

CPP 44: Wetting, Fluidics and Liquids at Interfaces and Surfaces II (joint session CPP/DY)

Time: Thursday 9:30–13:00

Location: MER 02

CPP 44.1 Thu 9:30 MER 02

Dynamic wetting of concentrated granular suspensions — ●REZA AZIZMALAYERI, PEYMAN ROSTAMI, and GÜNTER K. AUERNHAMMER — Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

Concentrated granular suspensions are employed in a variety of processes where the contact line dynamics and internal structure of the suspension interact. The process can be characterized using individual particle analysis and average suspension descriptions. Along the contact line, particles interact with each other and the substrate, and the shear rate influence the suspension's non-Newtonian rheological behavior. In this study, we use fluorescently-labeled tracer particles in a refractive index-matched silica suspension. We track the motion of the tracer particles in the concentrated suspension with astigmatism particle tracking velocimetry (APTV). Averaging over single tracks gives the flow profile in a droplet near the advancing contact line. In addition, side-view allows characterizing the drop shape. The behavior of high-concentration suspensions near contact lines differs significantly from that of simple liquids. Near the advancing contact line, we observe the fast-moving layering of suspensions close to the substrate, which is controlled by the suspension's rheology. Near the receding contact line, the suspension adheres to its previous layer and moves on top of it. Initially, there is an unsteady motion, which becomes stationary with time.

CPP 44.2 Thu 9:45 MER 02

Sliding drops: towards a universal law of friction — XIAOMEI LI¹, FRANCISCO BODZIONY², MARIANA YIN², HOLGER MARSHALL², RÜDIGER BERGER¹, and ●HANS-JÜRGEN BUTT¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz — ²Computational Multiphase Flows, Technische Universität Darmstadt, Alarich-Weiss-Straße 10, 64287 Darmstadt

Liquid drops moving on tilted surfaces are an everyday phenomenon and are important for many industrial applications. Still, it is not possible to predict their velocity. To make a step forward in quantitative understanding, we measured the velocity U , width w , length, advancing Θ_a , and receding contact angle Θ_r of liquid drops sliding down inclined flat surfaces. By solving the equation of motion, we determined the friction force versus slide velocity for different hydrophobic surfaces. The friction force acting on moving drops of polar and non-polar liquids with viscosities ranging from 10^{-3} to 1 Pa s can empirically be described by $F_f(U) = F_0 + \mu w Ca^\alpha$ for the whole relevant velocity range. Here, $Ca = U\eta/\gamma$ is the capillary number, in which η is the viscosity and γ the surface tension of the liquid. The friction coefficient μ is in the range of $1 - 3$ N/m for all liquid/surface combinations. For viscosities above 0.006 Pa s, we find $\alpha = 1.0$. Bulk and wedge viscous dissipation can fully account for the velocity-dependent friction force. These results were confirmed by direct numerical diffuse-interface simulations of the flow pattern inside sliding drops. We demonstrate that the Furmidge-Kawasaki equation, is also valid in the dynamic case.

CPP 44.3 Thu 10:00 MER 02

Spreading of soft elasto-viscoplastic droplets — ●MAZIYAR JALAAL¹, CASSIO OISHI¹, and HUGO FRANÇA^{1,2} — ¹Institute of Physics, University of Amsterdam, Amsterdam, The Netherlands — ²Sao Paulo State University, Sao Paulo, Brazil

The spreading under surface tension of a droplet of complex fluid with elastic and plastic properties is studied. Unlike Newtonian fluids, the droplet converges to a final equilibrium shape once the driving stresses inside the droplet fall below the critical yield stress. Scaling laws are presented for the final radius and complemented with an asymptotic analysis for shallow droplets. Moreover, numerical simulations using the volume-of-fluid method and an elastoviscoplastic (EVP) constitutive law, and experiments with an aqueous solution of Carbopol, are presented.

CPP 44.4 Thu 10:15 MER 02

Stick-slip Contact Line Dynamics in Forced Wetting of Polymer Brushes — ●DANIEL GREVE¹, SIMON HARTMANN¹, and UWE THIELE^{1,2} — ¹Institut für Theoretische Physik, WWU Münster — ²Center for Nonlinear Science (CeNoS), WWU Münster

We study the wetting of adaptive substrates using a mesoscopic hydrodynamic model for a liquid droplet on a polymer brush, refining the model in [1]. First, we show that Young's law still holds for the macroscopic equilibrium contact angle and that on the mesoscale a Neumann-type law governs the shape of the wetting ridge (comparable to the case of elastic substrates [2]). Further, we numerically examine the wetting ridge dynamics for a moving meniscus, i.e., we consider an "inverse Landau-Levich geometry" where a brush-covered plate is introduced into a bath. We find stick-slip motion in good qualitative agreement with experimental observations [3,4] and discuss criteria for the onset of the corresponding instability.

