Project Description – Project Proposals

Michael Hirtz, Karlsruhe Institute of Technology (KIT)

Highly localized preparation, tuning, and characterization of liquid-infused surfaces for a better understanding of (de)wetting dynamics

Proposal for a Project in the Priority Programme “Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces” (SPP 2171)

Project Description

1 State of the art and preliminary work

The project proposal aims to elucidate the micro-/mesoscopic dynamics and mechanisms associated with the non-equilibrium (de)wetting dynamics of droplets on liquid-infused surfaces (LIS) as an example for an adaptive, flexible and potentially switchable substrate. For this, we will develop a new method, based on a FluidFM setup, to allow static and dynamic force measurements during wetting and liquid exchange in LIS and – in a collaborative approach – deliver the obtained data to theory groups for incorporation in their models.

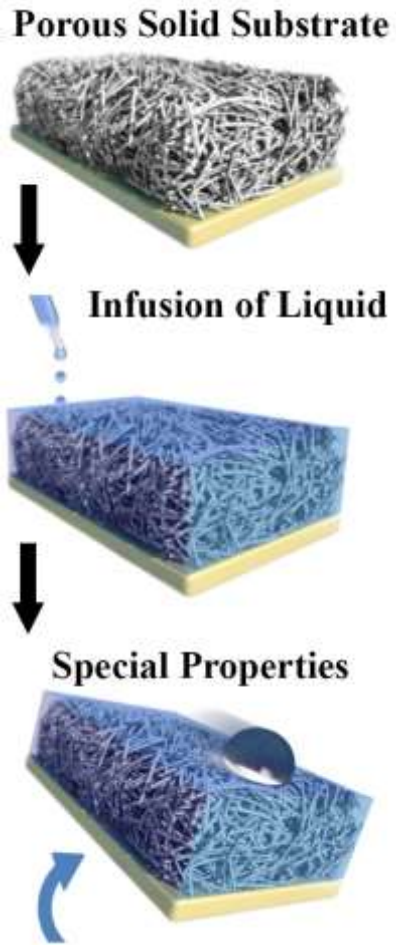

Fig.1: Principle of SLIPS. A porous solid substrate is infused with a liquid. Resulting are novel special porperties, as e.g. superhydrophobicity, anti-fouling or self-cleaning. Adapted from Wyss Institute website.[1] Credit: Wyss Institute at Harvard University.

Motivation

LIS and the narrower defined slippery liquid-infused porous surfaces (SLIPS) (Figure 1) are a fairly new approach to surfaces with special wetting properties and found various applications in surface engineering. They show a high potential for uses in self-cleaning/anti-fouling surfaces,[1,2] medical applications,[3,4] and even for screening[5] and patterning purposes.[6] With rising interest in these systems, a better understanding of the underlying mechanism becomes crucial for rational design for new applications. New methodologies becoming available recently open up novel approaches for in-depth characterization of these systems.

One key issue in the understanding of LIS/SLIPS systems is the dynamics of liquid exchange. This poses the extremes of the wetting states in such a system, as the infused liquid is exchanged by another liquid probing from the air/LIS interface. This process is on the one

[1] https://wyss.harvard.edu/technology/slips-slippery-liquid-infused-porous-surfaces/ (visited 12.10.2018)

hand the hallmark of LIS failure (meaning it loses e.g. its anti-fouling/self-cleaning capability), but on the other hand can also be exploited for fabricating liquid/liquid patterns on surfaces e.g. for screening purposes.[6] As interesting extreme case in the system and with the prospect of gaining precision control and even reversible switching by chemical substrate functionalization in the future we chose the liquid exchange in a SLIPS system as model system for our project.

General Approach and Methodologies

In the spirit of the well-known Feynman quote “What I cannot create, I do not understand”,[7] we will implement a three-tier approach of (I) characterization, (II) fabrication/functionalization, and (III) modelling of the LIS/SLIPS system (Figure 2). All three tracks of activity will inform each other and finally together built a better understanding of the dynamics in SLIPS liquid exchange.

