Project description – Project Proposals

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Project title: Dynamic wetting phenomena and contact angle hysteresis of drops on polymer brushes and gels

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1 State of the art and preliminary work

1.1 State of the art

In the past few decades, the interest in designing novel surfaces to understand and control the wetting and friction of liquid drops has been steadily growing.[1,2,3] Super-liquid-repellent surfaces show particularly low lateral adhesion and friction, i.e., a deposited drop rolls off as soon as the surface is tilted by less than 10°.[4] Three distinct approaches exist for achieving super-liquid repellency: Superhydro(amphi)phobicity,[5] lubricant impregnated surfaces[6,7] and liquid-like surfaces[8] (Fig. 1).

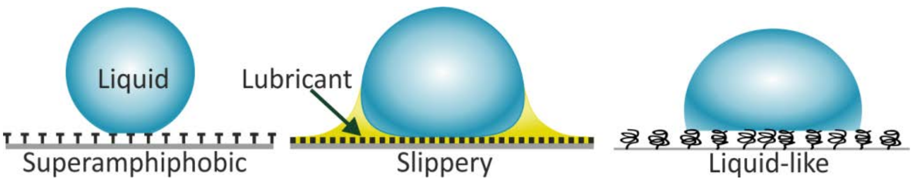

Figure 1: Recent strategies to make super-liquid repellent surfaces.

Super-liquid-repellent surfaces: Both *superhydrophobicity and superamphiphobicity* rely on the presence of air gaps within the nano- and/or microstructured surface asperities, effectively reducing

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[1] Bonn, D. et. al., Wetting and spreading. *Reviews of Modern Physics* **2009,** *81* (2), 739-805.
[2] de Gennes, P. G., et. al., *Capillarity and wetting phenomena*. Springer: New York, 2004; p 291.
[3] Snoeijer, J. H. & Andreotti, B., Moving Contact Lines: Scales, Regimes, and Dynamical Transitions. In *Annual Review of Fluid Mechanics, Vol 45*, Davis, S. H.; Moin, P., Eds. 2013; Vol. 45, pp 269.
[4] Barthlott, W. & Neinhuis, C., Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **202**, 1 (1997).
[5] Quéré, D. Superhydrophobic states. Nature Mater. **2**, 457 (2003).
[6] Lafuma, A.& Quéré, D., Slippery pre-suffused surfaces. *EPL****, 96***, 56001 (2011).
[7] Wong T.S. et. al. Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. Nature **477**, 443 (2011).
[8] McCarthy, T. J. Covalently Attached Liquids: Instant Omniphobic Surfaces with Unprecedented Repellency. Angew. Chem. Int. Ed., 55, 244 (2015).

the solid-liquid contact area. Because in this proposal we aim to understand wetting of polymer brushes and gels, we will not discuss superhydro(amphi)phobic surfaces.

In *lubricant impregnated surfaces,* a porous material is infused by a liquid or a weakly crosslinked lubricant, i.e. a soft gel. The porous material provides the mechanical stability of the coating and the capillary forces help to keep the lubricants in place. For high capillary forces, the lubricant needs to be chemically compatible with the surface of the porous material and its pore size needs to be small. Still, liquid lubricants (e.g. oil, ionic liquid) can be removed easily due to evaporation or continuity of shear stresses over the drop-lubricant interface.[9] Soft gels (swollen polydimethylsiloxanes, hydrogels) show better long term stability. A consequence of lubrication is that liquid drops experiences greatly reduced lateral adhesion when moving over the impregnated surfaces. To minimize friction, the drop should not make contact with the top faces of the porous material. Whether that is the case depends on the interplay of the liquid—substrate γ_{WS}, liquid—lubricant γ_{WL}, and lubricant—substrate γ_{LS} interfacial tensions, i.e. if the spreading parameter S is positive or negative, $S = \gamma_{WS} - (\gamma_{WL} + \gamma_{LS})$.[10] Furthermore, the Van der Waals interaction needs to be repulsive, $F_{VdW} \sim A_H/x$, where A_H is the Hamaker constant and x the thickness of the liquid layer, separating the substrate and the drop.[11]

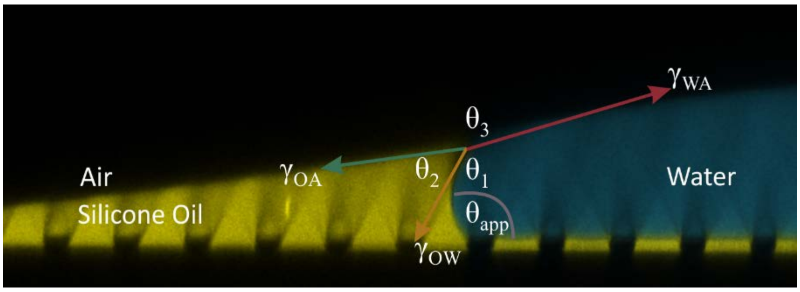

Figure 2: Confocal image of a water drop resting on a micropillar array infiltrated with decanol. γ_{ij} are the interfacial tensions, Θ_i the Neumann angles and Θ_{app} the apparent contact angle.

A characteristic property of lubricant impregnated surfaces is that the deposited drops are surrounded by an annular wetting ridge. It is induced by the vertical component of the interfacial tension (Fig. 2). For positive spreading parameter the drop is cloaked by a few nanometers thick film. The shape and dynamics of wetting ridge change if the liquid lubricant is replaced by an infiltrated gel.[12] The thickness of the wetting ridge decreases for thin lubricating layers. If the thickness of the infiltrated gel reduces to a few nanometers, lubricant impregnated surfaces resemble liquid-like surfaces.

In the so termed *liquid-like surfaces*, a nanometric layer of polydimethylsiloxane (PDMS) is attached to the target surface.[8] The siloxane repeating group (-O-Si-O-) adds high flexibility to the grafted molecules. Because only one end of the PDMS is covalently grafted to the substrate, the remaining part of the PDMS maintains its high mobility through rotational and/or bending motions. However, it is still unclear whether unbound siloxane molecules are necessary to achieve the low roll-off angle. Closely related to this question is the specific role played by the siloxane groups. Can PDMS be replaced by other polymers?

Lateral adhesion force and friction: As mentioned, super-liquid-repellent surfaces have in common that drops move easily over these surfaces. Deposited drops roll off as soon as the surface is tilted by

[9] Wexler, J. S., Jacobi, I., andStone, H. A., Shear-driven failure of liquid-infused surfaces. *Phys Rev Lett* **114**, 168301 (2015).
[10] Smith J. D., et al. Droplet mobility on lubricant-impregnated surfaces. *Soft Matter* **9**, 1772 (2013).
[11] Daniel D., et. al. Oleoplaning droplets on lubricated surfaces. *Nature Physics* **13**, 1020 (2017).
[12] Karpitschka S., et. al. Droplets move over viscoelastic substrates by surfing a ridge. *Nat. Comm.* **6**, 7891 (2015).

less than 10°. This raises the question how to measure and understand this particularly low lateral adhesion and friction force. It has been shown that the roll-off angle α results from the interplay of the gravitational $F_G = \rho V g \sin\alpha$ and the lateral adhesion forces, $F_{LA} = k\gamma w\left(\cos\theta_{\mathrm{rec}} - \cos\theta_{\mathrm{adv}}\right)$.[13] Here ρ is the density of the liquid, V the volume of the drop, g the gravitational constant, γ is the surface tension, w is the contact width of the droplet with the surface, and k is a dimensionless factor that accounts for the precise shape of the solid—liquid—air three-phase contact line.[3] For angles above α the gravitational force overcomes the adhesion force F_{LA}, i.e. $F_G > F_{LA}$, respectively $\rho V g \sin\alpha > k\gamma w\left(\cos\theta_{\mathrm{rec}} - \cos\theta_{\mathrm{adv}}\right)$. However, this macroscopic description does not provide information on the molecular or hydrodynamic origins which cause friction. The friction mechanism of droplets moving on lubricant-impregnated surfaces is complex due to the coexistence of four phases: lubricant, drop, air, and solid. Firstly, one needs to distinguish whether the viscosity of the lubricant exceeds that of the drop or vice versa. As shown by David Quéré et. al., for highly viscous drops, friction is dominated by the drop's hydrodynamics (Stoke's friction law).[14] However, the drop typically consists of water and the viscosity of the organic lubricant exceeds that of the drop. For that case, Kripa Varanasi was the first to show that viscous dissipation in the wetting ridge dominates dissipation in and underneath the drop.[10] David Quéré showed that for droplets moving over infiltrated micropillar arrays, dissipation in the wetting ridge is dominated by dissipation in the front or back part of the wetting ridge. The predictions derived by scaling laws were confirmed by monitoring the motion of drops on tilted surfaces, using drops and lubricants of greatly varying viscosity.[14]

Stefan Karpitschka et. al. modelled how liquid drops move over soft gels.[12] The interplay of capillary and elastic forces results in strong deformations of the gel. Notably, the moving drop causes the formation of sharp ridges. The shape of the ridge depends on the drop's velocity. For sufficiently high velocities they observed a periodic formation of the ridges, reflected in a stick-slip motion.

