Project Description - Project Proposals

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Impact of co-nonsolvency effects on dynamic wetting

Project Description

1   State of the art and preliminary work
1.0.1   State of the art

Surfaces that respond to environmental stimuli offer great promise for the development of "smart" materials for sensing applications, including in switchable surfaces and controlled drug release, but also offers a platform for studying the fundamentals of surface wetting. Amongst those, polymer brushes have become an increasingly important component for tailoring materials with specific environmental responses. Polymer brushes consist of end-tethered polymer chains stretched away from a surface. Under appropriate conditions, the brush height (h) is larger than the random-walk end-to-end distance of the polymer chain ($< r^2 >^{1/2}$)[1-4]. Resulting from a close coupling between adjacent chains, polymer brushes can rapidly transduce signals from environmental stimuli leading to macroscopically observed responses[5,6], where the response can be triggered from subtle local changes in solvation environment that become amplified due to the close packing of polymer chains. Importantly, a grafted brush of thickness of only a few nanometers can impart striking differences to surface wetting properties. For example, in nature thin polyelectrolyte glycoprotein brushes can modulate the surface wettability of cartilage in joints and the periciliary brushes that lubricate the surfaces of lung tissue[7].

Recent methods for grafting polymers to a surface with precise control over density[8] and polydispersity[9] from different building blocks[10], have allowed specific responses to ionic strength[11], pH[12], magnetic fields[13], temperature[10], light[14], and carbohydrates[15] to be achieved. Much work has been devoted to developing surfaces with switchable antifouling and lubrication properties[16,17], stemming from the interactions between adjacent polymer chains, and those on opposing surfaces. The key parameter of interest is a control over the surface wettability that is often determined through macroscopic contact angle measurements[18]. The ability of surfaces to change and adapt to a surface droplet is due to a complex modulation of polymer side-chain reorientation, solvent diffusion/interaction, adsorption of surfactants, and formation of charged double layers[19]. This adaptation of a surface to its environment can not only be induced by liquid interfaces, but also by the vapor above a polymer brush surface[20,21]. This has wide ranging applications in modelling biological structures, vapor analyte sensing, and manufacturing active layers for gas separation technologies[22]. Crucially, the vapor-induced response of polymer brushes towards droplets offers another dimension for modelling the underlying physics of surface wettability.

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A variety of models have been developed for predicting the contact angle and relaxation dynamics of drops on a surface, which include combinations of phase changes, diffusion, advection, and surface forces[23]. The dynamics and effective wetting of a polymer brush by a droplet therefore depends not only on hydrodynamics of the drop, but also on the properties of the underlying surface polymer[24], and entropic interactions of the solvent within the polymer brush[25]. This interplay of forces that determines surface wettability is therefore complex and is yet to be fully understood. In this proposal, we aim to investigate the effects of small changes in aqueous environmental conditions on wetting dynamics through the co-nonsolvency effect, with an emphasis on contributions from the vapor phase. Our key goal is to elucidate and model the dominating mechanism(s) of surface wettability that results from specific polymer brush interactions with co-nonsolvents in a drop.

Co-nonsolvency
The co-nonsolvency effect describes the counterintuitive phenomenon that a polymer can under certain circumstances become insoluble in a mixture of two good solvents. The effect has recently been in the center of both experimental studies[26-29] as well as theory and modelling[25,30-32]. Using a generic approach considering the competition of the two solvents for the polymer several aspects such as the discontinuous transitions in polymer brushes and solutions, and the reentry swelling/mixing behavior under variation of the solvent composition is predicted[25,30]. While the effect has been studied experimentally for polymers in solution and for gels[33], there are relatively few studies for co-nonsolvency effects for surface layers[26-29,34]. Based on the conformational changes found in solution and gels, one expects, however, strong effects for polymer brushes.

Essentially a polymer brush will react towards co-nonsolvency similar as to a change from good to poor solvent environment and collapse, but in contrast to the latter the transition can be jump-like under smooth variation of system parameters such as concentration of cosolvent and temperature. The collapse transition also changes the mechanical properties of the brush, e.g., the interactions between brush-coated surfaces[27] or between the brush and other substrates[26,28,35]. Moreover, by adding a third component, the co-nonsolvency effect can be fine-tuned and multiple response of physical properties of the brush can be expected. Besides the concentration effect temperature is an independent control parameter for the transition.

To study the conformational transitions in polymer brushes a number of different experimental methods including surface probe microscopy[35-37], attenuated total refraction[38], quartz crystal microbalance with dissipation (QCM-D)[39,40], and ellipsometry (SE)[41] have been explored in detail. Especially spectroscopic ellipsometry techniques can be used to analyze the swelling of polymer brushes (uncharged and polyelectrolytes) under different solvent conditions and investigate the influence of external stimuli on the composition-depth profile of the brush systems. The changes in mechanical properties are directly accessible via AFM-based techniques, like colloidal probe AFM[42,43] [E4 – E6]. Briefly, a colloidal particle is glued onto a tipless AFM cantilever such that direct force-distance measurements can be carried out in a sphere-plate geometry[42,43]. Using the dependency on solvent conditions, the mechanical properties of polymer brushes showing co-nonsolvency can be tuned and determined with AFM-based techniques[28,29,35,44-46] or the surface force apparatus (SFA)[47].

Brushes showing co-nonsolvency effects do not react instantaneously to changes in the solvent quality, where the kinetics of the brush transition can take 10 or even 30 minutes[26,45]. We have some hints that there is additionally an initial fast kinetics, but no clear data is available yet. The slow kinetics can be attributed to the fact that these thickness changes also involve reorganization processes in the brush related to a longer equilibration of the brush to the environment[19].

Advancing and receding the contact angles
On almost all practically relevant surfaces, the advancing contact angle θ_a differs from the receding contact angle θ_r. Contact angle hysteresis, i.e., the difference $\theta_a - \theta_r$, can be caused by several effects[48,49], e.g., surface roughness, heterogeneity of the surface, adsorption of contaminants at the contact line. Additionally, as Butt et al. pointed out[19], swelling of a thin film on a hard substrate changes the surface energy of the substrate. The swelling state of the substrate

influences the contact angles of droplets deposited on the substrate. Often pinning of the contact line due to surface roughness or chemical heterogeneity leads to similar effects. Beyond the Wenzel model for contact angles on rough surfaces[50], pinning of the contact line has been observed. The influence of pinning has been studied experimentally[51-54] and theoretically[48,55]. Changes in the roughness (even below 100 nm roughness) of the substrate may induce strong influences in the receding contact angle.[54]

For moving contact lines, the dynamic contact angle depends on additional parameters. Even for otherwise simple systems (hard substrate and simple liquids) a velocity dependent contribution to the contact angle is observed. This is often attributed to either molecular kinetics[56,57] or hydrodynamic effects[58-60].

Formation of wetting ridges on soft substrates
Soft substrates can be deformed under the influence of drops sitting on the substrate[61,62]. The major reason is the unbalanced vertical component of the surface tension along the contact line that is counterbalanced by an elastic force in the substrate. This mechanism is always present, independent of the elastic modulus of the substrate. However, only for soft enough substrates, the deformation along the contact line can be observed, e.g., by confocal microscopy[63,64]. As Long et al. described, this mechanism is not limited to thick soft materials. It can also be present in polymer brushes[65,66]. This finding makes these substrate deformations relevant for the present proposal. As Snoeijer and coworkers have shown, there is also a substantial contribution of the substrate deformation to the dynamics of the moving contact lines[67].

Sitting drops and their interaction with the gas phase around them
The thermodynamic equilibrium between a flat liquid surface (even of mixtures) and a gas phase above this surface is well-known.[68] For drops additional effects have to be considered for all contact angles different from 90°. In this case, the evaporation rate varies over the drop surface[69]. For this reason, even minor variations of the partial pressures of the gas phase can lead to non-homogeneous evaporation. This will cause Marangoni convection inside the drop (either due to temperature or concentration differences), which is expected within the drop[70,71].

For liquid mixtures, it must be considered that in equilibrium the composition of the liquid and the coexisting gas phase can be strongly different. This has been studied for various aqueous solutions, especially in the water/ethanol mixtures that will be used in this work[68,72].

When two miscible drops of different surface tension meet, this difference induces Marangoni flows in liquids that can alter significantly the drop coalescence[73]. In the same way, the exposure to vapor of a liquid that changes surface tension can induce Marangoni flows[74], even without direct contact of the liquids.

1.0.2   Prelimary Work

This proposal combines the complementary competences of the three involved groups.

The Auernhammer group has experience in studying the dynamics of wetting [E1 – E3]. Over the last years, various expereimental approaches to wetting have been applied and developed in the Auernhammer group: Drop impact and fast spreading of drops[75-78], dynamic dewetting with well-defined contact line velocities[79-81] [E2], measuring flow profiles using particle tracking [E2], and studying the surface rheology of liquid solutions[82-84]. To control the contact line velocity in wetting experiments, a drop slider[85] and rotating drum setup[79-81] [E2] have been developed in the Auernhammer group. With these setups, the contact line velocity can be controlled between a few µm/s up to several tens of cm/s. To determine flow profiles, the Auernhammer group has a long experience in particle tracking methods [86] [E2, E3]. Especially, the drop slider can be combined to the home built confocal microscope[85,86].

