CPP 36: Wetting, Micro and nanofluidics I

Time: Thursday 15:00–18:45 Location: C 264

Topical Talk CPP 36.1 Thu 15:00 C 264

From superhydrophobic to superamphiphobic coatings: How to tune wetting — •Doris Vollmer, Xu Deng, Lena Mammen, Periklis Papadopoulos, and Hans-Jürgen Butt — MPI for Polymer Research, Mainz, Germany

Many surfaces in nature are superhydrophobic, for example lotus leaves. Microscopic pockets of air are trapped beneath the water drops. This composite interface leads to an increase in the macroscopic contact angle and a reduced contact angle hysteresis [1]. However, the addition of an organic liquid such as alcohol or oil, decreases the interfacial tension sufficiently to induce homogeneous wetting. Drops, initially resting on air pockets, pass the transition to complete wetting (Wenzel state). Coatings that are simultaneously superhydrophobic and superoleophobic, i.e. superamphiphobic, are rare. For superamphiphobicity, surface roughness, low surface energy and topography are essential. We designed a transparent superamphiphobic using candle soot as a template [2]. Soot consists of a fractal-like assembly of nano-spheres. Convex small-scale roughness can provide a sufficient energy barrier against wetting, even if the Wenzel state is the thermodynamic equilibrium state. Finally, we discuss the coating resistance against drop impact.

[1] D'Acunzi, L. Mammen, M. Singh, X. Deng, M. Roth, G.K. Auernhammer, H.-J. Butt, and D. Vollmer, Faraday Discus. 146 (2010), 35.

[2] X. Deng, L. Mammen, H.-J. Butt, and D. Vollmer; Transformation of black candle soot into a transparent robust superamphiphobic coating, Science in press.

CPP 36.2 Thu 15:30 C 264

Influence of surfactant concentration and transport on forced dynamic wetting — •Daniela Fell[1,2], Ngamjarassrivichai Pawanrat[1,3], Manos Anyfantakis[1], Elmar Bonaccurso[2], Hans-Jürgen Butt[1], and Günter K. Auernhammer[1] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Center of Smart Interfaces, Darmstadt, Germany — [3]Chulalongkorn University, Bangkok, Thailand

We study the influence of surfactants as well as their local and non-local transport processes on dynamic contact angles in a rotating drum setup. Therefore contact angles of surfactant solutions at concentrations well below the critical micelle concentration (cmc) are measured as a function of wetting/dewetting velocity. Surface transport of surfactant is hindered by the axis holding the cylinder. Changing the filling height from half filled to slightly below or above the axis removes this hindrance. For blocking surface as well as bulk transport an additional metallic barrier is added to a half filled bath.

With increasing surfactant concentration the receding contact angle decreased. Stronger surfactants (low cmc) show a larger decrease of the contact angle than weaker ones. Additionally, at a constant concentration the receding contact angle decreased when increasing the hindrance to surfactant transport. Dynamic contact angles are therefore not only influenced by short-range effects like Marangoni stresses, but also by long-range transport processes like diffusion and advection between regions close to the advancing and receding contact lines.

CPP 36.3 Thu 15:45 C 264

Dynamics of Wet Granulates under Shear Deformation — •Somnath Karmakar[1], Marc Schaber[1], Marco Di Michiel[2], Mario Scheel[2], and Ralf Seemann[1,3] — [1]Saarland University, Saarbrücken, Germany — [2]ESRF, Grenoble, France — [3]Max Planck Institute for Dynamics and Self-Organization, Göttingen, Germany

Adding liquid to dry granular matter typically leads to stiffening of the granulate which arises due the formation of wet contacts between individual granules by the virtue of capillary forces. We study the mechanical properties of wet granulates which are composed of spherical glass or basalt beads. The glass is almost perfectly wetted by water whereas the basalt beads have a rather large contact angle with water. Our main focus is on the yield strength which is measured using a particularly designed shear cell which allows to vary shear speed, shear amplitude and absolute pressure. Due to the different wettability, the yield strength of glass granulates depend on the applied shear rate whereas for non-wetting basalt granules, the yield strength is independent of the applied shear rate. Surprisingly, for large absolute pressure, the stiffening of a wet granulate might be inversed and the liquid might rather act as a 'lubricant' lowering the yield strength with respect to dry granulates. With time resolved X-ray tomography, we could shed some light on the peculiar mechanical properties of wet granulates and could identify a liquid exchange process occurring between the individual liquid morphologies which depends on the wettability of wet granular systems.

