

CPP 18: Wetting, Superamphiphobicity, Micro- and Nanofluidics I

Time: Tuesday 9:30–12:45

Location: ZEU 222

CPP 18.1 Tue 9:30 ZEU 222

A liquid-vapor interface at equilibrium in the vicinity of structured substrates: a mean-field approach — ●NIKITA TRETYAKOV, BURKHARD DÜNWEIG, and KOSTAS DAOULAS — Max Planck Institute for Polymer Research, Mainz, Germany

We study static properties of a liquid-vapor interface in the vicinity of structured substrates employing a mean-field approach [1]. As opposed to the particle-based simulations [2], this is a continuum method based on thermodynamics and statistical physics. To this end, the Hamiltonian of the system is written to account for the bulk phases, the interface [3] and the interaction with the solid. The model is then proved by a series of case-studies. Later on, we use different geometries of the substrate to investigate the interface' response to external pressure and support our simulations with analytical results.

[1] K. M. Hong and J. Noolandi, "Theory of inhomogeneous multicomponent polymer systems", *Macromolecules*, vol. 14, no. 3, pp. 727-736, 1981.

[2] N. Tretyakov and M. Müller, "Correlation between surface topography and slippage: a molecular dynamics study", *Soft Matter*, vol. 9, pp. 3613-3623, 2013.

[3] K. R. Mecke and S. Dietrich, "Effective hamiltonian for liquid-vapor interfaces", *Phys. Rev. E*, vol. 59, pp. 6766-6784, 1999.

CPP 18.2 Tue 9:45 ZEU 222

Understanding the effect of temperature on hydrophobic wetting through molecular dynamics simulations — ●FRÉDÉRIC LEROY — Technische Universität Darmstadt, Darmstadt, Germany

Hydrophobic surfaces usually yield water contact angles which weakly depend on temperature. To explain this observation, we address the thermodynamics of formation of interfaces between rigid non-polar solid surfaces and water. The work of adhesion of water can be separated in its enthalpy and entropy contributions per unit area $W = \Delta H/A - T\Delta S/A$. [1] While the enthalpy relates to the energy loss upon separating the liquid and the solid phases, the entropy change characterizes the entropy gain of water upon separation. Inspired by the analogy between the solvation of particles in water and the formation of solid-liquid contacts, a clear microscopic interpretation of both contributions in terms of intermolecular interaction potentials is given. [2] We illustrate how the determination of ΔH and ΔS by means of molecular simulations of water on rigid non-polar surfaces explains why the work of adhesion has a greater temperature dependence on hydrophobic than on hydrophilic surfaces. [3,4]

[1] Taherian, F.; Marcon, V.; van der Vegt, N.F.A and Leroy, F. "What is the Contact Angle of Water on Graphene?" *Langmuir* 29, 1457-1465 (2013) [2] Taherian, F.; Leroy, F and van der Vegt, N.F.A. "Interfacial Entropy of Water on Rigid Hydrophobic Surfaces" *Langmuir* 29, 9807-9813 (2013) [3] Kumar, V. and Errington, J.R. "Wetting Behavior of Water near Nonpolar Surfaces", *J. Phys. Chem. C* 117, 23017-23026 (2013) [4] Leroy, F., in preparation

CPP 18.3 Tue 10:00 ZEU 222

Liquid drops on a surface: using density functional theory to calculate the binding potential and drop profiles and comparing with results from mesoscopic modelling — ●ADAM P. HUGHES¹, UWE THIELE^{1,2}, and ANDREW J. ARCHER¹ — ¹Department of Mathematical Sciences, Loughborough University, UK — ²Institut für Theoretische Physik, Universität Münster, Germany

