

## B. Project description

# Dynamic advancing and receding contact angles on adaptive surfaces

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## Summary

Surface adaptation is predicted to be one cause for contact angle hysteresis (Langmuir 2018, 34, 11292). The aim of our project is to experimentally verify this prediction. We plan to measure the kinetics of the adaptation process for thin polymer films. With the kinetics and our adaption theory, we can calculate the dynamic advancing and receding contact angles. Finally, the predicted dynamic contact angles will be compared with the velocity-dependent contact angles of moving drops measured on the same polymer films. To measure advancing and receding contact angle versus speed of the contact line we will use our home built Drop Adhesion Force Instrument and we plan to build up a tilted plane setup to monitor the dynamic contact angles at velocities up to 1 m/s. In case we can validate our theory, the measurement of the velocity dependence of the dynamic contact angles will allow us calculating the adaption kinetics of surfaces. If successful, we will have a relatively universal framework for quantitative modeling of dynamic contact angles and contact angle hysteresis caused by adaptation processes.

## 1 State of the art and preliminary work

### State of the art

For ideal surfaces, which are inert, rigid, smooth and homogeneous, a quantitative description of wetting dynamics of liquids is still a challenge<sup>1, 2, 3</sup> because different length and times scales are involved.<sup>4</sup> Contact angles depend on the speed of the three-phase contact line  $v$ , here briefly called contact line. The dynamic advancing contact angle  $\Theta_a(v)$  increases with wetting speed until it reaches  $180^\circ$  and air is entrapped. The dynamic receding contact angle  $\Theta_r(v)$  decreases with dewetting speed until it becomes zero and film formation sets in. Often, velocity dependent contact angles are described by the molecular kinetic theory (MKT) or hydrodynamic theory.<sup>1, 5, 6, 7, 8, 9</sup> MKT is based on thermally activated adsorption/desorption processes at an advancing/receding liquid front. Hydrodynamic and MKT theory describe velocity dependent contact angles. For many practical cases, however, in particular for low velocities, hydrodynamic theory does not describe measured  $\Theta_{a/r}$ -vs- $v$  curves. Often, the MKT leads to fitting parameters, which are not plausible with respect to the underlying physical process.

The challenge becomes even bigger for adaptive surfaces. Adaptive surfaces change their physico-chemical properties due to the presence of a liquid or its vapor. Examples of adaptive processes occurring on common or deliberately synthesized surfaces are:

- (i) Polymer surfaces often reconstruct due to a reorientation of side groups or a selective exposure of specific segments.<sup>10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20</sup>

- (ii) Liquid can diffuse into a polymer<sup>21, 22</sup>; a well-known example is water diffusing into polydimethylsiloxane (PDMS).<sup>23, 24</sup> Polymer swell in solvents.<sup>25, 26, 27, 28</sup>
- (iii) Mixed polymer brushes or blockcopolymers expose the more compatible component to the fluid.<sup>29, 30, 31, 32, 33, 34, 35, 36, 37, 38</sup>
- (iv) Some organic monolayers change their structure depending on the specific liquid, temperature or pH.<sup>39, 40, 41, 42, 43</sup>
- (v) As soon as a surface is exposed to air, water and airborne hydrocarbons adsorb; when such a surface is wetted, the adsorbed layer remains at the interface and can change its structure or it is replaced.
- (vi) In liquids, molecules adapt to the presence of the solid and change their structure close to the interface. The ordering of molecules changes according to whether they are in contact with a specific solid or air. That this molecular structure may change the dynamic contact angles was already pointed out by Hansen & Miotto and Elliot & Riddiford.<sup>44, 45</sup>
- (vii) If the liquid contains surfactants or other solutes, these may adsorb to the interfaces.<sup>8, 46, 47, 48</sup> In polar liquid, usually electric double-layers will form.

Here, we also consider the vice-versa process that is the liquid adapts to the presence of the interface. This interface can be a solid surface or the surrounding air. The dynamic advancing and receding contact angles as well as contact angle hysteresis change upon the above-mentioned adaptive processes. Therefore, we recently proposed a theory to describe wetting of adaptive surfaces.<sup>49</sup>

Our theory quantitatively predicts the velocity dependence of the advancing and receding contact angles based on a specific adaptation kinetics. The approach provides a quantitative framework to describe the wetting of surfaces that are deliberately made adaptive. In addition, we anticipate that in many common wetting situations, adaptation process lead to the observed velocity dependence of contact angles. In these cases, contact angle measurements provide a means to study the kinetics of adaptation.

## Preliminary work

**Theory.** The model is general and does not refer to a particular adaptation process. The aim of the proposed theoretical model is to provide a quantitative description of adaptive wetting and to link changes in contact angles to microscopic adaptation processes. By introducing exponentially relaxing interfacial energies and applying Young's equation locally, we predict a change of advancing  $\Theta_a$  and receding contact angles  $\Theta_r$  depending on the velocity of the contact line  $v$ :

$$\cos \Theta_a = \cos \Theta^\infty - \frac{\Delta\gamma_{SL}}{\gamma_L^\infty} e^{-l/v\tau_{SL}} \quad (1)$$

$$\cos \Theta_r = \cos \Theta^\infty + \frac{\Delta\gamma_S}{\gamma_L^\infty} e^{-l/v\tau_S} \quad (2)$$

$\Theta^\infty$  is the contact angle in thermodynamic equilibrium (that is for  $v \rightarrow 0$ ),  $\gamma_L^\infty$  is the surface tension of the liquid,  $\Delta\gamma_{SL}$  quantifies the change in solid/liquid interfacial energy due to adaption, and  $\Delta\gamma_S$  quantifies the change in solid surface energy due to adaption after the surface becomes dry (Fig. 1A). The relaxation times for the adaption processes of the solid surface after it gets into contact with the liquid and falls dry again are  $\tau_{SL}$  and  $\tau_S$ , respectively. We call  $l$  "peripheral thickness". The peripheral thickness  $l$  is the width of contact region, which influences the contact angle.

Even for perfectly homogeneous and smooth surfaces, a dynamic contact angle hysteresis will be obtained for adaptive processes. At the advancing side the contact angle increases (Fig. 1B), at the receding side it decreases with increasing velocity of the contact line (Fig. 1C). The relevant parameters are the ratios of the peripheral thickness,  $l$ , and the relaxation times  $\tau_{SL}$  and  $\tau_s$ . We define  $v_{SL} \equiv l/\tau_{SL}$  as the “adaptation velocities” at the wetting and  $v_s \equiv l/\tau_s$  at the dewetting side, respectively.