CPP 36.4 Thu 16:00 C 264

Liquid transport in wet granular packings — •Ciro Semprebon, Stephan Herminghaus, and Martin Brinkmann — Max Plank Institute for Dynamic and Self Organization, Goettingen

Liquid transport in a static pile of spherical beads can proceed through the formation of a thin wetting film on the surface or through the vapor phase. At sufficiently high surface liquid coverage a wetting film can be formed that percolates through the surface roughness. Assuming a constant effective mobility of this film and stationary flow conditions the local pressure in the film satisfies Laplace's equation with Dirichlet boundary conditions given by the Laplace pressure on the contact line of the bridges. The conductance of the film on a spherical surface in the presence of two bridges can be solved exactly by conformal mapping. Employing a perturbative method we arrive at a simplified model to calculate the matrix elements of the complete conductance matrix for arbitrary bridge configurations. Comparison to finite element methods shows that this approximation is sufficiently precise under certain conditions. The simplified model can be implemented in coarse grained numerical simulations aiming at the liquid transport through large static packings of spherical beads at different liquid saturations.

CPP 36.5 Thu 16:15 C 264

Pore-scale dynamics of multiphase fluid flow through porous media using synchrotron X-ray tomography — •Kamaljit Singh[1,2], Hagen Scholl[3], Marco Di Michiel[1], Mario Scheel[1], Stephan Herminghaus[2], and Ralf Seemann[2,3] — [1]ESRF, Grenoble, France — [2]MPI-DS, Goettingen, Germany — [3]Saarland University, Saarbruecken, Germany

The dynamic behavior of water-oil fronts during a water flood into an initially oil filled porous medium was investigated using ultrafast X-ray tomography at the European Synchrotron Radiation Facility. This type of multiphase flow is similar to a situation which can be found for oil recovery and soil decontamination. We investigated the effect of wettability, flow velocity, porosity and gravity. The findings reveal that the water-oil front is more compact in basalt beads, whereas the front in glass beads progresses in elongated fingers. The fingering in the glass beads results in a higher final residual oil saturation due to bypassing of several oil-filled pores. Secondly, a significant oil movement was observed behind the main front in the case of basalt beads, therefore sweeping the rest of the oil resulting in less trapping after a complete water flood. We further analyzed the time-series of tomograms to identify preferential pathways during forced-imbibition. These flow paths are overlain by corresponding pore-throat network to investigate the properties of pores and throats allowing water-oil interfaces to migrate. From this analysis, it seems that capillary forces dominate the flow behavior instead of hydraulic resistance. Finally, the velocity does not seem to play a significant role in water-oil front behavior.

CPP 36.6 Thu 16:30 C 264

Dielectric Capillary Rise in Mesoporous Vycor-Glass — •Beatrice Hallouet, Erika Robert, Patrick Huber, and Rolf Pelster — FR 7.2 Experimentalphysik, Universität des Saarlandes, Campus E26, 66123 Saarbrücken

We present a new method to follow the capillary rise of liquids in mesoporous samples by means of dielectric spectroscopy. The mesoporous material is Vycor®, a 3D network with a mean pore radius of about 4 nm and a porosity of about 30 %. The liquids are 1-alcohols (hexanol up to undecanol) which are carbons-chains molecules with one polar group. By measuring the time dependence of the permittivity, we are able to show that the capillary rise follows the so-called Lucas-Washburn law $h(t) = c_h\sqrt{t}$, where c_h depends on fluid parameters (viscosity, surface tension) and matrix parameters (porosity, radius

...). The combination of dielectric and gravimetric measurements allows us to evaluate quantities like the initial porosity or the hydrodynamic radius. We discuss the influence of humidity, i.e. of adsorbed water layers on the pore walls. The flow of all alcohols seems to be characterized by the same hydrodynamic radius but the contact angle may vary as a function of the chain length.