The contribution to the excess free energy for a film of liquid of thickness h on a solid surface, due to the interactions between the solid-liquid and liquid-gas interfaces is given by the binding potential, $W(h)$. The precise form of $W(h)$ determines whether or not the liquid wets the surface. Note that differentiating $W(h)$ gives the Derjaguin or disjoining pressure. We develop a microscopic density functional theory (DFT) based method for calculating $W(h)$, allowing us to relate the form of $W(h)$ to the nature of the molecular interactions in the system. We present results using a simple lattice gas model to demonstrate the procedure. In order to describe non-uniform liquid films and drops, a mesoscopic free energy based on $W(h)$ is often used. We calculate such film height profiles and also directly calculate using DFT the corresponding density profiles for liquid drops on surfaces. Comparing quantities such as the contact angle and also the shape of the drops, we find good agreement between the two methods. We also study in

detail the effect on $W(h)$ of truncating the range of the dispersion forces, both those between the fluid molecules and those between the fluid and wall. We find that truncating can have a significant effect on $W(h)$ and the associated wetting behaviour of the fluid.

CPP 18.4 Tue 10:15 ZEU 222

Droplet morphologies upon volume change on structured substrates — ●CARSTEN HERRMANN¹, CIRO SEMPREBON², MARTIN BRINKMANN^{1,2}, and RALF SEEMANN^{1,2} — ¹Saarland University, 66041 Saarbrücken — ²Max Planck Institute for Dynamics and Self-Organization, 37018 Göttingen

We experimentally investigate the general behavior of droplet morphologies sitting on micro-structured substrates upon volume change. The substrates provide geometries like triangular, rectangular, sinusoidal and trapezoidal cross section. The droplet morphologies are characterized by their eccentricity, i.e. the ratio of width to length, as function of the number of wetted grooves. The eccentricity of small droplets wetting just a few grooves characteristically varies upon an increase in drop volume and arrives at a constant value for sufficiently large droplets. The morphological changes depend sensitively on the wettability, aspect ratio and geometry of the underlying grooved substrate. The experimental results are compared quantitatively with numerical results computed by minimizing surface energies

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How superhydrophobicity breaks down — ●PERIKLIS PAPANIKOLAOU, FRANK SCHELLENBERGER, LENA MAMMEN, XU DENG, DORIS VOLLMER, and HANS-JÜRGEN BUTT — Max Planck Institute for Polymer Research, D-55128 Mainz, Germany

Droplets on superhydrophobic surfaces roll off easily, leaving the surface dry and clean. This property is due to a surface geometry that favors the entrainment of air beneath the drop, leading to the so-called Cassie state. This state competes with the Wenzel (impaled) state, in which the liquid fully wets the substrate. Despite the fact that thermodynamically the Wenzel state is often more stable, the geometry imposes an energy barrier that prevents the liquid from wetting the structure. The transition dynamics is still poorly understood due to difficulties in monitoring the temporal evolution of the liquid-air meniscus between the asperities with sufficient spatial resolution. Here, we study the Cassie-to-Wenzel transition of water drops evaporating on arrays of hydrophobic micropillars. To understand the underlying processes, we image the impalement dynamics in three dimensions by confocal microscopy. As evaporation proceeds, the curvature of the drop and the Laplace pressure increase. The three-phase contact line remains pinned until the contact angle reaches the advancing contact angle of the material. Then the water slides down the pillars. Alternatively, at large pillar spacing the curved water surface can touch the bottom of the substrate triggering an instantaneous Cassie-to-Wenzel transition. [1] Papadopoulos P., Mammen L., Deng X., Vollmer D., Butt H.-J., *PNAS* 110, 3254-3258 (2013)

CPP 18.6 Tue 10:45 ZEU 222

Superamphiphobic particles - how small can we go? — MING YE, XU DENG, JAVED ALLY, PERIKLIS PAPANIKOLAOU, FRANK SCHELLENBERGER, DORIS VOLLMER, MICHAEL KAPPL, and ●HANS-JÜRGEN BUTT — Max-Planck-Institut für Polymerforschung, Mainz, Germany

Water and oil repellent coatings - so called superamphiphobic coatings - greatly reduce the interaction between a liquid and a solid. So far only flat or weakly curved superhydrophobic and superamphiphobic surfaces have been designed. This raises the question whether highly curved structures or microspheres are feasible.