The Fery group has experience in AFM based investigation of polymer brushes and multilayers with internal brush compartments [E4 – E6]. We have recently studied brushes of poly(N-

isopropylacrylamide) (PNiPAAm) in ethanol/water mixtures and found [E7] a pronounced dependency of brush thickness on ethanol/water mixing ratio with a brush collapse around 15-17 vol% ethanol concentration. Further unpublished results indicate that the transition can be modified when changing the co-solvent.

The Uhlmann group has expertise in the field of polymer brushes as a tool box for the creation of multifunctional nanofilms and hybrid layers [E10]. The group is investigating switching mechanisms of brushes in detail [E8] and studying stimuli induced swelling and interfacial interactions *in-situ* by using ATR, QCM-D, and spectroscopic VIS-ellipsometry [E9]. For this proposal, we will use grafting-to method to synthesize the brushes. The primary advantage of the "grafting-to" method is that it is a technically simple processing step consuming low quantities of an accurately characterized pre-formed polymer.

Normal ellipsometry is only able to determine a combination of the refractive index of the thin film with and its thickness. However, using multiple wavelengths (spectroscopic VIS-ellipsometry) at a fixed angle and an suitable modelling of the data, it is possible to disentangle the information on the thickness and the refractive index[87]. This method has been developed and used in our groups over last years.

Test measurements of dynamic wetting on PNiPAAm brushes
During the while preparing this proposal, we performed a couple of test experiments (Fig. 1). These preliminary results illustrate that (i) the static and dynamic wetting on brushes showing co-nonsolvency effects depends on the composition of the liquid, (ii) the dynamics dewetting depends on the solvent history of the brush, (iii) the pinning of the contact line depends on contact line speed.
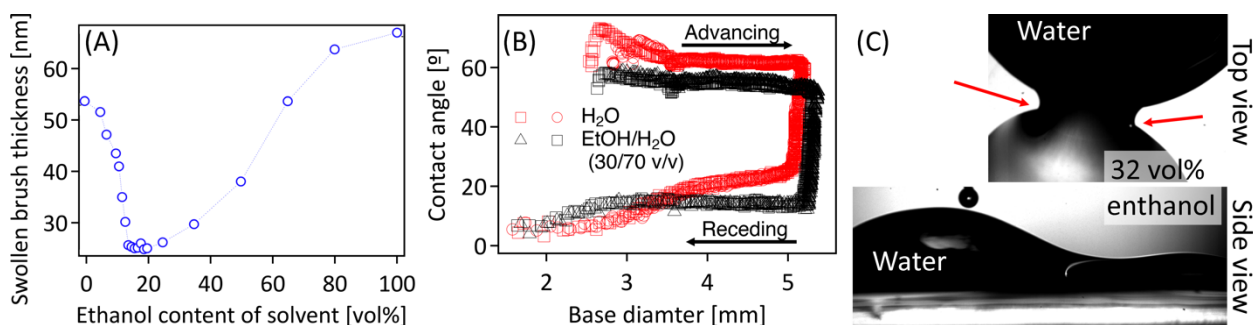

Figure 1: Illustration of our preliminary results. (A) The brush layer thickness as a function of composition of the liquid mixture (water/ethanol) about the brush. The strongest co-nonsolvency effect is observed for a ethanol concentration of 15 – 17 vol%, adapted from [E7]. (B) Contact angle on a brush similar to (A) for pure water (red, good solvent) and 30 vol% ethanol in water (black, bad solvent). Whereas the advancing contact angle (always wetting fresh surface) is constant, the receding contact angle shows a clear dependence on the contact time. Hereby, the characteristic time for the bad solvent mixture (black) is clearly longer than for the good solvent condition. (C) During drop coalescence, a strong pinning of the contact line is observed which manifests itself, e.g., in sharp kinks in the contact line (red arrows).

1.1   Project-related publications
1.1.1   Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.

[E1] Fell, D., M. Sokuler, A. Lembach, T. Eibach, C. Liu, E. Bonaccurso, G. K. Auernhammer and H.-J. Butt (2013). "Drop impact on surfactant films and solutions." Colloid and Polymer Science **291**(8): 1963-1976.

[E2] Henrich, F., D. Fell, D. Truszkowska, M. Weirich, M. Anyfantakis, T.-H. Nguyen, M. Wagner, G. K. Auernhammer and H.-J. Butt (2016). "Influence of surfactants in forced dynamic dewetting." Soft Matter **12**: 7782 - 7791.

[E3] Huang, S., K. Gawlitza, R. von Klitzing, W. Steffen and G. K. Auernhammer (2017). "Structure and Rheology of Microgel Monolayers at the Water/Oil Interface." Macromolecules **50**(9): 3680 - 3689.

[E4] Marschelke, C., I. Raguzin, A. Matura, A. Fery and A. Synytska (2017). "Controlled and tunable design of polymer interface for immobilization of enzymes: does curvature matter?" Soft Matter **13**(5): 1074-1084.

[E5] Bünsow, J., J. Erath, P. M. Biesheuvel, A. Fery and W. T. S. Huck (2011). "Direct Correlation between Local Pressure and Fluorescence Output in Mechanoresponsive Polyelectrolyte Brushes." Angewandte Chemie International Edition **50**(41): 9629-9632.

[E6] Gensel, J., I. Dewald, J. Erath, E. Betthausen, A. H. E. Müller and A. Fery (2013). "Reversible swelling transitions in stimuli-responsive layer-by-layer films containing block copolymer micelles." Chemical Science **4**(1): 325-334.

[E7] Yong, H., S. Rauch, K.-J. Eichhorn, P. Uhlmann, A. Fery and J.-U. Sommer (2018). "Cononsolvency Transition of Polymer Brushes: A Combined Experimental and Theoretical Study." Materials **11**(6): 991.

[E8] A. Furchner, A. Kroning, S. Rauch, P. Uhlmann, K.-J. Eichhorn, K. Hinrichs (2017), Molecular Interactions and Hydration States of Ultrathin Functional Films at the Solid-Liquid Interface, Analytical Chemistry, **89**, 3240-3244.

[E9] E. Psarra, U. König, Y. Ueda, C. Bellmann, A. Janke, E.Bittrich, K.-J. Eichhorn, P. Uhlmann (2015), Nanostructured biointerfaces: Nanoarchitectonics of thermoresponsive polymer brushes impact protein adsorption and cell adhesion, ACS Applied Materials & Interfaces, **7**, 12516-12529.

[E10] S. Rauch, K.-J. Eichhorn, D. Kuckling, M. Stamm, P. Uhlmann (2013) Chain extension of stimuli-responsive polymer brushes: a general strategy to overcome the drawbacks of the "Grafting-to" approach, Advanced Functional Materials, **23**, 5675-5681.

1.1.2   Other publications – not applicable
1.1.3   Patents
1.1.3.1   Pending – not applicable
1.1.3.2   Issued – not applicable

2   Objectives and work programme
2.1   Anticipated total duration of the project

The project is planned for 6 years. Here we ask for funding for 3 years.

2.2   Objectives

For a good responsiveness of a substrate to external conditions, a clear answer of the substrate on the stimulus is needed. In the proposed work, we want to investigate the changes in the dynamics of wetting on polymer brushes showing co-nonsolvency effects. Such substrates change from good solvent conditions (swollen state of the brush) to bad solvent conditions (collapsed state) in a relatively small range of solvent composition (Fig. 1A). These changes in the swelling state also induce changes in the dynamic wetting properties (Fig. 1B and C).

The goals of this project are:
- To study the statics and dynamics of the wetting of drops that induce swelling or collapse of the brush through co-nonsolvency effects
- To investigate a potential competition of the solvent conditions between the gas phase and the drop or between two drops of different composition
- To identify dominating dependencies and develop a physical model

To achieve these goals, we combine various strategies.
- Studying the dynamics of wetting in a broad range of well-defined contact lines velocities (from µm/s to tens of cm/s, using various experimental setups, see section 1.0.2).

- Combination of the wetting experiments with complementary experimental approaches (including imaging and spectroscopic VIS-ellipsometry to determine the brush layer thickness, AFM-based techniques for the mechanical characterization, and particle tracking methods to determine flow profiles).
- Systematic variations of the experimental parameters, like the properties of the brush (grafting density, molecular weight, brush layer thickness), the time scales and contact lines velocities (see above), and the composition of the liquid (drop) and gas phase involved in the wetting.
- Development of a physical model of the observed behavior, e.g., in collaboration with colleagues working on theoretical approaches.

Brushes showing co-nonsolvency exhibit a richer response to solvent drops than normal (swellable) brushes. Co-nonsolvency brushes show a responsiveness to the liquid (e.g. swelling), however, this swelling depends on the composition of the liquid and (perhaps) the gas phase around. We emphasize that the major focus of this proposal is not the simple swelling of the brushes, but the specific co-nonsolvency effects of the brushes.

The key ingredients to this project are: the polymer brush showing co-nonsolvency effects, at least one liquid drop (of well-defined composition) moving over this brush in a well-defined atmosphere. Specifically, we will use poly(N-isopropylacrylamide) (PNiPAAm) brushes prepared by a grafting-to method that allows for a well-defined molecular weight, grafting density and brush layer thickness. When the gas phase is in equilibrium to the liquid phase we have a tunable adaptiveness (through the composition of the gas and liquid phase) of the brush. When the gas and liquid phase favor different swelling states of the brush, a competition between both effects occurs and the co-nonsolvency (and its kinetics) interacts directly with the dynamics of wetting. The abovementioned combination of experimental methods will allow us to investigate the kinetics and dynamics of the system over a broad range of length and time scales.