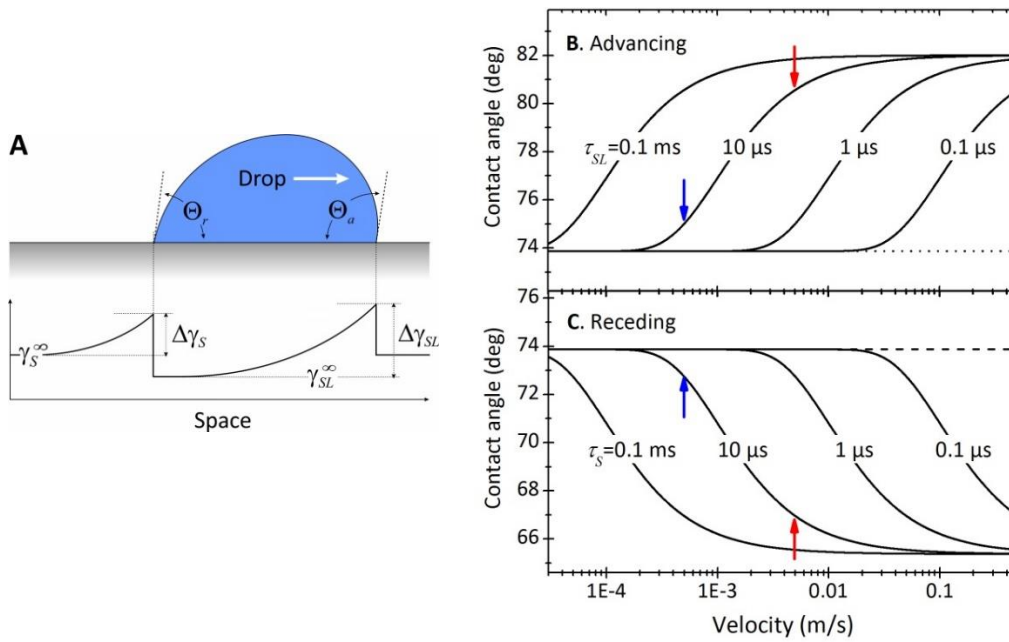
These changes in the dynamic contact angles described by Eqs. (1) and (2) are in addition to other processes such as hydrodynamics and adsorption desorption as described by MKT.

Our model predicts that energy is dissipated at the advancing and receding contact lines:

$$p_a = v\Delta\gamma_{SL}e^{-v_{SL}/v} \text{ and } p_r = v\Delta\gamma_s e^{-v_s/v}, \quad (3)$$

Here,  $p_a$  and  $p_r$  are in units of energy per time and unit length of contact line.

One of the critical parameters in our model is the peripheral thickness,  $l$ . Within our proposal, we want to study adaptive processes in polymer brush systems that can (selectively) swell. The aim is to calculate the peripheral thickness and attribute this value to the dynamics of the reorganization of polymers at different interfaces.

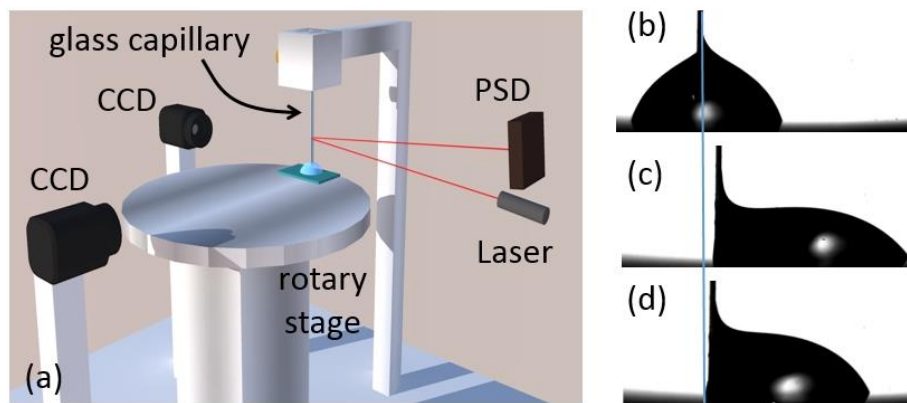


**Figure 1.** (A) Schematic of a moving drop. For a drop moving over an adaptive surface the change in interfacial energy leads to a position-dependent interfacial tension. (B) Dynamic advancing and (C) receding contact angles for water ( $\gamma_L^\infty=0.072$  N/m) versus velocity of the contact line for different relaxation times. Contact angles were calculated with Eqs. (1) and (2) inserting  $\gamma_s^\infty=0.06$  N/m,  $\gamma_{SL}^\infty=0.04$  N/m, and  $\Delta\gamma_s=\Delta\gamma_{SL}=0.01$  N/m. Based on the typical range of surface forces and mechanical stress applied by the contact line to the solid<sup>50, 51</sup> we speculate that  $l=10$  nm is of the right order of magnitude. For blue and red arrows see work programme, WP3.

One way to investigate adaptive processes is to study the lateral adhesion force of sliding drops. Sliding is opposed by capillary forces. They are associated with a contact angle difference between the rear and the front of the drop. The lateral adhesion force  $F_{LA}$  is given by:<sup>52, 53, 54, 55, 56, 57</sup>

$$F_{LA} = kL\gamma_L^\infty \cdot (\cos \Theta_r - \cos \Theta_a). \quad (4)$$

Here,  $k$  is a dimensionless factor and accounts for the precise shape of the solid–liquid–air three-phase contact line of the drop.  $L$  is the width of the drop. In order to study lateral adhesion forces, we have developed a **Drop Adhesion Force Instrument (DAFI)**.<sup>58, 59</sup> The DAFI allows us to measure lateral adhesion forces while the drop is sliding at different velocities from 1  $\mu\text{m/s}$  to 50  $\text{mm/s}$  (Fig. 2a). We measure the lateral adhesion force between a drop of liquid and a solid substrate, by positioning a capillary in the center of a drop (Fig. 2b). The substrate with the drop is moved sideways against the capillary at a constant velocity. When the capillary reaches the edge of the drop, it sticks to the drop. Consequently, the motion of the substrate is accompanied by a deformation of the drop as well as a deflection of the capillary. Initially, the drop remains pinned to the substrate. Once the capillary exerts a certain critical force, the drop overcomes the lateral adhesion to the substrate (Fig. 2c). At this point the front and rear side of the drop start moving. The deflection  $\delta$  of the capillary is measured by recording the position of a reflected laser beam with a position-sensitive detector (PSD). Then, the lateral adhesion force acting on the drop can be calculated by  $F_{LA} = \kappa\delta$ , where  $\kappa$  is the spring constant of the capillary. Simultaneously, the drop's shape is monitored by two cameras, which are synchronized with the force measurement. In this way the lateral adhesion force can be correlated with the contact angles of the sliding drop at constant velocity (Fig. 2d).



