CPP 23: Interfaces and Thin Films I (joint session CPP, DS)

Time: Tuesday 10:00–12:30 Location: C 243

CPP 23.1 Tue 10:00 C 243

What is the result of a tensiometer measurement to do with the surface tension? — •Markus Bier — Max Planck Institute IS and University of Stuttgart, Germany

The surface tension of liquids is routinely measured with various types of tensiometers under ambient pressure conditions [1]. For, e.g., water at room temperture this leads to the well-known value of 0.07 N/m [1]. However, the surface tension is strictly defined only under conditions of liquid-vapour bulk coexistence, whereas, e.g., water at room temperature and ambient pressure is deep in the one-phase region of the phase diagram, far away from phase coexistence. Hence the above-mentioned tensiometer measurements are actually performed at interfaces under non-equilibrium conditions. This leads to the question whether it is legitimate at all to identify the result of a tensiometer measurement of a non-equilibrium interface with the surface tension. This contribution gives an answer to that question [2].

References:
[1] D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics, 82nd edition* (CRC Press, Boca Raton, 2001).
[2] M. Bier and D. Arnold, Phys. Rev. E **88**, 062307 (2013).

CPP 23.2 Tue 10:15 C 243

Morphometric thermodynamics and interface conventions — •Andreas Reindl, Markus Bier, and S. Dietrich — Max Planck Institute IS, University of Stuttgart, Germany

Several model fluids with small number densities in contact with planar, spherical and cylindrical walls are investigated within density functional theory. The dependence of the interfacial tension on the curvature of spherical and cylindrical walls is examined and compared to the expression derived within the framework of morphometric thermodynamics. Particular attention is paid to the influence of the choice of the interface location, which underlies the definition of the interfacial tension. We found that morphometric thermodynamics is never exact for the considered systems and that its quality as an approximation depends on the choice of the interface.

CPP 23.3 Tue 10:30 C 243

The surface tension anomaly of water — •Marcello Sega[1], George Horvai[2], and Pal Jedlovszky[3] — [1]University of Vienna, Institut für Computergestützte Biologische Chemie, Vienna, Austria — [2]MTA-BME Research Group of Technical Analytical Chemistry, Budapest, Hungary — [3]Department of Chemistry, EKF Training School, Eger, Hungary

The surface tension of water is characterised by an anomalous dependence on the temperature that manifests itself in the form of an inflection point [1]. So far, a microscopic explanation of this phenomenon was missing. By using intrinsic surface analysis on the liquid/vapour interface, simulated using six different water models, we managed to establish a link between the surface tension inflection and the topological properties of the hydrogen-bond network of the surface layer. We discovered that the inflection temperature coincides with the percolation threshold of the hydrogen bond network in the first molecular layer at the liquid/vapour interface. This provides strong evidence that the sudden breakup of the network, which takes place at the percolation threshold, is the underlying microscopic mechanism at the origin of this surface tension anomaly of water [2,3].

[1] J. S. Rowlinson and B. Widom. Molecular Theory of Capillarity; Dover Publications: Mineola, NY, 2002; p 11.

[2] M. Sega, G. Horvai and P. Jedlovszky, Langmuir 30, 2969 (2014)

[3] M. Sega, G. Horvai and P. Jedlovszky, J. Chem. Phys. 141, 054707 (2014)

CPP 23.4 Tue 10:45 C 243

Liquid drops on a surface: comparing results from microscopic density functional theory (DFT) with mesoscopic modelling and a method for calculating the binding potential — Adam Hughes[1], Uwe Thiele[2], and •Andrew Archer[1] — [1]Department of Mathematical Sciences, Loughborough University, Loughborough, LE11 3TU, UK — [2]Westfälische Wilhelms-Universität Münster, Institut für Theorestische Physik, Wilhelm-Klemm-Str. 9, 48149 Münster, Deutschland

We present a microscopic DFT based method for calculating the binding potential $g(h)$ for a film of liquid on a solid surface, where h is the thickness of the liquid film. The form of $g(h)$ determines whether or not the liquid wets the surface. We study in detail the effect on $g(h)$ of truncating the range of the dispersion forces, both those between the fluid molecules and those between the fluid and wall. We find this can have a significant effect on the form of $g(h)$ and therefore also on whether the liquid is predicted to wet the surface or not. We also calculate density profiles for liquid drops on a surface, using both DFT and also from inputing $g(h)$ into a mesoscopic free energy. Comparing quantities such as the contact angle and the shape of the drops, we find good agreement between the two methods.

15 min. break

CPP 23.5 Tue 11:15 C 243

Crack-Free Hierarchical Wrinkle Patterns — •Bernhard Glatz and Andreas Fery — Physical Chemistry II, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany

Wrinkling is a mechanical instability phenomenon of thin films: Wrinkles form, if a system consisting of a hard, thin layer in strong adhesive contact with a soft, thick elastomer is subject to in plane compression. Under these conditions, a buckling instability results in a periodic surface corrugation with well-defined wavelength. In that regard PDMS is a well-established elastomer since it allows the in-situ generation of a glassy layer by oxidization processes as plasma or UVO. It comprises however side features as cracks and line defects, which form in most wrinkling process and are not predictable yet. We demonstrate a crack-free method where line defects are arranged by modifying the substrate: A stiffness gradient between two covalently linked PDMS phases induces a change in the wrinkle periodicity along the border of both. We tuned the ratio of the phases and so received several hierarchical line defect patterns. Furthermore computer simulations helped us to understand the observed structures. Such crack-free wrinkles with predictable defect positions allow applications as channel junctions in microfluidics or templates for particle alignment.

