CPP 22: Focus: Wetting on smooth and rough surfaces: From spreading to superhydrophobicity I

Wetting determines the morphology and dynamics of a liquid on a surface. In particular for rough, structured, or deformable surfaces the dynamic contact angles are poorly understood. Progress in experimental and numerical techniques permit time resolved three-dimensional investigations of wetting, providing new insight into the interplay between the contact angle, hysteresis, and pinning.

Organizers: Hans-Jürgen Butt (Mainz), Stephan Herminghaus (Göttingen), Doris Vollmer (Mainz)

Time: Wednesday 9:30–13:00 Location: H34

Invited Talk CPP 22.1 Wed 9:30 H34

Liquid drops on soft solids — •Jacco Snoeijer — University of Twente, The Netherlands

The wetting of a liquid on a solid usually assumes the substrate to be perfectly rigid. However, this is no longer appropriate when the substrate is very soft: capillary forces can induce substantial elastic deformations, as has been demonstrated e.g. for drops on elastomers. In this talk we discuss the fundamentals of elasto-capillary interactions. Theory, simulations and experiments reveal the surprising nature of capillary forces, which turn out to be different from anything proposed in the literature. We also discuss how the law for the contact angle (Young's law) is modified for soft substrates.

CPP 22.2 Wed 10:00 H34

How soft viscoelastic surfaces control the time scales of drop spreading — Longquan Chen[1], •Elmar Bonaccurso[1], and Martin Shanahan[2] — [1]Center of Smart Interfaces, Technische Universität Darmstadt, Petersenstr. 17, 64287 Darmstadt, Germany — [2]Univ. Bordeaux, I2M, UMR 5295, F-33400 Talence, France

It is known that liquid droplets spreading on a soft, viscoelastic substrate can be slowed down considerably by the formation of a wetting ridge, or protrusion of the substrate near the triple phase contact line (TPCL) due to capillary forces. Viscoelastic dissipation in the substrate can prevail over viscous dissipation in the liquid and dominate the spreading process. In this contribution we show how the internal time scales of the viscoelastic solid interact with a spreding droplet.

After contact of a droplet and a viscoelastic substrate a short, rapid spreading stage occurs. The necessary balance determining speed of motion of the TPCL is initially between capillary and inertial forces. As spreading proceeds, inertia lessens while the lower spreading speed allows for viscoelastic effects to emerge. We study the transition between inertial and viscoelastic regime by high-speed video microscopy and propose a simple model for relating the transition time with properties of the liquid and the viscoelastic substrate.

CPP 22.3 Wed 10:15 H34

The wetting properties of graphene in the light of molecular dynamics simulations — •Frédéric Leroy, Fereshte Taherian-Tabasi, Valentina Marcon, and Nico van der Vegt — Center of Smart Interfaces, TU Darmstadt, Darmstadt, Germany

It has recently been shown that monolayer graphene may serve as a protective coating for metals and nonpolar solid substrates while preserving the wetting properties of these surfaces with respect to water. The question arises as to whether such coating would preserve the wetting properties of all nonpolar surfaces.

To answer this question, the contact angle of water droplets on suspended isolated graphene must be known. Experimental work suggests that graphene may yield a value of the contact angle as high as 127°, whereas other studies suggest a weak enhancement in comparison with the value of 95° on graphite.

We have developed an argumentation supported by molecular dynamics simulations to show that a value of the contact angle of water on graphene cannot exceed 100°. In agreement with recent experimental work, it is thus anticipated that graphene coating is not transparent to the wetting properties of nonpolar subtrates which yield contact angles larger than 100°.

Furthermore, our study leads to the conclusion that the work of adhesion of water on graphene includes a non-negligible entropy contribution. Based on the theory of solvation, we introduce the idea that this entropy contribution is related to the fluctuations in the water-substrate interaction energy.

CPP 22.4 Wed 10:30 H34

History-dependent dynamic receding contact angles of aque-ous surfactant solution slugs flowing through polymeric capillaries — Manos Anyfantakis, Daniela Fell, Hans-Jürgen Butt, and •Günter K. Auernhammer — Max Planck Institute for Polymer Research, Mainz, D-55128, Germany

The time-dependent dewetting behavior of surfactant solution slugs which are forced to move in fluorinated ethylene propylene (FEP) micro-tubes was experimentally investigated. The dynamic receding contact angle at a given wetting velocity, measured by high-speed imaging of the receding menisci, was found to decrease as the solid-liquid contact time increased. Long-time kinetics of several hundred s led to a final state displaying a 0o dynamic receding contact angle. The receding contact angle kinetics was found to strongly depend on the slug velocity. Higher speeds led to a faster decrease in the receding contact angles. Qualitatively similar results were obtained for anionic (sodium dodecyl sulfate) and cationic (hexadecyltrimethylammonium bromide) aqueous surfactant solutions at concentrations below and equal to the corresponding critical micellar concentration. Employing a different hydrophobic surface (polycarbonate micro-tubes) led to an analogous dewetting behavior, presumably indicating a generic effect for hydrophobic solid surfaces. This history effect was absent in simple liquids (2-propanol, water), where the dynamic receding contact angle does not depend on the contact time.