2.3   Work program incl. proposed research methods

The contribution of the three applicants in this project are closely inter-connected. For a good overview over the planed work, we present the project as a whole. To make the contribution of each applicant clear, we finish each section with a summary that emphasizes the contribution of each applicant.

The parameter space in this project has many dimensions (various properties of the brush, composition of the gas and liquid phase, etc.). The initial work packages (WP1 and WP2) are intended to use systematic parameter variation to identify the parameter region in which the strongest effects are to be expected. The following work package (WP3) will then start from the identified parameter region to build the experimental basis for a physical modelling.

2.3.1   WP 1: Basic investigations (6 person months)
2.3.1.1   Quasi-static properties of poly(N-isopropylacrylamide) (PNiPAAm) brushes

Parameter range of the brushes
As explained in the section on our preliminary work, we developed a method to prepare well-defined polymer brushes with a grafting-to method[87]. This gives us the advantage of detailed knowledge of the molecular weight distribution of the polymer brush, while keeping the possibility to control brush thickness and grafting density. We will perform our studies on PNiPAAm brushes, because we have detailed knowledge on their co-nonsolvency properties[88] using ethanol and water as competing good solvents. In the following sections, a systematic variation of the brush properties is planned. Especially, the molecular weight of the grafted polymer, the grafting density and the brush thickness shall be considered. The brush thickness will be systematically varied between approximately 5nm and 20 nm, corresponding to variations in the molecular weight of the grafted polymer in the range of 25-178 kg/ mol.

Vapor swelling

The swelling behavior of brushes or thin films showing co-nonsolvency has been studied by several authors, when the brushes or thin films are in contact with the solvent[28,29,35,44-47]. From brushes using different polymers, it is known that they also swell in the solvent vapor[20-22]. To the best of our knowledge, no information is published how brushes showing co-nonsolvency react towards solvent vapor. For the present proposal the vapor swelling is, however, an essential issue. In the presence of a contact line, the brush is exposed to the liquid solvent and the solvent vapor in closely neighboring areas. *To what extend are the properties of the brush influenced by the gas phase outside the drop?*

To answer this question, we distinguish between situations in which the gas phase is either in equilibrium with the drop or not (evaporation or condensation takes place or not, compare section 1.0.1). Note that the actual mixing ratios will be different in the drop and the gas phase[68,72].

We extend our previous studies by investigating layer thickness changes in PNiPAAm brushes as a function the composition (e.g. the water/ethanol ratio) and composition changes of either liquid or gas above the brush. We will monitor the kinetics of these changes in detail using spectroscopic VIS-ellipsometry (as described in section 1.0.2) to provide data for the following work packages. The time scales identified in this work package will define the time scales of the work packages below. For the rest of this proposal, equilibrium swelling refers to the final state of this process (which might be obtained after 10 to 30 minutes[26]) and quasi-equilibrium refers to earlier times. Note that the time needed to perform many of the (static or dynamic) contact angle measurements below is much shorter (few minutes) than the expected equilibration time of the PNiPAAm brushes.

The swelling of the brush has two important consequences for the work proposed here: i) The surface energy of the substrate depends on its swelling state. ii) The elastic modulus of the film also depends on the swelling state of the substrate. Whereas the former one is hard to be measured directly, the latter will be measured using AFM-based techniques (as a function of the composition of the gas and liquid phase above the film). Using these mechanical data and the models for the formation of wetting ridges available in the literature[61,62,65-67], the properties of the wetting ridge can be estimated.

2.3.1.2   Contact angle hysteresis when drop and gas phase are in equilibrium

The purpose of this work package is twofold: build-up of a good environmental control and studying the contact angle hysteresis of drops on PNiPAAm brushes.

A good control of the environmental conditions (temperature and composition of the gas phase) is essential for this project. The laboratory is equipped with a control of the temperature T that guarantees $T = 23\,°C \pm 0.2\,°C$. To obtain a defined composition of the gas phase, we will make a setup as sketched in Fig. 2 (left). The key ingredient in this setup is the usage for three independent vapor lines with a precise control of the individual flow rates for (i) dry nitrogen, (ii) water saturated nitrogen, and (iii) ethanol saturated nitrogen (or any other co-solvent). The climate chamber that will be constructed in this work package will be compatible with the different contact setups that we have to measure the contact angle (OCA, DataPhysics and the asymmetric drop shape analysis, (ADSA), ASTRA, Toronto, Canada).

Later in the project, we will enforce a constant composition in the drop through a continuous (but slow) exchange of the liquid in the drop, see Fig. 2 (left). This should prevent potential condensation and evaporation effects from changing the drop volume. Two precise syringe pumps and a coaxial needle for two liquid flows will be used to continuously exchange the drop volume. To keep the drop volume constant both syringe pumps have the same flow rate (with opposite sign). Any mismatch in the flowrates can be used to increase or decrease the drop volume. The flow rate through the drop has to be small enough that effects on the measured

contact angle can be excluded or at least minimized. This will be checked within this work package.
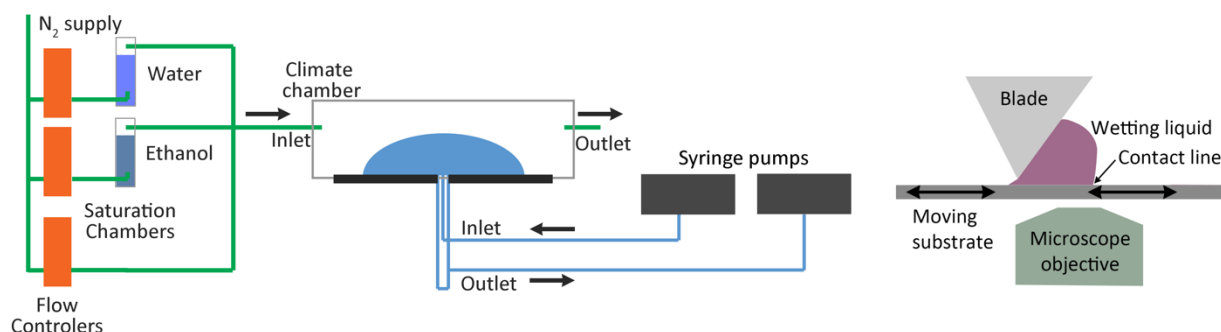

Figure 2: Left: For well-controlled experimental conditions, both the liquid and the gas phase need the possibilities for a continuous exchange. For the gas phase, we will realise this by a combination of three gas flows with controlled flow rates (left side). The liquid phase can be exchanged by two syringe pumps containing the same solvent mixture. Depending of the difference between the flow rates, the drop either keeps its volume, expands or shrinks. For high saturation levels, the saturation chambers have to be combined in one line. **Right:** Schematic of the drop slider of a microscopic observation close to the contact line.

The scientific goal of this work package is to establish a good data base of contact angle hysteresis on PNiPAAm brushes as a function of the composition of the drop, the properties of the brush (molecular weight, thickness, etc.) and the contact time between drop and substrate. This measurement with our contact angle devices (OCA and ADSA) will allow us to answer the question: *To what extend does the swelling state and kinetics of the brush (section 2.2.1.1) influence the contact angle hysteresis?* For the receding contact angle, we expect a dependency on the contact time of the drop before receding the contact line.

Distribution of the work:
The PhD student under the guidance of Günter K. Auernhammer (and co-supervised by Andreas Fery) performs the major part of the experiments. The technician under the guidance of Petra Uhlmann prepares the samples. The student assistant under the guidance Andreas Fery supports the PhD student in preparing, performing and analyzing the AFM and colloidal probe AFM experiments. All applicants will contribute to the discussion and interpretation of the obtained data and decide on the most promising next steps.

2.3.2   WP 2: Non-equilibrium between gas phase and drop (12 person months)

When the drop and the gas phase are in equilibrium, the PNiPAAm brush reacts similarly to the gas and to the liquid phase, i.e., the drop advances on a brush that has experienced similar solvent conditions in the gas phase. In this work package we will now address the question: *How do different swelling state under the gas and liquid phases influence the contact angle hysteresis?*

We will investigate what effects arise, when a drop with good solvent conditions (inducing swelling of the brush) advances over a brush in an atmosphere that favors a collapsed brush (or vice versa). We limit ourselves here to slow contact line velocities, i.e., we measure the static advancing and receding contact angles. Also, the overall composition of the liquid and gas phase will be kept constant through a continuous exchange of the liquid and gas. A number of different mechanisms can influence these contact angles (Fig. 3).

(i) The non-equilibrium between the gas phase and the drop will induce condensation or evaporation of one (or both) components. Presumably this will induce convection in the drop. We quantify the convection and compare it to the limits of liquid flow rates determined in section 2.2.1.2. We will use particle tracking methods for the determination of the flow profile. Besides the published methods used by us[83,94,95], the Auernhammer group develops a confocal micro

particle tracking velocimetry and astigmatic particle tracking velocimetry within the SFB 1194. These methods will also be available to the proposed project.
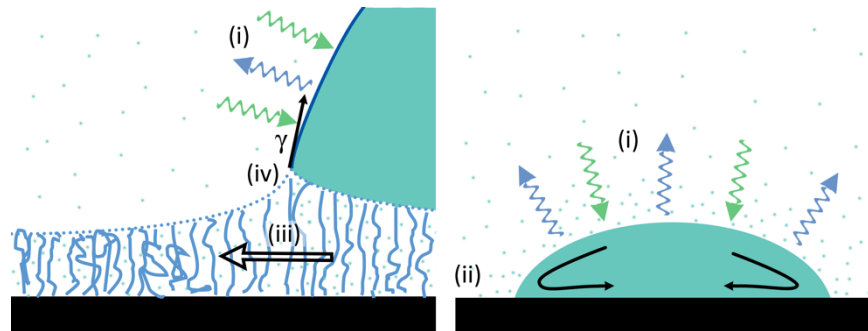

Figure 3: Schematic representation of the mechanisms involved for drops surrounded by atmosphere that is not in equilibrium to the drop composition (left microscopic and right macroscopic view). The roman numbers correspond to the explanations in the main text.

