CPP 58: Fluids and Interfaces II

Time: Thursday 10:15–12:45 Location: ZEU 255

CPP 58.1 Thu 10:15 ZEU 255

Elastic capsules at liquid-liquid interfaces — •Jonas Hegemann[1], Horst-Holger Boltz[2], and Jan Kierfeld[1] — [1]TU Dortmund, 44221 Dortmund, Germany — [2]Georg-August-Universität Göttingen, 37077 Göttingen, Germany

We investigate capsules consisting of a hollow spherical shell filled with an incompressible liquid. We consider shells made from isotropic and thin materials with Hookean bending and stretching elasticity. When adsorbing to a liquid-liquid interface, initially spherical capsules undergo equatorial expansion due to isotropic in-plane tension and become discus-shaped. During spreading within the liquid-liquid interface, the adsorption energy increases significantly leading to mechanical stabilization of the interface. The full range of shapes is bounded between the spherical rest shape and a liquid lense, whose shape is solely determined by balance between the set of surface tensions and pressure differences. The intermediate regime can be explored in terms of the shell's elastic moduli. By use of non-linear elastic shell theory, we calculate capsule shapes at liquid-liquid interfaces and provide a method, which allows for estimating the elastic moduli from experimental setups.

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Structuring of micro particle assemblies at the solid liquid interface by light driven diffusioosmosis — •David Feldmann[1], Salim Maduar[2], Olga I. Vinogradova[2,3,4], and Svetlana Santer[1] — [1]Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany — [2]A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia — [3]Department of Physics, M. V. Lomonosov Moscow State University, 119991 Moscow, Russia — [4]DWI-Leibniz Institute for Interactive Materials, RWTH Aachen, 52056 Aachen, Germany

Light-induced diffusioosmotic flows can be used to manipulate and structure particle assemblies at the solid liquid interface.[1] The main player is an azobenzene containing cationic surfactant. Azobenzene switches from a trans to a cis state under UV and back under visible light or by thermal relaxation. A particle-surfactant dispersion is pipetted onto a substrate and placed under a microscope, in which two lasers (UV, green) are coupled. Surfactant adsorbs to the surface, depending on isomer and surface properties, and creates an electrical double layer(EDL). Local irradiation induces a gradient in surfactant concentration creating a diffusioosmotic flow in the EDL, which drags particles on the surface either away (UV) or to (green) the laser spot, with velocities around 1μm/s. With these flows we clean, gather, and structure particles assemblies on flat surfaces or direct particles along patterned surfaces.[1]Feldmann, D. et al. Sci. Rep. 6, 36443; doi: 10.1038/srep36443 (2016).

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Deriving interaction potentials to simulate self-assembly of graphene particles at the oil-water interface — •Vikram Reddy Ardham and Frédéric Leroy — Eduard-Zintl-Institut für Anorganische und Physikalische Chemie,TU Darmstadt

High interfacial tension between immiscible liquids can provide necessary driving force for the self-assembly of nano-particles at the interface. Particularly, water-oil interfaces have been exploited to synthesize networks of highly inter-connected graphene flakes of only up to a few layers thick. To simulate and study these systems, we derive coarse-grained (CG) force-fields for particle-liquid interactions. CG potentials derived using the standard approaches often give rise to free energies far from the reference system and might not lead to any self-assembly at the interface, since the entire process is possible only within a narrow window of interfacial free energies determined by the wetting coefficient (ω) [Polym. Bull. 1991, 25 (2), 265-271]. Therefore, we derive CG particle-liquid interaction potentials [J. Chem. Phys. 2015, 143 (24)] to get the right free energy balance and therefore the right 'ω'. The derived coarse-grained potentials provide accelerated dynamics of up to a few orders of magnitude without losing the thermodynamic or much of the structural information. Further, we illustrate the applicability of method by simulating a relatively large water-oil interface with graphene particles forming an inter-connected network using the derived coarse-grain model. The method might find applications in multi-scale modeling of polymer nano-composites where a great deal of solid-liquid interface is to be modelled accurately.

Invited Talk CPP 58.4 Thu 11:00 ZEU 255

Molecular Scale Structure of Ionic Liquid Surfaces — •Markus Mezger — Institut für Physik, Johannes Gutenberg-Universität Mainz — Max-Planck-Institut für Polymerforschung, Mainz

Ionic Liquids (ILs) are promising candidates in a variety of applications such as heterogeneous catalysis. For understanding and optimizing the transport properties of reactants and products at IL interfaces, knowledge of their interfacial structure on the molecular length scale is highly desirable. Our x-ray reflectivity (XRR) studies of IL based electrolytes provide density profiles across liquid/vapor interfaces with sub-nanometer resolution. Depending on the molecular architecture of anions and cations, we observe the pinning of bulk correlations at the surface and surface induced smectic order. As model system for blends containing dielectric solvents, we studied the near surface structure of an alkane containing IL. Analysis of the experimental data revealed surface segregation of the alkanes that induce ordered structures, affecting the interfacial ion profiles over a length scale up to 50 nm.
M. Mezger et al., Proc. Natl. Acad. Sci. USA 110, 3733 (2013).
M. Mezger, et al., J. Chem. Phys. 142, 164707 (2015).