Lattice Boltzmann simulations: The shape of the wetting ridge and the location of viscous dissipation for drops moving on liquid infused surfaces were modeled by Halim Kusumaatmaja et. al. making use of Lattice Boltzmann simulations.[15] The liquid drop of constant volume was driven by a body force over a micropillar array which was infused by a lubricating liquid. Because the drop made contact with the top faces of the pillars (partial wetting), motion was hindered by pinning of the contact line to the pillars top faces and viscous dissipation in the ridge. They showed that the relative importance of viscous dissipation not only depends on the relative importance of viscous dissipation in the lubricant ridge but also on the shape of the wetting ridge, i.e. the ratio of the height and width of the ridge. They tuned the aspect ratio by varying the wettability of the drop on the lubricating layer. From the viscous dissipation they derived the drop's velocity. Small wetting ridges and good wettability result in high drops' velocity.

Molecular Dynamics simulations: Coarse-grained simulations were used to study different aspects of droplet structures and fluid flow on liquid-like polymer-coated surfaces. Müller and coworkers have studied the properties of rolling polymeric droplets on various surfaces: They first studied the flow profiles and dissipation mechanisms in rolling polymeric droplets on corrugated surfaces, showing that the dissipation mechanism depends on the droplet size[16]. For small droplets, the friction at the contact surface dominates, whereas for larger droplets, the main dissipation occurs due to flows inside the droplet. Subsequently, they investigated polymeric droplets on polymeric brush substrates and demonstrated the existence of wetting ridges even in such a simple, lubricant free system, which

[13] ElSherbini A., & Jacobi A., J. Colloid Interface Sci. **299**, 841 (2006).
[14] Keiser, A. et. al., Drop friction on liquid-infused materials. *Soft Matter* **13**, 6981 (2017).
[15] Sadullah M.S. et. al. Drop Dynamics on Liquid Infused Surfaces: The Role of the Lubricant Ridge, *Langmuir* **34**, 8112 (2018).
[16] Servantie C & Müller M, Statics and dynamics of a cylindrical droplet under an external body force, J. Chem. Phys. **128**, 014709 (2008).

were however rather small[17]. They also investigated the hydrodynamic boundary conditions generated by brushes on polymer melts and showed that they are not compatible with a simple partial slip boundary [18].

Lee et. al.[19] have studied the flow of simple liquids on polymer brushes and have shown that the behavior qualitatively differs for liquids that are good or poor solvents for the polymers. Good solvents penetrate into the brush up to a penetration length in good agreement with the Alexander-de Gennes theory, whereas brushes in contact with a bad solvent collapse and form complex patterns. Speyer and Pastorino studied droplet transport in a microchannel coated by semiflexible polymers[20] and established a correlation between the brush dynamics and the droplet velocity.

However, to our best knowledge, the dynamics of simple fluids or of fluid droplets on a lubricant-impregnated polymer brush or gel has not yet been studied by molecular simulations. However, it can be expected that it will greatly influence viscous dissipation.

1.2. Preliminary work

In this project we aim to understand the *shape and reorganization of the wetting ridge and contact angle hysteresis on polymer brushes and gel*s. Furthermore, we aim to correlate the deformation and reorganization of the wetting ridge to the lateral adhesion and friction force. Next, we review relevant aspect of our previous work to achieve this goal, approaching it from the experimental (Vollmer) and numerical side (Schmid).

Space and time resolved imaging: We showed that laser scanning confocal microscopy (in the following termed confocal microscopy) is well suited to investigate static and dynamic properties of drops on super-liquid repellent surfaces in 3D.[21] In contrast to classical video microscopy where the boundaries of drop and the lubricant cannot be discerned, confocal microscopy allows us to visualize the shape of the different interfaces, Fig. 2 [DV1]. A Leica TCS SP5 II - STED CW inverted confocal microscope with five detectors was employed. The microscope permits to measure the emission from three different dyes and the reflected light from the interfaces simultaneously. The adsorption spectra of the dyes shouldn't overlap and the dyes may not be interfacial active, i.e. the dye should not change the interfacial tensions. Depending on the objective, a horizontal resolution of approximately 300 nm, a vertical resolution of approximately 1 µm and a temporal resolution of 8 kHz per line can be achieved. Thus, all interfaces can be resolved with a resolution better than two micrometers at a temporal resolution of one 3D image per second. On micropillar arrays the contact angle of the buried interface (lubricant/drop) at the front and rear of a resting drop were measured.

[17] Léonforte, F. & Müller, M., Statics of polymer droplets on deformable surfaces. *J. Chem. Phys.* **135**, 214703 (2011).

[18] Müller, M.; Pastorino, C. & Servantie, J., Hydrodynamic boundary condition of polymer melts at simple and complex surfaces. *Comp. Phys. Com.* **180**, 600 (2009). Léonforte, F; Servantie, J., Pastorino, C. & Müller, M, Molecular transport and flow past hard and soft surfaces: Computer simulation of model systems. *J. Phys.: Cond. Matter* **23**, 184105 (2011).

[19] Lee, T.; Hendy, S. C. & Neto, C., Interfacial flow of simple liquids on polymer brushes: Effect of solvent quality and grafting density. *Macromolecules* **45**. 6241 (2012).

[20] Speyer K. & Pastorino C., Brushes of semiflexible polymers in equilibrium and under flow in a super-hydrophobic regime, *Soft Matter* **11**, 5473 (2015). Speyer, K. & Pastorino, C., Droplet transport in a nanochannel coated by hydrophobic semiflexible polymer brushes: The effect of chain stiffness, *Langmuir* **33**, 10753 (2017).

[21] Papadopoulos P., et. al., How superhydrophobicity breaks down. *Proc. Natl. Acad. Sci.* **110**, 3254 (2013).

Notably, they can change by more than 30°. The advancing contact angle reaches its fundamental limit of 180° [DV2]. Using a low numerical aperture objective, we have monitored the variations of the distance between a drop and a glass substrate with a resolution better than 20 nm. Therefore, we have analyzed the interference of light reflected at the lower side of the water drop and the top side of the glass substrate [DV3].

To investigate moving drops by confocal microscopy, we designed a strategy to move drops over the surface. This can be done using gravity as body force[22] or by pulling/pushing a drop with the help of a capillary (Fig. 3). Both driving forces permit the detailed observation of how a drop advances over a lubricant infiltrated micropillar array in slow motion. Single pinning and depinning events can be resolved. From the bending of the capillary, the friction force can be calculated by applying Hooke's law. So far, we have shown that is the lateral adhesion and friction force can be measured using a moving stage [DV4]. In the future we aim to measure the friction force and the shape of the wetting ridge simultaneously by confocal microscopy.

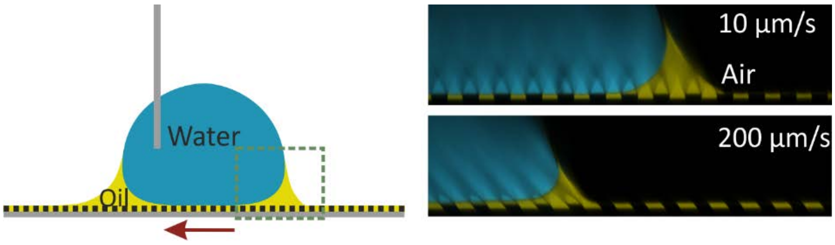

Figure 3: A water droplet is pulled over a lubricant infiltrated micropillar array. The viscosity of the lubricant, silicone oil, was 1 Pa s. For better visualization of the shape of the wetting ridge, the drop was not dyed. The shape, height and volume of the wetting ridge depend on the velocity.