**Figure 2.** (a) Schematic drawing of DAFI. Within this setup we can use linear as well as rotating stages. (b) Static drop shape when the stage is not moving. (c) The stage moves to the right side and the capillary deflects. Accordingly, the drop deforms. (d) Drop shape and deflection of the capillary when the stage moves at constant velocity in steady state. The vertical blue line indicates the position of the non-bent capillary.

By using DAFI we can investigate the development of forces acting on the drop when the contact angles change during the adaption process. In particular, we can vary the speed of the moving stages to match the time scales of the adaption processes.

In order to enable measurements of drop velocity  $>50 \text{ mm/s}$ , we plan to perform **tilted plane** experiments. With respect to the tilted plane setup, we have experience with observing drops at high speeds, e.g. in drop impact,<sup>60, 61, 62</sup> and automatic image analysis.

**Polymer brushes.** In our group we have experience in surface-initiated atom-transfer radical polymerization (ATRP) starting from e.g. bromosilanes on silicon oxide. We reach brush thicknesses of typically 30-50 nm (dry state). Brush thickness can be measured by ellipsometry in the dry state. Polydimethylsiloxane layers will be made by grafting from with a recently developed method on metal-oxid photocatalysts.<sup>63</sup>

## 1.1 List of project related publications

1. Bumbu, G. G., M. Wolkenhauer, G. Kircher, J.S. Gutmann & R. Berger: Micromechanical cantilever technique: A tool for investigating the swelling of polymer brushes. *Langmuir* **2007**, 23, 2203-2207. [49 cit.](#)
2. Ochsmann, J. W.; S. Lenz, P. Lellig, S.G.J. Emmerling, A.A. Golriz, P. Reichert, J.C. You, J. Perlich, S.V. Roth, R. Berger & J.S. Gutmann: Stress-structure correlation in PS-PMMA mixed polymer brushes. *Macromolecules* **2012**, 45, 3129-3136. [11 cit.](#)
3. Pilat, D.W., P. Papadopoulos, D. Schäffel, D. Vollmer, R. Berger & H.-J. Butt: Dynamic measurement of the force required for moving a liquid drop on a solid surface. *Langmuir* **2012**, 28, 16812-16820. [34 cit.](#)
4. Schellenberger, F., N. Encinas, D. Vollmer, H.-J. Butt: How water advances on superhydrophobic surfaces. *Phys. Rev. Lett.* **2016**, 116, 096101. Highlighted by: P. Ball, *Nature Mater.* **2016**, 15, 376; L. Courbin, *Physics* **2016**, 29, 23. [54 cit.](#)
5. Butt, H.-J., N. Gao, P. Papadopoulos, W. Steffen, M. Kappl & R. Berger: Energy dissipation of moving drops on superhydrophobic and superoleophobic surfaces. *Langmuir* **2017**, 33, 107-116. [12 cit.](#)
6. Zhou, H., Ch. Xue, P. Weis, Y. Suzuki, S. Huang, K. Koynov, G.K. Auernhammer, R. Berger, H.-J. Butt & S. Wu: Photoswitching of glass transition temperatures of azobenzene-containing polymers induces reversible solid-to-liquid transitions. *Nature Chemistry* **2017**, 9, 145-151. [65 cit.](#)
7. Wooh, S., N. Encinas García, D. Vollmer & H.-J. Butt: Stable hydrophobic metal-oxide photocatalysts via grafting polydimethylsiloxane brush. *Adv. Mater.* **2017**, 29, 1604637. [9 cit.](#)
8. Tress, M., S. Karpitschka, P. Papadopoulos, J.H. Snoeijer, D. Vollmer & Hans-Jürgen Butt: Shape of a sessile drop on a flat surface covered with a liquid film. *Soft Matter* **2017**, 13, 3760-3767. [1 cit.](#)
9. Gao, N., F. Geyer, D.W. Pilat, S. Wooh, D. Vollmer, H.-J. Butt & R. Berger: How drops start sliding over solid surfaces. *Nature Physics* **2018**, 14, 191-196. [2 cit.](#)
10. Butt, H.-J., R. Berger, W. Steffen, D. Vollmer, S.A.L. Weber: Adaptive wetting – adaptation in wetting. *Langmuir* **2018**, 34, 11292-11304.

Number of citations are from the Web of Science Core Collection.

## 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

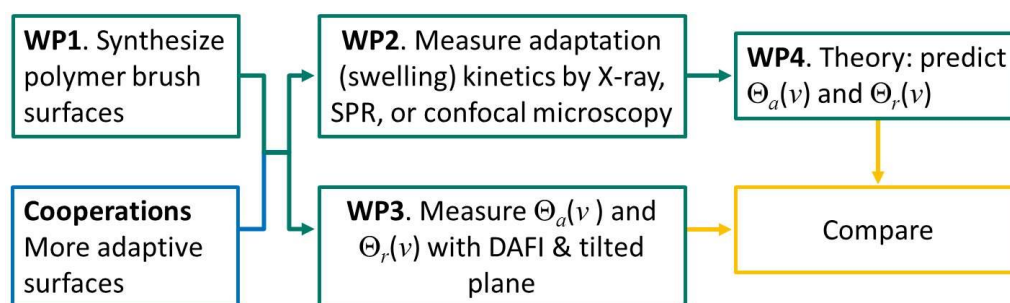
**The primary objective of the project is to test the above depicted theory of adaptive wetting.** Therefore, we, first, need to measure the relaxation times of specific adaptation processes. How fast does the surface structure change when it is exposed to the liquid or, vice versa, when it becomes dry again? Second, based on the theory we calculate how the advancing  $\Theta_a$  and receding contact angles  $\Theta_r$  depend on the velocity  $v$  of the moving contact line. Third, in order to verify the theory, we need to measure the advancing and receding contact angles of the moving drop at different velocity. Fourth, in case the theory describes dynamic contact angles

adequately, the width of contact region, which influences the contact angle (peripheral thickness) can be calculated. This peripheral thickness needs to be interpreted and compared to the range of surface forces or surface stresses in the solid at the contact line.

The secondary objective is to establish adaptation of surfaces as one source for contact angle hysteresis and velocity dependence of dynamic contact angles, in particular at slow velocity. To reach this aim **we will pursue various cooperations within this Priority Programme:** Dynamic wetting experiments with different concepts of adaptive surfaces will be performed with DAFI or a tilted plane setup. Furthermore, we will facilitate training of early career researchers for both setups. Those experiments will allow quantifying adaptation kinetics of different kinds of surfaces and processes.

### 2.3 Work programme including proposed research methods

The above objectives will be can be reached by the following work program, which is divided into four workpackages (Fig. 3).



**Figure 3.** Schematic of how we intend to proceed. The blue box indicates major cooperations within the SPP with respect to a wider spectrum of adaptive surfaces.