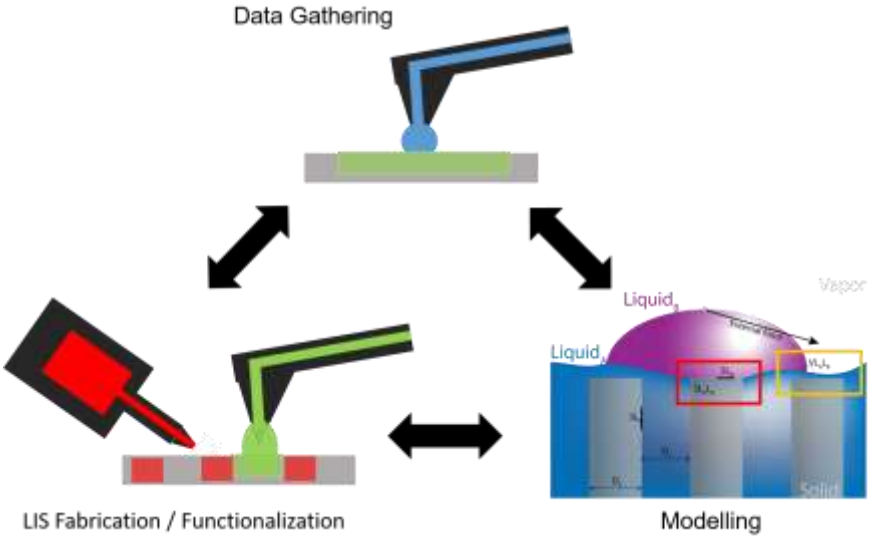

Fig.2: Layout of project concept: In order to understand the liquid exchange dynamics on a LIS, we will gather data on local wetting via liquid probe force microscopy (which will be developed during the project), functionalize surfaces for tuning / tailoring LIS and to monitor LIS formation, and inform models of LIS with the obtained data. The model can feed back into the experimental parts by suggesting specific functionalizations to tune the liquid exchange and to probe the LIS with particular solvents.

In order to understand the principle dynamics in the wetting/dewetting of two liquids in a LIS system two different interfaces need to be addressed: The liquid-liquid interface and the liquid solid interface (yellow, repectively red box in the model in Figure 2). To inform models with empirical data, a high-resolution method for probing these interfaces and realistic probes are needed. At the same time, it would be highly beneficial to be able to tune the local properties with similar resolution, as this allows to validate predictions from the model experimentally by tuning a surface according to model particularities. A recently installed instrument at our group, the FluidFM, offers a high potential for opening up a route to combine both of these requirements, local measurement and tuning.

The FluidFM technology consists of an atomic force microscope (AFM) that is equipped with a micromachined hollow AFM tip.[8,9] These setups allow the delivery or aspiration of small amounts of liquids (down to attoliter range) in air and liquid environments.[10] At the same time, the high sensitity of an AFM for force measurements is available to the user. This allowed e.g. the quantification of adhesion forces on a single cell level for yeast and mammalian cells without needs of chemical attachment of the cells to the cantilever as this is done by applying suction to the cell through the hollow AFM tip.[11]

Currently, FluidFM is mainly used in biological applications; in addition to the aforementioned application in cell adhesion,[11] also uses of injecting in or sampling small volumes of cytosol of

single cells,[12] cell and bacteria manipulation,[13–15] and delivering viral particles to study infection on single cell level[16] were reported. Additionally, the FluidFM can also be used for nanolithography, as was demonstrated by depositing fluorophores and nanoparticles by this technique.[17,18]

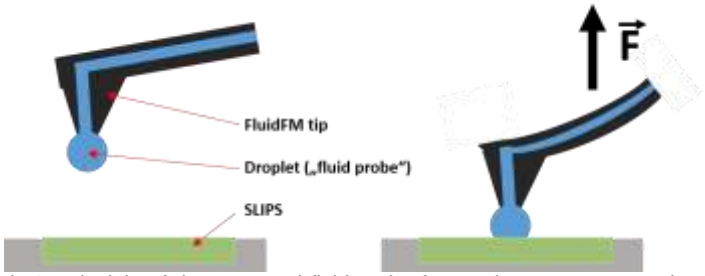

Fig.3: Principle of the proposed fluid probe force microscopy approach. A FluidFM tip generates a small microdroplet of a probing liquid (left). This "fluid probe" is then lowered onto the SLIPS until contact is achieved. This allows then to do force spectroscopy measurements in a highly localized manner, different probing liquids, and in-situ regeneration of the fluid probe.

We propose to use this technology to develop a new measurement process we will term "liquid probe force microscopy" (LPFM): a small micron-sized droplet of a probing liquid is released by the hollow cantilever of a FluidFM and used as highly localized probe able to implement force spectroscopy on surfaces (Figure 3). This technique could be seen as an advanced approach of a recently reported techniques for force measurements that utilize millimeter sized droplets attached to a SU-8 disc mounted on a force probe.[19] Compared to this setup, which already allowed to measure wetting variation on a butterfly wing in a resolution of about 200µm, an approach utilizing the FluidFM setup would have several advantages, especially for the intended use in a LIS/SLIPS system:

- highly local measurements with the specific probe liquid (low micron to submicron)
- enabling of liquid-in-liquid measurements, e.g. to probe wider ranges of surface tension or to prevent evaporation of probing liquid
- in-situ regeneration of liquid probe, which will be especially important for dynamic measurements where the probe liquid is exchanged with the LIS liquid. The rapid renewal of probes enables frequent repetition of the experiment for statistics and phase space screening
- full control over tip/probe movement, allowing to also measure friction forces when moving the probing droplet while in contact with the surface.