[1] B. A. Glatz and co-workers (in preparation)

CPP 23.6 Tue 11:30 C 243

Condensation of methane in metal organic frameworks (MOFs): Novel phase transitions — •Nicolas Höft and Jürgen Horbach — Institut für Theoretische Physik II: Soft Matter, Heinrich-Heine-Universität Düsseldorf, Germany

Metal-Organic frameworks (MOFs) are nanoporous crystalline materials where where metal oxide complexes are to connected to each other by organic linkers. Due to the large inner surface, MOFs are well-suited for applications associated with gas adsorption. Experimentally, adsorption isotherms have been studied for molecules such as CH_4, CO_2, H_2O, etc., indicating the possibility of a phase-transition in various MOF structures. However, the nature of these transitions is not well understood, in particular with respect to the interplay between layering on the inner surface and gas-liquid coexistence in the porous structure.

We use grand canonical Monte Carlo simulations in conjunction with successive umbrella sampling to study the condensation of CH_4 in the MOF systems IRMOF-1, IRMOF-8, and IRMOF-16. We find a very rich phase behaviour in these systems and analyse in detail the occurring coexisting phases as well as the critical behaviour.

CPP 23.7 Tue 11:45 C 243

Extreme Surface Propensity of Halide Ions in Water — •Ellen H.G. Backus[1], Lukasz Piatkowski[2], Zhen Zhang[1], Huib J. Bakker[2], and Mischa Bonn[1] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]FOM Institute AMOLF, Amsterdam, the Netherlands

The dominant part of water on earth is not pure water; it contains salts. Moreover, especially in atmospheric chemistry the ions present at the interface are important for various reactions occurring at these interfaces. These ions are potentially reactive and/or determine the water structure, thereby influencing the surface reactivity. Experimentally, it is very challenging to determine the local concentration of ions in the outermost molecular monolayer region of aqueous solutions. Here, we show how two-dimensional sum frequency generation spectroscopy can be used to determine this concentration by measuring the energy transfer rate between water molecules. The presence of ions leads to a reduction of this transfer rate. The data reveal a high surface propensity for iodide anions corresponding to a surface concentration three times higher than the bulk concentration.

CPP 23.8 Tue 12:00 C 243

Pressure induced adsorption of lysozyme at the solid-liquid interface — •Paul Salmen[1], Julia Nase[1], Susanne Dogan[1], Holger Göhring[1], Irena Kiesel[1,3], Johannes Möller[1,2], Christopher Weis[1], Florian Wirkert[1], Michael Paulus[1], and Metin Tolan[1] — [1]Fakultät Physik/DELTA, TU Dortmund, 44221 Dortmund, Germany — [2]ESRF - The European Synchrotron, 71 Avenue des Martyrs, F-38043 Grenoble, France — [3]Institut Laue-Langevin, 71 Avenue des Martyrs, 38000 Grenoble, France

The pressure-induced adsorption of proteins at hydrophilic and hydrophobic interfaces was studied by x-ray reflectivity measurements. In our custom-built cell for x-ray reflectivity (XRR) measurements [1], we are able to apply pressures up to 5 kbar and study the solid/liquid interface in-situ with Angstrom resolution. As hydrophobic surfaces, silicon wafers covered with octadecyltrichlorosilane (OTS) were used, while bare silicon wafers with a native silicon dioxide layer provide charged, hydrophilic interfaces. Lysozyme was used in 20 mM BisTris buffer (pH 7.1) at a concentration of 0.1 mg/ml. The measurements were performed at the synchrotron light sources DELTA (Dortmund, Germany), ESRF (Grenoble, France) and SLS (Villigen, Switzerland) using high energy x-ray radiation. At low pressures, only a monolayer of lysozyme adsorbs at both interfaces. When pressure is increased, a second layer of lysozyme adsorbs. Because the thickness of the first layer decreases in this process, we suppose a partial collapse of the first lysozyme layer. [1] F. J. Wirkert et al., Journal of Synchrotron Radiation 2014 (21) doi:10.1107/S1600577513021516

CPP 23.9 Tue 12:15 C 243

A Standing-Wave Approach in Ambient Pressure Photoemission: Chemical State and Depth Resolved Concentration Profiles of Solid/Liquid and Liquid/Gas Interfaces — •Slavomir Nemsak[1], Hendrik Bluhm[2], Charles Fadley[3], and Claus Schneider[1] — [1]Peter Grünberg Institut 6, Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Chemical Sciences Division, Lawrence Berkeley National Laboratory, 94720 Berkeley, CA, USA — [3]Department of Physics, University of California, 95616 Davis, CA, USA

A standing wave approach in the ambient pressure photoelectron spectroscopy is a new and powerful technique to study heterogeneous processes in solid/gas, liquid/gas and solid/liquid interfaces [1]. Advantages of the technique, such as superb depth resolution and chemical sensitivity, are demonstrated on several model systems with relevance to energy research, heterogeneous catalysis, electrochemistry, and atmospheric and environmental science. A strong standing-wave is generated using a multi-layer Si/Mo mirror as a substrate and phase of the standing wave is tailored through the interface of interest by rocking the sample around the Bragg angle. Photoemission signal from different species is then analyzed in order to provide their spatial arrangement, as well as local potential variations, along the direction perpendicular to the interface with sub-nm accuracy. Pros and cons of using harder X-ray excitation are discussed in terms of a photoemission signal strength and a standing wave effects amplitude.

[1] Nemsak et. al, Nature Communications 5, 2014.