[1] U. Thiele and S. Hartmann, *Eur. Phys. J.-Spec. Top.*, 2020, 229, 1819-1832.
 [2] B. Andreotti and J. H. Snoeijer, *Annu. Rev. Fluid Mech.*, 2020, 52, 285-308.
 [3] S. Schubotz et al., *Adv. Colloid Interface Sci.*, 2021, 294, 102442.
 [4] L. Wan, X. Meng, Y. Yang, J. Tian and Z. Xu, *Sci. China Chem.*, 2010, 53, 183-189.

CPP 44.5 Thu 10:30 MER 02

Demixing of liquid PDMS during dewetting into the equilibrium state — ●KHALIL REMINI¹, LEONIE SCHMELLER², DIRK PESCHKA², BARBARA WAGNER², and RALF SEEMANN¹ — ¹Experimental Physics, Saarland University, Saarbrücken, Germany — ²Weierstrass-Institute, Berlin University, Berlin, Germany

The study of micrometer-sized equilibrium droplets on elastic substrates is of great interest because, due to negligible gravity, other interactions such as elastic or capillary forces and their mutual influence can easily be investigated, so deviations from the expected behaviour at larger scales becomes visible. This applies in particular to soft solids like PDMS that are typically considered as ideal rubbers on the macro scale. Our experimental system is composed of liquid polystyrene (PS) droplets on a viscoelastic substrate consisting of cross-linked polydimethylsiloxane (PDMS) of different elasticities. Using atomic force microscopy (AFM), we analyse the topography of the materials and thus their contact angles with high precision, we also use AFM to demonstrate the existence of non-cross-linked liquid PDMS that migrates from the elastic PDMS toward the three-phase contact line TPCL to form a demixed liquid ring around the dewetted PS droplet. In that situation, on the nanometer distance around the TPCL, liquid PS meets liquid PDMS instead of being in direct contact with the soft solid PDMS. Further analysis allows us to say that this phenomenon also exists during the dewetting of liquid polystyrene in the same type of elastic solids.

CPP 44.6 Thu 10:45 MER 02

How droplets dry on stretched soft substrates — ●BINYU ZHAO, YIXUAN DU, and GÜNTER K. AUERNHAMMER — Leibniz Institute of Polymer Research Dresden, Dresden 01069, Germany

Droplets evaporation on solid substrates is a ubiquitous phenomenon and relevant in many natural and industrial processes. Well known are the coffee-ring. Many studies have succeeded in promoting, suppressing or even reversing the formation of coffee-ring by using non-spherical particles, surfactants, patterned substrates, and so on.

Here, we show that a uniaxial stretching of soft substrates strongly controls the dynamics of droplet evaporation and particle deposition through controlling the contact line motion. Water droplet evaporates with an elongated non-circular contact line on the stretched substrates and switches the elongation direction during evaporation. The contact line evolution depends on the orientation of the contact line relative to the stretching direction. When nanoparticles are added into the liquid, the circular deposition pattern, i.e., the so-called coffee-ring, becomes elongated along the direction perpendicular to the stretching direction. Particularly, such non-circular deposition pattern exhibits periodic height gradients along its rim. The finer structure of the pattern can be controlled by applying different stretching ratios to the soft substrate and thus are correlated to the anisotropic surface stresses near the contact line. The findings broaden our understanding of droplet wetting and evaporation on soft and anisotropic substrates, and open the way to reshaping the coffee-ring to allow anisotropic, non-circular patterning.

CPP 44.7 Thu 11:00 MER 02

Gradient dynamics model for sessile drop evaporation in a gap: from simple to applied scenarios — ●SIMON HARTMANN¹, UWE THIELE¹, CHRISTIAN DIDDENS², and MAZIYAR JALAA³ — ¹Institut für Theoretische Physik and Center for Nonlinear Science, Universität Münster — ²Physics of Fluids group, Max Planck Center Twente for Complex Fluid Dynamics, and J. M. Burgers Center for Fluid Dynamics, University of Twente — ³Van der Waals-Zeeman Institute, Institute of Physics, University of Amsterdam

We consider an evaporating drop of volatile partially wetting liquid on a rigid solid substrate. In addition, the setup is covered with a plate, forming a narrow gap with the substrate. First, we develop an efficient mesoscopic description of the liquid and vapor dynamics in a gradient dynamics form. It couples the diffusive dynamics of the vertically averaged vapour density in the narrow gap to an evolution equation for the drop profile. The dynamics is purely driven by a free energy functional that incorporates wetting, bulk and interface energies of the liquid as well as vapour entropy.