#### WP1 Prepare polymer brush surfaces (6 person months)

We focus on silicon oxide surfaces coated with polymer brushes. By varying the chemical nature of the polymer, its compatibility with the liquid and the thickness of the brush, the speed and extend of polymer swelling will be varied.

**Surfaces.** We plan to use surface-initiated atom-transfer radical polymerization (ATRP) which is well established at the MPIP.<sup>64, 65</sup> Starting with bromosilanes we intend to synthesize thin polymer brush films of poly(N-isopropylacrylamide (PNIPAM) and poly(2-hydroxyethyl methacrylate) (PHEMA).<sup>1</sup> In addition, well-defined high molecular weight PNIPAM films will be provided by the Fery-group from IPF in Dresden within the SPP.<sup>68</sup> PNIPAM and PHEMA swell in polar liquids. For non-polar liquids, we plan to synthesize polymethylmethacrylat (PMMA) and polystyrene (PS) brush layers. By varying the reaction time and the concentration of initiator in bulk solution we already synthesized brush with a thickness of up to  $\approx 50$  nm. There are reports in the literature of making even thicker films of polyacrylates by ATRP (e.g. 66).

<sup>1</sup> PNIPAM brush films change from hydrophilic to more hydrophobic upon increasing their temperature above 32°C. There are numerous reports in the literature that also their contact angle with water changes at this temperature. However, many papers mention that measuring contact angles on PNIPAM above 32°C is problematic. For example, Gilcreest mentions "...that the angle at which the droplet slips is not reproducible, leading to a large spread in the angles measured".<sup>67</sup> Therefore, PNIPAM will not be our preferred choice and therefore we consider mainly other polymers.

Polydimethylsiloxane (PDMS) brushes will be made by a recently developed method on  $\text{TiO}_2$ .<sup>63</sup> This is accomplished by immersing the sample in PDMS and simply shine UV-A light for 10 min. By using PDMS with different molar mass, we vary the polymer film thickness between 2 – 10 nm.

Silicon oxide can be coated with a thin PDMS film by immersion in the melt and heating to 60°C for few hours.<sup>69, 70</sup>

Furthermore, we plan to fabricate adapting surfaces by synthesis of two-component polymer brush layers. Here the two polymers need to be sensitive to selective solvents. A widely used two-component polymer system is polystyrene (PS) and poly(2-vinylpyridine) (PVP).<sup>71</sup> We will focus on this system as the advancing contact angles of a PS-PVP binary brush layer can be switched from 90° to 36° upon exposure to water (pH 2.5). In particular, we will use the pH value of the water drop to adjust the contact angle. Minko et al. reported that the switching time can be tuned by the fraction and grafting density of the two polymers. Switching times from minutes to hours (large fraction of the hydrophobic polymer) were reported. In a similar way, we will vary composition and grafting density to realize different relaxing interfacial energies.

Finding a non-adaptive reference surface is not trivial. Taking the polymer brush which does not swell in a liquid may not be sufficient. Even small amounts of liquid diffusing into the polymer may change the surface energy. One example is PDMS. Although it is hydrophobic, up to 30 mM of water diffuse into PDMS. For this reason, we intend to measure dynamic contact angles of liquids on seemingly non-swelling polymer brushes such as water/PDMS. In addition, we will test wetting of silicon oxide hydrophobized with silane monolayers (trichloro(octyl)silane, trichloro(1H,1H,2H,2H-perfluorooctyl)silane, 1H,1H,2H,2H-perfluorodecyltrichlorosilane).

**Liquids.** We need suitable combinations of polymers and liquids. On one hand, the liquid should enter the brush and partially mix with the polymer so that the interfacial energy of the surface changes. On the other hand, it should not lead to a high degree of swelling. Strong swelling changes the topography significantly and softens the surface. On soft surfaces, stick-slip motion can occur<sup>72</sup> and obscure the view on the adaption process. We prefer liquids with low vapor pressure to avoid evaporation and avoid temperature induced Marangoni effects. Liquids should not have surface tensions above 40 mN/m to have contact angles significantly above zero. We plan to try the following liquids in addition to water:

Liquid	Surface tension (mN/m)	Vapor pressure (Pa)	Viscosity (mPa s)
Water	72.0	3169	0.89
Glycerol	63.5 (20)	<130	1469 (20)
Glycerol with 10% water	64.5 (20)	<130	219 (20)
Ethylene glycol ( $\text{C}_2\text{H}_6(\text{OH})_2$ )	48.0	7.9 (20)	16.1
Diiodomethane ( $\text{CH}_2\text{I}_2$ )	49.9	172	2.6
Formamide ( $\text{CHONH}_2$ )	57.0	<130	3.3
Emim <sup>+</sup> NTf <sub>2</sub> <sup>-</sup>	35.8 (20)	<100	34
$\text{C}_{11}\text{H}_{17}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$	34.6	<100	98

**Table 1:** Liquids planned to use for dynamic wetting studies and their properties at 25°C (if not indicated otherwise). Glycerol at ~40% relative humidity (typical in our laboratory) takes up 10% water.<sup>73</sup> Emim<sup>+</sup>NTf<sub>2</sub><sup>-</sup>: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.<sup>74, 75</sup>



As ionic liquids we intend to use commercial 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Sigma, purity 99%) or 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ( $C_{11}H_{17}F_6N_3O_4S_2$ ), since we used this liquid before in wetting studies.<sup>59, 74</sup>

## WP2 Measure swelling kinetics of polymer brushes (6 person months)

We will focus on polymer brush systems in the first 36 months of the SPP because the penetration of liquid and the resulting swelling can be quantified with existing methods at MPIP. In WP2 we will determine the characteristic times for an initially dry polymer layer to swell after it has been brought into contact with a liquid. In addition, we plan to measure the reverse process: How long does it take to dry again? Processes are most likely limited by diffusion of liquid molecules in the polymer layer. The associated relaxation time is connected to the diffusion constant  $D$  by

$$\tau_d \approx h^2/D \quad (5)$$

Here,  $h$  is the thickness of the polymer layer. Thus, by changing the layer thickness, we can sensitively adjust the relaxation time.