(ii) Evaporation and condensation on the drop will change the gas composition in the vicinity of the drop. The size of the gas volume that is influenced by evaporation and condensation will depend on the gas flow profile and flow rate in the environmental chamber, which we will vary systematically. To quantify local variations in the swelling of the brush, we will measure the brush layer thickness as a function of distance from the contact line. For a detailed analysis of these effects Dr. Eva Bittrich has agreed a collaboration. Eva Bittrich is an expert on advanced ellipsometric measurements and heads a lab with various ellipsometric techniques (including sprectroscopic VIS-ellipsomtery). Within this collaboration, we will use an anisotropic contrast optical microscope[96] that gives similar information than imaging ellipsometers. The spatial resolution of these measurements will be limited to some 10 µm, i.e., details very close to the contact line cannot be directly obtained (see also section 2.3.5.2).

(iii) Additional to the diffusion through the gas phase, lateral diffusion through the brush is possible. Since gas diffusion constants typically exceed diffusion constants in liquids of polymeric environments by orders of magnitude, we expect that the diffusion through the brush only plays a minor role.

(iv) Along the contact line, a wetting ridge will form. The spatial extension of this ridge is too small to be observed with our techniques, but the mechanical measurements of section 2.2.1.1 should give reliable data to estimate the height of this ridge.

Within this work package we will combine the mentioned techniques with slow (quasi-static) contact angle measurements under well-controlled conditions to disentangle the consequences of these mechanisms. As in the previous work package, the receding contact line moves over a surface that has been in contact with the liquid for a well-known, but variable time.

Advancing contact lines, however, always meet a surface that was pre-exposed to the gas phase. For long enough waiting times, this can be assumed to lead to a stationary state of the substrate. Within this work package, we will limit ourselves to this situation. Consequently, it is easier to observe the effects of the non-equilibrium between liquid and gas phase on the advancing contact angle. For the interpretation of our data and the development of a physical model describing the effects studied in the first two work packages, we plan to continue the collaboration with the Sommer group at the IPF in Dresden. Prof. Jens-Uwe Sommer is an expert in theory and in computer simulations of co-nonsolvency effects.[30,31] The experiments within this collaboration and the provided data will be coordinated with the Sommer group.

Distribution of the work:
The PhD student under the guidance of Günter K. Auernhammer (and co-supervised by Andreas Fery) performs the major part of the experiments. The technician under the guidance of Petra

Uhlmann prepares the samples. The student assistant under the guidance Andreas Fery supports the PhD student in preparing, performing and analyzing the AFM and colloidal probe AFM experiments. All applicants will contribute to the discussion and interpretation of the obtained data and decide on the most promising next steps.

2.3.3 WP 3: Co-nonsolvency effects versus simple adaptiveness in dynamic wetting (18 person months)

Within the first two work packages we studied the quasi-static effects of swelling and collapse of PNiPAAm brushes on the wetting properties, i.e., we studied the adaptiveness and responsiveness of the brushes to (mainly) external conditions. Now we turn to truly dynamic situations.

Various models predict a dependency of the dynamic contact angle on velocity: for simple liquid there are molecular kinetic[56,57] and hydrodynamic models[58-60], for soft surfaces the formation of a wetting ridge influences the dynamics of the contact line[65-67], for responsive surfaces the surface energy of the substrate is a function of the contact time of the substrate with the swelling solvent or vapor[19].

In a similar approach to the previous work package, we will study the effect of the competition between the swelling properties of the brush due to the solvent conditions of the liquid and gas phase. Experimentally, we will use the methodology existing in the group: drop slider[85] for contact line velocities up to a few cm/s, the rotating drum setup[95] for contact line velocities up to 1 m/s, and for very high speeds drop impacts with high speed imaging. Again, we will keep the composition in the liquid and gas phase mainly constant through continuous flow.

The focus of this work package is to identify similarities and differences between dynamic wetting on adaptive brushes and brushes showing co-nonsolvency. In our system both cases can be easily realized. When the drop and the gas phase are in equilibrium to each other, the dynamics of wetting should correspond to other cases of adaptive wetting. However, PNiPAAm brushes allow for changing the amount of adaptiveness (swelling) through composition of the liquid and gas phase. *But how can the co-nonsolvency effects on (dynamic) wetting be separated from the simple adaptiveness effects of any swelling polymer brush?*

In contrast, co-nonsolvency effects are expected to be observed, when there is a competition between the liquid and the gas phase considering the swelling state of the PNiPAAm brush. Such a competition can be either realized through liquid and gas phases for good and bad solvents of the brush (or vice versa), respectively. Alternatively, one can choose the composition of the liquid and gas phase both as good solvents (e.g. water and ethanol vapor, respectively). This might generate bad solvent conditions only close to the contact line, where both phases meet.

Within this work package we will survey the kinetics of the change of the solvent condition through the differences in the dynamic contact angle on the same substrate but under varying solvent conditions of the gas and liquid phase (see pervious paragraph). This comparison will allow us to separate the co-nonsolvency effects on dynamic wetting from the simple adaptiveness effects that these PNiPAAm brushes also exhibit. Through systematic variation of contact line speed, properties of the PNiPAAm brush, and the composition of the liquid and gas phase, we will identify regions in the parameter space where the co-nonsolvency effects can be clearly separated from the simple adaptiveness effects. The experiments in this parameter range are an especially important input for modelling efforts.

Additionally to our own experiments described above, we will collaborate with the Butt/Berger group to use their drop adhesion force instrument (DAFI).[97,98] The experiments described so far, concentrate on the advancing and receding contact angle. i.e., the front and back side of a moving drop. With DAFI measures the integral force needed to move a drop, i.e., additionally changes in the shape of the footprint contribute to the measured force.

We will also compare our results of the co-non solvency effect on the dynamic wetting of PNIPAM microgel layers with the results on PNiPAAm brushes obtained by the von Klitzing group (TU Darmstadt). Since the von Klitzing groups uses layers of microgels, we are able to validate the effect of molecular architecture and thickness of the PNiPAAm layer.

For the modelling of these effects we agreed additionally on a collaboration with the Thiele group (Uni Münster). This comparison seems to be especially applicable to the experiments with moving contact lines, i.e. dynamic experiments. The experiments within this collaboration and the provided data will be coordinated with the Thiele group. Furthermore, the Thiele group intends to include the gas phase in their modelling. We intend to compare our experimental results on the influence of the gas phase to the modelling of the Thiele group.

Distribution of the work:
The PhD student under the guidance of Günter K. Auernhammer (and co-supervised by Andreas Fery) performs the major part of the experiments. The technician under the guidance of Petra Uhlmann prepares the samples. The student assistant under the guidance Andreas Fery supports the PhD student in preparing, performing and analyzing the AFM and colloidal probe AFM experiments. All applicants will contribute to the discussion and interpretation of the obtained data and decide on the most promising next steps.

2.3.4   Contribution to the training of young scientists

In this project we use some experimental methods that are perhaps not widespread: The **drop slider**, the **rotating drum setup** and the **asymmetric drop shape analysis** (ADSA). Within the framework of the priority program 2171, we will offer young scientists of other projects to perform measurements with our setups and get a hands-on training on these devices.

In this framework we already agreed with the von Klitzing group to offer them the possibility to measure dynamic contact angles at higher contact line velocities using the drop slider and the rotating drum.

2.3.5   Outlook to the second funding period
2.3.5.1   Changes of the wetting conditions through the changes in the gas phase.

From our initial test experiments and the work describe so far, it is anticipated that there will be an influence of the co-nonsolvency effects on the dynamics of wetting. As a long term goal, we want to address the question: *Can this be used to change the behavior of a drop already sitting on a substrate only through changes in the gas phase?*

For such an investigation that composition of a good solvent (water) drop on a PNiPAAm brush will be modified through addition of ethanol in the gas phase. Condensation of ethanol on the water drop might change it to bad solvent conditions, and consequently also change its wetting properties.

2.3.5.2   Microscopic insight into the properties of the brush

To get a more microscopic insight into the dynamics of the PNiPAAm brushes, we propose to synthesize PNiPAAm brushes on glass slides by surface-initiated ATRP, where the polymerization will involve a combination of NiPAAm and fluorophore monomers following the strategy reported by Wu et al.[99]. The result will be a surface-anchored PNiPAAm brush that contains small amounts of covalently tethered fluorophores that will be chosen as a Förster resonant energy transfer (FRET) donor. The conjugation density will be chosen so as to not influence the solvation dynamics of the PNiPAAm brush. When a drop containing the corresponding FRET acceptor is placed on the slide, and observed by fluorescence confocal microscopy, the FRET response will give information of the density of the fluorophores, i.e., on the relative swelling state of the brush. This can then be measured with a lateral resolution of about 300 nm. This will give local information on the brush close to the contact line with a lateral

resolution one to two orders of magnitude better than the imaging ellipsometers can give. However, the chemical effort is beyond the plans of the first funding period.