Subsequently, we employ numerical simulations to validate the model against both experiments and simulations based on Stokes equation. Finally, we show that the gradient dynamics approach allows for extensions of our model to cover more intricate scenarios, e.g., spreading drops of volatile liquid on polymer brushes or on porous media.

15 min. break

CPP 44.8 Thu 11:30 MER 02

Modeling the temporal evolution and stability of thin evaporating films for wafer surface processing — ●MAX HUBER^{1,2,3}, XIAO HU^{1,2,3}, ANDREAS ZIENERT^{1,2,3}, and JÖRG SCHUSTER^{1,2,3} — ¹Fraunhofer Institute for Electronic Nano Systems ENAS, Technologie-Campus 3, 09126 Chemnitz, Germany — ²Center for Materials, Architectures and Integration of Nanomembranes (MAIN), Chemnitz University of Technology, Rosenbergr. 6, 09126 Chemnitz, Germany — ³Center for Microtechnologies, Chemnitz University of Technology, Reichenhainer Str. 70, 09126 Chemnitz, Germany

Thin liquid films play a crucial role for many applications, e.g., coating, particle deposition, wafer bonding, and the cooling of electronic devices. As an example, we investigate the evaporation of thin water films on LiTaO₃. *Ab initio* density functional theory is used to calculate the Gibbs free energy of adsorption. These results are fitted to an expression of the Gibbs free energy which is derived from the disjoining pressure, consisting of molecular and structural components. In this way, the parameters for the disjoining pressure can be determined. A combination of literature-known models for spin drying and evaporation is used to analyze the temporal evolution of the water layer. The vapor above the water layer is modeled by diffusion and a mass balance is applied at the water-air interface. The results can be used to optimize the process time needed to reach the equilibrium thickness of the water layer. In addition, computational fluid dynamics simulations are utilized to investigate the evaporation in a wafer bond chamber during pump-down.

CPP 44.9 Thu 11:45 MER 02

Electrokinetic, electrochemical and electrostatic surface potentials of the pristine water liquid-vapor interface — ●MAXIMILIAN R BECKER and ROLAND R NETZ — Freie Universität Berlin, Berlin, Germany

Although conceptually simple, the interface between liquid water and vapor displays rich behavior and is subject to intense experimental and theoretical investigations. Different definitions of the electrostatic surface potential as well as different calculation methods, each relevant for distinct experimental scenarios, lead to widely varying potential magnitudes. Here, based on density-functional-theory (DFT) molecular dynamics (MD) simulations, different surface potentials are evaluated and compared to force-field (FF) MD simulations. The laterally averaged electrostatic surface potential, accessible to electron holography, is dominated by the trace of the water molecular quadrupole moment and therefore differs strongly between DFT and FF MD. Thus, when predicting electrostatic potentials within water molecules DFT simulation methods need to be used. The electrochemical surface potential inside a neutral atom, relevant for ion transfer reactions and ion surface adsorption, is much smaller and depends specifically on the atom radius. Charge transfer between interfacial water molecules leads to a sizable surface potential as well. However, when probing electrokinetics by explicitly applying a lateral electric field in DFT-MD simulations, the electrokinetic zeta-potential turns out to be negligible.

Thus, interfacial polarization charges from charge transfer between water molecules do not lead to a significant electrokinetic mobility.

CPP 44.10 Thu 12:00 MER 02

How Charges Separate at Moving Contact Lines — ●AARON D. RATSCHOW¹, LISA S. BAUER¹, PRAVASH BISTA², STEFAN A. L. WEBER^{2,3}, HANS-JÜRGEN BUTT², and STEFFEN HARDT¹ — ¹Technische Universität Darmstadt, Darmstadt, Germany — ²Max Planck Institute for Polymer Research, Mainz, Germany — ³Johannes Gutenberg Universität, Mainz, Germany

