

## CPP 40: Focus: Van der Waals at soft matter interfaces: structure and dynamics

While vdW interactions are successfully taken into account to explain adhesion and repulsion of soft matter at solid interfaces, it is yet not fully understood how dynamic processes are affected. The focus session is aimed to give an overview over recent studies and to address open questions concerning the influence of vdW interactions on structure and dynamics at interfaces including soft matter.

Organizers: Daniela Täuber (Chemnitz) and Karin Jacobs (Saarbrücken)

Time: Thursday 9:30–11:15

Location: H39

**Invited Talk** CPP 40.1 Thu 9:30 H39  
**Collective van der Waals Interactions in Molecules, Solids, and Interfaces** — ●ALEXANDRE TKATCHENKO — Fritz-Haber-Institut der MPG, Berlin, Germany

Van der Waals (vdW) interactions are ubiquitous in molecules, condensed matter, and hybrid organic/inorganic interfaces. These interactions are inherently quantum mechanical phenomena that arise from concerted fluctuations between many electrons within a given molecular system. Despite this fact, the vast majority of theoretical calculations determine long-range vdW interactions based on a simple effective interatomic pairwise model. We have recently introduced efficient methods that accurately describe the long-range many-body vdW energy for molecules and materials [PRL 108, 236402 (2012); PNAS 109, 14791 (2012); PRL 108, 146103 (2012)]. In this talk, we demonstrate that many-body vdW interactions can successfully explain the recent experimental observations that vdW interactions act at much longer distances than conventionally assumed, and their contribution can significantly exceed the highly coveted “chemical accuracy” for molecules and materials. Our findings suggest that inclusion of the many-body vdW energy is essential for obtaining quantitative and sometimes even qualitatively correct results in materials modeling.

CPP 40.2 Thu 10:00 H39

**Enhanced surface tension of liquid–vapour interfaces at mesoscopic scales** — ●FELIX HÖFLING and SIEGFRIED DIETRICH — Max Planck Institute for Intelligent Systems, Stuttgart, and Institute for Theoretical Physics IV, Universität Stuttgart, Germany

Due to the simultaneous presence of bulk-like and interfacial fluctuations the understanding of the structure of liquid–vapour interfaces poses a long-lasting and ongoing challenge for experiments, theory, and simulations. In this context, we have generated high-quality molecular dynamics data for a Lennard-Jones fluid mimicking long-ranged van der Waals attraction. Upon lowering the temperature from that of the critical point to that of the triple point, the wavenumber-dependent surface tension develops a maximum at non-zero wavenumber so that its functional form changes from concave to convex at mesoscopic length scales.

**Invited Talk** CPP 40.3 Thu 10:15 H39  
**The influence of van der Waals interactions on the adsorption of proteins to solid/liquid interfaces** — ●HENDRIK HÄHL — Institute of Physical Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

Protein adsorption to interfaces is an ubiquitous phenomenon. In particular on solid/liquid boundaries, adsorbed proteins precondition the surface for a later biofilm colonization. Therefore, a better understanding of this first step in biofilm development is highly desirable. The adsorption of proteins to the solid/liquid interface is driven by the interactions between proteins and substrates. Yet, particularly van der Waals (vdW) forces and their dependence on the substrate’s composition are mostly neglected in experiments as well as in simulations.

For the investigation of the influence of vdW forces on protein adsorption, we judiciously chose substrates, with which only the vdW potential could be varied. Therefore, silicon wafers with different sil-

icon oxide thicknesses proved to be an excellent substrate system [1]. Adsorption kinetics as well as the structure of the final adsorbate of several globular proteins were determined on these substrates. Varying the oxide layer thickness caused changes in adsorption rates, course of the adsorption kinetics as well as in the density of the adsorbate irrespective of the surface energy [2]. Thus, it could be shown that the vdW forces between substrate and protein influence the adsorption process and the relaxation of the adsorbate in particular.

[1] P. Loskill et al. *Adv. Coll. Interf. Sci.* **107** (2012) 179182.

[2] H. Hähl et al. *Langmuir* **28** (2012) 7747.

CPP 40.4 Thu 10:45 H39

**Influence of van der Waals interactions on morphology and dynamics in ultrathin liquid films at silicon oxide interfaces** — ●DANIELA TÄUBER and CHRISTIAN VON BORCZYKOWSKI — nanoMA, TU-Chemnitz, Institut für Physik

Liquids show molecular layering close to interfaces with solids [1]. Its extend is influenced by substrate roughness, humidity and the type of liquid. From studies on wetting behavior, the influence of substrate material on film thickness is known, while also structure formation and dynamics in thin liquid crystal films appeared to depend on the type and thickness of the silicon oxide [2]. Single molecule tracer diffusion studies of evaporating ultrathin tetrakis-2-ethyl-hexoxysilane (TEHOS) films on silicon with 100 nm thermal oxide reveal a slowdown of the tracer mobility 1-2 nm above the substrate [3]. An ellipsometric study of thinning TEHOS films on silicon with 100 nm thermal or 2 nm native oxide yields further information. On the thermal oxide, a lateral flow of the liquid is observed, while the film on the native oxide forms an almost flat surface and shows negligible flow. In addition, we found a significantly smaller initial film thickness in case of the native oxide. We ascribe these differences to van der Waals interactions with the underlying silicon in case of the native oxide, whereas the thermal oxide suffices to shield those interactions [3].

[1] M. L. Forcada, C. M. Mate, *Nature* 363 (1993) 527. [2] B. Schulz, D. Täuber, J. Schuster, T. Baumgärtel, and C. von Borczykowski, *Soft Matter* 7 (2011) 7431. [3] D. Täuber, I. Trenkmann, and C. von Borczykowski, submitted.

CPP 40.5 Thu 11:00 H39

**Interface effects on the glass transition temperature in thin supported polymer layers** — ●DOMINIK WÖLL<sup>1,2</sup>, BEATE STEMPELE<sup>1</sup>, BENTE FLIER<sup>1</sup>, and ANDREAS ZUMBUSCH<sup>1</sup> — <sup>1</sup>Fachbereich Chemie, Universität Konstanz, 78457 Konstanz — <sup>2</sup>Zukunftskolleg, Universität Konstanz, 78457 Konstanz

Experimental approaches to study the influence of interfaces on polymer dynamics are challenging. In our contribution, we present wide-field fluorescence microscopy studies to investigate the motion of single dye molecules of different size in thin glass-supported polystyrene films up to temperatures of 150 °C. Heterogeneities in the diffusion coefficients of single molecules were attributed to interface effects influencing the glass transition temperature. Monte Carlo random walk simulations with glass transition temperature profiles taken from literature could rationalize our experimental results, thus confirming that changes in the glass transition temperature at the polymer-air interface can reach only few nm into the polymer film.