2.3.5.3   Highly dynamic situations: Drop coalescence

During coalescence of the drops, variations of the so far characterized effects will play a role. Additionally, the contact line speed varies strongly during the process. Although the experiments are easy to perform, a full understanding of the process and the involved mechanisms seems only possible using the results of the experiments with controlled contact line speed described in the WP1 through WP3.

2.4   Data handling

Storage and archiving of the produced data will be done according the rules of the DFG. The Leibniz Institute for Polymer Research offers the IT infrastructure for this, including network drives for the working group, backup systems and capabilities for long-time storage and archiving. For data exchange between collaborating groups we will use the cloud storage infrastructure also provided by the Leibniz Institute for Polymer Research.

2.5   Other information – not applicable
2.6   Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern ‑ not applicable
2.7   Information on scientific and financial involvement of international cooperation partners ‑ not applicable

3   Bibliography

1   Minko, S. Responsive Polymer Brushes. *Journal of Macromolecular Science, Part C: Polymer Reviews* **46**, 397-420, doi:10.1080/15583720600945402 (2006).
2   Milner, S. T. Polymer Brushes. *Science* **251**, 905 (1991).
3   Halperin, A., Tirrell, M. & Lodge, T. P. in *Macromolecules: Synthesis, Order and Advanced Properties*   31-71 (Springer Berlin Heidelberg, 1992).
4   Brittain, W. J. & Minko, S. A structural definition of polymer brushes. *Journal of Polymer Science Part A: Polymer Chemistry* **45**, 3505-3512, doi:10.1002/pola.22180 (2007).
5   Chen, T., Ferris, R., Zhang, J., Ducker, R. & Zauscher, S. Stimulus-responsive polymer brushes on surfaces: Transduction mechanisms and applications. *Progress in Polymer Science* **35**, 94-112, doi:10.1016/j.progpolymsci.2009.11.004 (2010).
6   Stuart, M. A. *et al.* Emerging applications of stimuli-responsive polymer materials. *Nat Mater* **9**, 101-113, doi:10.1038/nmat2614 (2010).
7   Conrad, J. C. & Robertson, M. L. Towards mimicking biological function with responsive surface-grafted polymer brushes. *Current Opinion in Solid State and Materials Science*, https://doi.org/10.1016/j.cossms.2018.09.004 (2018).
8   Zhou, T., Qi, H., Han, L., Barbash, D. & Li, C. Y. Towards controlled polymer brushes via a self-assembly-assisted-grafting-to approach. *Nat Commun* **7**, 11119, doi:10.1038/ncomms11119 (2016).
9   Qi, S. *et al.* Tuning Transition Properties of Stimuli-Responsive Brushes by Polydispersity. *Advanced Functional Materials*, doi:10.1002/adfm.201800745 (2018).
10   Adam, S. *et al.* Quartz crystal microbalance with coupled spectroscopic ellipsometry-study of temperature-responsive polymer brush systems. *Applied Surface Science* **421**, 843-851, doi:10.1016/j.apsusc.2017.02.078 (2017).
11   Yang, J. *et al.* Salt-Responsive Zwitterionic Polymer Brushes with Tunable Friction and Antifouling Properties. *Langmuir* **31**, 9125-9133, doi:10.1021/acs.langmuir.5b02119 (2015).
12   Cheng, N., Bao, P., Evans, S. D., Leggett, G. J. & Armes, S. P. Facile Formation of Highly Mobile Supported Lipid Bilayers on Surface-Quaternized pH-Responsive Polymer Brushes. *Macromolecules* **48**, 3095-3103, doi:10.1021/acs.macromol.5b00435 (2015).
13   Yang, C., Wu, L. & Li, G. Magnetically Responsive Superhydrophobic Surface: In Situ Reversible Switching of Water Droplet Wettability and Adhesion for Droplet Manipulation. *ACS Appl Mater Interfaces* **10**, 20150-20158, doi:10.1021/acsami.8b04190 (2018).
14   Kollarigowda, R. H. *et al.* Light-responsive polymer brushes: active topographic cues for cell culture applications. *Polymer Chemistry* **8**, 3271-3278, doi:10.1039/c7py00462a (2017).

15   Lamping, S., Otremba, T. & Ravoo, B. J. Carbohydrate-Responsive Surface Adhesion Based on the Dynamic Covalent Chemistry of Phenylboronic Acid- and Catechol-Containing Polymer Brushes. *Angew Chem Int Ed Engl* **57**, 2474-2478, doi:10.1002/anie.201711529 (2018).

16   Demirci, S., Kinali-Demirci, S. & Jiang, S. A switchable polymer brush system for antifouling and controlled detection. *Chem Commun (Camb)* **53**, 3713-3716, doi:10.1039/c7cc00193b (2017).

17   Kang, T. *et al.* Mussel-Inspired Anchoring of Polymer Loops That Provide Superior Surface Lubrication and Antifouling Properties. *ACS Nano* **10**, 930-937, doi:10.1021/acsnano.5b06066 (2016).

18   Huang, X., Sun, Y. & Soh, S. Stimuli-Responsive Surfaces for Tunable and Reversible Control of Wettability. *Adv Mater* **27**, 4062-4068, doi:10.1002/adma.201501578 (2015).

19   Butt, H.-J., Berger, R., Steffen, W., Vollmer, D. & Weber, S. A. L. Adaptive Wetting—Adaptation in Wetting. *Langmuir* **34**, 11292-11304, doi:10.1021/acs.langmuir.8b01783 (2018).

20   Biesalski, M. & Rühe, J. Swelling of a Polyelectrolyte Brush in Humid Air. *Langmuir* **16**, 1943 - 1950 (2000).

21   Orski, S. V., Sheridan, R. J., Chan, E. P. & Beers, K. L. Utilizing vapor swelling of surface-initiated polymer brushes to develop quantitative measurements of brush thermodynamics and grafting density. *Polymer* **72**, 471-478, https://doi.org/10.1016/j.polymer.2015.05.030 (2015).

22   Galvin, C. J., Dimitriou, M. D., Satija, S. K. & Genzer, J. Swelling of polyelectrolyte and polyzwitterion brushes by humid vapors. *J Am Chem Soc* **136**, 12737-12745, doi:10.1021/ja5065334 (2014).

23   van der Heijden, T. W. G., Darhuber, A. A. & van der Schoot, P. Macroscopic Model for Sessile Droplet Evaporation on a Flat Surface. *Langmuir*, doi:10.1021/acs.langmuir.8b02374 (2018).

24   Lhermerout, R., Perrin, H., Rolley, E., Andreotti, B. & Davitt, K. A moving contact line as a rheometer for nanometric interfacial layers. *Nat Commun* **7**, 12545, doi:10.1038/ncomms12545 (2016).

25   Mukherji, D., Marques, C. M. & Kremer, K. Polymer collapse in miscible good solvents is a generic phenomenon driven by preferential adsorption. *Nature Communications* **5**, 4882, doi:10.1038/ncomms5882 (2014).

26   Chen, Q. *et al.* Collapse from the top: brushes of poly(N-isopropylacrylamide) in co-nonsolvent mixtures. *Soft Matter* **10**, 3134-3142, doi:10.1039/c4sm00195h (2014).

27   Yu, Y., Kieviet, B. D., Kutnyanszky, E., Vancso, G. J. & de Beer, S. Cosolvency-Induced Switching of the Adhesion between Poly(methyl methacrylate) Brushes. *ACS Macro Letters* **4**, 75-79, doi:10.1021/mz500775w (2015).

28   Yu, Y. *et al.* Tunable friction by employment of co-non-solvency of PNIPAM brushes. *Polymer* **102**, 372-378, https://doi.org/10.1016/j.polymer.2016.08.029 (2016).

29   Yu, Y. *et al.* Pick up, move and release of nanoparticles utilizing co-non-solvency of PNIPAM brushes. *Nanoscale* **9**, 1670-1675, doi:10.1039/C6NR09245D (2017).

30   Sommer, J.-U. Adsorption–Attraction Model for Co-Nonsolvency in Polymer Brushes. *Macromolecules* **50**, 2219-2228, doi:10.1021/acs.macromol.6b02231 (2017).

31   Sommer, J.-U. Gluonic and Regulatory Solvents: A Paradigm for Tunable Phase Segregation in Polymers. *Macromolecules* **51**, 3066-3074, doi:10.1021/acs.macromol.8b00370 (2018).

32   Debashish, M., Carlos, M. M. & Kurt, K. Collapse in two good solvents, swelling in two poor solvents: defying the laws of polymer solubility? *Journal of Physics: Condensed Matter* **30**, 024002 (2018).

33   Scherzinger, C., Schwarz, A., Bardow, A., Leonhard, K. & Richtering, W. Cononsolvency of poly-N-isopropyl acrylamide (PNIPAM): Microgels versus linear chains and macrogels. *Current Opinion in Colloid & Interface Science* **19**, 84-94, https://doi.org/10.1016/j.cocis.2014.03.011 (2014).

34   Edmondson, S., Nguyen, N. T., Lewis, A. L. & Armes, S. P. Co-Nonsolvency Effects for Surface-Initiated Poly(2-(methacryloyloxy)ethyl phosphorylcholine) Brushes in Alcohol/Water Mixtures. *Langmuir* **26**, 7216-7226, doi:10.1021/la904346j (2010).

35   Backes, S., Krause, P., Tabaka, W., Witt, M. U. & von Klitzing, R. Combined Cononsolvency and Temperature Effects on Adsorbed PNIPAM Microgels. *Langmuir* **33**, 14269-14277, doi:10.1021/acs.langmuir.7b02903 (2017).

