

CPP 20: Wetting, Fluidics and Liquids at Interfaces and Surfaces (joint session CPP/DY)

Time: Tuesday 9:30–13:00

Location: H13

CPP 20.1 Tue 9:30 H13

Non-monotonous wetting of graphene-mica and MoS₂-mica interfaces with a molecular layer of water — ●ABDUL RAUF, ANDRE SCHILO, NIKOLAI SEVERIN, IGOR M. SOKOLOV, and JÜRGEN P. RABE — Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Hydration of interfaces with a layer of water is a ubiquitous phenomenon. Nevertheless, the understanding of the wetting process is still limited, since it is experimentally difficult to follow. Here, graphene and monolayers of MoS₂ deposited on dry mica are used to investigate wetting of the 2D material-mica interfaces with a molecularly thin layer of water employing scanning force microscopy in different modes. Wetting starts at relative humidities (RH) of 10-17% for graphenes and 8-9% for MoS₂, and it concludes with a homogeneous layer at 25-30% and 15-20%, respectively. Wetting occurs non-monotonously in time and space for both types of interfaces. Initially a highly compliant and unstable layer of water spreads, which subsequently stabilizes by developing labyrinthine nanostructures. These nanostructures exhibit distinct mechanical deformability and dissipation, which is ascribed to different densities of the confined water layer. The laterally structured morphology is explained by the interplay of counteracting long-range dipole-dipole repulsion and short-range line tension, associated with the mechanical deformation of the 2D material. The proposed origins of the interactions are common for thin layers of polar molecules at interfaces, implying that the lateral structuring of thin wetting layers may also be a quite general phenomenon.

CPP 20.2 Tue 9:45 H13

Molecular Hydrophobicity at a Macroscopic Hydrophilic Surface — ●JENEE D. CYRAN¹, MICHAEL DONOVAN¹, DORIS VOLLMER¹, FLAVIO SIRO BRIGIANO², SIMONE PEZZOTTI², DARIA R. GALIMBERTI², MARIE-PIERRE GAIGEOT², MISCHA BONN¹, and ELLEN H.G. BACKUS¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²LAMBRE, Univ Evry, Université Paris-Saclay, Evry, France

Chemical and physical interactions between water and silicates are ubiquitous and relevant for geochemistry and industrial processes, including chromatography, oil extraction and coatings. Characterizing the silica/water interface is important to not only understand the fundamental properties for natural occurring processes but also to improve existing technologies, such as silica coatings, which rely on wettability and thermal-resistant properties to remain effective. At the silica/water interface, we compare the microscopic water organization, from both surface sensitive vibrational sum frequency generation experiments and molecular dynamics simulations, to macroscopic information about the hydrophobicity obtained from contact angle measurements. At the microscopic level, weakly hydrogen-bonded OH groups, typical for hydrophobic interfaces, are observed that originate from water molecules interacting with hydrophobic sites of the silica surface. Surprisingly, we observe the presence of hydrophobic water at a macroscopically hydrophilic water surface.

CPP 20.3 Tue 10:00 H13

Interfacial premelting of ice in nano composite materials — ●MARKUS MEZGER^{1,2}, HAILONG LI¹, JULIAN MARS^{1,2}, and MARKUS BIER^{3,4} — ¹Max Planck Institute for Polymer Research, Mainz — ²Institute of Physics, Johannes Gutenberg University Mainz — ³Max Planck Institute for Intelligent Systems, Stuttgart — ⁴University of Applied Sciences Würzburg-Schweinfurt

The interfacial premelting in ice/clay nano composites was studied by high energy X-ray diffraction. Below the melting point of bulk water, the formation of liquid water was observed for the ice/vermiculite and ice/kaolin system. For the quantitative description of the molten water fraction in wet clay minerals we developed a continuum model for short range interactions and arbitrary pore size distributions. This model quantitatively describes the experimental data over the entire temperature range. Model parameters were obtained by fitting using a maximum entropy approach. Pronounced differences in the deviation from Antonow's rule relating interfacial free energy between ice, water, and clay are observed for the charged vermiculite and uncharged kaolin minerals. The resultant parameters are discussed in terms of their ice nucleation efficiency. Using well defined and characterized

ice/clay nano composite samples, this work bridges the gap between studies on single crystalline ice/solid model interfaces and naturally occurring soils and permafrost.