Therefore, we coated microspheres with a superamphiphobic layer and measured the force between the spheres and a liquid. A qualitatively different dependence of the adhesion force on the applied load for superamphiphobic and smooth spheres is detected. Furthermore we demonstrate both experimentally and theoretically that superamphiphobicity fails below a critical particle radius, depending on topological details and type of liquid. Therefore, this study sets a fundamental physical limit to the application of superamphiphobic layers for small objects with high curvature.

15 min. break

CPP 18.7 Tue 11:15 ZEU 222

Gibbs condition for a volatile completely wetting liquid — ●MARIANO GALVAGNO¹, IOANNIS TSOUMPAS², PIERRE COLINET², and UWE THIELE^{1,3} — ¹Department of Mathematical Sciences, Loughborough University, UK — ²TIPs-Fluid Physics, Université Libre de Bruxelles, Belgium — ³Institut für Theoretische Physik, Universität Münster, Germany

We study the profile of evaporating liquid drops on substrates with a corner. A continuous influx allows us to study steady drops of different volume even in this non-equilibrium situation. Experimental results are qualitatively reproduced employing a 2d long-wave mesoscopic hydrodynamic description that incorporates wettability via a Derjaguin (disjoining) pressure. In particular, we study (i) the dependence of the evaporation-induced apparent contact angle on the position of the contact line and (ii) the pinning and depinning of a droplet at a corner - that is for non-volatile liquids well described by Gibbs' criterion. Our results suggest that for volatile liquids, a simple modification of Gibbs' criterion is valid: replacing the equilibrium contact angle by the evaporation-caused apparent contact angle. Most importantly, the calculations confirm the experimental observation, that there exists a dynamically produced critical angle for depinning that increases with the evaporation rate.

CPP 18.8 Tue 11:30 ZEU 222

Slip effects in dewetting polymer microdroplets — ●JOSHUA D. MCGRAW¹, THOMAS SALEZ², SIMON MAURER¹, TAK SHING CHAN^{1,3}, MICHAEL BENZAQUEN², JONAS HEPPE¹, MARTIN BRINKMANN^{1,3}, ÉLIE RAPHAËL², and KARIN JACOBS¹ — ¹Saarland University, Experimental Physics, D-66041 Saarbrücken — ²Laboratoire de Physico-Chimie Théorique, UMR CNRS Gulliver 7083, ESPCI, Paris, France — ³Max Planck Institute for Dynamics & Self-Organization, 37077 Göttingen

Spherical caps on a substrate with less than equilibrium contact angles contract as a result of capillary forces. Applying the classical no-slip condition at the liquid-substrate interface results in diverging stress at the contact line. This divergence can be alleviated, however, by allowing finite flow velocity at the substrate, corresponding to the slip boundary condition. Experiments have been conducted in which glassy polystyrene microdroplets are placed upon, as substrates, different self-assembled monolayers (SAMs). The spherical caps are prepared such that initial contact angles are much less than the equilibrium contact angle. Above the glass transition temperature, a capillary induced flow is observed; the droplet radii shrink while their heights grow. Furthermore, the intermediate height profiles are highly non-spherical. Different SAMs give rise to differing slip lengths, resulting in dramatic changes to the temporal and morphological path these tiny droplets take toward their equilibrium spherical cap shapes.

CPP 18.9 Tue 11:45 ZEU 222

Wetting and electrowetting — MARKUS BIER and ●INGRID IBAGON — MPI for Intelligent Systems, Stuttgart, Germany

The phenomenon of electrowetting, i.e., the dependence of the macroscopic contact angle of a fluid on the electrostatic potential of the substrate, is analyzed in terms of the density functional theory of wetting. A comparison with the traditional scheme based on capacitor models reveals qualitative errors of the latter approach. Within density functional theory one accounts for the formation of a microscopically thin film which (partially) wets the substrate. By that means one obtains an improved expression for the electrowetting number as a function of the voltage. The improved theory is compared with available experimental results and with predictions of the traditional approach. An experimental setup is proposed to differentiate between the traditional and the density functional approach to electrowetting.

