# CPP 30: Poster: Focus: Wetting on smooth and rough surfaces: From spreading to superhydrophobicity

Time: Wednesday 16:30–18:30 Location: Poster C

CPP 30.1 Wed 16:30 Poster C

**Polymer brushes in poor solvent - A Monte Carlo Study** — •Christoph Jentzsch[1,2] and Jens-Uwe Sommer[1,2] — [1]Leibniz-Institut für Polymerforschung Dresden, Germany — [2]TU-Dresden, Intitut für theoretische Pyhsik, Germany

We use a new variant of the bond fluctuation model with explicit solvent to study polymer brushes under poor solvent conditions. Extensive simulations were performed in order to cover a wide range of grafting densitys for large systems. For high grafting densitys we observe a dense uniform brush. By decreasing the grafting density, we observe stable holes penetrating through the brush. A further decrease of the grafting density leads to a semicontinous morphology due to a segregation between the solvent and the polymers. For very low grafting densitys we observe octopus micelles of different sizes. We investigate those regimes and their transitions.

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**Droplet morphologies upon growing and shrinking on triangular grooved substrates** — •Carsten Herrmann[1], Ciro Semprebon[2], Martin Brinkmann[1,2], and Ralf Seemann[1] — [1]Saarland University, 66041 Saarbrücken — [2]Max Planck Institute for Dynamics and Self-Organization, 37018 Göttingen

We experimentally investigate the morphologies of droplets sitting on triangular grooved micro-structures upon volume change. 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. In contrast droplets are almost perfectly round upon volume reduction for sufficiently small droplet volumes. In both cases the morphological changes depend sensitively on the wettability and the wedge angle of the triangular grooved substrate. The experimental results are compared quantitatively with numerical results computed by minimizing surface energies.

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**Liquid-liquid dewetting** — •Stefan Bommer[1], Sebastian Jachalski[2], Dirk Peschka[2], Ralf Seemann[1], and Barbara Wagner[2] — [1]Saarland University, 66041 Saarbrücken — [2]Weierstraß-Institute, 10117 Berlin

The transient morphologies towards equilibrium of liquid droplets dewetting on another liquid are considered experimentally and theoretically. As liquids short chained polystyrene and polymethylmethacrylate are used which are glassy at room temperature and which can be considered as Newtonian liquids well above their glass transition temperatures. The liquid/air interfaces are imaged in situ by scanning force microscopy whereas the liquid/liquid interface is imaged after solidifying the sample and removing the dewetting polystyrene. The obtained droplet shapes are compared to numerical results in lubrication approximation which are calculated for the surface tensions and contact angles which are extracted from the equilibrium shapes of the droplets. A remarkably independence of the transient shapes on the start conditions was found for sufficiently 'mature' droplets which allows for the quantitative comparison.

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**Light induced switching of surface wetting of azobenzene decorated silicon nanograss surfaces** — •Jonas Groten and Jürgen Rühe — Universität Freiburg, IMTEK

The wetting behavior of high aspect ratio nanorough surfaces depends on the surface energy of the involved materials. Depending on the value of the surface energy superwetting, Wenzel type wetting or superhydrophobicity can be observed. These wetting regimes are separated by sharp transitions at well defined surface energies. We have coated a silicon surface consisting of high aspect ratio nanoscale needles ("black silicon") with a polymer monolayer containing a fluorinated azobenzene moiety. The azobenzene moiety can be switched between the cis and the trans state through illumination with light of appropriate wavelengths. In the described system the surface energy of the polymer coating is adjusted to the energy value which separates the distinct wetting regimes of the nanorough surface. This coupling allows for large changes in the surface wetting behavior even when the surface energy upon illumination is only rather small. As a consequence the surface can be reversibly switched from a superhydrophobic state with roll off tilt angle $< 2°$ to a completely sticky surface with no roll off at all or from a strong Wenzel-type wetting state to a superwetting surface.