15 min break

CPP 36.7 Thu 17:00 C 264

Imaging of wetting dynamics of a molecularly thin fluid film in a soft graphene-mica slit pore — •Nikolai Severin, Philipp Lange, Igor M. Sokolov, and Jürgen P. Rabe — Department of Physics, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

The behavior of water and other molecular liquids confined to the nanoscale is of fundamental importance, e.g., in biology, material science, nanofluidics and tribology. Direct microscopic imaging of wetting dynamics in sub-nanometer pores is however challenging. We demonstrate high resolution imaging of a molecularly thin water film wetting the interface between mica and graphene. Ambient humidity allows to control the wetting and dewetting of the film. We follow these processes in space and time using scanning force microscopy imaging of the graphene conforming to the film. At sufficiently high humidity a continuous molecularly thin water film wets the interface between the graphene and mica. At lower humidities the film dewets with fractal depressions exhibiting dimensions around 1.7 and depths comparable to the size of a water molecule. The soft graphene cover offers a previously unexplored semi-hydrophilic slit pore of self-adjustable size, which enables high resolution imaging of confined molecularly thin fluid films. Moreover, the self-adjusting slit pore geometry implies prospects to experiment with other liquids and liquid mixtures with molecules of variable sizes. The soft electrically conducting cover offers interesting opportunities for the fabrication of novel nano-fluidic devices including an electrically driven pump.

CPP 36.8 Thu 17:15 C 264

Wetting and adsorption properties of monolayer interfaces — •Jens Smiatek[1], Hendrik Wagner[2], Armido Studer[2], and Andreas Heuer[1] — [1]Institut für Physikalische Chemie, WWU Münster, D-48149 Münster, Germany — [2]Institut für Organische Chemie, WWU Münster, D-48149 Münster, Germany

We present the results of mesoscopic Dissipative Particle Dynamics (DPD) simulations concerning monolayers with varying length in contact with an explicit solvent. Our results indicate different solvent interface concentrations for varying monolayer thicknesses. Additionally we have calculated the free binding energy for a test particle. Our results demonstrate that the test particle is stronger adsorbed at thinner monolayers due to a decreased solvent content and a higher monomer density at the interfacial region. The numerical findings are in good agreement with experimental observations.

CPP 36.9 Thu 17:30 C 264

Parameter passing between Molecular Dynamics and thin film hydrodynamics — •Nikita Tretyakov[1], Marcus Müller[1], Desislava Todorova[2], and Uwe Thiele[2] — [1]Institut für Theoretische Physik, Georg-August-Universität, Göttingen, Germany — [2]Department of Mathematical Sciences, Loughborough University, Loughborough, UK

First, we study the wetting properties of coarse-grained polymer liquids by Molecular Dynamics (MD) simulation. The system consist of a LJ-polymer liquid on a fcc lattice substrate. The temperature is controlled by a DPD thermostat, which locally conserves momentum. The values of the contact angle are dictated by the strength of the substrate-liquid interaction.

At small thicknesses of a polymer film the interaction of the substrate-liquid and liquid-vapor interfaces can be expressed by the Derjaguin (or disjoining) pressure. In the MD simulations we measure the Derjaguin pressure and the surface tension through the anisotropy of the pressure tensor using a slab geometry. The Derjaguin pressure and surface tension are then employed to predict the shape of droplets using two continuum models that correspond to the static limit of a hydrodynamic thin film equation in full-curvature and long-wave formulation, respectively. The results are compared to the averaged profiles in particle simulation.

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CPP 36.10 Thu 17:45 C 264

The influence of nano-roughness on solid-liquid surface free energies. A molecular dynamics simulations contribution. — •Frédéric Leroy — TU-Darmstadt, Darmstadt, Germany

We address the question of the determination of the surface free energies of rugged solid-liquid interfaces. We aim to describe interfaces whose roughness dimension is of the order of 1-10 nanometers. Although such surfaces are ubiquitous, the way nanostructures influence the solid-liquid surface free energy remains largely unexplored. This is mainly due to the impossibility to carry out direct measurements of this quantity. Its estimation relies on droplets contact angles measurements and on the use of equations to connect surface free energies and contact angles. There is experimental evidence that this task is not always straightforward to be performed. It is also legitimate to wonder whether continuum equations have the ability to describe situations where molecular details may matter.

