CPP 10: Interfaces and Thin Films II

Time: Tuesday 9:30–13:00 Location: C 130

Topical Talk CPP 10.1 Tue 9:30 C 130

PEG Functionalized Lipid Bilayers at the Solid / Liquid Interface: Protrusions versus Blisters — •Beate Klösgen[1], Giovanna Fragneto[2], Avi Halperin[3], Ole G. Mouritsen[1], Patricia Hardas[4], and Michele Sferrazza[4] — [1]University of Southern Denmark, Odense, Denmark — [2]Institute Laue-Langevin, Grenoble, France — [3]Université Joseph Fourier, Grenoble, France — [4]Université Libre de Bruxelles, Bruxelles, Belgique

PEGylated lipids inoculated into fluid membranes constitute a membrane disturbance due to conformational restrictions of the polymer when grafted to the membrane interface. Blisters and protrusions were both discussed as possible responses to the hydrophilic pull. Neutron reflectivity of adsorbed lipid membranes at the solid/water interface supports the protrusion model. Results are shown from an asymmetric system with an inner leaflet consisting of 1,2-distearoyl-sn-glycero-3-phosphorylcholine (DSPC) and an outer leaflet composed of DSPC and Polyethylene glycol (PEG) functionalized 1,2-distearoyl-sn-glycero-3-phosphoethanolamine (DSPE-PEG). DSPC headgroups were deuterated to enhance sensitivity and mark the lipid headgroup/water interface. A narrow water layer at the inner interface allows for some membrane deformation, equally found for the outer headgroup layer in the absence of polymer. This roughness is enhanced when PEG chains are present; the roughness of the inner headgroup layer is about constant. The outer headgroup layer roughness increases with PEG-lipid mole fraction and temperature. The findings suggest that PEG chains favour headgroup protrusions rather than blister like deformations.

CPP 10.2 Tue 10:00 C 130

Interactions and stability of foam films from oppositely charged polyelectrolyte/surfactant mixtures — •Nora Kristen-Hochrein, Heiko Fauser, Martin Uhlig, and Regine von Klitzing — Stranski-Laboratorium, Institut für Chemie, TU Berlin, Germany

Polyelectrolyte/surfactant mixtures in foams play an important role in many technical applications. To control the properties of the foam it is important to investigate single foam films. A measure of the interactions between the two film interfaces is the disjoining pressure, which is the sum of electrostatic, van der Waals and steric forces. The disjoining pressure as a function of film thickness is measured with a Thin Film Pressure Balance (TFPB). In this study we focus on the influence of negatively charged polyelectrolytes on foam films stabilized with cationic surfactant. At low polyelectrolyte concentrations the charge at the surface is positive. With increasing amount of polyelectrolyte the charge of the complexes is reduced and then reversed. However, surface characterization indicates that no charge reversal occurs at the film interfaces. To test the influence of the polyelectrolyte and surfactant hydrophobicity[1,2], results on the stability of films with different polyelectrolytes and surfactants are shown and compared with surface tension and elasticity and neutron reflectometry measurements.

[1] N. Kristen, V. Simulescu, A. Vüllings, A. Laschewsky, R. Miller and R. v. Klitzing, J. Phys. Chem B (2009) 113 7985.

[2] N. Kristen-Hochrein, A. Laschewsky, R. Miller, R. v. Klitzing, J. Phys. Chem B, (2011) DOI: 10.1021/jp206964k

CPP 10.3 Tue 10:15 C 130

Hydration Interactions between Biological Membranes: Molecular Dynamics Analysis — •Matej Kanduc[1], Emanuel Schneck[2], and Roland Netz[1] — [1]Freie Universität Berlin — [2]Technische Universität München

Interactions between biological surfaces result from the interplay of various physical contributions. Dispersion interactions and screened electrostatics have been successfully treated in a continuum approximation, whereas the so-called hydration interaction caused by water structuring at interfaces, still elude a quantitative description. In fact, the interaction between charge-neutral phospholipid membranes is dominated by this contribution in a wide range of separations. Despite the qualitative agreements of various theories, it has become a consensus view during the last decades that in order to explain the hydration interaction on a quantitative level, the structure of the solvent has to be taken into account explicitly. This insight has drawn the attention towards the application of atomistic simulations, where water molecules are treated explicitly including all relevant degrees of freedom. We introduce a novel thermodynamic extrapolation method that provides greatly improved interaction measurements in Molecular Dynamics simulations. The results are quantitatively compared with classical membrane swelling experiments.