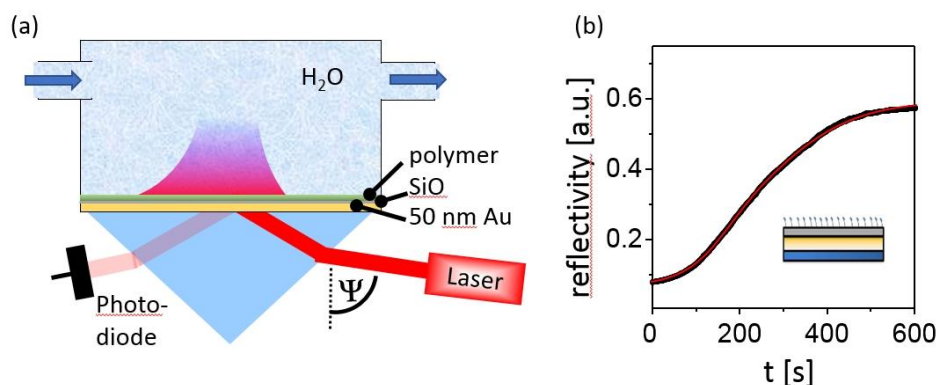
We found three examples for diffusion coefficient of liquids in polymers (at low concentration of liquid molecules): Water diffusing in a plasma-polymerized polynorbornene film gives  $D = 1.4 \times 10^{-13} \text{ m}^2/\text{s}$ <sup>22</sup> or in polyamides results in  $D = 4.6 \times 10^{-13} \text{ m}^2/\text{s}$ <sup>76</sup> and toluene diffusing in crosslinked polystyrene with  $D \approx 4 \times 10^{-12} \text{ m}^2/\text{s}$ .<sup>25</sup> With  $h = 40 \text{ nm}$  we get relaxation times of 0.4 – 11 ms.

We plan to apply three methods to measure the kinetics of polymer swelling:

**X-ray reflectometry (XRR)** will be employed to study the swelling of polymer brushes in the range between 2 - 100 nm thickness at buried solid/liquid interfaces. XRR provides information on the film thickness, density, and surface roughness. Mo  $K\alpha$  radiation (17.5 keV) allows penetrating several millimeters of water (absorption length 6 mm) providing access to deeply buried solid/liquid interfaces. Experiments on the adsorption and **swelling dynamics with resolution on the 10 ms time scale will be performed using synchrotron radiation** (e.g. at beamline P08, PETRA III, DESY, Hamburg). These experiments will be carried out together with Jun.-Prof. Markus Mezger, an expert in X-ray diffraction at interfaces and a member of our group.

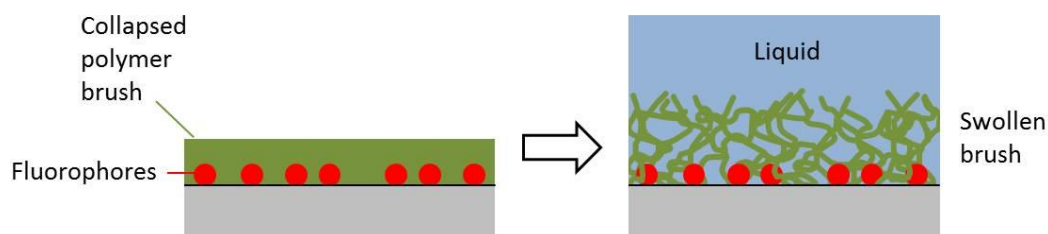
**Surface plasmon resonance (SPR).** Dynamic SPR allows monitoring the swelling kinetics of polymer brushes upon exposure to different liquids or air in situ. The swelling of the polymer brush layer leads to a change in refractive index and thickness of the polymer brush and thus to a shift of the plasmon resonance as observable. In principle, the swelling kinetics can be monitored with a time resolution down to 10 ns, depending on the proper choice of amplifier, AD converter and detection scheme.<sup>77, 78</sup> **With the home-build setup available at MPIP we can realize a time resolution of 10  $\mu\text{s}$ .** Here we will use a closed liquid cell where we push in the liquid at high speed (Fig. 4). This setup will be operated in cooperation with Prof. Werner Steffen at the MPIP, who is a member of our group. In order to study grafted polymer films we sputter a 10 nm thick layer of  $\text{SiO}_x$  onto the gold. This influences the surface plasmon polariton and thus the experiment only marginally. Alternatively, a 500 to 2000 nm thick  $\text{SiO}_x$  layer can be sputtered on gold. Then we will utilize waveguides excited in the  $\text{SiO}_x$  and their evanescent field into the ad-layer above for the same experiment to track swelling kinetics.





**Figure 4.** (a) SPR in Kretschmann configuration. The polymer is grafted onto a thin  $\text{SiO}_x$  layer. (b) Build-up of CTAB layer on PMMA having a final thickness of 2.5 nm.

**Confocal microscopy.** Many fluorophores change their fluorescent properties depending on the polarity or viscosity of the environment<sup>79, 80</sup>. Therefore, they can be used as sensors to detect the presence of liquid around them. We intend to bind fluorophores to silicon oxide surfaces (Fig. 5). Then a polymer brush will be formed. The conditions are chosen such that the grafting density of the polymers is much higher than the density of fluorophores. The fluorophores will therefore be positioned at the bottom of the brush, close to the solid substrate. When a liquid is placed on top of the brush the fluorophores notice when the liquid has reached the bottom of the brush. To detect the fluorescent properties we will place the samples onto a laser scanning confocal microscope or a normal fluorescent microscope. We plan to measure changes in fluorescence intensity rather than measuring changes of lifetimes, because sub millisecond time resolution can be achieved. As fluorophores we consider Prodan, Laurdan or borondipyrromethene (Bodipy) derivatives. Via a silane linker we intend to attach them to a glass substrate. These experiments will be carried out together with Dr. Kaloian Koynov and Prof. Dr. Vollmer, our experts in the group for confocal microscopy and fluorescence correlation spectroscopy.



**Figure 5.** Schematic of how we propose to measure the diffusion time with fluorescent probes at the solid/polymer interface.

In the initial phase and in close cooperation with Markus Mezger, Werner Steffen, Kaloian Koynov, Doris Vollmer we will first explore all three methods (3 person months). Once we found out which method is most suitable and promising we concentrate on this method. In this method the PhD student should become an expert and conduct the measurements of adaptation times (3 person months).