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**Transformation of black candle soot into a transparent robust superamphiphobic coating** — •Xu Deng, Lena Mammen, Periklis Papadopoulos, Maxime Paven, Hans-Jürgen Butt, and Doris Vollmer — Max Planck Institute for Polymer Research,Ackermannweg 10, D-55128, Mainz, Germany

Coating is an essential step in adjusting the surface properties of materials. Superhydrophobic coatings with contact angles greater than 150° and roll off angles below 10° for water have been developed, based on low energy surfaces and roughness on the nano- and micrometer scales. However, these surfaces are still wetted by organic liquids such as surfactant-based solutions, alcohols, or alkanes. Coatings that are simultaneously superhydrophobic and superoleophobic are rare. We designed an easily fabricated, transparent, and oil-rebounding superamphiphobic coating. A porous deposit of candle soot was coated with a 25 nm thick silica shell. The black coating became transparent after calcination at 600°C. After silanization the coating is superamphiphobic and remained so even after its top layer was damaged by sand impingement.

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**The Salvinia Effect: Superhydrophobic Surfaces with Hydrophilic Pins for Air Retention Under Water** — •Daniel Gandyra[1], Birte Böhnlein[1], Matthias Mail[1,2], Aaron Kobler[1], Anke Kaltenmeier[1], Matthias Barczewski[1], Stefan Walheim[1], Kerstin Koch[4], Jan-Erik Melskotte[3], Martin Brede[3], Alfred Leder[3], Wilhelm Barthlott[2], and Thomas Schimmel[1] — [1]Institute of Applied Physics, Institute of Nanotechnology, and Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology — [2]Nees Institute for Biodiversity of Plants, University of Bonn — [3]Chair of Fluid Mechanics, University of Rostock — [4]Biology and Nanobiology, Hochschule Rhein-Waal

Air-retaining surfaces are of great technological, economic and ecological interest, e.g., for low-friction fluid transport and drag reduction in ship coatings. An innovative mechanism for long-term air retention under water is found in the sophisticated surface design of water fern Salvinia molesta. Its floating leaves are evenly covered with complex hydrophobic hairs retaining a layer of air when submerged under water. The terminal cells of the hairs, however, are hydrophilic. These hydrophilic patches at the end of the hairs pin the air-water interface, thus preventing the loss of air by preventing the formation and detachment of air bubbles [1]. This "Salvinia Effect" opens intriguing perspectives for developing artificial, biomimetic surfaces with long-term air retention under water. [1] W. Barthlott, T. Schimmel et al.: The Salvinia Paradox. Advanced Materials 22, 2325-2328, 2010.

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**Drop impact on superamphiphobic surfaces** — •Xu Deng[1], Frank Schellenberg[1], Periklis Papadopoulos[1], Longquan Chen[2], Maxime Paven[1], Lena Mammen[1], Jihua Zhang[1], Doris Vollmer[1], and Hans-Jürgen Butt[1] — [1]Max Planck Institute for Polymer Research, Mainz — [2]Center of Smart Interfaces, Technical University Darmstadt

The spreading and retraction kinetics of liquid drops impacting on superamphiphobic,[1] i.e. superhydrophobic and superoleophobic, surfaces is studied by high speed video microscopy. To investigate the influence of interfacial tension and viscosity on spreading and retraction kinetics mixtures of ethanol-water and glycerin-water are chosen. The main findings are identical for both systems, including the dependence of the impact scenario on drops' Weber and Reynolds number. At low impact velocity the drops rebound, however, the contact time increases when approaching the pinning regime. Drop spreading is dominated by inertia, independent of whether a drop rebounds or pins on the surface. The retraction phase is split into two regimes: a fast inertia dominated retraction of the drop's contour, followed by a slow decrease of the drop's contact diameter for diameters below the initial diameter of the drop before impact. Impact causes partial penetration and pinning of the liquid in the coating, even though the drop rebounds completely.

[1] X. Deng, L. Mammen, H.-J. Butt, and D. Vollmer; Candle soot as a template for a transparent robust superamphiphobic coating, Science, 335 (2012), 67-70.