[1] H. Li et al., Phys. Chem. Chem. Phys. DOI: 10.1039/c8cp05604h (2018)

CPP 20.4 Tue 10:15 H13

A Direct Inversion Approach to Local Permittivity at Liquid-Liquid Interfaces — ●DAVID EGGER, CHRISTOPH SCHEURER, and KARSTEN REUTER — Theoretische Chemie, TU München

Realistic models for catalytic reactions at liquid-liquid interfaces (LLIs) require a profound knowledge of the electrostatic properties in the vicinity of the solvated catalytic complex. For polar fluids like water, these properties as described by the static dielectric constant, ϵ , can be related to thermal equilibrium fluctuations of the polarization at zero field.

The Kirkwood-Fröhlich (KF) approach usually applied in the derivation of such formulas faces two major difficulties: First, correlated polarization fluctuations are long-range and subject to slow convergence, making KF expensive in simulations. Second, the difficulty of the electrostatic boundary value problem one needs to solve in a KF ansatz increases with the systems' complexity. In this contribution, we present a possible alternative procedure, following the reciprocal space formalism described by Neumann for wave-vectors at finite wavelength [1].

Exploiting the convolutional relation between dipole-dipole interaction tensor and polarization, we present a cavity kernel based approach in reciprocal space in order to arrive at local real space averages to calculate a spatially resolved $\epsilon(r)$ from spheroidal gaussian cavities of different shape and volume, avoiding difficulties with geometry-induced boundary conditions in the electrostatic description. Results are discussed for water bulk and water-dichloroethane LLI systems.

[1] M. Neumann, Mol. Phys. 57:1, 97-121, 1986

CPP 20.5 Tue 10:30 H13

Testing dielectric continuum theory at interfaces by atomistic simulations — ●PHILIP LOCHE¹, CIHAN AYAZ¹, ALEXANDER SCHLAICH^{1,2}, DOUWE JAN BONTHUIS¹, and ROLAND R. NETZ¹ — ¹Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Laboratoire Interdisciplinaire de Physique, CNRS and Université Grenoble Alpes, UMR CNRS 5588, 38000 Grenoble, France

Based on fully atomistic simulations of ions in water, we discuss the validity of continuum models for the dielectric response at aqueous interfaces. For the electrostatic energy of an ion in the vicinity of a hydrophobic graphene surface we find the electrostatic contribution to be dominated by the non-electrostatic contribution. Linear dielectric theory breaks down, and to quantitatively describe the linear dielectric contribution an anisotropic tensorial dielectric model is needed. This demonstrates the limitation of current continuum models for the dielectric response at interfaces.

Invited Talk

CPP 20.6 Tue 10:45 H13

Dynamic surface tension of soft solids — MATHIJS VAN GORCUM¹, BRUNO ANDREOTTI², JACCO SNOEIJER¹, and ●STEFAN KARPITSCHKA³ — ¹University of Twente, Enschede, Netherlands — ²Université Paris-Diderot, Paris, France — ³MPI-DS, Göttingen, Germany

The contact line of a liquid drop on top of a solid surface exerts a nano-metrically sharp surface traction, providing an unprecedented tool to study highly localized and dynamic deformations of soft polymer networks. The morphology is determined not only by bulk viscoelasticity, but also by solid surface tension. The latter may depend on strain, known as the Shuttleworth effect. Its impact on soft wetting is controversially discussed in recent literature. One of the outstanding problems in this context is the stick-slip instability of a moving contact line, which is observed above a critical velocity. Times-resolved measurements of the solid deformation are challenging, and the mechanism of dynamical depinning has remained elusive. Here we present direct visualizations of dynamic wetting ridges. Unexpectedly, the opening angle of the wetting ridge increases with speed, which cannot be attributed to bulk rheology. Instead, this effect points to an increase of

solid surface tension not only in response to strain, but also depending on the rate of strain. Under this assumption, a criterion for depinning can be derived which is confirmed experimentally. We conclude that the surface tension of a solid is a truly dynamical quantity, following from a surface rheology that is different from the bulk, similar to what is known from liquid interfaces with surfactants.