M. Anyfantakis et al., Chem. Lett. 2012, 41, 1232

CPP 22.5 Wed 10:45 H34

Mixed Wettability on the Mesoscopic scale: Effect of wetting correlation length in porous media — •Julie Murison[1], Benoit Semin[2], Jean-Christophe Baret[1], Stephan Herminghaus[1], Matthias Schröter[1], and Martin Brinkmann[1] — [1]Max Planck Institute of Dynamics and Self Organisation, Göttingen, Germany — [2]Laboratoire de Physique Statistique, ENS, Paris, France

In order to better understand the behavior of immiscible two phase flow through mixed wetting porous media, we have designed a series of experiments to test the effect of isolated and controlled microscopic heterogeneities (sub-grain) on a larger sample scale (20 mm). Here we present the effect of wetting correlation length on the sub-pore to multi-pore (aprox 1mm) scale. Initial results indicate that sample composition alone cannot adequately describe the fluids behavior, but rather the size of the heterogeneity creates different wetting environments. In particular sub-pore heterogeniety causes large hysteresis in fluid displacement profiles. Recently we combine gravametric measurements of fluid displacement with X-ray microtomography to characterise and quantify effective trapping environments for droplets within the porous media.

CPP 22.6 Wed 11:00 H34

Dewetting of mixtures as described by a gradient dynamics model — •Uwe Thiele, Desislava Todorova, and Hender Lopez — Department of Mathematical Sciences, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

We show that the dynamics of free surface films of mixtures (polymer blends, nanoparticle suspensions) may be described by a hydrodynamic long-wave model that is written thermodynamically inspired gradient dynamics form based on an underlying free energy functional (accounting for wettability and capillarity). For an ideal mixture whose components do not differ in their wettability, the *classical* hydrodynamic model used, e.g., in Refs. [1,2] is recovered. The gradient dynamics form allows us to extend the model to incorporate (i) solute-dependent wettability, and (ii) solute-solvent decomposition [3]. We illustrate extension (i) by an investigation of the dewetting of a film of a mixture and show that a film may become unstable through the coupling of film height and concentration fluctuations. The resulting nonlinear dynamic behaviour and equilibrium states are discussed [4]. The outlook discusses how the idea also applies to surfactant-covered films [5].

[1] M. Warner, R. Craster and O. Matar. J. Colloid Interface Sci. 267, 92 (2003). [2] L. Frastia, A.J. Archer, U. Thiele, Phys. Rev. Lett. 106, 077801 (2011); Soft Matter 8, 11363 (2012). [3] U. Thiele, Eur. Phys. J. Special Topics, 197, 213-220 (2011). [4] D. Todorova, H. Lopez and U. Thiele, in prep. [5] U. Thiele, A.J. Archer and M. Plapp, Phys. Fluids 24, 102107 (2012).

15 min. break

Invited Talk   **CPP 22.7   Wed 11:30   H34**
Wetting transitions in polymer decorated nanostructured surfaces — •Jürgen Rühe — Institut für Mikrosystemtechnik, Universität Freiburg, 79110 Freiburg

We describe the generation of well defined micro- and nanostructured surfaces with surface-attached polymer monolayers. To this high aspect ratio micro- and nanostructured surfaces are generated in silicon through lithography, the Bosch process or DRIE process. In the first case well defined post structures, in the latter silicon nanograss structures are obtained. The silicon structures are coated with self-assembled monolayers containing benzophenon groups. These monolayers are used for a photoinduced attachment of polymer monolayer to these surfaces. We study the wetting properties of such surfaces as a function of the surface energy of the polymer involved. Superwetting, Wenzel-type of wetting and superhydrophobic properties can be observed. In some cases roll-off angles well below $<1°$ are observed. It is found that such surfaces show very distinct wetting transitions, where even minor changes in the surface energy of the coating cause huge changes in the contact angle.

CPP 22.8   Wed 12:00   H34
Dynamics of water droplets on nanostructured hydrophobic surfaces with step gradients — •Tobias Neckernuss, Stefan Wiedemann, Alfred Plettl, and Paul Ziemann — Institute of Solid State Physics, University of Ulm

Droplets on a surface exhibiting different contact angles (CA) along their three-phase-contact-line experience a net force due to uncompensated Young forces. These forces play a major role in the dynamics of both, CA hysteresis and gradient-induced movement. A simple analytical model is developed based on these uncompensated Young components combined with geometrical constraints when a droplet laterally crosses a wettability step. Such steps are prepared with a micellar technique in combination with a hydrophobic Teflon-like coating leading to arrays of nanopillars (typical height: 100 nm, diameter: up to 40 nm). As a result, CAs of about $165°$ and $150°$ are observed for advancing and receding droplets, respectively. By varying parameters like pillar density and diameter, the forces acting on a moving droplet can be adjusted. The dynamics of moving droplets are investigated with a modified commercial CA measurement setup. To move a droplet towards the wettability step, the substrate can be tilted, allowing control of its shape and velocity in the vicinity of the step. Comparison of experimental data to the model prediction shows remarkable agreement.

