>2,3</sup> — <sup>1</sup>THEOS and NCCR MARVEL, EPFL, Switzerland — <sup>2</sup>IMPMC, Sorbonnes Universités, UPMC, UMR CNRS 7590, 4 place Jussieu, 75005 Paris, France — <sup>3</sup>ISC-CNR and Dept of Physics, Sapienza University of Rome, P.le A. Moro 5, 00185, Rome, Italy

Electron-phonon interactions and their role in the transport properties of 2D materials are conceptual milestones for tomorrow's nanoelectronics. Electron-phonon interactions depend strongly on dimensionality, especially when long-range Coulomb interactions are involved, as in screened couplings or the coupling to polar optical phonons.

A key limitation of plane-wave density-functional perturbation theory with local functionals for the simulation of 2D materials is the use of periodic boundary conditions, implying the presence of periodic images of the 2D system in the out-of-plane direction. Long-range Coulomb interactions between those periodic images lead to incorrect electron-phonon couplings in 2D materials such as graphene or MoS<sub>2</sub>.

We develop novel approaches to eliminate the interactions between

periodic images by truncating the Coulomb interaction in the out-of-plane direction. This is implemented for the calculation of total energy, forces, phonons and electron-phonon interactions, with possible addition of an asymmetric electric field to dope the 2D material. We use this method to investigate the peculiarity of the electron-phonon interaction in 2D materials like graphene and MoS<sub>2</sub>.

MM 41.8 Wed 17:45 H52

**Discovering complete pressure-temperature phase diagrams with Hamiltonian Monte Carlo nested sampling** — •ROBERT BALDOCK<sup>1</sup>, NOAM BERNSTEIN<sup>2</sup>, LIVIA PARTAY<sup>1</sup>, MICHAEL PAYNE<sup>1</sup>, and GABOR CSANYI<sup>1</sup> — <sup>1</sup>University of Cambridge, UK — <sup>2</sup>Naval Research Laboratory, USA

Nested sampling is a Monte Carlo algorithm that can be used to efficiently calculate the complete configurational density of states in a material that undergoes multiple first-order phase transitions. From the density of states one can calculate the partition function as an explicit function of temperature and perform statistical mechanics from first principles. Indeed, we have shown how nested sampling can be used to automatically discover complete pressure-temperature phase diagrams with no prior knowledge of the locations of phase transitions or the structures of phases. In this talk I will present a new version of the nested sampling algorithm, based on a modified Hamiltonian (“Hybrid”) Monte Carlo scheme. This new scheme reduces the scaling of a general nested sampling calculation. In particular the new algorithm expedites the sampling of atomic configuration spaces in condensed phases, and permits one to perform nested sampling calculations at a fraction of the cost required by ordinary nested sampling with standard Monte Carlo.