O 58: Mini-Symposium: Molecular scale investigations of liquid-vapor interfaces II

Time: Wednesday 10:30–12:30 Location: R1

Invited Talk O 58.1 Wed 10:30 R1

Simulating interfacial water with neural network potentials

— •Christoph Dellago[1], Oliver Wohlfahrt[1], and Marcello Sega[2] — [1]University of Vienna, Faculty of Physics, Vienna, Austria — [2]Forschungszentrum Jülich, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, Nürnberg, Germany

The strong, directed network of hydrogen bonds of water lies at the heart of its rich phase diagram and numerous anomalous properties and is responsible for the peculiar structure of its liquid/vapor interface. Detailed insights into the molecular structure and dynamics of bulk and interfacial water have been gleaned from first principles simulations, which provide an unbiased description of water at the atomic level and yield information on the underlying molecular forces. However, the computational cost of such simulations is still daunting, particularly for interfacial systems that require relatively large systems sizes as they suffer from finite size effects more than bulk systems. Recently, artificial neural networks have been proposed to overcome these limitations, yielding the accuracy of first principles simulations at a fraction of their computational cost. In this talk, I will report on the structural and thermodynamic properties of the water/vapor interface obtained using a neural network potential trained for bulk and interfacial water. In particular, I will discuss the liquid/vapor coexistence curve and its size dependence as well as the structure of the interface in terms of density profiles and molecular orientations.

O 58.2 Wed 11:00 R1

Modelling solvation at dielectric interfaces

— •Jakob Filser[1], Markus Sinstein[1], Konstantin Jakob[1], Karsten Reuter[2], and Harald Oberhofer[1] — [1]Technische Universität München — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft

Modelling solvation effects is a complex challenge in molecular simulations. The difficulty lies in unravelling classical electrostatic, quantum mechanical, nuclear, entropic and other free energy contributions in liquid systems. In reality these contributions interact with each other and a simplistic separation is not possible. Modelling this full complexity by accounting for all relevant degrees of freedom explicitly is often computationally intractable. Therefore, approximations are necessary. The family of implicit solvation models treats only the solute on an explicit, atomistic level and summarizes the degrees of freedom of all or all but few solvent molecules in a structurless dielectric medium.

The presence of dielectric interfaces in the system further complicates things. Different models which predict similar energies in bulk solvent can predict substantially different behaviour at a dielectric interface. We systematically construct a method which can implicitly model dielectric interfaces. It describes a solvent only by three parameters, the first of which is experimentally known: The relative permittivity, a dimensionless interaction distance and an effective interfacial tension with the explicit system. First predictions are compared to experimental results as well as predictions from explicit solvent models for an octanoic acid surfactant on water droplets.

Invited Talk O 58.3 Wed 11:20 R1

Surface activity of hydroxide and the hydrated proton

— •Ellen Backus — Institut für Physikalische Chemie, Wien, Österreich — Max-Planck-Institute für Polymerforschung, Mainz, Deutschland

The behavior of hydroxide and hydrated protons, the auto-ionization products of water, at surfaces is important for a wide range of applications and disciplines. Despite of its importance, the likelihood of surface adsorption of either of those two ions is controversially discussed in literature. By determining the onset concentration of surface adsorption at the water-air surface of hydrated protons and hydroxide ions, we can determine the relative surface-activity. To this order, we perform surface-sensitive vibrational sum frequency generation spectroscopy - basically providing the vibrational spectrum of just the interfacial layer - on the O-H stretch vibration. We will discuss how spectral changes in the response from hydrogen bonded molecules can be related to the surface adsorption of the hydrated ions. Moreover, changes in the spectral signature of the so-called free OH molecule sticking out in the air are used to determine the adsorption free energy of the proton.

O 58.4 Wed 11:50 R1

Vibrational Dynamics of Interfacial Ice Ih and Liquid Water

— •Prerna Sudera[1], Jenée D. Cyran[2], Malte Deiseroth[1], Marc-Jan van Zadel[1], Mischa Bonn[1], and Ellen Backus[3] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Baylor University, Waco, Texas, USA — [3]University of Vienna, Vienna, Austria

The dynamics of vibrational energy relaxation and dissipation at surfaces of aqueous systems is relevant for chemical conversion occurring at the surface of those systems: the energy flow pathways determine the likelihood of a reaction taking place on the surface. Subtle differences in energy dissipation mechanism can account for different photochemical activities of water and ice surfaces, relevant for atmospheric processes. We excite water and ice at 3100 and 3300 cm-1, the low- and high-frequency regions of the water stretch band, with femtosecond infrared excitation pulses of 150 cm-1 bandwidth and probe over the entire O-H stretch region with Sum Frequency Generation spectroscopy. Our results show extremely rapid spectral diffusion for both ice and water on sub-100 fs timescales, before vibrational relaxation and thermal redistribution of excess energy on several hundreds of fs timescales. The non-hydrogen bonded water molecules show relaxation dynamics on a picosecond timescale with ice being slower than water. By comparing the observed relaxation dynamics of water molecules at the surface of single-crystalline ice and the water-air interface, we discuss the potential implications of the results for chemical dynamics at the two surfaces.

O 58.5 Wed 12:10 R1

Mass transfer of water at organic aerosol interfaces

— •Matus E. Diveky, Michael Gleichweit, Sandra Roy, and Ruth Signorell — Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, CH-8093 Zürich, Switzerland

Interfacial mass transport plays a crucial role in defining growth rates of aerosols. To properly assess the potential of aerosols to behave as condensation nuclei, it is of paramount importance to unravel the kinetics of mass transport through the interface. The important parameter defining the probability of a gas-phase molecule accommodating to the surface upon collision is called mass accommodation coefficient. Despite the widespread relevance of accommodation coefficients, values for many important systems are still lacking.

We employ Photothermal Single-Particle Spectroscopy (PSPS) to investigate the water accommodation on miscible organic aerosol particles. Such systems remain largely uncharted despite the abundance of organic matter and gas-phase water molecules in the atmosphere. The PSPS technique combines photoacoustic spectroscopy with modulated Mie scattering performed simultaneously on a single-particle level.

Through a careful droplet manipulation inside an optical trap, we study the temperature and relative humidity dependence of the mass accommodation coefficient of water on organic miscible droplets. Our results hint at a negative correlation between accommodation coefficient and temperature. Lastly, we argue that the PSPS technique can be used to restrict the lower limit of the mass accommodation of water on liquid water.