CPP 22.9   Wed 12:15   H34
Dynamic Measurement of the Force Required for Moving a Liquid Drop on a Solid Surface — •Dominik Pilat, Periklis Papadopoulos, David Schäffel, Doris Vollmer, Rüdiger Berger, and Hans-Jürgen Butt — Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

A novel setup for direct measurement of the force needed to move a drop on a solid surface was developed. The forces were measured by means of a vertical deflectable capillary stuck in the drop. The drop adhesion force instrument (DAFI) allowed us to investigate the dynamic lateral adhesion force of water drops of 0.1 to 2 μL volume at defined velocities. On flat PDMS surfaces, the dynamic lateral adhesion force increases linearly with the diameter of the contact area of the solid liquid interface and linearly with the sliding velocity. We further investigated a 3D superhydrophobic pillar array. The depinning of the receding part of the rim of the drop occurred almost simultaneously for four to five pillars, giving rise to peaks in the lateral adhesion force. The spatial resolution of the lateral adhesion force, which is possible with the DAFI, is not only interesting for scientific applications, but also for industrial applications like quality control of surfaces made in large scale processes.

CPP 22.10   Wed 12:30   H34
Exploring the high-pressure wetting resistance of springtail skin by in situ plastron collapse tests and numerical simulations — •René Hensel[1], Ralf Helbig[1], Julia Nickerl[1], Sebastian Aland[2], Hans-Georg Braun[1], Axel Voigt[2], Christoph Neinhuis[3,4], and Carsten Werner[1,4] — [1]Max Bergmann Center of Biomaterials, Leibniz Institute of Polymer Research Dresden, Germany — [2]Institute of Scientific Computing, TU Dresden, Germany — [3]Institute of Botany, TU Dresden, Germany — [4]B CUBE Innovation Center for Molecular Bioengineering, TU Dresden, Germany

Springtails (Collembola),wingless arthropods are adapted to cutaneous respiration in temporarily rain-flooded habitats due to a non-wetting skin surface. They immediately form a plastron protecting them against suffocation upon immersion into water and even low-surface-tension liquids. Herein, we present the design principles for pressure resistance of such plastrons against collapse. Therefore, the skin morphology of springtails was studied by transmission electron microscopy. The micrographs reveal cavity side-wall profiles with characteristic overhangs. These were fitted by polynomials to allow access for analytical calculations of the breakthrough pressure, i.e., the barrier against plastron collapse. The actual dynamics of an enforced wetting transition from heterogeneous to homogeneous wetting state were performed by in situ plastron collapse tests and numerical simulations based on a diffuse interface approach for two phase flow. Furthermore, model profiles with well-defined geometries were used to develop a general design principle for the most robust surface structures.

CPP 22.11   Wed 12:45   H34
Design of the self-repairable materials using colloidal particles — •Nikolay Puretskiy[1,2], Georgi Stoychev[1,2], Alla Synytska[1], and Leonid Ionov[1] — [1]Leibniz-IPF Dresden, 01069 Dresden, Germany — [2]TU Dresden, 01062 Dresden, Germany

We suggest an approach for the design of materials with self-repairable switchable and hydrophobic properties. The approach is based on use of colloidal particles located on a surface of hydrophobic oil. Due to surface forces, the colloidal particles segregate at the wax surface after melting and change its wetting properties. Since the degree of particle immersion in the wax depends on the environment (hydrophilic or hydrophobic), the roughness, as well as the wetting properties of the particle-wax composite surface, can be switched. The obtained morphology can be "frozen" by cooling down below oil melting point [1]. Notably, since the colloidal particles are homogeneously distributed in the wax bulk, removal of the topmost particle-wax layer does not result in disappear of switchable properties. After remelting the particles segregate again at newly formed surface and switchable properties are recovered. The similar approach is used for the design of materials with self-repairable ultrahydrophobic properties. The materials are based on perfuorinated decane with incorporated colloidal particles. Due to the highly pronounced tendency of this perfuorinated decane to crystallize, the formation of blends with rough fractal surfaces was observed [2]. [1] N. Puretskiy, G. Stoychev, M. Stamm and L. Ionov; ACS Applied Materials and Interfaces, 2010, 2, 2944-2948 [2] N. Puretskiy, G. Stoychev, A. Synytska and L. Ionov; Langmuir, 2012, 28, 3679-3682