CPP 18.10 Tue 12:00 ZEU 222

Liquid transport on rough substrates — CIRO SEMPREBON, ●STEPHAN HERMINGHAUS, and MARTIN BRINKMANN — MPI-DS Göttingen

The ability of liquids to form continuous films on solids is essential for many technical applications such as surface coatings or liquid transport in granulates. In this work we investigate the morphological evolution and transport properties of wetting layers adhering to an irregular rough substrate. To avoid explicit modelling of contact lines, we consider a thin film model with a precursor film and minimize the total interfacial energy. The generic short range interface potential accounts for a finite apparent contact angle of the macroscopically thick regions of the film. Based on the static interfacial profiles obtained by energy minimization, we numerically solve the linearized steady thin film equation and compute the effective mobility of the liquid. Various types of roughness and material contact angles are investigated, either prescribing the pressure in or the volume of the liquid film. Our results show that the connectivity between the domains of macroscopically thick films can be correlated to the effective liquid mobility.

CPP 18.11 Tue 12:15 ZEU 222

Forced multiphase flow on the pore scale explored in 3D — ●HAGEN SCHOLL¹, KAMALJIT SINGH², ALEN KABDENOV¹, MARIO SCHEEL², and STEPHAN HERMINGHAUS³ — ¹Saarland University, Saarbrücken, Germany — ²ESRF, Grenoble, France — ³MPI-DS, Göttingen, Germany

Using ultra fast x-ray tomography the forced imbibition of an aqueous phase into an initially oil filled matrix is studied. The water is volume controlled flushed into cylindrical columns filled with oil saturated spherical bead packs and the forced imbibition is imaged in real time using ultrafast x-ray tomography. The 3d time series are analyzed in terms of oil content, front area and the pore throat filling behavior. For typical flow parameter at low capillary numbers, as e.g. relevant for oil recover, the multiphase flow hardly depends on gravitational effects and details of the pore space. Capillary forces, however, are a key to understand the forced multiphase flow. A compact front develops for a wettable invading phase whereas a branched front develops for a non-wettable invading phase.

CPP 18.12 Tue 12:30 ZEU 222

Adsorption kinetics of surfactants in droplet-based microfluidics using pH measurements at the micron scale — ●BIRTE RIECHERS, QUENTIN BROUSSEAU, FLORINE MAES, and JEAN-CHRISTOPHE BARET — Max Planck Institute for Dynamics and Self-Organization, Göttingen, Germany

Interfaces are omnipresent in biological and man-made systems like emulsions and foams. In biology, interfaces are particularly important for encapsulation and compartmentalization [Theberge et al. *Ange wandte* 2010]. They can be stabilized using surfactants which, upon adsorption, influence properties of the interface (e.g. surface tension and interfacial rheology) and of the bulk phases (e.g. pH) [Baret *LabChip* 2012]. The determination of interfacial properties (equilibrium, adsorption kinetics to the interface) at the scale of the emulsion droplets is crucial for their use in biotechnological applications and solves a fundamental problem.

We present a new method for the determination of the dynamics of surfactant adsorption and surfactant coverage at the interface using droplet-based microfluidics. Water-in-oil emulsions are studied using a fluorescence setup. In combination with a pH sensitive dye inside the droplets, adsorption kinetics of an acidic surfactant are monitored. As the surfactant adsorbs to the interface and deprotonates, it changes the pH inside the dispersed phase giving rise to adsorption and equilibrium properties. We show the effectiveness of surfactant adsorption in droplet-based microfluidics and unravel the kinetics of adsorption at the micron scale with a millisecond time-resolution.