Profiling the wetting ridge on prewetted films: When placing a liquid drop on a prewetted surface, where the two liquids are immiscible, a wetting ridge forms. But how does it form? To gain insight into this question we placed a water drop on a glass slide which was prewetted with silicone oil, Fig. 4 [DV 5]. At the transition zone where the meniscus connects to the film region, the film is depleted and a local minimum film thickness, h_{min}, is observed before the film reaches its initial thickness h_0 far away from the meniscus, Fig. 4, right. The reason for the formation of h_{min} is that the Laplace pressure inside the meniscus is lower than the pressure of the flat film region, due to the concave curvature of the oil surface. The pressure drop follows from the Young–Laplace equation $\Delta P = \gamma\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$, where r_1 and r_2 are the radii describing the meniscus curvature. The negative Laplace pressure in the meniscus initiates a pressure-gradient-driven capillary suction of oil from the film region into the meniscus. Eventually, the local minimum in film thickness will disappear and the transition zone will be given a monotonically decreasing profile. Pressure-gradient-driven capillary suction increases the size of the ridge until the pressure difference between the meniscus and the film region vanished. Because of the minimum film thickness in front of the meniscus, balancing the pressure difference can take several hours – or even days – depending on the geometry of the system and viscosity of the liquid. In order to visualize the flow inside the meniscus, we added polystyrene tracer particles in the silicone oil. The capillary flow of the oil from the film region follows the oil–air interface up the meniscus. This induces continuous circulative convection of the oil within the meniscus.

[22] Schellenberger F. et. al., How Water Advances on Superhydrophobic Surfaces. *Phys. Rev. Lett.* **116**, 096101 (2016).

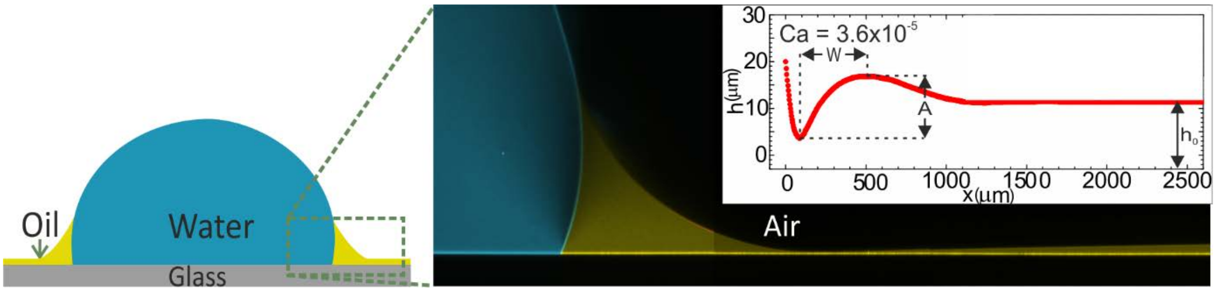

Figure 4: Left: Sketch of a drop on a prewetted glass slide. A compiled laser scanning confocal microscopy image showing a 0.5 µL dyed water drop (cyan) resting on a dyed silicone oil film (yellow, η = 50 mPa s, γ = 21 mN/m) on a smooth glass substrate (side view). The image was captured 1–2 min after placing the water drop on the oil film. Local minimum film thickness (h_{min} ≈ 1 µm, see inset) is visible at the transition zone where the meniscus connects to the film region. Inset: Shape of the meniscus at enlarged magnification. The half-wavelength (W) and the amplitude (A) are determined as the distance and the height difference. h_0 denotes the film thickness far away from the meniscus at the smooth film region.

Friction of drop on infiltrated micropillar arrays: The friction force can be obtained using gravity as body force. In one set of experiments (in cooperation with D. Quéré), we placed a water drop on a micropillar array infiltrated with silicone oil. The lateral adhesion force follows from the tilting angle α, where the drop starts moving. The friction force follows from the terminal velocity.[14] To model viscous dissipation we divided the wetting ridge into six regions, were viscous dissipation can be localizes (Fig. 5a). For water drops moving over a silicone oil infiltrated surface, friction is dominated by dissipation in the wetting ridge. The wetting ridge deforms dynamically (Fig. 3), i.e. its shape depends on velocity or capillary number $Ca = \eta_o v/\gamma$ where η_o is the viscosity of oil ($Ca = \eta_o v/\gamma_{wo}$ in region 2, $Ca = \eta_o v/\gamma_o$ in region 4), Fig. 5. At low velocities and for high pillars, dissipation is localized in region 1 and can be modelled considering the interplay of viscous and capillary forces. At high velocities and low pillar heights, a Landau Levich film[23,24] forms. Now dissipation in region 2 adds up. Remarkably, frictions on the front side (regions 1 and 3) and rear side (region 2 and 4) of the wetting ridge scale as $\gamma R Ca^{2/3}$, despite different physical contents. To verify that friction scales with the number of surfaces, we doubled the number of surfaces by using a Hele-Shaw cell. Now, the water drop is confined between two micropillar arrays (Fig. 5b, inset) infiltrated with silicon oil and separated by a distance *H.* Data inside the Hele-Shaw cell show the same scaling behavior, but the prefactor is multiplied by 2, in line with the doubling of the number of surfaces.

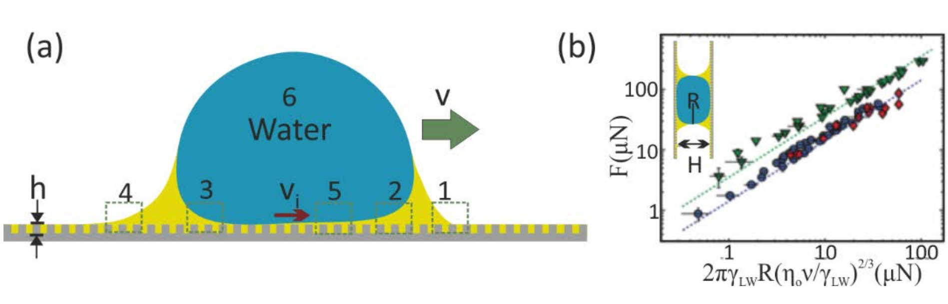

Figure 5: (a) Schematic of a drop moving at a speed *v* over a lubricant-infused micropillar array. Water is blue, while the oil lubricating the system is orange. Six main dynamical regions can be defined. Four of them concern the oil meniscus around the drop: regions 1 and 3 correspond to advancing oil meniscus, while the receding parts are regions 2 and 4. The two final regions are the

[23] Maleki M., et. al., Landau-Levich menisci. *J.Coll. Int. Sci.,* **354,** 359 (2011).

[24] Landau L. & Levich B., Dragging of a liquid by a moving plate. *Acta Physicochimica Urss,* **17**, 42 (1942).

drop itself (region 6) and the oil film whose typical thickness is set by the texture height *h* (region 5). v and v_i (close up in region 5) are respectively the drop and the water/oil interface velocities. The oil meniscus is supposed asymmetric, with an advancing angle φ at the front (region 1) and a film of thickness ε at the rear (region 2). **b)** Friction force *F* of drops or bubbles as a function of the scaling parameter $2\pi\gamma_{ow}R\ (\eta_o v/\gamma_{ow})^{2/3}$ for drops running down a lubricant infused surface (blue circles), drops falling in a Hele-Shaw cell (green triangles) and bubbles rising up lubricant infused surfaces (red diamonds). All surfaces have the same texture (square lattice of circular pillars, *h* = 20 µm, area fraction of 23%). The drop volume is varied between 5 and 20 µL and the tilt angle between 1° and 90°.

