

## CPP 48: Focus: The Physics of Water Interactions with Biological Matter (joint session BP/ CPP, organized by CPP)

Organizers: Emanuel Schneck (MPIKG Potsdam), Regine von Klitzing (TU Berlin), Tristan Berau (MPIP Mainz)

The role of water in biological systems is not simply to act as a solute for biomolecules. Water mediates the interaction between biological interfaces and has to be considered an integral component of biomolecular assemblies. These interactions can alter the properties of both water and the biomolecules in significant ways. Recent methodological progress in experimental techniques and computer simulations provides us with improved tools to gain insight into the relevant physics, from quantum-chemical details of individual molecules, to collective behavior at interfaces, to hydration-dependent structures of biomaterials. The purpose of this Focus Session is to bring scientists from various disciplines to search for solutions to integrate hydration phenomena on different length scales.

Time: Thursday 9:30–12:45

Location: H37

### Invited Talk

CPP 48.1 Thu 9:30 H37

**It is water what matters: THz absorption spectroscopy as a new tool to study solvation dynamics** — ●MARTINA HAVENITH — Physikalisches Chemie II, Ruhr-Universität Bochum, Bochum, Germany

Terahertz (THz) absorption spectroscopy is a powerful tool to study (bio)molecular hydration. Experimental advances in the development of new THz sources had to go hand in hand with the development of new theoretical concepts which are able to describe the underlying solute-induced sub-picosecond dynamics of the hydration shell.

Recent results show the significance of hydrogen bond dynamics for molecular recognition. We find a gradient of water motion toward functional sites of proteins, the so-called "hydration funnel", which is found to be essential for biomolecular function.

Transient THz spectroscopy can be used to record snapshots of the low frequency spectrum of a solvated proteins during protein folding, thus capturing changes during hydrophobic collapse in real time during biological function. Within the talk I will present examples of low frequency spectra of hydration water around solutes which can be correlated to changes in entropy.

V. Conti Nibali, M. Havenith New insights into the role of water in biological function: Studying solvated biomolecules using terahertz absorption spectroscopy in conjunction with molecular dynamics simulations *J. Am. Chem. Soc.* 136(37), 12800-12807 (2014)

CPP 48.2 Thu 10:00 H37

**The Effect of Zwitterionic Ectoine on Local Water Dynamics** — ●JOHANNES ZEMAN and JENS SMIAITEK — Institute for Computational Physics, University of Stuttgart, Germany

Ectoine is known to have a stabilizing effect on proteins in aqueous solution. In order to investigate the plausibility of a suggested indirect mechanism [1], its effect on the local water dynamics at low molar concentrations has been examined by means of Molecular Dynamics simulations. The simulation data has been analyzed in terms of diffusion coefficients, hydrogen bond life times and angular distributions, power spectra, as well as dielectric spectra.

The observed influence of zwitterionic ectoine on water dynamics indicate a pronounced structural strengthening and therefore support the hypothesis of an indirect stabilization mechanism.

For comparison, similar simulations and analyses have been carried out with urea in aqueous solution, as urea is known to have a denaturing effect on proteins. As expected [2], the influence of urea on the local water dynamics is comparatively small.

[1] M. B. Hahn et al., The Influence of the Compatible Solute Ectoine on the Local Water Structure: Implications for the Binding of the Protein G5P to DNA, *J. Phys. Chem. B* (Nov 10, 2015) [Epub ahead of print]

[2] D. Bandyopadhyay et al., Molecular Dynamics Simulation of Aqueous Urea Solution: Is Urea a Structure Breaker?, *J. Phys. Chem. B*, 118 (40), pp 11757–11768 (2014)

### Invited Talk

CPP 48.3 Thu 10:15 H37

**Dielectric and diffusional aspects of hydration water** — ●ROLAND NETZ and MATEJ KANDUC — Physics Department, FU Berlin, Germany

The molecular layer of water molecules on surfaces is important for

the properties of neutral and charged solutes and surfaces. We study how hydration and dielectric properties of interfacial water layers can be used to explain diverse phenomena such as the hydration repulsion between polar surfaces, dielectric spectra of salt solutions, and conformational transitions of polymers.

CPP 48.4 Thu 10:45 H37

**Salt Induced Hydrophobic Polymer Collapse Theoretical Model vs. Simulation** — ●JAN HEYDA<sup>1</sup> and JOACHIM DZUBIELLA<sup>2,3</sup> — <sup>1</sup>Department of Physical Chemistry, University of Chemistry and Technology, Prague, Czech Republic — <sup>2</sup>Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin, Hahn-Meitner Platz 1, 14109 Berlin, Germany — <sup>3</sup>Department of Physics, Humboldt-University Berlin, Newtonstr. 15, 12489 Berlin, Germany

Smart materials are perspective due to their versatility. A soft-matter example are thermoresponsive polymers, which undergo volume transition, when crossing the lower critical solution temperature (LCST). Near the LCST, they become sensitive to other stimuli, such as salt type and concentration ([dx.doi.org/10.1021/ja0546424](https://doi.org/10.1021/ja0546424)).

In this contribution, we employed a hydrophobic polymer model ([dx.doi.org/10.1073/pnas.0605139104](https://doi.org/10.1073/pnas.0605139104)), which possesses 2-state behavior, to study ion-specific effects. We performed replica-exchange molecular dynamics simulations and analyzed the data thermodynamically as well as in terms of Kirkwood-Buff theory, i.e., the preferential binding of salt over water to the polymer was determined.

We have found that the effect on LCST change of salts excluded from hydrophobic interfaces, such as KF and NaCl is strikingly different from attracted salts, such as NaI or GndCl. The surface area based model performs well for the first, but fail for the second group of salts.