CPP 10.4 Tue 10:30 C 130

Temperature-induced transition from odd-even to even-odd effect in polyelectrolyte multilayers due to interpolyelectrolyte interactions — •Peter Nestler[1], Stephan Block[2], and Christiane A. Helm[1] — [1]Institut für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, 17487 Greifswald, Germany — [2]ZIK HIKE, Uni Greifswald, Fleischmannstr. 42 - 44, D-17487 Greifswald, Germany

Within a liquid cell the linear growth of polyelectrolyte multilayers by LbL technique is observed using multiple angle null-ellipsometry. Poly(styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) are used. The salt content is varied between 1 and 4 mol/L NaCl, the temperature between 20 and 55°C. The outermost layer is investigated. At low temperature a top PSS layer is twice as thick as a top PAH layer (odd-even effect), consistent with the respective monomer volume and the same water content for both polyelectrolytes. On heating, the thickness of a polycation/polyanion bilayer increases. For temperatures exceeding T_{x-over} a top PAH layer is thicker than a top PSS layer (even-odd effect). In this case, the index of refraction of the respective top layers indicates a compact PSS and a swollen PAH layer. At temperatures above T_{x-over} the dried films destabilize, an increased roughness and a random pattern of holes is observed. It is suggested that at elevated temperature and high salt-conditions, secondary forces gain importance in comparison to electrostatic forces: therefore a transition from an odd-even to an even-odd effect occurs, as well as the decreased film stability on drying.

CPP 10.5 Tue 10:45 C 130

Diffusion study in thin free-standing liquid crystal films — •Benjamin Schulz and Christian Bahr — MPI für Dynamik und Selbstorganisation, 37077 Göttingen

Free-standing liquid crystal films are liquid films that are spanned over a supporting frame and stable without an underlying substrate. Hence it becomes possible to study the pure material properties in thin films as no surface interaction comes into play. However, not much is known about the changes in diffusion in such films as compared to bulk properties.

We study the translational molecular dynamics in free-standing films using single molecule tracking. For this we dissolve a small amount of dye molecules to then image their diffusive behaviour. This allows us to directly study the dynamics in the film on molecular level. We focus on the diffusion in films at the transition to complete 2-dimensional systems with a thickness of only a few layers, which leads to a strong increase in diffusion for some materials. Also we look into the diffusion properties in proximity to phase transitions as for some materials it is known that they show layer-by-layer phase transitions in the layers directly at the free surface [1].

[1] Jin et. al., Phys. Rev. E. 49 (1994), R4791-R4794

CPP 10.6 Tue 11:00 C 130

Interfacial effects on single dye dynamics in ultrathin liquid and thin liquid crystal films — •Daniela Täuber and Christian von Borczyskowski — nanoMA, TU-Chemnitz, Institut für Physik

Silica surfaces are widely used e.q. in the fabrication of organic electronic devices. Minimization of devices thereby induces strong confinement on the organic compound and thus enhances interfacial effects. Yet many details of the interactions between silica surfaces and organic molecules which are crucial for their electrical properties and thus for device performance are not fully understood. Here we use single molecule methods to explore the dynamics of dye molecules within ultrathin liquid films [1,2] and thin liquid crystal films [3] on differently treated silica surfaces. This allows us to draw conclusions on diffusion coefficients and physio-chemical binding affinities depending on the chemical structure of participating molecules and silica surfaces.