Friction of drop on infiltrated micropillar arrays: To gain insight into the friction a drop experiences when moving on a lubricant infiltrated surface, we measured the velocity of drops deposited on a micropillar array using gravity as body force. These measurements were done in Paris in the group of D. Quéré. The lateral adhesion force follows from the tilting angle α, where the drop starts moving. The friction force follows from the terminal velocity. This setup has the advantage that the viscosity of the drop and the lubricating oil can be varied by several orders of magnitude. To model viscous dissipation we divided the wetting ridge into six regions, were viscous dissipation can be localized (Fig. 5a). For water drops moving over a silicone oil infiltrated surface, friction is dominated by dissipation in the wetting ridge. The wetting ridge deforms dynamically (Fig. 3), i.e. its shape depends on velocity or capillary number $Ca = \eta_o v/\gamma$ where η_o is the viscosity of oil ($Ca = \eta_o v/\gamma_{wo}$ in region 2, $Ca = \eta_o v/\gamma_o$ in region 4), Fig. 5. At low velocities and for high pillars, dissipation is localized in region 1 and can be modelled considering the interplay of viscous and capillary forces. At high velocities and low pillar heights, a Landau Levich film forms. Now dissipation in region 2 adds up. Remarkably, frictions on the front side (regions 1 and 3) and rear side (region 2 and 4) of the wetting ridge scale as $\gamma R Ca^{2/3}$, despite different physical contents. To verify that friction scales with the number of surfaces, we doubled the number of surfaces by using a Hele-Shaw cell. Now, the water drop is confined between two micropillar arrays (Fig. 5b, inset) infiltrated with silicon oil and separated by a distance *H.* Data inside the Hele-Shaw cell show the same scaling behavior, but the prefactor is multiplied by 2, in line with the doubling of the number of surfaces. Our confocal microscopy data show that the size of the wetting ridge decreases with increasing velocity. So far it is unclear how this affects viscous dissipation.

Low adhesive infiltrated polymer brushes: Instead of micropillar arrays infiltrated with silicone oil, low friction has also been observed for PDMS brushes grafted to a glass surface or silicon wafer. We started to investigate thin PDMS films and PDMS brushes infiltrated with silicone oil. Our data hint that even after rinsing the infiltrated surfaces in good solvents for silicone oil, mobile molecules remain in the PDMS brush or film, providing the liquid-like nature to the layer. The low friction force is reflected in the low roll off angle [DV6]. In that respect, infiltrated thin PDMS films or brushes resemble infiltrated PDMS gels. However, the size of the wetting ridge is greatly reduced, i.e. making thin PDMS films and PDMS brushes ideal surfaces for molecular dynamic simulations.

Coarse-grained simulations: To gain a microscopic understanding of the relation between the structure of the wetting ridge and the dynamical and adhesive properties of the liquid drops, we will complement the experiments by coarse-grained molecular simulations. These will be based on the dissipative particle dynamics (DPD) method and carried out in the group of the PI Friederike Schmid as detailed below in the work programme. F. Schmid has a long-standing expertise in coarse-grained simulations of flows and of polymeric systems.

For example, we have solved a problem that has previously plagued flow simulations based on the DPD method: The implementation of the correct hydrodynamic boundary conditions. We have developed a “tunable-slip” DPD method that allows adjusting the surface slip to arbitrary desired values [FS1] and can also be used on patterned surfaces[25,26]. Furthermore, we have clarified how to use the Green-Kubo formalism for determining bulk and shear viscosities from DPD simulations – in particular, how to correctly account for dissipative and stochastic forces [FS2]. We have also proposed a set of non-equilibrium methods that allows determining bulk viscosities in steady-state elongational flows [FS2].

In recent studies, we have investigated the internal structure of polymer brushes with focus on polydispersity effects, which are omnipresent in all real brushes [FS3, FS4]. In particular, we have considered the penetration length of solvent into the brush, and shown that it is not fundamentally affected by a moderate level of polydispersity [FS3]. We have also proposed a new design for smart switchable polymer brushes, which could potentially also be used to dynamically control droplet motion [FS4].

1.1 List of project-related publications

[DV1] Papadopoulos P, Deng X, Mammen L, Drotlef DM, Battagliarin G, Li C, Mullen K, Landfester K, del Campo A, Butt HJ & Vollmer D: **Wetting on the Microscale - Shape of a Liquid Drop on a Microstructured Surface at Different Length Scales**. *Langmuir* **2012**, *28*, 8392.

[DV2] Schellenberger F, Xie J, Encinas N, Hardy A, Klapper M, Papadopoulos P, Butt HJ, Vollmer D: **Direct observation of drops on slippery lubricant-infused surfaces**. *Soft Matter* **2015**, *11*, 7617.

[DV3] Papadopoulos P, Vollmer D & Butt HJ: **Long-Term Repellency of Liquids by Superoleophobic Surfaces.** *Physical Review Letters* **2016**, *117*, 046102.

[DV4] Gao N, Geyer F, Pilat DW, Wooh S, Vollmer D, Butt HJ & Berger R: **How drops start sliding over solid surfaces**. *Nature Physics* **2018**, *14*, 191.

[DV5] Teisala H, Schönecker C, Kaltbeitzel A, Steffen W, Butt HJ & Vollmer D: **Wetting over pre-existing liquid films**. *Physical Review Fluids* **2018**, *3*, 084002.

[DV6] Wooh S & Vollmer D: **Silicone Brushes - Omniphobic Surfaces with Low Sliding Angles**. *Angewandte Chemie-International Edition* **2016**, *55*, 6822.

[FS1] Smiatek J, Allen MP & Schmid F: **Tunable-slip boundaries for coarse-grained simulations of fluid flow**. *European Physical Journal E* **2008**, *26*, 115.

[FS2] Jung G & Schmid F: **Computing bulk and shear viscosities from simulations of fluids with dissipative and stochastic interactions**. *Journal Chemical Physics* **2016**, *144*, 204104.

[FS3] Qi S, Klushin LI, Skvortsov AM & Schmid F: **Polydisperse polymer brushes: Internal structure, critical behavior, and interaction with flow**. *Macromolecules* **2015**, *49*, 9665.

[FS4] Qi S, Klushin LI, Skvortsov AM, Liu M, Zhou J & Schmid F: **Tuning transition properties of stimuli-responsive brushes by polydispersity**. *Advanced Functional Materials*, **2018**, to appear. doi:10.1002/adfm.201800745

[25] Zhou J., Belyaev A., Schmid F. & Vinogradova, O, Anisotropic flow in striped superhydrophobic channels, *J. Chem. Phys.* **136**, 194706 (2012).

[26] Nizkaya TV, Asmolov ES, Zhou J., Schmid F. & Vinogradova, O, Flows and mixing in channels with misaligned superhydrophobic walls, *Phys. Rev. E.* **91**, 033020 (2015).

2 Objectives and work programme

2.1 Anticipated total duration of the project

72 months total duration. We apply for a period of 36 months.

2.2 Objectives

Within this project we aim to understand the shape of the wetting ridge surrounding an aqueous droplet, its reorganization when the droplet starts moving (Fig. 6) and the resulting mechanisms of viscous dissipation for substrates covered by polymer gels and brushes. As model systems, we intend to focus on PDMS gels and PDMS brushes with and without immersed free polymer chains, Fig. 7. We plan to vary the film thickness of the brush/gel, the molecular weight of the brushes, the crosslinking density of the gel, and the viscosity of the infiltrated liquid and the velocity of the drop moving on the surfaces. As a free polymer, we plan to use silicone oil because it is non-volatile and shows excellent chemical compatibility with PDMS. To vary the wettability of the drop on a gel, hydrogels will be investigated for comparison. We plan to combine experimental investigations (confocal microscopy complemented by interference microscopy and friction measurements) and theory (coarse-grained molecular simulations) to obtain complementary and in depth insight into the dynamic wetting phenomena.

Figure 6: Central problem to be studied in the proposed project. A droplet is surrounded by a wetting ridge. If the droplet moves, the ridge deforms and reorganizes. This dissipates energy and generates friction. We plan to study the relation between the deformation and reorganization of the wetting ridge with the lateral adhesion and friction forces acting on the droplet for different liquid-like substrates stabilized by a polymeric matrix.

Specifically, we plan to address the following questions:

- How does the lubricant affect the structure of the surface and the shape of the wetting ridge at equilibrium and nonequilibrium (i.e., if the droplet is moving)?
- How do the contact angles and the structure and shape of the wetting ridge evolve with time?
- Which factors determine the lateral adhesion and the friction forces of droplets and how can they be manipulated by using lubricants, surface patterning etc.?