36   Elmahdy, M. M., Drechsler, A., Uhlmann, P. & Stamm, M. Swelling and Surface Interactions of End-Grafted Poly(2-vinylpyridine) Layers in Acidic Solution: Influence of Grafting Density and Salt Concentration. *Langmuir* **32**, 5451-5459, doi:10.1021/acs.langmuir.6b00316 (2016).

37   Drechsler, A., Synytska, A., Uhlmann, P., Stamm, M. & Kremer, F. Tuning the Adhesion of Silica Microparticles to a Poly(2-vinyl pyridine) Brush: An AFM Force Measurement Study. *Langmuir* **28**, 15555-15565, doi:10.1021/la303131d (2012).

38   Müller, M. *et al.* In-situ ATR-FTIR for characterization of thin biorelated polymer films. *Thin Solid Films* **556**, 1-8, https://doi.org/10.1016/j.tsf.2013.12.025 (2014).

39   Bittrich, E. *et al.* Protein adsorption on and swelling of polyelectrolyte brushes: A simultaneous ellipsometry-quartz crystal microbalance study. *Biointerphases* **5**, 159-167, doi:10.1116/1.3530841 (2010).

40   Koenig, M. *et al.* Combined QCM-D/GE as a tool to characterize stimuli-responsive swelling of and protein adsorption on polymer brushes grafted onto 3D-nanostructures. *Analytical and Bioanalytical Chemistry* **406**, 7233-7242, doi:10.1007/s00216-014-8154-4 (2014).

41   Kroning, A. *et al.* In Situ Infrared Ellipsometry for Protein Adsorption Studies on Ultrathin Smart Polymer Brushes in Aqueous Environment. *ACS Applied Materials & Interfaces* **7**, 12430-12439, doi:10.1021/am5075997 (2015).

42   Butt, H.-J. Measuring electrostatic, van der Waals, and hydration forces in electrolyte solutions with an atomic force microscope. *Biophysical Journal* **60**, 1438-1444 (1991).

43   Ducker, W. A., Senden, T. J. & Pashley, R. M. Direct measurement of colloidal forces using an atomic force microscope. *Nature* **353**, 239, doi:10.1038/353239a0 (1991).

44   Backes, S. *et al.* Poly(N-isopropylacrylamide) Microgels under Alcoholic Intoxication: When a LCST Polymer Shows Swelling with Increasing Temperature. *ACS Macro Letters* **6**, 1042-1046, doi:10.1021/acsmacrolett.7b00557 (2017).

45   Sui, X., Chen, Q., Hempenius, M. A. & Vancso, G. J. Probing the Collapse Dynamics of Poly(N-isopropylacrylamide) Brushes by AFM: Effects of Co-nonsolvency and Grafting Densities. *Small* **7**, 1440-1447, doi:10.1002/smll.201002229 (2011).

46   Drobek, T. & Spencer, N. D. Nanotribology of Surface-Grafted PEG Layers in an Aqueous Environment. *Langmuir* **24**, 1484-1488, doi:10.1021/la702289n (2008).

47   Espinosa-Marzal, R. M., Nalam, P. C., Bolisetty, S. & Spencer, N. D. Impact of solvation on equilibrium conformation of polymer brushes in solvent mixtures. *Soft Matter* **9**, 4045-4057, doi:10.1039/C3SM27726G (2013).

48   Joanny, J. F. & Gennes, P. G. d. A model for contact angle hysteresis. *J. Chem. Phys.* **81**, 552 - 562 (1984).

49   Extrand, C. W. & Kumagai, Y. An Experimental Study of Contact Angle Hysteresis. *Journal of Colloid and Interface Science* **191**, 378-383 (1997).

50   Wenzel, R. N. RESISTANCE OF SOLID SURFACES TO WETTING BY WATER. *INDUSTRIAL AND ENGINEERING CHEMISTRY* **28**, 988 - 994 (1936).

51   Bartell, F. E. & Shepard, J. W. Surface Roughness as Related to Hysteresis of Contact Angles. II. The Systems Paraffin–3 Molar Calcium Chloride Solution–Air and Paraffin–Glycerol–Air. *The Journal of Physical Chemistry* **57**, 455-458, doi:10.1021/j150505a015 (1953).

52   Schwartz, A. M. & Tejada, S. B. Studies of dynamic contact angles on solids. *Journal of Colloid and Interface Science* **38**, 359-375, doi:http://dx.doi.org/10.1016/0021-9797(72)90252-4 (1972).

53   Kanungo, M., Mettu, S., Law, K.-Y. & Daniel, S. Effect of Roughness Geometry on Wetting and Dewetting of Rough PDMS Surfaces. *Langmuir* **30**, 7358-7368, doi:10.1021/la404343n (2014).

54   Pittoni, P. G., Lin, C.-H., Yu, T.-S. & Lin, S.-Y. On the Uniqueness of the Receding Contact Angle: Effects of Substrate Roughness and Humidity on Evaporation of Water Drops. *Langmuir* **30**, 9346-9354, doi:10.1021/la501455d (2014).

55   Chamakos, N. T., Kavousanakis, M. E., Boudouvis, A. G. & Papathanasiou, A. G. Droplet spreading on rough surfaces: Tackling the contact line boundary condition. *Physics of Fluids* **28**, 022105, http://dx.doi.org/10.1063/1.4941577 (2016).

56   BLAKE, T. D. & HAYNES, J. M. Kinetics of liquid/ liquid Displacement. *J. Colloid Interf. Sci.* **30**, 421 - 423 (1969).

57   Blake, T. D. The physics of moving wetting lines. *Journal of Colloid and Interface Science* **299**, 1-13, doi:10.1016/j.jcis.2006.03.051 (2006).

58   COX, R. G. The dynamics of the spreading of liquids on a solid surface. Part 1. Viscous flow. *J. Fluid Mech.* **168**, 169 - 194 (1986).

59   Voinov, O. V. Hydrodynamics of wetting. *Fluid Dynamics* **11**, 714-721, doi:10.1007/bf01012963 (1976).

60   Snoeijer, J. H. & Andreotti, B. Moving Contact Lines: Scales, Regimes, and Dynamical Transitions. *Annual Review of Fluid Mechanics* **45**, 269-292, doi:10.1146/annurev-fluid-011212-140734 (2013).

61   Rusanov, A. I. Theory of Wetting of Elastically Deformed Bodies.1. Deformation with a Finite Contact-Angle. *Colloid Journal of the Ussr* **37**, 614-622 (1975).

62   Rusanov, A. I. THEORY OF WETTING OF ELASTICALLY DEFORMED BODIES .2. EQUILIBRIUM CONDITIONS AND WORK OF DEFORMATION WITH A FINITE CONTACT-ANGLE. *Colloid Journal of the Ussr* **37**, 623-628 (1975).

63   Pericet-Camara, R., Best, A., Butt, H. J. & Bonaccurso, E. Effect of capillary pressure and surface tension on the deformation of elastic surfaces by sessile liquid microdrops: An experimental investigation. *Langmuir* **24**, 10565-10568 (2008).

64   Pericet-Camara, R. *et al.* Solid-supported thin elastomer films deformed by microdrops. *Soft Matter* **5**, 3611 -- 3617 (2009).

65   Long, D., Ajdari, A. & Leibler, L. How Do Grafted Polymer Layers Alter the Dynamics of Wetting? *Langmuir* **12**, 1675-1680 (1996).

66   Long, D., Ajdari, A. & Leibler, L. Static and Dynamic Wetting Properties of Thin Rubber Films. *Langmuir* **12**, 5221-5230, doi:10.1021/la9604700 (1996).

67   Karpitschka, S. *et al.* Droplets move over viscoelastic substrates by surfing a ridge. *Nat Commun* **6**, doi:10.1038/ncomms8891 (2015).

68   Wakisaka, A. & Iwakami, T. Molecular clustering inherent in the liquid state: Effect of relativity in intermolecular interaction energy. *Journal of Molecular Liquids* **189**, 44-51, https://doi.org/10.1016/j.molliq.2013.05.025 (2014).

69   Hu, H. & Larson, R. G. Evaporation of a sessile droplet on a substrate. *Journal of Physical Chemistry B* **106**, 1334-1344, doi:10.1021/jp0118322 (2002).

70   Jaijus, P. J. & Singh, A. Flow visualization and solute transport in evaporating droplets. *AIChE Journal* **56**, 1674-1683, doi:10.1002/aic.12096 (2010).

71   Manukyan, S. *et al.* Imaging internal flows in a drying sessile polymer dispersion drop using Spectral Radar Optical Coherence Tomography (SR-OCT). *Journal of Colloid and Interface Science* **395**, 287-293, http://dx.doi.org/10.1016/j.jcis.2012.11.037 (2013).

72   Wakisaka, A., Matsuura, K., Uranaga, M., Sekimoto, T. & Takahashi, M. Azeotropy of alcohol–water mixtures from the viewpoint of cluster-level structures. *Journal of Molecular Liquids* **160**, 103-108, https://doi.org/10.1016/j.molliq.2011.03.002 (2011).

73   Karpitschka, S., Hanske, C., Fery, A. & Riegler, H. Coalescence and Noncoalescence of Sessile Drops: Impact of Surface Forces. *Langmuir* **30**, 6826-6830, doi:10.1021/la500459v (2014).

74   Hernández-Sánchez, J. F., Eddi, A. & Snoeijer, J. H. Marangoni spreading due to a localized alcohol supply on a thin water film. *Physics of Fluids (1994-present)* **27**, 032003, http://dx.doi.org/10.1063/1.4915283 (2015).

