

## MM 17: Computational Materials Modelling - Methods II

Time: Monday 17:00–17:45

Location: IFW D

MM 17.1 Mon 17:00 IFW D

**Phase Transitions Investigated by Variationally Enhanced Sampling with Permutationally Invariant Collective Variables** — •BIN SONG<sup>1</sup>, GARETH TRIBELLO<sup>2</sup>, KURT KREMER<sup>1</sup>, and OMAR VALSSON<sup>1</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany — <sup>2</sup>Queen’s University of Belfast, Belfast, United Kingdom

Phase transitions are a common theme in our physical world, which are performed over various acts in crystallization of atomic or molecular crystals and transformations between various phases of nanoalloys or soft matters. These phenomena could affect catalytic activity of a catalyst, the bioavailability of a drug molecule, and the stability of metal structures. For understanding phase transitions, molecular dynamic (MD) simulations have become an indispensable tool that is versatile and capable to provide mechanistic insights. Despite the advancement of computing hardware and development of algorithms, the timescale of MD simulations is still limited. Our group has been developing Variationally Enhanced Sampling (VES) method to transcend this limit placed upon MD practitioners. VES builds a bespoke bias potential in the collective variable (CV) space to drive the systems to visit different states and achieve ergodicity, with the collective variables being functions of the configuration space. In this work, we have extended the functionality of VES to use local Permutationally Invariant Collective Variables in situations when global CVs are not viable. We demonstrate the merits of method through studies of phase transition of LJ clusters, and crystallization and melting of bulk sodium.

MM 17.2 Mon 17:15 IFW D

**New basis functions and optimization algorithms for Variationally Enhanced Sampling** — •BENJAMIN PAMPEL and OMAR VALSSON — Max Planck Institute for Polymer Research, Mainz, Germany

Variationally Enhanced Sampling is an advanced sampling method for molecular dynamics simulations based on a variational principle. A bias potential is constructed by minimizing a convex functional, to obtain thermodynamic and kinetic information of rare event systems.

So far mostly orthogonal polynomials have been used as basis functions for the expansion of the bias potential. While there have been proposals for alternatives, this was for specific problems and not with a general evaluation of the performance of the method in mind. There-

fore, the most efficient choice of basis functions is an open question.

Another important ingredient of the VES method is the employed optimization algorithm. While the Bach’s averaged stochastic gradient decent used so far has generally performed fine, more recent algorithms from the field of machine learning might perform better.

To answer these two open questions, we first implemented and evaluated the performance of new sets of basis functions, including Gaussians and cubic splines, by testing them on various systems. We find the usage of Daubechies Wavelets favorable for many applications.

For the optimization, besides implementing some of the popular algorithms like Adagrad or Adam, we also propose our own modifications. Here the conclusions are less clear, as only in few cases the Adam algorithm is able to outperform Bach’s algorithm.

MM 17.3 Mon 17:30 IFW D

**Self-consistent site-dependent DFT+U(+V) for defects** — CHIARA RICCA<sup>1</sup>, IURI TIMROV<sup>2</sup>, MATTEO COCCIONI<sup>2,3</sup>, NICOLA MARZARI<sup>2</sup>, and •ULRICH ASCHAUER<sup>1</sup> — <sup>1</sup>University of Bern, Bern, Switzerland — <sup>2</sup>Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland — <sup>3</sup>University of Pavia, Pavia, Italy

DFT calculations of defects in transition metal oxides often require advanced methods such as hybrid functionals to yield a reasonable description of the electronic structure. When properties of defects at dilute concentrations are desired, the - often incompatible - need for large supercells is added to the above functional requirement. We have recently established self-consistent, site-dependent DFT+U and DFT+U+V as promising approaches to address the challenge of simultaneously meeting these requirements. The minimal added cost of DFT+U(+V) compared to a semi-local functional enables the treatment of large supercells, yet the structural and electronic properties relevant for point-defect calculations agree well with hybrid-functionals. We ascribe this to both the self-consistent determination of the Hubbard parameters that leads to an internal consistency of results, as well as the site dependence, which for localized defect states captures chemical changes on multivalent ions around the defect. We will highlight the performance of the method for oxygen vacancies in the perovskite oxides SrTiO<sub>3</sub> and SrMnO<sub>3</sub>. In the former self-consistent DFT+U+V leads to an electronic structure of oxygen vacancies that agrees well with that of hybrid functionals, which also translates to similar formation energies that agree well with experiment.