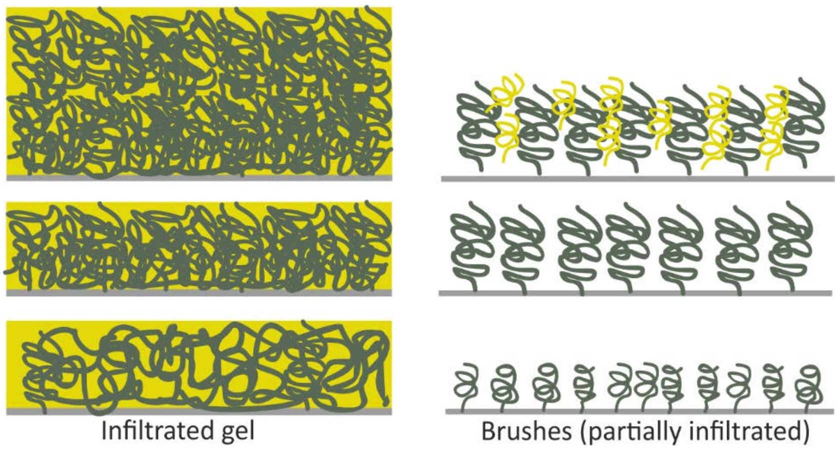

Figure 7: Model surfaces considered in this work

2.3 Work programme including proposed research methods

2.3.1 Methods

In the experiments, we will use laser scanning confocal microscopy and interference microscopy to optically resolve the shapes of the drops on the polymer gels with micrometric resolution. Static and dynamic wetting ridges above a height of 1 µm can be resolved in fluorescence mode, adding a dye to the gel. Submicrometer changes can be resolved using interference microscopy. Flow profiles will be measured by adding tracer particles.[27] To characterize the reorganization of the wetting ridge we are going to move the droplet at controlled velocity while monitoring the shape of the ridge. Simultaneously, we are going to measure the lateral adhesion and friction force from the deflection of the capillary holding a drop which is deposited on a moving plate.

In the simulations, we will study the physical mechanisms governing the dynamic interactions between droplets and the solvent using coarse-grained particle models. We will predominantly use the dissipative particle dynamics (DPD) method[28]. In this approach, coarse-grained particles interact by soft, short-ranged conservative interactions and additional Galilean-invariant friction forces. It is particularly suited for studying hydrodynamic phenomena in soft matter. The original (and most widely used) version only includes repulsive pair interactions and can therefore not capture liquid-vapor coexistence. Therefore, we will use an extension, the so-called multibody DPD (MDPD method), where an additional adhesive density dependent interaction in the EAM (embedded atom spirit) is added[29]. We have used this method earlier to study droplets of conducting fluids[30]. The polymers will be set up as simple spring-bead chains and the droplet fluid is made of individual beads. In order to be able to run fast simulations of large systems, we plan to use graphics processing units (GPUs). We will set up the simulations using the openly available particle simulation toolkit HOOMD-blue[31], where both standard DPD interactions [32]and EAM potentials[33] have already been implemented. The hydrodynamic boundaries at the substrate will be implemented using our tunable slip method [FS1].

As described in the work program below, we plan to systematically vary critical parameters such as the interfacial tensions, the swelling properties of the brush in the presence of free chains, the elasticity of the gel, the mesh size etc., as well as the hydrodynamic properties of the wetting fluids. To this end, we will vary the conservative and dissipative MDPD interaction parameters, the bond

[27] Chen Q., Rame E. & Garoff S., The velocity field near moving contact lines, *J. of Fluid Mechanics,* **337**, 49 (1997).
[28] Hoogerbrugge P & Koelman J, Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics. *Europhys. Lett.* **19**, 155 (1992).
[29] Pagonabarrago I & Frenkel D, Dissipative particle dynamics for interacting systems. *J. Chem. Phys.* **115**, 5015 (2001); Warren P, Vapor-liquid coexistence in many-body dissipative particle dynamics, *Physical Review E* **68**, 066702 (2003).
[30] Joulaian M.; Pisheva, A.; Khajepor, S.; Schmid, F. & Afshar, Y., A new algorithm for simulating flows of conducting fluids in the presence of electric fields, *Comp. Phys. Comm.* **183**, 2405 (2012).
[31] Anderson J.A, Lorenz C.D & Travesset A, General purpose molecular dynamics simulations fully implemented on graphics processing units, *J. Comp. Phys*. **227** 5342 (2008); Glaser J.; Nguyen T.D., Anderson J.A, Liu P., Spiga F., Millan J.C., Morse D.C. & Glotzer S.C., Strong scaling of general-purpose molecular simulations on GPUs, *Comp. Phys. Comm.* **192**, 97 (2015).
[32] Phillips C.L., Anderson J.A. & Glotzer S.C., Pseudo-random number generation for Brownian dynamics and Dissipative Particle Dynamics simulations on GPU devices. *J. Comp. Phys.* **230**, 7191 (2011).
[33] Morozov I.V., Kazennova A.M., Bystryia R.G., Normana G.E., Pisareva V.V. & Stegailova V.V., Molecular dynamics simulations of the relaxation processes in condensed matter on GPUs. *Comp. Phys. Comm.* **182**, 1974 (2011).

interactions and the chain architectures. The resulting interfacial tension will be determined using the virial theorem, and the viscosities using appropriate Green-Kubo relations [FS2].

2.3.2 Work plan

The work will be carried out by a tandem of two PhD students, one mainly doing the experiments, and one the simulations. Both students will collaborate regarding the theoretical analysis of their results. To ensure a close interaction between the two students, we will arrange regular discussion meeting. Furthermore, both will undertake an “internship” (at least four weeks) in the partner student’s lab in the second year of their thesis, after the basic setup has been completed on both sides. The experimental PhD student will then study a selected problem by simulations, and the theoretical PhD student will carry out a set of straightforward measurements. The student doing the internship will mainly be supervised by their partner student.

The experimental part of the work will be carried out under the supervision of the PI D. Vollmer and divided in 5 work packages as follows, where WP2 and3 and WP4 and 5 are closely interlinked.

WP E1: Fabrication of surfaces (6 months, distributed over the whole duration of the project)

First the students will learn how to prepare and characterize polymer brushes and gels. As we aim for a student with a background in physics or physical chemistry, the fabrication of the surfaces will be done in cooperation with M. D’Acunzi, a postdoc in PI Vollmer’s group. PDMS brushes will be synthesized using trimethylsiloxy terminated linear polydimethylsiloxane molecules, the most common silicone fluids. They have highly polarized inorganic silicon (Si)–oxygen (O) backbone with two organic methyl side groups ($-CH_3$) attached to each silicon atom. PDMS reacts with silicon oxide surfaces. Brushes will be grown by applying heat[11-12] or UV light[13]. The chemically attached PDMS molecules grow linearly, forming nm-thick and optically clear coating films. The PDMS gels are formed by mixing a prepolymer and crosslinker (Sylgard 184), degassing the mixture and spin coating the mixture onto glass slides. The elasticity of the mixture can be tuned by controlling the ratio of the prepolymer and the crosslinking agent. Gels with an elastic modulus as low as 5 kPa can be obtained. For hydrogels we intend to test the thermoresponsive hydrogel PNIPAM, which can be chemically bonded to the surface. Alternatively, we will tune the viscosity of the gel by adding a polyelectrolyte, for example the strong polyelectrolyte poly(sodium styrene sulfonate)(PSS), or the weak polyelectrolyte polyacrylic acid(PAA). The thickness of the films will be determined by ellipsometry and the elastic and viscous modulus by bulk rheology. For the aqueous drop, we will use water, water-glycerin mixtures or ionic liquids if evaporation needs to be excluded.

WP E2: Monitoring the wetting properties under static conditions (9 months).

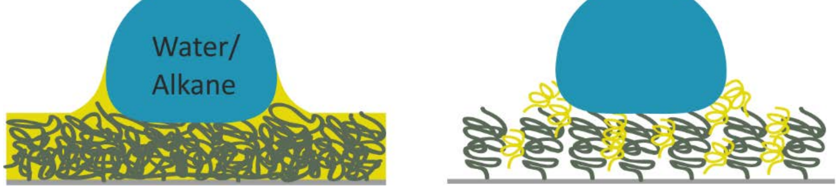

Figure 8: Drop on a thin gel and an infiltrated polymer brush.