15 min. break

CPP 20.7 Tue 11:30 H13

Raman spectroscopic evaluation of concentration gradients in small drops in binary mixtures on different substrates and in 3d printed small channels — ●ALENA BELL and ROBERT STARK — Physics of Surfaces, Materialwissenschaften, TU Darmstadt, Alarich-Weiss-Str. 16, 64287 Darmstadt, Deutschland

The evaluation of concentration gradients plays a big role in medical technology and chemotaxis. Microchannels are used in lab-on-chip devices for quick tests to test fluids directly, for example. Microchannels are also used for chemotaxis applications to mix fluids. The amount of liquid which is needed for these tests is in the microliter range. Raman spectroscopy is a powerful technique to detect changes in molecular structures within reactions in lab-on-chip devices and in chemotaxis devices. Therefore, different fluids are directed through 3d printed channels and changes are measured via Raman spectroscopy. In a first step, these generated fluid mixtures are measured as drops on different substrates. The concentration gradients that build up in the mixtures is measured in the drops. In the next step the gradients are measured in small channels. The concentration gradients are calculated by comparing relative peak intensities and correlating these results with calibration curves.

CPP 20.8 Tue 11:45 H13

Shallow water lattice Boltzmann simulations of thin film flows — ●STEFAN ZITZ¹, ANDREA SCAGLIARINI², SURYANARAYANA MADDU KONDAIAH³, ANTON DARHUBER⁴, and JENS HARTING^{1,4} — ¹Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Nürnberg, Germany — ²Institute for Applied Mathematics "M. Picone" (IAC-CNR), Rome, Italy — ³Center for System Biology (MPL-CBG), Dresden, Germany — ⁴Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands

We propose a novel approach to the numerical simulation of thin film flows, based on the viscopillary shallow water equations. The integration is performed by the means of a suitably devised lattice Boltzmann method.

The numerical scheme is applied to the viscous Rayleigh-Taylor instability of a thin film under the influence of gravity as well as the spreading of a sessile drop towards its equilibrium contact angle. During the spreading we observe a linear correlation between the spreading speed and the contact angle, as theoretically predicted by the Cox-Voinov law.

Further we address the problem of a droplet sliding on an inclined plane. Due to the choice of the substrate friction we observe a pinning region for low forcing. When increasing the forcing by varying the droplet volume the droplet starts to slide and the Capillary number scales linearly with the Bond number.

CPP 20.9 Tue 12:00 H13

Complex Wetting: flow profiles close to three phase contact lines — ●BENEDIKT STRAUB¹, FRANZISKA HENRICH¹, and GÜNTER K. AUERNHAMMER² — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Leibniz Institute for Polymer Research, Dresden, Germany

Wetting and dewetting behavior on solid surfaces is the crucial process underlying many natural phenomena as well as technical applications like printing or coating of surfaces. Our aim is to study the wetting behavior of surfactant solutions on solid surfaces. Especially the flow profile close to the three phase contact line is highly interesting for modelling efforts.

Three-dimensional flow profiles are measured with an astigmatism particle tracking velocity setup.

Measurements of a receding contact line for pure water show that the theoretical prediction can be reproduced, which is used to validate the system. First results show that surfactants cause a deviation of the flow field in comparison to theoretical predictions for pure liquids.

In the case of a receding contact line new air-liquid interface is formed at the three phase contact line. The freshly formed interface is, in comparison to the already existing air-liquid interface, not completely occupied by surfactants. This causes a Marangoni tension in the direction of the contact line along the interface. This Marangoni tension opposes the bulk flow close to the air-liquid interface and causes a deviation of the flow field. In special cases this can lead to an opposing interface flow compared to the bulk flow.