[1] D. Täuber, C. von Borczyskowski et al: Diff. Fund. J. 11 (2009) 76.

[2] D. Täuber, Dissertation, TU Chemnitz, 2011.

[3] B. Schulz, D. Täuber, J. Schuster, T. Baumgärtel, and C. von Bor-

czyskowski, Soft Matter 7 (2011) 7431.

15 min break

CPP 10.7 Tue 11:30 C 130

Coherent acoustic phonon propagation through organic interface layers — •Mike Hettich, Karl Jacob, Martin Schubert, Oliver Ristow, Axel Bruchhausen, and Thomas Dekorsy — Department of Physics and Center of Applied Photonics, Universität Konstanz, D-78457 Konstanz, Germany

The damping of coherent acoustic phonons in thin gold films was investigated by asynchronous optical sampling (ASOPS) [1]. A distinct change of the damping time of the gold film's breathing mode is observed depending on the acoustic phonon frequency, when self assembled molecular layers (SAMs) are introduced at the interface between the film and a substrate [2]. We thoroughly characterized this system by varying the thickness of the organic interface layer from a single monolayer ($\approx$ 0.7nm) up to 12 nm. This allowed the investigation of the elastic properties of the SAMs in a transition regime that highlights the limitations of the elastic-continuum description when reducing the size of the organic interlayer to the nanometer scale.

References
[1] A. Bartels et al., Rev. Sci. Instr. **78**, 035107 (2007)
[2] M. Hettich et al., Appl. Phys. Lett. **98**, 261908 (2011)

CPP 10.8 Tue 11:45 C 130

Phase separation dynamics in a two-dimensional magnetic mixture — •Ken Lichtner[1], Andrew J. Archer[2], and Sabine H. L. Klapp[1] — [1]Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany — [2]Department of Mathematical Sciences, Loughborough University, Leicestershire, LE11 3TU, UK

Based on classical density functional theory (DFT), we investigate the demixing phase transition of a two-dimensional, binary Heisenberg fluid mixture [1]. The particles in the mixture are modeled as Gaussian soft spheres, where one component is characterized by an additional classical spin-spin interaction of Heisenberg type. Within the DFT we treat the particle interactions using a mean-field approximation. For certain magnetic coupling strengths, we calculate phase diagrams in the density-concentration plane. For sufficiently large coupling strengths and densities, we find a demixing phase transition driven by the ferromagnetic interactions of the magnetic species showing a complex behaviour of the particles similar as in [2]. We also provide a microscopic description (i.e., density profiles) of the resulting non-magnetic/magnetic fluid-fluid interface. Finally, we investigate the phase separation using dynamical density functional theory (DDFT) [3], considering both nucleation processes and spinodal demixing.
[1] K. Lichtner, A. J. Archer, S. H. L. Klapp, J. Chem. Phys., accepted.
[2] R. Rungsawang et al., Phys. Rev. Lett. 104 (2010) 255703.
[3] A. J. Archer and R. Evans, J. Chem. Phys. 121 (2004) 4246.

CPP 10.9 Tue 12:00 C 130

Homogeneous and patterned deposition from a meniscus of an evaporating suspension onto a moving substrate — •Hender Lopez and Uwe Thiele — Department of Mathematical Sciences, Loughborough University, Leicestershire LE11 3TU, UK

A dynamical model is used to study the deposition process observed when an inclined plate is drawn from a bath of a volatile solution or suspension. Based on the gradient dynamics formulation proposed by Thiele [*Eur. Phys. J. Special Topics* 197, 213 (2011)] we derived two coupled equations that describe the film height profile and mean solute concentration. These equations were solved numerically for a large parameter set and the effect of the plate velocity, U, was studied systematically. Our model captures the two main regimens that have been observed in a wide range of experimental setup): at low U, the deposit thickness decreases with U (evaporative regime), and at high U, the deposit thickness increases with U (Landau-Levich regime). An important feature is that for a range of U in the evaporative regime we observe a stick-slip motion of the contact line that is related to the formation of regular lines deposits. This phenomenon is frequently reported in experiments, but often not covered by previous models. We acknowledge support by the EU (PITN-GA-2008-214919).