The shape of the wetting ridge in presence of a drop will be investigated by confocal microscopy. Here, we will add a water soluble dye to the drop (Atto488) and a second dye to the lubricant, showing a well-separated emission spectrum. To verify that the dyes do not influence the results, we will compare the results with data obtained from the analysis the reflection of light from the interfaces. First we aim to measure the contact angles for all regions of the wetting ridge, Fig. 5. Next we will slowly inflate and deflate the drop to get the advancing and receding contact angles and thus the contact angle hysteresis. In particular, we aim to investigate how the contact angles and the shape of the ridge correlate to the thickness and elasticity of the gel. Under which conditions are the angles independent of the properties of the gel? The thickness of the gel underneath the drop can be measured by interference microscopy. Aside from the angle the drop forms with the lubricating layer (region 2 & 3 in Fig. 5), we aim to characterize the angle at the front part of the ridge, region 1 & 4 in Fig. 5. However, it is not fully clear yet, whether this angle can be defined because the ridge might smoothly merge into the gel layer. In the case of very soft gels the drop might even rest on a liquid film (e.g. silicone oil), preventing the definition of a contact angle. In that case we will focus on the analysis of the curvatures of the interfaces. From the analysis of the curvatures the Laplace pressure in the drop and wetting ridge will be calculated.

If the thickness of the gel is below 50 nm Van der Waals interactions will come into play. These influence the contact angles. Unfortunately, for low thicknesses, confocal microscopy is insufficiently sensitive to resolve the shape of the wetting ridge. Now, an apparent advancing and an apparent receding angle will be measured. By varying the thickness of the gel, we aim to gain information on how the "real" angles (region 2 & 3 in Fig. 5) relate to the apparent angles. From a comparison with the results of the theoretical tandem student we hope to decide whether the angles can be extrapolated or whether Van der Waals interactions and further mechanisms need to be considered. Furthermore, we want to investigate how the apparent angles change if the thin gel is replaced by a brush?

For comparison, we like to investigate the changes of the contact angles if the properties of the lubricant are switched by light (project of Jiaxi Cui and Böker/Reinicke) or when the drop is exposed to low amplitude vibrations (project of Müller/Hasse/Langenbach/Antonyuk).

WP E3: Flow profile in the drop and wetting ridge (6 months, overlapping with WP E2)

From the curvature of the interfaces we can calculate the Laplace pressure in the drop and wetting ridge. Until the wetting ridge has achieved its equilibrium shape, the Laplace pressure in the ridge is negative, giving rise to a flow of lubricant from the gel phase into the ridge. To understand how the Laplace pressure and viscous dissipation relates to the flow profile in the drop and the wetting ridge, we intend to quantify the flow profiles by particle tracking. Therefore, we will add tracer particles to the drop and gel and follow the trajectories by confocal microscopy [DV5]. To uniquely track the particles by confocal microscopy, the particles' velocity needs to be adjusted by varying the viscosity of the drop or the gel. The velocity of the particles may not exceed 1 µm per second. To monitor the flow pattern in the drop, the viscosity of the aqueous phase will be adjusted by adding glycerin or a polyelectrolyte to the aqueous phase. To quantify the flow in the wetting ridge its height and width need to exceed a few micrometers and its viscosity by varying the molecular weight of the silicone oil. For PDMS gels this can be done by varying the degree of cross-linking or the viscosity of silicone oil. Fast particles velocities will be measured and evaluated in collaboration with the SPP project of Kirsten Hardt. As tracer particles, 1 µm sized dyed polystyrene particles are well-suited. Their density is close to water, reducing fast sedimentation of the particles. The particles can be coated with a silica shell to optimize the chemical compatibility between the particles and drop and hydrophobic lubricant. The particles trajectories and velocities will be obtained using the tracking tools implemented in Fiji. The interpretation of the flow profiles with regards to viscous dissipation will be done in close interaction with the theoretical tandem student.

WP E4: Reorganization of the wetting ridge when the drop starts moving (9 months, overlapping with WP E2)

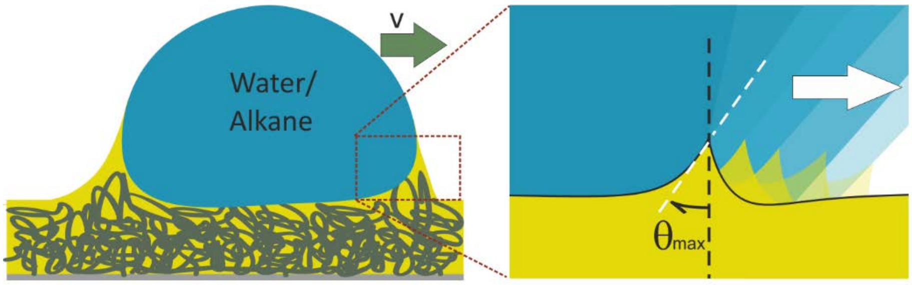

Figure 9: Drop moving over a thin gel. How does the wetting ridge deform?

In WP 2 we analyzed the contact angles and contact angle hysteresis when inflating/deflating a drop. To understand viscous dissipation (WP5) the drop needs to move over the polymer brush/gel. In this work package, we plan to investigate how a drop starts moving. The drop can be pulled/pushed by a capillary while the surface is kept at rest. For comparison, we will keep the drop in place by a capillary while moving the plate underneath at a well-defined velocity. This has the advantage that we can monitor the reorganization of the shape of the wetting ridge while the substrates are moved over several cm. This allows us to study the reorganization of the ridge in the presence and absence of inertia. The current setup allows varying the velocity by approximately 4 orders of magnitude, i.e. up to 1mm/s.

We aim to understand under which conditions the drop performs a stick-slip motion, and under which conditions the drop moves smoothly over the infiltrated gel or brush? How does the height and volume of the ridge depend on velocity? From the measurement of the curvatures we will gain information on the velocity dependence of the pressure variation within the ridge. The formation of a Landau Levich film will be checked by interference microscopy, because of its higher vertical resolution. In cooperation with the theoretically working tandem student, we also aim to understand the influence of the presence/absence of free polymers on velocity dependent reorganization of the ridge.

WP E5: Lateral adhesion and friction forces (6 months, overlapping with WP E4)

After different mechanisms of the reorganization of the wetting ridge are discerned, for a few cases the mechanisms of reorganization will be related to the lateral adhesion and friction force. Again, the drop is kept in place by a capillary, while the plate underneath the drop is moving at a controlled velocity. The forces will be measured from the bending of the capillary (Hooke's law), using capillaries of well-known spring constant.

For example, we aim to understand how viscous dissipation depends on the thickness and cross-linking density of the gel? Does dissipation of PDMS gels and brushes differ? If yes, what causes the differences? How does dissipation depend on the amount of free molecules in the brush? Furthermore, we will test the influence of wettability of the drop and the lubricating layer on dissipation. This can be experimentally realized by moving a crosslinked hydrogel drop over a hydrogel layer. Alternatively, a weakly crosslinked PDMS drop can be pulled over a PDMS gel. The measurements on lateral adhesion and friction force of PDMS brushes will be done in close cooperation with Berger/Butt and the interpretation in cooperation with the tandem student.

The theoretical / simulation work will be carried out under the supervision of the PI F. Schmid.

WP T1: Setup of the system (3-6 months)

In the first step, the simulation must be set up. The HOOMD-blue package provides a toolkit, but the student must still write a simulation code (in Python), and test and validate it. A basic set of interaction parameters must be determined which will serve as a starting point for the subsequent investigations. It will be chosen such that the droplet fluid coexists with a vapor, the lubricant polymers swell the brush (brush and lubricant polymers are of the same type), and the fluid does not swell the bare brush. Furthermore, the code must provide the option to crosslink the brush polymers such that we can also study gels.

WP T2: Basic characterization (1 year)

In the second step, different aspects of the system are investigated systematically and separately. Starting from the basic parameter set specified in WP T1, we will

a) Determine the viscosities of the liquid and the pure polymer melt
b) Determine the interfacial tensions between liquid/vapor, the bare polymer melt/vapor
c) Determine the pressure tension profile of the pure brush in contact with the liquid and in contact with the vapor. This should allow us to extract an interfacial tension for the brush surface.
d) Repeat the analysis c) for gels (crosslinked brushes) with different mesh sizes.
e) Calculate the slip properties of the liquid on the bare brushes and the bare gels

From the interfacial tensions, we can also determine the contact angle at equilibrium. The model parameters will then be varied systematically to assess their influence on the various physical parameters. At the end of WP T2, we will redefine the “basic” parameter set such that the physical parameters match the experimental values as closely as possible.