75   Muralidhar, P., Bonaccurso, E., Auernhammer, G. K. & Butt, H.-J. Fast dynamic wetting of polymer surfaces by miscible and immiscible liquids. *Colloid Polym. Sci.* **289**, 1609-1615, doi:10.1007/s00396-011-2475-z (2011).

76   Chen, L., Auernhammer, G. K. & Bonaccurso, E. Short time wetting dynamics on soft surfaces. *Soft Matter* **7**, 9084-9089 (2011).

77   Chen, L., Li, C., van der Vegt, N. F. A., Auernhammer, G. K. & Bonaccurso, E. Initial Electrospreading of Aqueous Electrolyte Drops. *Phys. Rev. Lett.* **110**, 026103 (2013).

78   Cruz-Aceves, I. *et al.* Multiple Active Contours Driven by Particle Swarm Optimization for Cardiac Medical Image Segmentation. *Computational and Mathematical Methods in Medicine* **2013**, 13, doi:10.1155/2013/132953 (2013).

79   Fell, D. *et al.* Influence of Surfactant Concentration and Background Salt on Forced Dynamic Wetting and Dewetting. *Langmuir* **27**, 2112-2117, doi:10.1021/la104675t (2011).

80   Fell, D., Pawanrat, N., Bonaccurso, E., Butt, H.-J. & Auernhammer, G. K. Influence of surfactant transport suppression on dynamic contact angle hysteresis. *Colloid Polym. Sci.* **291**, 361 - 366, doi:10.1007/s00396-012-2759-y (2012).

81   Eibach, T. F., Fell, D., Nguyen, H., Butt, H. J. & Auernhammer, G. K. Measuring contact angle and meniscus shape with a reflected laser beam. *Review of Scientific Instruments* **85**, 013703, http://dx.doi.org/10.1063/1.4861188 (2014).

82   Truszkowska, D. *et al.* Forced dewetting dynamics of high molecular weight surfactant solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **521**, 30-37, http://doi.org/10.1016/j.colsurfa.2016.07.073 (2017).

83   Huang, S., Gawlitza, K., von Klitzing, R., Steffen, W. & Auernhammer, G. K. Structure and Rheology of Microgel Monolayers at the Water/Oil Interface. *Macromolecules* **50**, 3680 - 3689, doi:10.1021/acs.macromol.6b02779 (2017).

84   Schümann, M. *et al.* A characterization of the magnetically induced movement of NdFeB-particles in magnetorheological elastomers. *Smart Materials and Structures* **26**, 095018, doi:10.1088/1361-665X/aa788a (2017).

85   Henrich, F. M. *Dynamic dewetting of surfactant solutions*, Technische Universität, (2018).

86   Roth, M., Schilde, C., Lellig, P., Kwade, A. & Auernhammer, G. K. Colloidal aggregates tested via nanoindentation and simultaneous 3D imaging. *Eur. Phys. J. E* **35**, 124, doi:10.1140/epje/i2012-12124-8 (2012).

87   Rauch, S. *et al.* Temperature responsive polymer brushes with clicked rhodamine B: synthesis, characterization and swelling dynamics studied by spectroscopic ellipsometry. *Soft Matter* **8**, 10260-10270, doi:10.1039/C2SM26571K (2012).

88   Yong, H. *et al.* Cononsolvency Transition of Polymer Brushes: A Combined Experimental and Theoretical Study. *Materials* **11**, 991 (2018).

89   Holtzer, L., Meckel, T. & Schmidt, T. Nanometric three-dimensional tracking of individual quantum dots in cells. *Applied Physics Letters* **90**, 053902, doi:10.1063/1.2437066 (2007).

90   Hsu, W.-Y. *et al.* Development of the fast astigmatic auto-focus microscope system. *Measurement Science and Technology* **20**, doi:10.1088/0957-0233/20/4/045902 (2009).

91   Cierpka, C., Rossi, M., Segura, R., Mastrangelo, F. & Kähler, C. J. A comparative analysis of the uncertainty of astigmatism-µPTV, stereo-µPIV, and µPIV. *Experiments in Fluids* **52**, 605-615, doi:10.1007/s00348-011-1075-5 (2012).

92   Ichikawa, Y., Yamamoto, K. & Motosuke, M. Three-dimensional flow velocity and wall shear stress distribution measurement on a micropillar-arrayed surface using astigmatism PTV to understand the influence of microstructures on the flow field. *Microfluidics and Nanofluidics* **22**, 73, doi:10.1007/s10404-018-2095-8 (2018).

93   Borcia, R., Menzel, S., Bestehorn, M., Karpitschka, S. & Riegler, H. Delayed coalescence of droplets with miscible liquids: Lubrication and phase field theories. *Eur. Phys. J. E* **34**, 1-9, doi:10.1140/epje/i2011-11024-9 (2011).

94   Wenzl, J., Seto, R., Roth, M., Butt, H.-J. & Auernhammer, G. K. Measurement of rotation of individual spherical particles in cohesive granulates. *Granular Matter* **15**, 391-400, doi:10.1007/s10035-012-0383-7 (2013).

95   Henrich, F. *et al.* Influence of surfactants in forced dynamic dewetting. *Soft Matter* **12**, 7782 - 7791, doi:10.1039/C6SM00997B (2016).

96   Peev, D. *et al.* Anisotropic contrast optical microscope. *Review of Scientific Instruments* **87**, 113701, doi:10.1063/1.4965878 (2016).

97   Pilat, D. W. *et al.* Dynamic Measurement of the Force Required to Move a Liquid Drop on a Solid Surface. *Langmuir* **28**, 16812-16820, doi:10.1021/la3041067 (2012).

98   Gao, N. *et al.* How drops start sliding over solid surfaces. *Nature Physics* **14**, 191, doi:10.1038/nphys4305 (2017).

99   Wu, T., Zou, G., Hu, J. & Liu, S. Fabrication of Photoswitchable and Thermotunable Multicolor Fluorescent Hybrid Silica Nanoparticles Coated with Dye-Labeled Poly(N-isopropylacrylamide) Brushes. *Chemistry of Materials* **21**, 3788-3798, doi:10.1021/cm901072g (2009).

4   Requested modules/funds
4.1   Basic Module
4.1.1   Funding for Staff

Dr. Auernhammer, Günter K.:
1 PhD student 75% of a full position
The PhD student will perform the experiments describe in the proposal, interpret the data and develop (together with the supervisors and collaboration partners) a model. Due to the requirements in the experiments and the data interpretation the student should have a strong background in physical modelling, e.g., having studied physics or a closely related field. The PhD student will be supervised by Andreas Fery and Günter K. Auernhammer.

Prof. Dr. Fery, Andreas:
1 student assistant 6000 € per year
The student assistant will support the PhD student in performing and analyzing the preparation of the AFM and colloidal probe AFM experiments. Analogous to the PhD student, the student assistant should have a strong background in physics.

Dr. Uhlmann, Petra:
1 technician 33% of a full position (4 months per year)
The technician should prepare the brushes on the substrates and support the PhD student with their characterization. Carolin Böhm in the Uhlmann group has a lot of experience in the preparation and characterization of PNiPAAm brushes. She would be available for this position.

4.1.2   Direct Project Costs
4.1.2.1   Equipment up to Euro 10,000, Software and Consumables

Dr. Günter K. Auernhammer
3x Flow controllers (Model 35829, Analyt-MTC) 1459 € each
The flow controllers will be used to establish a climate chamber that is able to control two different vapor pressures (see Fig. 2).

Particles for particle tracking (e.g. 1µm hollow particles from Polysciences) 500 € per year
Neutral buoyancy tracer particles are necessary for the tracking of the flow fields. The price for 500 mg particles is 224.- €. We estimate the yearly costs for the particles to 500 €.

2x Syringe Pump (KD Scientific Legato 100) 2615 € each
A high-quality syringe pump is essential for the generation of well-defined drops for the sitting drop experiments and the drop impact experiments. For the starting period, we have a syringe pump that can be borrowed from another project (project A02a of the SFB 1194). For continuous measurements this is, however, not possible, because the syringe pump will be used in the other measurements.

Hamilton syringes for precise dosage of the liquids (2 per year). 500 € per year.
Glass syringes are essential to avoid impurities that might arise from plastic syringes. 500 € per year correspond to 2 syringes and 6 needles per year.

Modular Coaxial needles (Linari NanoTech)
The complete setup amounts to 2205 € initial investment.
We estimate the running costs to 2 pairs of needles per year, plus exchange of sealings: 400 € per year.
To keep the composition in the drop constant, even under solvent exchange with the gas phase through evaporation and condensation, a constant flow of liquid will be provided through the drop. The best way of realizing this is through a coaxial needle.

Dr. Petra Uhlmann
Special chemicals for the brush synthesis: 2500 € per year

4.1.2.2 Travel Expenses

Dr. Günter K. Auernhammer
One national conference per year: 1000 € per year
One international conference per funding period: 2000 €
Presenting the results of the proposed research is an integral part of the research. We plan for the PhD student for one national conference per year and one international conference per funding period. We estimate the costs for a national conference to 1000 € and 2000 € for an international conference.

Visits to cooperation partners: 1500 € per year
The described collaborations will involve visits to the collaboration partners. We estimate the costs per visit per person and week to 500 € (travel and hotel costs). We plan on average with two to three weeks of collaboration visits per year (mainly for the PhD student, occasionally also together with one of the PIs).