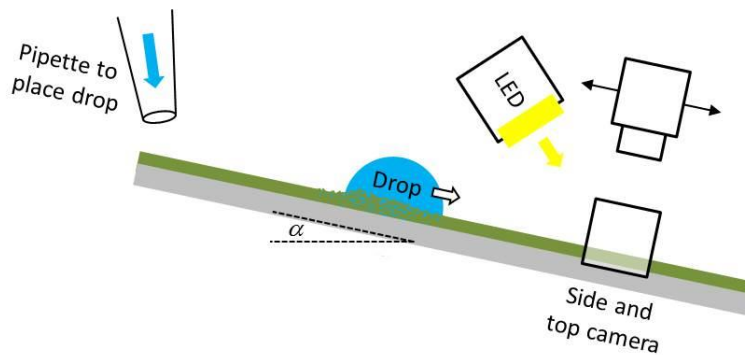
### WP3 Measure advancing and receding contact angles versus velocity (18 person months)

For sliding velocities up to  $\approx 50$  mm/s we apply our home-built DAFI to measure advancing and receding contact angles versus velocity. DAFI allows a precisely controlled movement of the drop and a simultaneous measurement of the lateral force. More explicitly, with DAFI we can move

drops over surfaces at velocity being slower or faster than the relaxation times for the adaption processes (Fig. 1A). With the example shown in figure 1B, C and a relaxation time of 10  $\mu$ s, we obtain an advancing contact angle of 75° and receding contact angle of 73° at a velocity of 50  $\mu$ m/s (blue arrows). For a speed of 0.5 mm/s angles of 81° and 67° are obtained (red arrows). Thus according to Eq. (4) and assuming a constant width of the contact area  $L$  the force would change by a factor of

$$\frac{F_{LA}(0.5\text{mm/s})}{F_{LA}(50\mu\text{m/s})} \approx 7.$$

For velocities 50 mm/s up to 1000 mm/s, we plan to construct a tilting stage (Fig. 6), following the design of.<sup>81</sup> Drops of typically 4 - 20  $\mu$ L size are deposited by a micropipette on a horizontal surface. The stage will be able to support samples of up to 20 cm length. It is then slowly tilted by a low-vibration motor. The angle  $\alpha$  at which the drop starts to move down the incline is recorded. Then the contact angles and the contact area are measured by high speed cameras from the side and the top. If the contact angles are above 90° we will try to use transparent substrates and image from below.



**Figure 6:** Schematic of a stage to tilt the planar surface and image a sliding drop. Technically, the cameras are rigidly fixed to the tilting stage to ensure that the optical axis of the camera does not change. The sample will be illuminated by a light-emitting diode.

By shifting the camera at defined distance from the point of placement we will be able to probe different drop velocities. On superhydrophobic surfaces we expect accelerations up to 2  $\text{m/s}^2$ .<sup>81</sup> For sliding distances of 0.2 m the velocity can be up to 1 m/s. To be able to resolve contact angles up to such a speed we will use cameras with frame rate of 10000 fps which is available at MPIP (Photron - Mini UX). Within one frame the drop would move a distance of 10  $\mu$ m. Contact angle will be automatically extracted from video images by a home-written software in ImageJ.

The DAFI and tilted plane setup will be made available to other projects within the SPP. On the one hand, we can perform measurements on samples which will be provided by cooperation partners. On the other hand, we will engage in training of early career researchers in applying both methods:

- In cooperation with Dr. Alla Synytska (Leibniz-Institute for Polymerforschung Dresden e.V.) we will study the wetting properties of switchable anisotropic surfaces realized by freely rotating Janus-particles. We will investigate the development of forces acting on water drops during the adaption process. This cooperation will lead to a better understanding of the strength of interaction between the surface and water droplet. Furthermore, these results will help Dr. Alla Synytska to develop a theoretical description of adaptive wetting of surfaces made from Janus-particles.

- In cooperation with Dr. Leonid Ionov (University of Bayreuth) we will study switchable surfaces. In particular, the topography, the softness, and the wetting properties of surfaces will be switched based on stimuli-responsive polymers. From these experiments, we will estimate the dynamics and the character (elastic, viscoelastic) of the deformation of surfaces structures.
- In cooperation with the project of Auernhammer/Fery/Uhlmann (Leibniz-Institute for Polymerforschung Dresden e.V.) we will study PNIPAM brushes in contact with ethanol drops. With DAFI measurements will be able to provide information on the shape of the drops in addition to the advancing and receding contact angles.
- In cooperation with the project of Rainer Haag (Freie Universität Berlin) we will measure and analyze the dynamic advancing and receding contact angles of polymer coatings with different morphology from hairy coatings to roughness gradient coatings. These layers will be also modified with light switchable spiropyran photochromic molecules. We will compare the dynamic contact angles before and while light irradiation.
- In cooperation with Ellen Backus (Univ. Wien)/Mischa Bonn (MPI-P), we will study solvent induced restructuring and swelling effects in front of liquid drops by using sum frequency spectroscopy tools.
- In cooperation with Jiaxi Cui (Leibniz-Institut für Neue Materialien) we will perform experiments with the DAFI to study the collision of droplets resting on a different lubrication layers. Videos captured with a high-speed camera should provide details of droplet coalescence. In particular, we aim to understand the role of the apparent contact angle and the lubrication ridge for droplet coalescence.

For setting up the tilted plane and adapting ImageJ software we estimate 6 person months of work. Another 12 person months are estimated for carrying out measurements.

#### **WP4 Compare experimental results with theoretical predictions (6 person months)**

We measure the characteristic time for swelling and drying of the polymer brush and insert the obtained relaxation times  $\tau_{SL}$  and  $\tau_S$  into Eqs. (1) and (2). Then we fit measured contact angles-vs-velocity curves. We expect to obtain values for the peripheral thickness. By using brushes of different thickness, grafting density and compositions the relaxation can be adjusted systematically.

There are, however, three foreseeable problems. First, the diffusion of liquid into the polymer does most likely not follow first order kinetics. Swelling of a polymer brush is a complex process because diffusion, transport of liquid, and deformation of the brush are coupled. Furthermore, the diffusion constant depends on the degree of swelling<sup>26, 82, 83, 84, 85</sup>. Still, often the initial phase of swelling is phenomenologically described by a  $1 - e^{-t/\tau}$  time dependence (e.g. 84, 86). If it turns out that the swelling kinetics deviates significantly from first order kinetics, the theory has to be modified accordingly. Then the exponential functions in Eqs. (1) and (2) need to be replaced by a other kinetic models that will be developed in this work package.

In order to get a clearer picture of the swelling kinetics of polymer brushes in good solvents we will cooperate with the project of Vollmer (MPIP)/Schmid (University of Mainz). Friederike Schmid plans to carry out simulations of the infiltration dynamics of fluid particles (good solvent) in brushes. We will compare the simulated with the measured relaxation times of PMMA or PS brush layers. A more detailed knowledge of swelling kinetics will enable us to refine our kinetic model to describe adaptive surfaces.

Second, even on inert, non-adaptive surfaces one usually observes significant contact angle hysteresis. Since dry polymer brushes are smooth and homogeneous, we do not expect contact

angle hysteresis to exceed 10-20°. In Eq. (1) we insert the static advancing contact angle, in Eq. (2) we insert the static receding contact angle. Static means: The respective contact angle measured just before the contact line starts moving.