We introduce a thermodynamic integration algorithm to determine the surface free energy of smooth and rugged interfacial systems. We perform molecular dynamics calculations dealing with water in collapsed wetting states on model rugged graphite-based surfaces simultaneously exhibiting roughness and chemical heterogeneity. We show that the related continuum theory is able to predict the nanometer scale results under the condition that water does not experience too strong confinement. Our results also evidences that the origin of surface free energy, at least in the case of water on non-polar attractive substrates, is to be found in the very few first layers of adsorbed water.

CPP 36.11 Thu 18:00 C 264

Wetting and prewetting in electrolyte solutions — •Ingrid Ibagon, Markus Bier, and S. Dietrich — Max-Planck-Institut IS, Stuttgart, Germany

We investigate the wetting of a charged substrate by an electrolyte solution by means of classical density functional theory applied to a lattice model for an ionic fluid. Our lattice model consists of three species (solvent, anions and cations) that occupy the sites of a uniform lattice filling the half-space $z>0$. The three species have an attractive nearest-neighbor interaction. Moreover ions interact via Coulomb force and all three species interact with the substrate via an attractive external potential. The surface charge density and the ionic concentration are found to have an impact on the wetting behavior, in particular the influence on the wetting temperature and the prewetting transition are studied.

CPP 36.12 Thu 18:15 C 264

Dynamics of small droplets on solid surfaces — •Nasrollah Moradi[1], Fathollah Varnik[1,2], and Ingo Steinbach[1] — [1]ICAMS, Ruhr Universität Bochum — [2]Max-Planck Institut für Eisenforschung,

The behavior of individual microdrops on solid surfaces is very important in many practical processes [1,2]. Despite of its importance, many aspects of this behavior, however, are still not well understood. Here, we address some of these aspects. The main focus is on the behavior of small drops on a super hydrophobic surface with a gradient of roughness; the effect of a step wise change in the pillar density on the dynamics of drops is investigated via lattice Boltzmann (LB) simulations [3], and the dependence of the drop velocity on the surface tension and the gradient of pillar density is analytically modeled [4]. In addition to the case of drops on a gradient of roughness, based on a detailed LB survey of the local viscous dissipation inside sliding droplets on flat substrates, we model the dependence of the drop velocity on the equilibrium contact angle [5]. Finally, we study the behavior of droplets at situations in which the size of a droplet is comparable to the roughness scale of the solid substrate using LB simulations. In this case, possible morphologies and a so-called re-entrant transition are studied [6].

1- P. G. de Gennes, Rev. Mod. Phys. 57, 827 (1985) 2- C. Dorrer and J.Rühe, Soft Matter 5, 51 (2009) 3- M. R. Swift, W. R. Osborn and J. M. Yeomans, PRL 75, 830 (1995) 4- N. Moradi, F. Varnik and I. Steinbach, EPL 89, 22006 (2010) 5- N. Moradi, F. Varnik and I. Steinbach, EPL 95, 44003 (2011) 6- N. Moradi, F. Varnik and I. Steinbach, MSMSE 19, 45005 (2011)

CPP 36.13 Thu 18:30 C 264

Wetting of droplet ensembles on solid substrates — •Marouen Ben Said[1,2], Britta Nestler[1,2], Harald Garcke[3], and Michael Selzer[1,2] — [1]Institute of Materials and Processes, University of Applied Sciences, Karlsruhe, Germany — [2]Institute of Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany — [3]Faculty of

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We present a phase field model for multi-phase systems with preserved volume fractions and an accurate boundary condition to simulate wetting behaviors of droplet ensembles on solid substrates. The formulation of the boundary condition at the substrate surface ensures the correct macroscopic contact angles according to Young's law. The approach is related to the minimization of free energy of the system. Furthermore, we use the energy formulation proposed by Nestler et al. [1] with an additional substrate energy term describing the interactions between the solid- and the different liquid phases. We show 2D and 3D simulations of liquid droplet ensembles on flat and structured solid walls and discuss the results.

[1] Britta Nestler, Frank Wendler, Michael Selzer, Björn Stinner, and Harald Garcke. Phase field model for multi-phase systems with preserved volume fractions. *Phys. Rev. E*, 78(1):011604, Jul 2008.