WP T3: Properties of infiltrated brush (1 year, overlapping with WP T2)

In the third step, we will consider infiltrated brushes in contact with a liquid and a vapor. We will repeat some of the analysis of WP T2 for these swollen brushes. In particular, we will calculate the penetration depth of the lubricant into the brush, the interfacial tensions at the interface between the brush surface and the liquid or the vapor, and the influence of swelling on the slip of the fluid. The results of Lee et al for dry brushes[34] have suggested that dry brushes in contact with a bad solvent collapse in a laterally heterogeneous manner. As a result, the interface between the liquid and the droplet is corrugated. We expect that this effect will disappear for infiltrated brushes and the interface will be much smoother, which should have a significant impact on the effective slip.

Furthermore, we will specifically study the swelling dynamics after bringing the drop in contact with an initially dry brush. This topic is of particular interest for the SPP project Berger/Butt. Therefore, we will also study the swelling and reorganization dynamics after bringing in other “good solvents” of lower molecular weight and compare our results with experimental results in the Berger/Butt project.

WP T4: Static droplet properties (1 year, overlapping with WP T3)

In large scale simulations (of order 1 million particles), we will study the properties of droplets on dry brushes, dry gels, and infiltrated brushes and gels. We will characterize the wetting ridge at the border of the droplet by a geometrical analysis and extract a contact angle. We will compare the observed “local” contact value with the macroscopic value obtained from Young’s equation based on the interfacial tensions calculated in WP T2 and WP T3. We will rationalize our findings in terms of a simple elastic model that also includes the stretching energy of the brush and the possibility of a line

[34] Lee T., Hendy S.C. & Neto C., Interfacial flow of simple liquids on polymer brushes: Effect of solvent quality and grafting density. *Macromolecules* **45**. 6241 (2012).

tension. Here, we plan to closely collaborate with the SPP project of Thiele. The theory can be tested, e.g., by carrying out additional simulations for droplets of varying droplet size.

WP T5: Moving droplet (1.5 years, overlapping with WP T4)

In the final step, the droplet of WP T4 will be set into motion by applying a constant bulk force in one direction. We will characterize the resulting stationary state as a function of droplet velocity for dry brushes, dry gels, infiltrated brushes and infiltrated gels. We will determine the advancing and receding contact angle and compare it with the equilibrium contact angle. To obtain a more detailed theoretical picture, we will

- investigate the changes in the shape of the meniscus in the wetting ridge and the conformational changes in the chains, and calculate the elastic energy stored in the ridge deformations
- characterize the conformational changes in the chains and the chain dynamics, and determine the energy that is dissipated in the ridges.
- characterize the flow profiles inside the droplet (for droplets of different size) and determine the associated energy dissipation.

Based on this analysis, we will calculate the effective friction for rolling or sliding droplets and correlate it with the energy dissipation in the wetting ridge, at the contact surface between the droplet and the brush, and inside the droplet.

Finally, we will use our results to construct a hydrodynamic continuum model for our system, based on the elastic model derived in WP T4. This will be done in collaboration with the SPP project of Thiele in the framework of a gradient (hydro)dynamics, and will allow us to access even larger scales in simulations and pave the way for studying large, topologically structured, polymer grafted surfaces in the next funding period.

Figure 7 and Table 1 summarize the workflow and time schedule of the entire project.

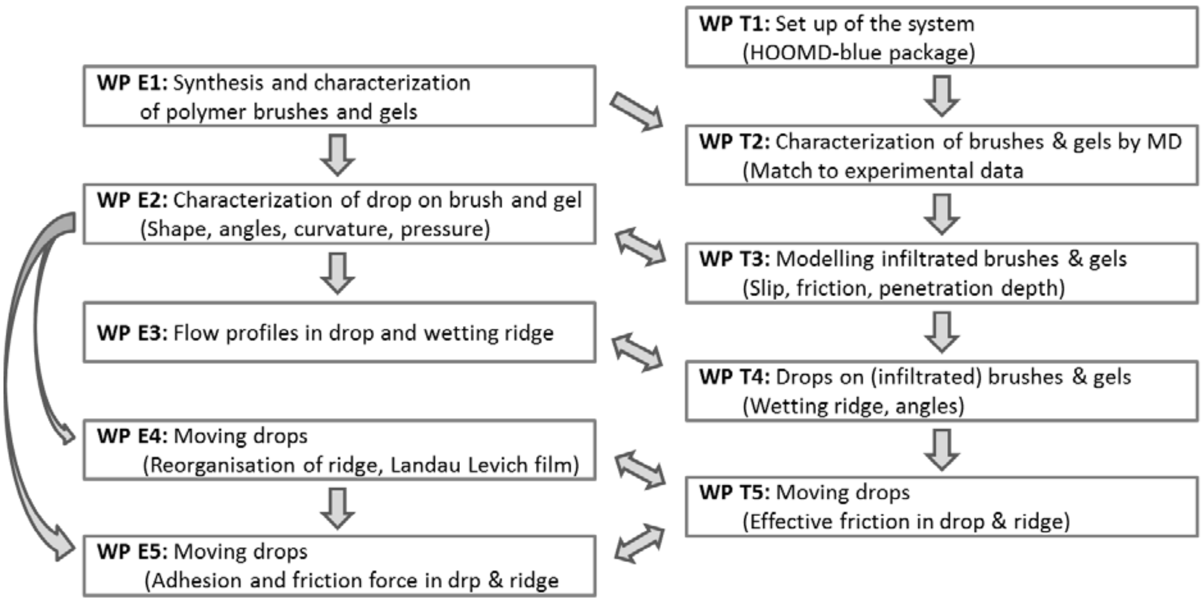

Figure 9: The roadmap of the experimental (left) and theoretical (right) approach and their interlinks

Table 1: Gant chart of the program

Year 1		Year 2		Year 3	
1-6 month	7-12 month	13-18 month	19-24 month	25-30 month	30-36 month
WP E1		WP E1			
WP E2					
	WP 3				
		WP E4			
				WP E5	
WP T1					
WP T2					
	WP T3				
		WP T4			
			WP T5		

2.4 Data handling

The applicants undertake to adhere to the recommendations of the DFG on good scientific practice. The handling of data is based on the guidelines provided by the DFG. All data are backed up several times and archived within the research groups thoroughly, timely, and securely. The MPIP provides a central facility to store data for least 10 years at two locations. Regular appraisal interviews make the proper data handling and backup a subject of discussion. Most data generated within this project will be images, videos or simulations. In total, the volume of the data obtained will not be a critical feature so that the present infrastructure in the group provides sufficient capacity for the storage as well as backup. The experimental research data (laboratory journals, analytical data) as well as the simulation data will be archived for at least ten years and the corresponding digital data will be stored on CDs and on an external hard drive. The working methods of the employees will be checked regularly. The results of the research will be published in established peer-reviewed journals in order to make them available to the broad readership. Detailed experimental data will be provided as supplementary information.

2.5 Other information

None.

2.6 Explanations on the proposed investigations

Experiments involving humans or human materials: Not applicable
Animal experiments: Not applicable
Dual Use Research of Concern: Not applicable

2.7 Information on scientific and financial involvement of international cooperation partners

Not applicable

3 Bibliography concerning the state of the art, the research objectives, and the work programme

The references are added as footnote at the end of the respective pages.

4 Requested modules/funds

4.1.1 Funding for staff

	Vollmer	Schmid
PhD student position, 75% EG 13, 36 months	145.125 €	145.125 €
Student research assistant, 40h/month, 30 months	16.800 €	16.800 €
Total (3 years)	**161.900 €**	**161.900 €**

To ensure a close cooperation between both students, the experimental student should be interested in modeling, too. A suitable candidate might be L. Hauer, who is currently doing his master thesis with us. Suitable candidates for the theoretical tandem student are students with a background in physics or physical chemistry.

4.1.2 Direct Project Costs

4.1.2.1 Equipment up to €12,000, Software and Consumables

	Vollmer	Schmid
Two Graphical cards (RTX 2080Ti or equivalent)		2.000 €
Consumables (dye, solvents, lab supplies, glassware)	5.000 € per year	
Total	**15.000 €**	**2.000 €**

Justification consumables: This sum represents approximations based on our experience gained from similar projects. For the confocal microscopy, special hydrophilic and hydrophobic dyes are required. It is important is that the dye is not interfacial active to ensure that they do not change the interfacial tensions. Suitable dyes are or example Alexa 488 Carboxy, Atto 532, Alexa Fluor 488, Alexa Fluor 546. The price for 1 mg is approximately (488 Carboxy: 140 €; Alexa Fluor 488: 350 €).