Third, advancing and receding contact angles are known to change with velocity due to viscous energy dissipation. We need to separate this hydrodynamic effect from adaptation. Separating adaptation-induced velocity effects from changes caused by other factors will indeed be a major issue. There are several ways to deal with this issue:

- Measure dynamic contact angles with liquids of similar viscosity and contact angle which do not diffuse into the polymer layer.
- Hydrodynamics is usually only significant for capillary numbers ( $Ca = \eta v / \gamma_L^\infty$ , with the viscosity  $\eta$ ) above  $\approx 0.5 - 1.0 \times 10^{-3}$  (e.g. <sup>87</sup>). For lower  $Ca$  it is usually negligible.
- The characteristic dependence of the contact angle on the velocity for hydrodynamics is different from the expected dependence of  $\Theta_a(v)$  and  $\Theta_r(v)$  expected from Eqs (1) and (2). From hydrodynamics we expect<sup>1, 5, 88</sup>

$$\Theta_{a/r}^3(v) = \Theta^{\infty 3} \pm \frac{9\eta v}{\gamma_L^\infty} \ln \frac{L_o}{L_i} \quad (5)$$

Here,  $L_o$  is an outer, macroscopic length scale.  $L_i$  represents an inner, microscopic, cutoff length scale, introduced to remove a singularity in the mathematical description.<sup>6</sup> Thus when plotting  $\Theta_{a/r}^3(v) - \Theta^{\infty 3}$  as straight line is expected (and verified for water<sup>87</sup>).

One long-term vision is to be able to measure relaxation kinetics from dynamic wetting experiments. That is: Measure  $\Theta_a(v)$  and  $\Theta_r(v)$  and determine via Eqs. (1) and (2) the relaxation times correlated with adaptation. If time allows we plan to test, if such a procedure is possible. Therefore, sample with polymer brushes of different thickness are prepared. They will be given to the student without her/him knowing the brush thickness. This way we want to test, if from dynamic wetting experiment a prediction of the brush thickness and the corresponding diffusion time is possible.

We envision to start our project 1.10.2019 and we summarized the personnel and tasks in the following time table.

Task/workpackage	Q4 2019	Q1 2019	Q2 2020	Q3 2020	Q4 2020	Q1 2021	Q2 2021	Q3 2021	Q4 2021	Q1 2022	Q2 2022	Q3 2022
WP1: Synthesis of polymer brush												
WP 1: Synthesis of binary polymer brush												
WP 2: Swelling kinetics												
WP 3: DAFI measurements												
WP 3: tilted plane setup												
WP 4: Comparison with theory and refinement												

**Time-table:** The tasks of the PhD student are outlined in green. The tasks of the Master thesis work in orange.

## 2.4 Data handling

Results will be stored and procedures documented according to DFG guidelines. Data are regularly stored and documented in the lab book. The MPIP provides a central facility to store data for least 10 years at two locations. Data handling is organized by the IT group of the Max Planck Institute for Polymer Research. Lab books are written in German or English and documentation is carried in such a way that data can be clearly correlated with stored files. Results/data of the project are sought to be published in peer-refereed journal, preferably open access journals. The data will be made available upon reasonable request.

## 2.5 Other information

## 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.

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#### **4 Requested modules/funds**

##### **4.1 Funding for Staff**

**1 PhD student** (preferably a physicist or engineer) Such an extensive program would normally require more resources than only one PhD student. Due to the good support by expert group leaders, the availability of major methods and the fact that a lab assistant will help preparing the polymer brushes we believe that one PhD student is able to carry out the planned experiments. At least the PhD student will learn the basic synthetic routes for preparing and analyzing polymer brushes.

E13, 75% for 48.375 € per year, 3 years 145.1250 €

**1 Student helper** (*studentische Hilfskraft*) for 18 months to prepare the polymer brush surfaces. The PhD student will be a physicist or engineer. Her/his skills and the time will not be sufficient to carry out all synthetic work. Therefore, a student helper (physical chemist or chemist) with first knowledge in chemical synthesis is required. This student helper is also guided by Gunnar Kircher, who has experience in synthesizing polymer brushes. Beginning of 2021 we plan to start a Master thesis on synthesis and analysis of binary polymer brushes.

560 €/month for 18 months = 10.080 €.

##### **4.2 Direct project costs**

###### **Consumables: 27.000 €**

This includes costs for parts for the electronic and mechanical shop to build the tilted plane setup, (automatic) micropipettes to generate drops, cables, motors, transmissions, lenses, illumination, etc. As materials we need quartz glass plates, silicon wafers, glass prisms and chemicals and glass ware (special designed Schlenk tubes made by our glass blower) to synthesize and characterize polymer brushes.

###### **Travel expense for SPP related events: 7.840 €**

Advanced school for employed researcher in 1<sup>st</sup> year (5 days): 600 €

SPP workshop 1<sup>st</sup> and 2<sup>nd</sup> year (4 days) for employed researcher and the PIs:  $6 \times 520 \text{ €} = 3.120 \text{ €}$

PhD workshop 2<sup>nd</sup> year (4 days) for employed researcher: 520 €

International conference 3<sup>rd</sup> year (5 days) for employed researcher and PIs:  $3 \times 1.200 \text{ €} = 3.600 \text{ €}$

###### **Publication costs: 2.250 €.**

We estimate 3 publications with a cost of 750 €.

## **Instrumentation: 0 €**

Additional instrumentation such as computers and the high-speed cameras for the tilted plane setup will be covered by our budget provided by the Max Planck Institute for Polymer Research.

## **5 Project requirements**

### **5.1 Employment status information**

Dr. Rüdiger Berger, group leader MPIP, permanently employed

Prof. Dr. Hans-Jürgen Butt, director MPIP, permanently employed

Both will jointly coordinate the project, supervise the PhD student, carry out literature searches and take responsibility of publication and writing. Dr. Berger will focus on the technical aspects (DAFI, setting up the tilted plane). Dr. Butt concentrates more on preparing the sample and comparing experimental results with theory.

### **5.2 First-time proposal data**

Not applicable.

### **5.3 Composition of the project group**

Dr. Rüdiger Berger, group leader at the Max Planck Institute of Polymer Research (MPIP)

Prof. Dr. Hans-Jürgen Butt, director MPIP

Gunnar Kircher, Chemical technician. He has experience in synthesizing polymer brushes by ATRP and will help preparing the samples.

Dr. Kaloian Koynov, group leader MPIP. He is an expert on confocal microscopy and fluorescence correlation spectroscopy.

Prof. Dr. Markus Mezger, Juniorprofessor at the University of Mainz, Physics Department, and group leader at the MPIP. He is an expert on X-ray diffraction at interfaces.

Alexander Saal, PhD student. He is mounting DAFI on an inverted confocal microscope to image the movement of the contact line on a moving drop.

Prof. Dr. Werner Steffen, group leader at the MPIP. He is an expert on light scattering at interfaces and surface plasmon spectroscopy.