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**Simulating immiscible multi-phase flow and wetting by means of stochastic rotation dynamics (SRD) - A 3D modeling approach** — •Thomas Hiller, Marta Sanchez de la Lama, Martin Brinkmann, and Stephan Herminghaus — Max Planck Institute for Dynamics and Self-Organization, Göttingen, Germany

We use the mesoscopic particle simulation method SRD to simulate immiscible multi-phase flow on the pore and sub-pore scale in three dimensions. As an extension to the standard SRD method, we present a novel approach on implementing complex wettability on heterogeneous surfaces. Our preliminary results demonstrate the capability of this method to address a variety of applications. For instance, on the pore-scale SRD is a valuable tool to study the formation of capillary bridges in an assembly of three or four spherical beads. Additionally, we show the simulation of flow through an artificial porous media (packing of spherical beads) where the substrate exhibits different spatial wetting characterisitcs and how this influences the dynamics, in terms of percolation and residual saturation, through the porous media. As an outlook we also present how SRD can be applied to simulate droplets flowing in microfluidic channels.

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**Transparent silica nano- and microchannels for microfluidic devices** — •Lena Mammen, Xu Deng, Kathrin Friedemann, Frank Schellenberger, Periklis Papadoupolos, Daniel Crespy, Hans-Jürgen Butt, and Doris Vollmer — Max Planck Institute for Polymer Research, Mainz, Germany

Nano- and microchannels are attractive model systems for fundamental studies like filling kinetics, diffusion processes or transport phenomena. In this work transparent nano- and few-micrometer-sized silica channels were prepared by coating different polymer fiber templates with silica performing a modified Stöber synthesis and subsequent removal of the organic material by calcination. As templates either PVA or polystyrene electrospun or spider silk fibers were used. The channels have a circular cross-section with uniform diameter and smooth surface. We measured the capillary filling speed of water and glycerol/water mixtures and castor oil using laser scanning confocal microscopy (LSCM) what is a convenient technique to observe the filling velocities close to the channel entrance. By comparing our results with the theoretically predicted values according to the classical Washburn kinetics we found a deviation for small filling times ($< 0.1$ s) from the power law.

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**Microcones and Nanograss: Towards mechanically robust superhydrophobic surfaces** — •Vitaliy Kondrashov and Jürgen Rühe — University of Freiburg, Freiburg, Germany

We report on the generation of superhydrophobic surfaces, which are resistant to strong mechanical forces, especially against high shear stress. To this we generate surfaces, which have two roughness levels: micrometer sized silicon microcones surrounded by superhydrophobic silicon nanograss. The fabrication process of the surface is mask-free, and both microcones and nanograss are fabricated in consecutive processes by Deep Reactive Ion Etching (DRIE) in the overpassivation regime. Varying the process parameters, microcones of different size and density were fabricated, while nanograss size and distribution were kept constant.

When shear is applied, the microcones take the load and prevent contact of the shearing surface with the mechanically instable silicon nanograss. As the microcones can cause pinning of the contact line, the height and density of the microcones are important parameters for the influence of wear onto the wetting properties. As result, the shear-stress experiments show that surfaces with high density of large microcones are able to sustain high shear loads without noticeable loss in superhydrophobicity. However, the larger the microstructures the larger shaved hydrophilic area which increases pinning to the drop. This shows that, the control over microcones size and density is a key factor in realization of mechanically robust superhydrophobic surfaces.