CPP 20.10 Tue 12:15 H13

Direct observation of gas meniscus formation on a superhydrophobic surface — ●DORIS VOLLMER¹, MIMMI ERIKSSON², AGNE SWERIN², HANNU TEISALA¹, MICHAEL KAPPL¹, and HANS-JÜRGEN BUTT¹ — ¹MPI for Polymer Research, Mainz, Germany — ²RISE Research Institutes of Sweden, Stockholm, Sweden

The formation of a bridging gas meniscus via cavitation or nanobubbles is considered the most likely origin of the long-range attractive forces measured between hydrophobic surfaces in aqueous solution. On a superhydrophobic surface a thin air layer is present and influences the interaction. Here, we report time and space resolved imaging of the formation and growth of a gas meniscus during force measurements between a superhydrophobic surface and a hydrophobic microsphere immersed in water. This is achieved by combining laser scanning confocal microscopy and colloidal probe force microscopy. The configuration allows determination of the volume and shape of the meniscus, together with direct calculation of the Young-Laplace capillary pressure. The long-range attractive interactions acting on separation are due to meniscus formation and volume growth as air is pulled from the surface layer.

CPP 20.11 Tue 12:30 H13

Wetting of n-Alkane Nano-Patterns: Evidence of Macroscopic Line Tension Effects and Adaptive Wetting — ●DIEGO DIAZ¹, TOMAS P. CORRALES², MARIA J. RETAMAL³, MARCELO CISTERNAS¹, NICOLAS MORAGA¹, RODRIGO CATALAN¹, MARK BUSCH⁴, PATRICK HUBER⁴, MARCO SOTO-ARRIAZA³, and ULRICH G. VOLKMANN¹ — ¹Institute of Physics and CIEN-UC, P. Univ. Catolica de Chile, Santiago, Chile — ²Department of Physics, UTFSM, Valparaiso, Chile — ³Faculty of Chemistry and CIEN-UC, P. Univ. Catolica de Chile, Santiago, Chile — ⁴TUHH, Hamburg, Germany

We present a wetting study of silicon samples coated with a single layer of n-alkane molecules self-assembled perpendicular to the surface by velocity-dependent dip-coating. The contact angle was measured with 2 microliters of ultrapure water for different n-alkane surface coverages. The results of the apparent contact angle versus coverage can be grouped in two regimes that depend linearly on coverage. This can be described by the Cassie wetting model along with the consideration of line tension effects. The two wetting regimes are characterized by two line tensions representing distinct alkane monolayer morphologies, i.e. dendritic and stripe patterns resulting from different dip-coating velocities. During drop evaporation, there is a restructuring of the alkane monolayer structure which could be related to adaptive wetting. Acknowledgements: FONDECYT Nos. 3160803 (MJR), 1180939 (UGV) 1171047 (MSA) and 11160664 (TPC), CONICYT Fellowship (MC) and CONICYT-PIA ACT 1409.

CPP 20.12 Tue 12:45 H13

Impact of Nanoparticles' Surface Properties on their Physico-Chemical Behavior in Pickering Emulsions — ●SEBASTIAN STOCK, DMITRIJ STEHL, SANDRA FORG, and REGINE VON KLITZING — TU Darmstadt, Darmstadt, Germany

Pickering Emulsions (PEs) were first studied by S. U. Pickering in the beginning of the last century and describe emulsions stabilized by particles that adsorb at the oil water interface and prevent coalescence of the droplets. In the present study Halloysite Nanotubes, fumed colloidal silica and Latex nanospheres are used to stabilize PEs. They display significant differences regarding their surface properties, size and shape. The surface of these particles is modified in order to investigate the influence of surface charge or hydrophobicity on the whole systems behavior including emulsion stability and reaction performance in homogeneous catalysis at the oil-water-interface. Additionally, the effect of the surface-active Rh-catalyst is investigated. The interaction between catalyst and particle surface plays a significant role for mass transfer and conversion.