15 min break

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Influence of surface charge on interfacial water arrangement — •Lisa Dreier[1,2], Ellen Backus[1], and Mischa Bonn[1] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Graduate School Materials Science in Mainz, Mainz, Germany

For a charged surface in contact with an aqueous solution, the decay of the electric potential towards bulk liquid has been described by various models for the electric double layer. Usually, the electrostatic behavior of charged lipid-water interfaces is interpreted in the same way, even though the charge at these interfaces is highly localized. Here, we test experimentally to what extent electric double layer models for solid-liquid interfaces are applicable for lipid-water interfaces, especially very close to the surface in these systems. We study the water organization at the water-lipid interface using the non-linear optical spectroscopy vibrational Sum-Frequency Generation (SFG). Requiring that symmetry is broken, SFG is highly surface-selective, and provides the vibrational spectrum of specifically interfacial molecules; the SFG intensity can be related to the degree of interfacial water alignment. The charge carried by the interface orients interfacial water molecules. By mixing positively and negatively charged lipids, we can vary the surface charge at constant area per lipid molecule. Surprisingly, one can change the lipid layer composition, and thus the surface charge, dramatically without substantially influencing the arrangement of the water molecules. The SFG intensity, and thus the water orientation, responds in a remarkably strong nonlinear fashion to changes in the surface charge.

CPP 58.6 Thu 12:00 ZEU 255

Hydrogen and Electric Power Generation from Liquid Microjets: Design Principles for Optimizing Conversion Efficiency — •Nadine Schwierz, Royce K. Lam, Phillip L. Geissler, and Richard J. Saykally — Department of Chemistry, University of California, Berkeley, California 94720, United States

Liquid water microjets have been successfully employed for both electrical power generation and gaseous hydrogen production, but the demonstrated efficiencies have been low. Here, we employ a combination of a modified Poisson Boltzmann description, continuum hydrodynamic equations, and microjet electrokinetic experiments to gain detailed insight into the origin of the streaming currents produced in pure water. We identify the contributions to the streaming current from specific ion adsorption at the solid/liquid interface and from long-ranged electrostatic interactions, finding that the portion originating from the latter dominate at charged surfaces. The detailed understanding afforded by theory and the close agreement with experimental results elucidates design principles for optimizing hydrogen production and power generation. Changing the sign of the surface charge density through targeted use of surface coatings via silanization switches the primary charge carrier between hydronium and hydroxide and therefore switches the corresponding production of molecular hydrogen to oxygen at the target electrode. Moreover, hydrophobic surface coatings reduce dissipation due to fluid/solid friction, thereby increasing the conversion efficiency.

CPP 58.7 Thu 12:15 ZEU 255

Bridging phases: Permittivity studies at interfaces for ITIES catalysts — •David Egger, Zhu Liu, Christoph Scheurer, and Karsten Reuter — Technische Universität München, Germany

"Interfaces between Two Immiscible Electrolyte Solutions" (ITIES) - typically, between an aqueous and an organic solvent (OS) - have recently emerged as promising environments for electrocatalytic processes. Amphiphilic MoS_2-based complexes at ITIES are of particular interest for photocatalytic water splitting. It is expected that an appropriate bandgap engineering could lead to a further boost in quantum efficiency that renders ITIES-based solar hydrogen generation technologically viable. Approaching this context from the perspective of predictive-quality first-principles electronic structure calculations a major challenge rests in the accurate, yet efficient representation of the effect of the ITIES environment on the catalytic complex. To this end, we present a tailored implicit solvation approach, in which the liquid-liquid interface surrounding the catalytic complex is coarse-grained to a spatially varying dielectric medium. Across interfaces, this transition function exhibits a strong electrostatic correlation, as recently shown for soft polar interfaces in aqueous environment [1]. Based on classical molecular dynamics simulations we present an approach to model consistent permittivity transition functions across the relevant phase interfaces of the ITIES system. We discuss first numerical results for the topologically significant interfaces of MoS_2-water, MoS_2-OS, as well as the triphase point MoS_2-water-OS. [1] A. Schlaich, E.W. Knapp, and R.R. Netz, Phys. Rev. Lett. **117**, 048001 (2016).

CPP 58.8 Thu 12:30 ZEU 255

Dielectric Permittivity Tensor of the Intrinsic Liquid-Liquid Interface — •Zhu Liu, Karsten Reuter, and Christoph Scheurer — Technische Universität München, Germany

As an important continuum response property of liquids at a shared interface, the dielectric permittivity tensor sensitively reflects the unique microscopic characteristics in the interfacial region. Simulations of interfacial dielectric properties have so far mostly considered the case of confined liquids at a rigid solid/mobile liquid interface [1]. Liquid/liquid interfaces are instead known to be intrinsically fluxional in nature [2,3]. This requires statistical procedures devised to analyze molecular dynamics simulations for the computation of the dielectric tensor fields to be adjusted accordingly. We present a novel approach to this problem which yields dielectric profiles with features of similar sharpness as for the solid/liquid case – if the statistical analysis is consistently referenced to the instantaneous liquid/liquid interface. In contrast, simple statistical analyses based on an average interface definition only result in broadened featureless dielectric profiles across the interface region. Numerical results will be presented for the prototypical 1,2-dichloroethane/water liquid/liquid interface, using a reparametrized force-field for the organic solvent.

[1] D.J. Bonthuis, *et al.*, Langmuir **28**, 7679 (2012).
[2] V. Privman, Int. J. Mod. Phys. C **3**, 857 (2012).
[3] A. Schlaich, *et al.*, Phys. Rev. Lett. **117**, 048001 (2016).