Spontaneous charge accumulation in sliding drops is ubiquitous in nature and has been the subject of research activities for over two decades. Despite the growing number of experimental investigations in recent years, the physical mechanism behind the charging remains poorly understood. We identify the origin of charge separation as the dewetting of the immobilized part of the electric double layer (EDL) by the moving contact line. This layer of physically or chemically bound surface charges depends strongly on the local EDL structure, which is disturbed by the vicinity of the gas-liquid interface and the flow in the liquid. We summarize the physics of charge separation in an analytical model that predicts parametric dependencies on surface chemistry, wetting, and liquid properties. The results agree well with our experiments and numerical simulations and uncover decreasing charge separation with decreasing dynamic contact angle and increasing contact line velocity. Our findings reveal the universal mechanism of charge separation at moving contact lines, not limited to drops, with broad implications for the field of wetting.

CPP 44.11 Thu 12:15 MER 02

Beyond the plate capacitor: Calculating the full dielectric tensor for arbitrary system geometries — ●DAVID EGGER, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Realistic models for catalytic reactions at aqueous interfaces require a profound understanding of the electrostatic properties in the vicinity of the solvated catalytic complex, in particular for (photo-)electrochemical reactions with charged intermediates. However, explicit quantum mechanical simulations of these systems on the required length- and time-scales remain oftentimes out of reach. Coarse-graining the electrostatic response of the molecular solvent into a continuum dielectric, described by the dielectric permittivity tensor ϵ , can hence be a necessity. Existing coarse-graining protocols for ϵ typically assume a separation of the dielectric response parallel and perpendicular to the active interface. This approximation is equivalent to two decoupled sets of in-series plate capacitors and ignores potential non-zero off-diagonal elements in the ϵ tensor.

In this contribution, we present a comprehensive and general formalism to coarse-grain molecular solvents into a truly anisotropic ϵ beyond this approximation. We obtain the full, spatially resolved dielectric tensor for arbitrary system geometries with no prior assumptions on boundary conditions. Common bulk and slab formulas are obtained as special cases. The approach is applied exemplarily to bulk water, water-dichloroethane liquid-liquid interfaces, and solvated platinum nanoparticles following from Wulff constructions.

CPP 44.12 Thu 12:30 MER 02

Asymmetric Sessile Compound Drops — ●JAN DIEKMANN and UWE THIELE — Westfälische Wilhelms-Universität, Münster, Germany

We consider compound drops of two immiscible liquids on a rigid solid substrate. Having established a mesoscopic model (amending [1]) consistent with the macroscopic description of [2,3], we show for one-dimensional (1D) substrates that asymmetric compound drops can be energetically favoured using continuation techniques. Furthermore, we investigate selected dewetting and coarsening processes and discuss emerging steady compound drops for two-dimensional (2D) substrates, thereby discussing the relation of 1D and 2D results.

[1] A. Pototsky et al., "Morphology changes in the evolution of liquid two-layer films". J. Chem. Phys. 122, 224711, 2005.

[2] L. Mahadevan, M. Adda-Bedia, and Y. Pomeau., "Four-phase merging in sessile compound drops". J. Fluid Mech. 451, 411-420, 2002.

[3] M. J. Neeson et al., "Compound sessile drops". Soft Matter 8, 11042-11050, 2012.

CPP 44.13 Thu 12:45 MER 02

Steering droplets on substrates with plane-wave wettabil-

ity patterns and deformations — •JOSUA GRAWITTER and HOLGER STARK — Technische Universität Berlin, Institut für Theoretische Physik, Straße des 17. Juni 135, 10623 Berlin

Droplets are set in motion on substrates with a spatio-temporal wettability pattern as generated, for example, on light-switchable surfaces. To study such cases, we implement the boundary-element method to solve the governing Stokes equations for the fluid flow field inside and on the surface of a droplet and supplement it by Cox–Voinov friction for the dynamics of the contact line. One objective of our research is targeted microfluidic transport of such droplets. In earlier work we investigated how a droplet can be steered by imposing a wettability

pattern on the substrate [Grawitter and Stark, *Soft Matter* **17**, 2454 (2021)]. As a next step, we have recently extended our method to include substrates the height profile of which varies temporally in a prescribed manner.

We compare two cases: First, we investigate a droplet on substrates with planar-wave wettability pattern by varying the speed and wave length of the pattern. Second, we investigate a droplet on substrates with a planar-wave height profile. In both scenarios, for small wave velocities the droplet moves steadily forward. In contrast, above a wave velocity the droplet performs steady oscillations. These speed oscillations correlate with oscillations in the shape of the droplet which decay linearly as a function of pattern speed.