### **5.4 Cooperation with other researchers**

**(a) Subject matter:** The proposed theory provides a relatively general framework to describe dynamic wetting of adaptive surfaces. It is therefore applicable to many of the surfaces prepared in this SPP. The theory may help to analyze wetting also for other projects with the SPP. Vice versa, results obtained in other projects are good test cases for the theory. Getting first hand results from diverse samples will help to explore the range of applicability of the theory.

Within the project we will develop techniques to measure advancing and receding contact angles of moving drops over a wide velocity range. These methods (DAFI, tilted plane) will be made available to other projects within the SPP. We have identified several groups submitting a proposal to the SPP who committed cooperation. They will either send samples or send a student for a few weeks to learn and perform dynamic contact angle measurements.

The group of scientists assembled in the DFG priority programme “Wetting of flexible, adaptive and switchable substrates” will be in the worldwide leading forefront of research. We want to be part of this discussion group. With our expertise we believe that we can contribute to the discussion in wetting and advance the knowledge. In particular, young researchers will profit from being exposed to such a discussion.

**(b) Organization:** The PIs plan to contribute to all workshops or advanced schools organized by the SPP. In addition, the PhD student and the Master student will participate at these SPP events. We are welcoming external researchers for a research stay for example they are interested in learning and using the DAFI method for adaptive surfaces.

#### **5.4.1 Researchers with whom you have agreed to cooperate on this project (alphabetic)**

We plan to cooperate with the projects of:

- Auernhammer/Fery/Uhlmann (Leibniz-Institute for Polymerforschung Dresden e.V.): With DAFI measurements will be able to provide information on the shape of the drops in addition to the advancing and receding contact angles.
- In cooperation with Ellen Backus (Univ. Wien)/Mischa Bonn (MPI-P), we will study solvent induced restructuring and swelling effects in front of liquid drops by using sum frequency spectroscopy tools.
- In cooperation with Markus Biesalski and Tobias Meckel (TU Darmstadt) we will study special paper substrates. Here the dynamic contact angles at high velocities will be interesting that we aim to reach with the tilted plane setup.
- Jiaxi Cui (Leibniz-Institut für Neue Materialien) will send a student to us in order to learn using the DAFI. We aim to understand the role of the contact angles and the lubrication ridge for droplet coalescence.
- Rainer Haag (FU Berlin): Dynamic contact angles.
- Leonid Ionov (University of Bayreuth): Wetting properties of surfaces which will be switched based on stimuli-responsive polymers.
- Alla Synytska (Leibniz-Institute for Polymerforschung Dresden e.V.): wetting properties of switchable anisotropic surfaces made from Janus-particles.
- With the group of Uwe Thiele (University of Münster) we will share details of the dynamic contact angle measured on (binary) polymer brush systems. Then he will adapt his generic gradient dynamics models and we will gain insight in details of the swelling process.
- Doris Vollmer (MPIP) and Friederike Schmid (Universität Mainz): Simulations of the infiltration dynamics of fluid molecules into brushes and Laser Scanning Confocal Microscopy.

Details of the cooperation are mentioned in our workpackages, respectively.

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

Gunther Andersson (Flinders Univ. South Australia, Adelaide), Jon P. Barnes (Univ. Glasgow, Scotland), Tom Brown (Univ. Oxford, UK), Kookheon Char (Seoul Natl. Univ.), Masao Doi (Beihang Univ., China), George Floudas (Univ. Ioannina, Greece), Syuji Fujii (Osaka Inst. Technol., Japan), Stephen Garoff, (Carnegie Mellon Univ. Pittsburgh), Xiahui Gui (China Univ. Min. & Technol., Xuzhou), Jochen S. Gutmann (Univ. Duisburg Essen & Deutsches Textilforschungszentrum), Mark Helm (Univ. Mainz, Inst. Pharmacy), Lucio Isa (ETH, Switzerland), Ulrich Jonas (Univ. Siegen), Xing-Jie Liang (Natl. Ctr. Nanosci. & Technol., Chinese Acad. Sci., Beijing), Detlef Lohse (Univ. Twente, NL), A. James Mason (Kings College London, Inst. Pharmaceut. Sci.), Kris Matyjaszewski (Carnegie

Mellon Univ. Pittsburgh), Filipe Natalio (Weizmann Inst. Sci., Rehovot, Israel), Hiroyuki Nishide (Waseda Univ., Tokyo), Periklis Papadopoulos (Univ. Ioannina, Greece), Bertrand Pouligny (Pessac, France), Markus Retsch (Univ. Bayreuth), Takamasa Sakai (Univ. Tokyo, Dept. Bioengn.), Ulrich Schubert (Univ. Jena), Roberto Simonutti (Univ. Milano Bicocca, Dept. Mat. Sci.), Jacco H. Snoeijer (Univ. Twente, NL), Martin Steinhart (Univ. Osnabrück), Wolfgang Tremel (Univ. Mainz, Inorgan. Chem.), Sanghyuk Wooh (Chung Ang Univ., Seoul), Shinichi Yusa (Univ. Hyogo, Japan), Xuehua Zhang (Univ. Alberta, Edmonton, Canada), Rudolf Zentel (Univ. Mainz, Organic Chemistry)

## 5.5 Scientific equipment

Commercial confocal laser scanning microscope LSM 880 (Carl Zeiss) equipped with broad range of excitation lasers and fluorescence detectors are available. In addition to confocal microscopy the device can be used also for total internal reflection (TIRF) and fluorescence life time imaging (FLIM) microscopy as well as for fluorescence correlation spectroscopy (FCS) studies. The SPR is a home-build machine.

Film thickness and roughness of polymer brushes will be determined by X-ray reflectivity using our multi-purpose diffractometer. For in-situ measurements on samples submerged in liquids, we are currently purchasing an X-ray reflectometer with molybdenum anode (Rigaku SmartLab 9kW). Fast time resolved experiments on the swelling dynamics will be conducted at synchrotron sources (P08 PETRAIII, ID31 ESRF etc.).

Contact angle measurement setups (Data Physics OCA35) and additional tools to characterize surfaces (Scanning Force Microscopes, Scanning Electron Microscopes, Transmission Electron Microscope, X-ray Photoelectron Spectrometer, Time of Flight Secondary Ion Mass Spectrometer) are readily available at the MPIP. In addition, analytical equipment for the polymer synthesis is available: Gel Permeation Chromatography (GPC) and GPC coupled with light scattering.

## 5.6 Project-relevant cooperation with commercial enterprises

Currently, we cooperate with Krüss GmbH, Borsteler Chaussee 85 in Hamburg. Krüss will implement the drop adhesion force instrument (DAFI) in their product line.

## 6 Additional information

We do not receive funding and we did not request funding for any project related to adaptive surface anywhere else. 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.

Mainz, den 12.10.2018,  
Prof. Dr. Hans-Jürgen Butt

Mainz, den 12.10.2018  
Dr. R. Berger