To interpret the effect of 'binding' salts, we have employed recently proposed bridging mechanism ([dx.doi.org/10.1021/ma302320y](https://doi.org/10.1021/ma302320y)) and chain configuration entropy approach ([dx.doi.org/10.1039/c4cp05314a](https://doi.org/10.1039/c4cp05314a)).

### 15 min. break

### Invited Talk

CPP 48.5 Thu 11:15 H37

**Neutron scattering clarifies the behaviour of water in cells** — ●GIUSEPPE ZACCAI — Institut Laue Langevin, Grenoble, France

Its essential role in biological structure and function is so well established that the search of extra-terrestrial Life is guided by a search of liquid water. Yet the H-bonding properties of water and their interactions with biological molecules are still not fully understood. Because of the strong H/D isotope effect in neutron scattering, neutron diffraction and neutron spectroscopy are particularly powerful experimental methods for the study of water in biology. Neutrons contributed important data to clarify the state of water in cells, following controversial reports on its dynamic state, which, by sustaining that in cell conditions are significantly different, put in question the relevance of in vitro studies. The atomic scale dynamics of intracellular water has been measured in vivo in mesophile and extreme halophile organisms. The results clearly show that intracellular water, other than in hydration interactions with macromolecules and membranes, flows as freely as bulk water, with similar effects on functional molecular dynamics as observed in vitro. Neutrons also characterised the state of water in the intracellular solvent of halotolerant bacteria, which contains molar concentrations of the compatible solute ectoine. All these observations

underline the biological requirement of maintaining, within the physiological environment, the remarkable H-bonding properties of liquid water.

CPP 48.6 Thu 11:45 H37

**Explicitly implicit solutions: Cavity optimization on the cheap** — •DAVID EGGER, CHRISTOPH SCHEURER, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München, Garching, Germany

In recent years the importance of the solvent response in catalytic, bio- and photochemical processes has become more and more apparent. Yet, in ab-initio computer simulations treating the solvent effect in an efficient but accurate manner is still a major challenge. Unfortunately, an explicit inclusion of solvent molecules significantly increases the associated computational costs. Therefore, continuum solvation models which treat the solute-solvent interaction implicitly through their dielectric permittivities, are often the method of choice. The transitions between these permittivities define a dielectric 'cavity' that is generally defined over free parameters.

In our contribution, we study the validity of such an approach by comparing the implicit potential response to that of explicit classical MD simulations. We reverse engineer an optimal cavity by minimizing the differences between explicit and implicit spatially resolved electrostatic reaction potential of the solvent. To this end we also investigate a number of different models of the permittivity transition function and cavity. Finally, we present optimization results for ions and small molecules in water.

**Invited Talk**

CPP 48.7 Thu 12:00 H37

**Controlling Water Evaporation: self-assembly at air/liquid interfaces** — •EMMA SPARR<sup>1</sup> and KEVIN ROGER<sup>2</sup> — <sup>1</sup>Physical chemistry, Lund University, Sweden — <sup>2</sup>Université de Toulouse, France

Land-living organisms face the challenge that the ambient air is much drier than what is found in a living cell. One strategy to counter this drying-out threat is through lipid-protein barrier membranes, like the human skin. One important property of the skin is that the evaporation rate across skin is nearly independent of the air humidity, which implies that skin is a responding membrane and its permeability depends on its boundary conditions.

Using aqueous solutions of amphiphilic molecules, we show that the response can be explained by changes in self-assembly structures in the water gradient across the interfacial layer. We have designed an experimental device coupled to a variety of characterization techniques (X-ray scattering, polarized & IR microscopy) to study the non-equilibrium time evolution at an air-liquid interface. Using this device we demonstrate for two model systems how multilayer interfacial structures are formed, and how these structures influence the water transport. We show that a dry phase with low water permeability forms at the air/liquid interface and adapts its thickness to counter changes in the air humidity. This responsive shield is a universal feature of systems for which the structure/permeability changes with the water content. Our findings can unveil mechanism of responding membrane in biological systems, for example, the skin, and it can lead to new possibilities to design robust and homogeneous coatings of amphiphilic molecules.

CPP 48.8 Thu 12:30 H37

**Anomalous and anisotropic diffusion of hydration water in fluid lipid membranes** — •FELIX ROOSEN-RUNGE<sup>1</sup>, LAURA TOPPOZINI<sup>2</sup>, and MAIKEL RHEINSTÄDTER<sup>2</sup> — <sup>1</sup>Institut Laue-Langevin, Grenoble, France — <sup>2</sup>McMaster University, Hamilton, Ontario, Canada

Water diffusion in heterogeneous environments is a relevant and frequently studied phenomenon in experiment, simulation and theory. We report on water diffusion between phospholipid membranes using incoherent quasi-elastic neutron scattering (QENS) and computer simulations [1]. The combination of a well-aligned stack of DMPC membranes with the large, 2-dimensional detectors available at the neutron spectrometer Let (ISIS, UK) allows for simultaneous access to water motions lateral and perpendicular to the membranes. The resulting 2-dimensional maps of relaxation time,  $\tau$ , and stretching exponent,  $\beta$ , evidence anomalous (sub-diffusive) and anisotropic diffusion of membrane hydration water varying on nanometer distances. By combining molecular dynamics and coarse-grained Brownian dynamics simulations, the overall behavior is reproduced, and the apparent features can be linked back to an intrinsic sub-diffusivity of water at picosecond time scales, and the anisotropy of confinement and local dynamical environments.

[1] Topozini et al. *Soft Matter* 11 (2015) 8354