CPP 10.10 Tue 12:15 C 130

Water interfaces from first principles: structure and spectroscopy — •Marialore Sulpizi — Johannes Gutenberg University Mainz, Staudinger Weg 7 55099 Mainz Germany.

Complex phenomena arise at solid-liquid interfaces, leading to surface induced changes that are not only important for the solid but also for the liquid. In that respect, water plays an important role in a number of interfacial phenomena encountered in biological, chemical and physical processes. Water properties at the interface can be quite different with respect to bulk properties and have been subject of recent research efforts. Here we present some simulation results on solid/water, namely quartz/water and alumina/water, and water/vapor interfaces based on Density Functional Theory. We aim to address the molecular details of the solvation structure and to include the electronic polarization effects. We calculate the acidity of oxide surfaces and we discuss the water structure at the interface to interpret recent experimental results from surface sensitive Sum Frequency Generation.

CPP 10.11 Tue 12:30 C 130

Second Generation Car-Parrinello Molecular Dynamics: Theory and Application to the Liquid/Vapor Interface — •Thomas Kühne — Johannes Gutenberg University Mainz, Institute of Physical Chemistry and Center for Computational Sciences, Staudinger Weg 9, D-55128 Mainz, Germany

A new method [1] to accelerate density functional theory-based ab-initio molecular dynamics simulations is presented. In the spirit of the Car-Parrinello [2] approach during the dynamics the electronic wavefunctions are not self-consistently optimized. However, in contrast to the original scheme, large integration time steps can be used. By this means the best of the Born-Oppenheimer and the Car-Parrinello methods are unified, which not only extends the scope of either approach, but allows for ab-initio simulations previously thought not feasible. The effectiveness of this new approach is demonstrated on liquid water at ambient conditions [3], and on the corresponding liquid/vapor interface [4].

[1] T. D. Kühne, M. Krack, F. Mohamed and M. Parrinello, Phys. Rev. Lett. 98, 066401 (2007). [2] R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985). [3] T. D. Kühne, M. Krack and M. Parrinello, J. Chem. Theory Comput. 5, 235 (2009). [4] T. D. Kühne, T. A. Pascal, E. Kaxiras and Y. Jung, J. Phys. Chem. Lett. 2, 105 (2011).

CPP 10.12 Tue 12:45 C 130

The mesoscopic structure of liquid–vapour interfaces — •Felix Höfling and Siegfried Dietrich — Max-Planck-Institut für Intelligente Systeme, Heisenbergstraße 3, 70569 Stuttgart, and Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart

The interfacial region between coexisting phases, e.g., between liquid and vapour, is broadened and roughened by thermal fluctuations. The spectrum of these fluctuations diverges for large wavelengths according to capillary wave theory; deviations have been predicted by density functional theory for inhomogeneous fluids [1]. In particular, an enhancement of fluctuations at mesoscopic wavenumbers is expected due to the long-ranged nature of the intermolecular dispersion forces. These predictions have been supported by scattering experiments, but previous computer simulations find a monotone spectrum.

We have performed extensive simulations for a simple liquid with Lennard–Jones interactions truncated at long distance. The investigation of large system sizes was considerably accelerated by a specifically developed simulation package employing high-end graphics processors [2]. Introducing an interfacial structure factor, the wavenumber-dependent surface tension is derived. It develops a maximum at mesoscopic scales as temperature is increased, indicating a relative suppression of fluctuations. We argue that the expected minimum may be masked by the emerging maximum.

[1] K. Mecke and S. Dietrich, Phys. Rev. E **59**, 6766 (1999).

[2] P. Colberg and F. Höfling, Comp. Phys. Comm. **182**, 1120 (2011).