Justification graphical cards: The simulations will be run on graphics cards. In order to enable local tests and code development, we apply for two graphical cards (GTX 2080 Ti or equivalent) – one for the PhD student working on the project and one for the PI. Based on these tests, large scale simulations will be carried out on the high-performance computing cluster of the University of Mainz.

4.1.2.2 Travel Expenses

	Vollmer	Schmid
Conferences	1.500 € per year	2.000 € per year
Cooperations and SPP meeting (travel and accommodation)	2000 € per year	2000 € per year
Total	**10.500 €**	**12.000 €**

This appropriation will be needed to join relevant specialist conferences. These are essentially meetings of the American Physical Society (APS), European Colloid and Interface Society, and conference related to wetting (i.e. “Bubbles and Drops”, “Fluid and Elasticity”). Additionally, this will fund travel and accommodation of the PI and the PhD student at the SPP schools and workshops, and the scientific visits of the PhD students to our collaborator within this SPP project.

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

None.

4.1.2.4 Expenses for Laboratory Animals

None.

4.1.2.5 Other Costs

None.

4.1.2.6 Project-related publication expenses

	Vollmer	Schmid
Publications in open access journals	750 € per year	750 € per year
Total	**2.250 €**	**2.250 €**

These funds will be used for color figures and open access costs.

5 Project requirements

5.1 Employment status information

Prof Dr. Doris Vollmer is a group leader in the department "Physics at interfaces" (Prof. Hans-Jürgen Butt) at the Max Planck Institute for Polymer Research, Mainz. She has a permanent position.

Prof. Friederike Schmid is a professor for theoretical physics at the University of Mainz. She has a permanent position.

Both will jointly coordinate the project, organize regular meetings, carry out literature research, perform analytical calculations (PI Schmid), and take responsibility of publication and writing. PI Vollmer will take over the main responsibility in the supervision of the experimental PhD student and PI Schmid of the theoretical tandem PhD student.

5.2 First-time proposal data

Not applicable.

5.3 Composition of the project group

Permanent staff:

Dr. Anke Kaltbeitzel, MPI for Polymer Research, stuff scientist
is an expert on confocal microscopy. She will contribute her expertise in laser scanning confocal microscopy and image analysis.

Staff employed from third party funding:

Abhinav Naga, PhD student, EU funded (No 722497)
will contribute his expertise in laser scanning confocal microscopy and image analysis. He is investigating slippery lubricant infused micropillar arrays under flow.

Dr. Maria D'Acunzi, Postdoctoral researcher, EU funded (No 722497)
is going to synthesize polymer gels and brushes.

Dr. Sriteja Mantha, Postdoctoral researcher, DFG funded (SFB TRR 146)
develops multiscale modeling methods for polymeric systems, will contribute his expertise on coarse-grained polymer models.

5.4 Cooperation with other researchers

5.4.1 Researchers with whom you have agreed to cooperate on this project

Speck/Virnau & Marcus Müller: On the side of molecular simulations, we will also collaborate with the SPP projects of Speck/Virnau and with the projects of Müller/Tanaka. Specifically, Müller/Tanaka plan to study the interactions of switchable multicomponent polymer brushes with vesicles. The methods in both projects are similar and similar problems will have to be solved. Therefore, we have agreed on a close collaboration in particular with Marcus Müller, and our students will visit each other to learn from each other and possibly use each other's methods.

Butt/Berger: As detailed in the work programme (work package WP T3), we plan to collaborate specifically with the SPP project by Berger/Butt in the simulation part of this work. As one part of work package WP T3, we plan to carry out simulations of the infiltration dynamics of fluid particles (good solvent) in brushes which can be compared with experiments. Furthermore, the measurements and analysis of the adhesion and friction forces will be done in close cooperation with H.-J. Butt and R. Berger.

Uwe Thiele: We plan to collaborate with the SPP project of Thiele regarding the connection of our simulations and experiments with a mesoscopic continuum model, as explained in work packages WP T4 and WP T5.

Kirsten Hardt: Confocal microscopy is too slow to study fast wetting dynamics on thin polymer films and brushed. Here we plan to cooperate with the SPP projects of K. Hardt. She uses digital holographic and interference microscopy (DHM) to image fast motion of spreading drops on thin polymer brushes and films. Our students will visit each other to learn and possibly use each other's methods.

Jiaxi Cui & Böker/Reinicke: Both are preparing switchable lubricant infused surfaces. We plan to exchange samples to investigate the consequences of switching on the deformation of the wetting ridge of moving drops.

Bonn/Backus: Apply SFG to characterize the properties of brushes in presence and absence of a liquid drop.

Müller/Hasse/Langenbach/Antonyuk: Preparing super-liquid repellent dosage needles and testing the wetting properties of drops under low amplitude vibrations.

Organization: As member of the coordination board, **PI Vollmer** aims to foster cooperation within this project by stimulating and supporting joint use of equipment and the exchange of personnel between groups. This includes organizing a list with expensive or unique equipment that is available within this SPP and can be used by other researchers. We are happy to offer our expertise in measuring and quantifying contact angles of resting and moving drops by laser scanning confocal microscopy to the other projects within this SPP

5.4.2 Researchers with whom you have collaborated scientifically within the past three years

Doris Vollmer:

Günter Auernhammer, Leibnitz Institute (Germany); Kookheon Char, Seoul National University (Korea); Xu Deng, Univ. Chengdu (China); Detlef Lohse, Twente University (The Netherlands); Chiara Neto, Univ. Syndney (Australia); Periklis Papadopoulos, Univ. Ioannina (Greece); David Quéré, ESPCI Paris (France); Jacco Snoijer, Twente University (The Netherlands); Zuankai Wang, City University of Hong Kong, China; Tobias Weidner, Aarhus University (Denmark); Julia Yeomans, Univ. Oxford (Great Britain).

Friederike Schmid:

Kookheon Char, Seoul National University (Korea); Klaus Drese, Hochschule Coburg (Germany); Jurgen Horbach, Düsseldorf University (Germany); Toshihiro Kawakatsu, Tohoku University (Japan); Leonid Klushin, Am. Univ. of Beirut (Lebanon); Michael Maskos, IMM Mainz (Germany); Giuseppe Milano, Yamagata University (Japan); Andrey Milchev, Bulgarian Academy of Sciences (Bulgaria); Shuanhu Qi, Beihang University (China); Richard Register, Princeton (USA); Agur Sevink, Leiden University (The Netherlands); Alexander Skvortsov, Institute of Molecular Compounds, St. Petersburg (Russia); Daniel Vega, Bahia Blanca (Argentina); Olga Vinogradova, Lomonosov State University (Russia); Zhen-Gang Wang, Caltech (USA); Dadong Yan, Beijing Normal University (China); Jiajia Zhou, Beihang University (China)

5.5 Scientific equipment

- Laboratories for the synthesis and characterization of polymer brushes and gels
- Inverted laser scanning confocal microscope, Leica TCS SP8
- Inverted white light microscope, Olympus IX83, with high speed cameras, Photron, Fastcam Mini UX
- Homebuilt confocal microscope with AFM head, MFP3D, Asylum
- Two high speed cameras, Photron, Fastcam Mini UX
- Contact angle measurement device, DataPhysics, OCA35
- Tensiometer, Dataphysics, DCAT11
- Scanning electron microscopy, Zeiss LEO 1530 Gemini SEM
- X-ray photoelectron spectrometer, Kratos Axis Ultra
- Imaging Ellipsometer, EP3 Nanofilm Nanofilm surface analysis

Large scale simulations will be carried out on the high-performance computing cluster of the university of Mainz ``Mogon'' (35520 AMD Interlagos cores at 2,1 Ghz) and "Mogon 2", which provides access to around 200 GPUs (mostly GTX 1080Ti).

5.6 Project-relevant cooperation with commercial enterprises

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6 Additional information

We have not requested funding for this project from any other sources. In the event that we submit such a request, we will inform the Deutsche Forschungsgemeinschaft immediately. In submitting a proposal for a research grant to the DFG, we agree to adhere to the DFG's rules of good scientific practice. In preparing the proposal, we have adhered to the guidelines for publication lists and bibliographies. The ombudsperson of the Deutsche Forschungsgemeinschaft at the University of Mainz and the general assembly of the Max Planck Society have been informed about the application.

Vollmer — F. Schmid

(Doris Vollmer) — (Friederike Schmid)