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**Influence of subsurface interactions on the dynamic contact angle of liquids on mixed organic monolayers** — David Polster[1] and •Harald Graaf[2] — [1]Department of Physics, University of Konstanz, D-78464 Konstanz, Germany — [2]nanoMA (Center for nanostructured Materials and Analytics), Chemnitz University of Technology, D-09107 Chemnitz, Germany

The functionalisation of surfaces by organic monolayers is a well known way to influence the surface properties e.g. the adhesion forces. Mixed monolayers consisting of similar molecules with two or more various headgroups can tune the obtained surface properties like the hydrophobicity. In the present study silicon surfaces are modified by alkene molecules. By using two different alkenes mixed monolayers of various ratios the hydrophilizity of the surface can be tuned. A water ring formation around single and double ester groups increase the effective hydrophilic area, which leads to a deviation from the expected change in static contact angle measurements.[1] In a recent study we found on such mixed monolayers a hysteresis of the dynamic contact angle of different liquids.[2] Several approaches are discussed in literatur the hysteresis (and also differences in wetting and dewetting energies) partially to long range interactions between the liquid and the underlying silicon, which is very reasonable as the monolayer thickness is only about two nanometers.

[1] Polster et al. Langmuir 26 (2010) 8301, [2] Polster et al. Appl.Surf.Sci. DOI 10.1016/j.apsusc.2012.10.128

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**Universal Phase Diagram for Wetting on Mesoscale Roughness** — •Stephan Herminghaus — MPI für Dynamik und Selbstorganisation

The wetting properties of solid substrates with mesoscale (between van der Waals tails and the capillary length) random roughness are considered as a function of the microscopic contact angle of the wetting liquid and its partial pressure in the surrounding gas phase. It is shown that the well-known transition occurring at Wenzel's angle is accompanied by a transition line at which a jump in the adsorbed liquid volume occurs. This should be present generally on surfaces bearing homogeneous, isotropic random roughness. While a similar abrupt filling transition has been reported before for certain idealized groove or trough geometries, it is identified here as a universal phenomenon. Its location can be analytically calculated under certain (rather mild) conditions.

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**Patterning of YVO4:Eu3+ luminescent films by soft lithography** — •Wenxin Wang[1], Ziyong Cheng[2], Jun Lin[2], and Yong Lei[1] — [1]Fachgebiet 3D-Nanostrukturierung, Institut fuer Physik & IMN MacroNano (ZIK), Institute for Physics and IMN MacroNano (ZIK), Technische Universitaet Ilmenau, Prof. Schmidt Str. 26, 98693 Ilmenau, Germany — [2]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, P.R.China

Ordered square and dot luminescent YVO4:Eu3+ array patterns were fabricated by two kinds of soft lithography processes, namely, microtransfer molding (uTM) and microcontact printing (uCP), respectively. Both soft-lithography processes utilize a PDMS elastomeric mold as the stamp combined with a Pechini-type sol-gel process to produce luminescent patterns on quartz plates. The difference is that square pattern can be direct obtained via uTM, but with method of uCP, we print hydrophobic SAMS on the hydrophilic quartz to induce the dewetting process of sol precursor to form dot pattern array. The ordered luminescent YVO4:Eu3+ patterns are revealed by optical microscopy and their microstructures, consisting of nanometer-scale particles, is unveiled by scanning electronic microscopy (SEM) observations. Additionally, photoluminescence and cathodoluminescence were carried out to characterize the patterned YVO4:Eu3+ samples.

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**Wetting of silica spheres on the micro-scale** — •Jennifer Wenzl, René Stangenberg, and Günter K. Auernhammer — Max Planck Institute for Polymer Research, Mainz, Germany

We present here a model system for wet granular matter on the micrometer scale, which we are able to observe in 3D with confocal microscopy. We use a 3-phase-system consisting of polydisperse silica particles, dispersed in a mixture of an aqueous salt solution (sodium thiocyanate) and an organic solvent (cis-decaline). By mere shaking of the sample mixture, we generate capillary bridges and pickering emulsion droplets with cis-decaline as the binder liquid. Surface modification with methyl silyl groups allows us to adjust a finite contact angle of the interface between the binder liquid and the aqueous salt solution. With the combination of the confocal microscopy and a home-build nano-manipulation, we are able to apply a compression or shear load and observe simultaneously the sample structure in 3D.

We investigated the particle-droplet structure in 3D under compression and shear. In this presentation we show the wetting behavior of this interface and discuss the change of the emulsion droplet number and the corresponding volumes with time. We present also the structural changes of the particles depending on the applied load.