4.1.2.3 **Visiting Researchers** (excluding Mercator Fellows) - **not applicable**
4.1.2.4 **Expenses for Laboratory Animals** - **not applicable**
4.1.2.5 **Other Costs – not applicable**
4.1.2.6 **Project-related publication expenses**

Dr. Günter K. Auernhammer
For color figures and open access publishing: 750 € per year

4.1.3 **Instrumentation**
4.1.3.1 **Equipment exceeding Euro 10,000 – not applicable**
4.1.3.2 **Major Instrumentation exceeding Euro 50,000 – not applicable**

4.2   Module Temporary Position for Principle Investigator - **not applicable**
4.3   Module Replacement Funding - **not applicable**
4.4   Module Temporary Clinician Substitute - **not applicable**
4.5   Module Mercator Fellows - **not applicable**
4.6   Module Workshop Funding - **not applicable**
4.7   Module Public Relations Funding – not applicable

5   Project requirements
5.1   Employment status information

Dr. Auernhammer, Günter K.: Permanent position
Prof. Dr. Fery, Andreas: Permanent position
Dr. Uhlmann, Petra: Permanent position

5.2   First-time proposal data - **not applicable**
5.3   Composition of the project group

Dr. Günter K. Auernhammer (permanent position)
-    Supervision of the PhD student.
-    Invests 20% of his working time in the project.
Prof. Dr. Andreas Fery (permanent position)
-    Co-supervision of the PhD student and supervision of the student assistant.
-    Invests 10% of his working time in the project.
Dr. Petra Uhlmann (permanent position)
-    Supervision of the technician and co-supervision of the PhD student
-    Invests 10% of her working time in the project.
Stefan Michel (permanent position)
-    Is very experienced in the usage of the different dynamic wetting setups at the IPF.
-    Support the PhD student in the experimental work.
-    Invests 10% of his working time in the project.
Dr. Andreas Janke (permanent position)
-    AFM characterization
-    Invests 10% of his working time in the project.

5.4   Cooperation with other researchers

As detailed in section 2.3.4, other researchers of the SPP 2171 are welcome visit our group and perform measurements using our experimental setup (drop slider, rotating drum and asymmetric drop shape analysis).

The PIs plan to contribute to the workshops and schools that will be organized by the SPP. The PhD student will participate in these events. In the same way, a contribution to the collaborative structure of the SPP (e.g., a digital communication platform/internal wiki or a structured knowledge base) is planned.

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

Prof. Dr. Antonyuk, TU Kaiserslautern
As an extension to the described experiments on non-moving substrates, we will perform experiments with the Antonyuk group on vibrating substrates to characterize the effect of mechanical excitation on the contact angle hysteresis.
Dr. Eva Bittrich, Leibniz Institute for Polymer Research, Dresden
Ellipsometric measurements to determine the width of the film influenced by the vapor of the drop.
Prof. Dr. Hans-Jürgen Butt and Dr. Rüdiger Berger, Max Planck Institute for Polymer Research (MPI-P), Mainz
The collaboration with the project Butt/Berger has two aspects:

1) Complementary to our experiments, we plan to perform measurements with the drop adhesion force instrument (DAFI) at the MPI-P. These measurements give additional information, because the friction force of drop while moving over the surface is influenced by the advancing and receding contact angle as well as the shape of the drop footprint on the substrate. So DAFI measurements give information on the motion of the sides of the drop that would otherwise not be available with our methods that focused on the dynamics of the advancing and receding contact angles. We will investigate situations with and without equilibrium between the liquid and the gas phase.

2) We provide samples of our polymer brushes to the Butt/Berger project. Details on the characteristics of the provided samples will be decided in close discussion with the Butt/Berger project.

Prof. Dr. Leonid Ionov, Uni Bayreuth

We will cooperate with the Ionov group on imaging the drop shape on their substrates using confocal microscopy and compare the results to the drop shapes observed on our co-nonsolvency surfaces.

Prof. Dr. Regine von Klitzing, TU Darmstadt

We will compare data on (dynamic) contact angle hysteresis with the von Klitzing group. The different approaches in the substrate preparation allow to check for effects of the molecular architecture and thickness of the PNiPAAm layer. We will also investigate the mutual influence between neighboring water and ethanol drops on their wetting behavior.

Dr. Gregory Lecrivain, Helmholtz-Zentrum Dresden-Rossendorf

We will provide access to our capabilities for measuring drop impact experiments with high speed cameras to the PhD student of the project of Dr. Gregory Lecrivain. The student of his project gets support in performing the experiments and the data analysis.

Dr. Alla Synytska, Leibniz Institute for Polymer Research

The collaboration with the Synytska group consists of several aspects:

- We will offer to the Synytska group our possibilities to use confocal microscopy and high-speed imaging to follow in-situ the reorientation of the Janus particles on the wax surface. For experiments at elevated temperature, will use air objectives to avoid cooling of the sample due to the heat capacity of the objective. In these experiments, we want to determine the kinetics of the reorientation process, its spatial homogeneity and its dependency on external parameters like the phase above the wax (gas or liquid).
- We will cooperate with the Synytska group on the chemical modification of the used surfaces.

Prof. Dr. Jens-Uwe Sommer, Leibniz Institute for Polymer Research

For the interpretation of our data and the development of a physical model describing the effects studied in the first two work packages, we plan to continue the collaboration with the Sommer group at the IPF in Dresden.

Prof. Dr. Uwe Thiele, Uni Münster

We will compare our experimental results to the gradient dynamics modeling developed in the Thiele group. Thereby the particular focus shall be on dynamic experiments, i.e., experiments with contact line motion and data they provide will be coordinated within this collaboration.

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

Günter K. Auernhammer: Prof. Dr. Hans-Jürgen Butt, Dr. Rüdiger Berger, Prof. Dr. George Floudas, Prof. Dr. Christian Holm, Prof. Dr. Regine von Klitzing, Dr. Kaloian Koynov, PD Dr. Andreas Menzel, Dr. Robert Müller, Prof. Dr. Stefan Odenbach, Prof. Dr. Wolfgang Tremel, Prof. Dr. H. Henning Winter, Dr. Si Wu, Prof. Aranzazu Del Campo

Andreas Fery: Prof. Helmut Cölfen, Dr. Claus Duschl, Prof. Stephan Förster, Prof. Gerald Gerlach, Prof. Andreas Greiner, Prof. Jürgen Groll, Prof. Thomas Hellweg, Prof. Leonid Ionov, Prof. Matthias Karg, Prof. Sergiy Minko, Prof. Martin Möller, Prof. Andrij Pich, Prof. Felix Plamper, Prof. Walter Richtering, Prof. Felix H. Schacher, Prof. Sebastian Seiffert, Prof. Jens-Uwe Sommer

Petra Uhlmann:
Prof. Dr. Torsten Fritz, Dr. Andreas Geißler, Dr.-Ing. Lars Giebeler, PD Dr. Karsten Hinrichs, Prof. S. Michael Kilbey, Dr. Meike König, Prof. Dr. Friedrich Kremer, Dr. Bradley S. Lokitz, Prof. Igor Luzinov, Prof. Sergiy Minko, Prof. Angela Pannier, Dr. Martin Reiche, Prof. Alexander Revzin, Dr. Keith Brian Rodenhausen, Prof. Mathias Schubert, Prof. F. Philipp Seib, Prof. Sabu Thomas, Dr. Jungmok You.

5.5   Scientific equipment

Two high-speed cameras
- Photron AX 100 and Photron AX 200, maximum frame of 540 kHz
- Setup for synchronous orthogonal imaging (e.g., side and top view) of the sample
- Equipped with macro-zoom optics (Navitar 12x) and suitable LED illumination.
- Along with these experimental setups the Auernhammer group has software that allows for 2D and 3D (using astigmatism) particle tracking.

Rotating drum setup
- Home build, observation with high speed cameras
- With different motors for dynamic wetting experiments with contact line velocities in the range of approximately 1 mm/s to 1000 mm/s (home built)

Contact angle measurement
- OCA DataPhysics
- Axissymmetric Drop Shape Analysis (ADSA). ASTRA, Toronto, Canada (A. W. Neumann). Variable setup sitting or pending drop, captive bubble and Constraint drop

Wilhelmy-Plate setup
- DCAT 21, DataPhysics

Drop Slider
- Home built, linear drop motion for velocities above approx. 100 µm/s, home built.
- Compatible with the home-built confocal microscopes (below)

Confocal microscopes
- The Auernhammer group has two home-build confocal microscopes that offer a high flexibility to additional setups to them.
- The slow mode microscope has a frame rate of ca. 1 Hz in 2D and allows for an optical resolution of ca. 300 nm laterally 700 nm along the beam direction.
- The fast mode allows for frame rates up to 1 kHz in 2D at a reduced resolution of about 1.5 µm laterally and 3 µm in beam direction.
- Along with these experimental setups, the Auernhammer group has software that allows for 2D and 3D particle tracking.

5.6   Project-relevant cooperation with commercial enterprises – not applicable
5.7   Project-relevant participation in commercial enterprises – not applicable

6   Additional information

Günter K. Auernhammer has two projects within the SFB 1194. In both project the focus is on wetting on hard, non-adaptive and non-responsive substrates. There is no direct overlap to the project proposed here. However, the proposed project will benefit from the knowhow and experimental methods developed within these projects in the SFB 1194.

In the event that we would get funding on a project similar to the present one, we will inform the Deutsche Forschungsgemeinschaft immediately.