

O 85: Molecular Simulations

Time: Thursday 17:45–19:00

Location: WIL B321

O 85.1 Thu 17:45 WIL B321

Representing Complex Potential Energy Surfaces by Artificial Neural Networks — ●CHRISTOPHER HANDLEY and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Computer simulations of large systems are computationally costly, and in many cases intractable, when using *ab initio* models. More efficient potentials are typically based on approximations representative of particular atomic interactions, and the fitting of these potentials is not straightforward. Neural Networks (NNs) recently have been shown to provide interatomic potentials that are comparable to the accuracy of quantum mechanical calculations[1,2]. They are flexible enough to fit complex functions, to quantum mechanical training data, accurate energies and forces. Here, we present the first steps towards a more transferable NN based upon electronic structure methods.

[1] C. M. Handley and P. L. A. Poplier, *J. Phys. Chem. A*, 114, 3371-3383, (2010).

[2] J. Behler, *PCCP*, 13, 17901-18232 (2011).

O 85.2 Thu 18:00 WIL B321

Accelerating *ab initio* molecular dynamics simulations of water by artificial neural networks — ●TOBIAS MORAWIETZ¹, ANDREAS SINGRABER², CHRISTOPH DELLAGO², and JÖRG BEHLER¹ — ¹Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany — ²Faculty of Physics, University of Vienna, Boltzmannngasse 5, 1090 Vienna, Austria

Ab initio molecular dynamics (AIMD) simulations based on density-functional theory (DFT) are a valuable tool to study processes involving water at the atomic level. However, many important properties of *ab initio* water are unknown because the costly evaluation of the forces restricts the simulation time. Artificial neural network (NNs) trained to DFT calculations provide an unbiased way to construct accurate and efficient interatomic potentials [1]. Here, we show that NN potentials closely reproduce the DFT potential-energy surface of water under a wide range of conditions, thus enabling us to study properties of water so far not accessible to AIMD simulations [2].

[1] J. Behler, *PCCP* **13**, 17930 (2011).

[2] T. Morawietz, A. Singraber, C. Dellago, and J. Behler, in preparation.

O 85.3 Thu 18:15 WIL B321

The dissociation constant of water at extreme conditions — ●OTTO E GONZALEZ VAZQUEZ¹, SANDRO SCANDOLO¹, and LUIGI GIACOMAZZI^{1,2} — ¹Abdus Salam International Centre for Theoretical Physics (ICTP), Trieste, Italy — ²International School for Advanced Studies (SISSA), Trieste, Italy

Only one out of 10^7 water molecules is dissociated in liquid water at ambient conditions, but the concentration of dissociated molecules increases with pressure and temperature, and water eventually reaches a fully dissociated state when pressure exceeds 50-100 GPa and temperature reaches a few thousand Kelvin. The behavior of the dissociation constant of water (pKa) at conditions intermediate between ambient and the fully dissociated state is poorly known. Yet, the water pKa is a parameter of primary importance in the aqueous geochemistry

as it controls the solubility of ions in geological fluids. We present results of molecular dynamics calculations of the pKa water at extreme conditions. Free-energy differences between the undissociated and the dissociated state are calculated by thermodynamic integration along the dissociation path. The calculations are based on a recently developed all-atom polarizable force-field for water, parametrized on density-functional theory calculations.

O 85.4 Thu 18:30 WIL B321

Simulating the non-equilibrium growth of complex molecules: the influence of anisotropy — ●NICOLA KLEPPMANN and SABINE H. L. KLAPP — Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

In the last decade complex organic molecules have become of increasing importance. Their large charge carrier densities and tuneable energies make them ideal candidates for applications in semiconductor devices. However the efficiency of such devices strongly depends on the structure formed by the adsorbed molecules, which depends on a complex interplay of growth conditions and molecular properties.

Recent *ab initio* calculations and experiments [1] inspire us to examine the growth of sexiphenyl (6P) on ZnO(10-10) as a model system to understand the influence of molecular anisotropy on structure formation during growth. We use kinetic Monte Carlo simulations to examine the real-space surface and single-particle dynamics as a function of time. The interaction hamiltonian of 6P molecules is modelled using a Gay-Berne potential and a linear quadrupole interaction term with additional substrate influence. Thus, we examine the influence of the molecular anisotropy on growth and on the self-assembled structures formed during growth, based on our previous studies of C60 epitaxy [2]. This system has macroscopic structures characterized by morphological quantities such as island density and layer coverage, but also microscopic ordering of molecules within the islands.

[1] F. Della Sala et al., *PRL* 107, 146401 (2011)

[2] S. Bommel, N. Kleppmann et al., submitted to *PRL*

O 85.5 Thu 18:45 WIL B321

Free energy surface reconstruction from umbrella samples using Gaussian process regression — ●THOMAS STECHER^{1,2}, NOAM BERNSTEIN³, and GÁBOR CSÁNYI¹ — ¹Department Chemie, TU München, Garching, Deutschland — ²Department of Engineering, University of Cambridge, Cambridge, UK — ³Naval Research Laboratory, Center for Computational Materials Science, Washington, DC, USA

We demonstrate how a prior assumption of smoothness can be used to enhance the reconstruction of free energy profiles from multiple umbrella sampling simulations using the Bayesian Gaussian process regression approach. The method we derive allows the concurrent use of histograms and free energy gradients and can easily be extended to include further data. In a system with one collective variable we demonstrate improved performance with respect to the weighted histogram analysis method and obtain meaningful error bars without any significant additional computation. In the case of multiple collective variables we compare to a reconstruction using least squares fitting of radial basis functions and find substantial improvements in the regimes of spatially sparse data or short sampling trajectories.