The other side of the experimental parts will deal with the local tuning of surfaces for changing their dynamics in LIS/ SLIPS formation. Here, we can rely on a host of scanning probe techniques like dip-pen nanolithography (DPN),[20] polymer pen lithography (PPL),[21] and microchannel cantilever spotting (µCS).[22] We have a broad experience in utilizing these techniques for surface modifications, e.g. in the functionalization of graphene,[23–26] click-chemistry arraying,[22,27–29] applications in biomedical research,[30–35] and functionalization of pre-structures as e.g. photonic devices.[36–39] In particular, we also established the use of these methods for porous substrates (Figure 4).[40–43] Depending on the chosen technique, functionalizations restricted to the surface,[41] but also infusion of liquids[40] that allow for chemically altering the bulk of the porous material[42] are

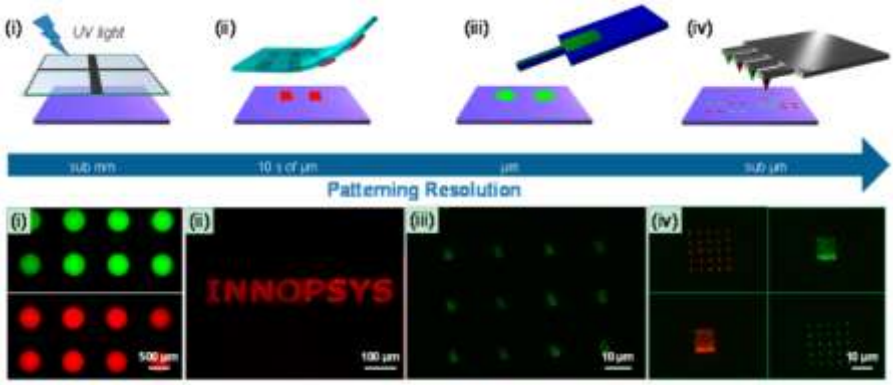

Fig.4: Use of different patterning techniques on porous substrates. Resulting patterning resolution spans from the sub mm (photo patterning, i) over tens of microns (microcontact printing, ii) to micrometer (µCS, iii) and sub micrometer (DPN, iv). The lower images show corresponding examples of fluorophores patterned on a porous substrate. Adapted from [41].

possible. In the present project, these methods will be employed to tailor the substrates with local modifications in wetting properties that will influence the LIS/SLIPS formation. This allows to experiment with pattern and scale effects and enables us to implement interesting experimental boundary conditions that might be suggested by the models during the course of the project. Of particular interest in the project will be to produce patterned substrates that allow the probing of different surface wetting next to each other (instead of different samples) and the implementation of wetting gradients.

In addition to the established methods, the Fluid FM will also offer new options for surface modifications: the closed microfluidic system allows to deposit functionalization inks that would dry to quickly for delivery via µCS (were the open microchannel used in delivery inflicts the need for admixings to avoid premature drying of ink on the tip) and modifications in liquid (instead only be able to work in air). Furthermore, the active delivery by microfluidics in FluidFM is independent of capillary forces that are the sole means of transport in µCS (therefore making it hard to pattern inks that have a higher affinity to the µCS tip than to the substrate they are intended to be written to). Finally, the FluidFM will be able to actively monitor forces during the transition of the fluids from tip to the LIS/SLIPS system, thus allowing to directly measure forces as time-evolution during LIS/SLIPS formation.

The establishing of these experimental characterization and fabrication methods will be closely intertwined with theoretical models in collaborative efforts. The PhD student developing the experimental processes will be supported by the group of Christian Brandl (KIT) to develop a model for the liquid exchange in the specific SLIPS system. Furthermore, we will reach out to other projects within the SPP 2171 that are in need of similar data on surface wetting properties as input for their models. Also, models previously developed by members of the SPP, e.g. for two-liquid film systems,[44,45] will be adjusted for the description of the LIS/SLIPS. This can be implemented by student exchanges and supported in form of master theses coupled to the project.

Intended collaboration and interaction within the SPP

We expect many fruitful interactions with the broader community of the SPP 2171. In particular, experimental data on micro-/nanoscopic surface properties obtained by the methods developed within the proposed project can be used in other projects as basis for model validation or as input for model parameters. Furthermore, we can also use the fabrication methods and nano-lithography tools to precisely implement specific LIS setups motivated by theoretical models and validate their predictions.

As one specific activity, we plan for an exchange with the mesoscopic models of the project by **Jacco Snoeijer/Uwe Thiele** as liquid-infused substrates form a limiting case of their viscoelastic substrates. Here, we will deliver experimental input to complement their models with additional information from our mesoscale data obtained with the FluidFM setup. In return, this collaboration will strengthen our own theoretical approaches and understanding of the examined LIS/SLIPS system.

In particular, we will closely work together with **Pavel Levkin** (specialist for LIS/SLIPS), who is also submitting an SPP 2171 project and will kindly provide us with the porous substrates for the measurements. Reciprocally, we will provide this project with data on local wetting properties of their sample and highly localized altering of these via scanning probe lithography. We can furthermore exploit the vicinity of our labs and the already established collaborations on other topics to enable constant exchange between the PhD students intended to implement the proposed project.

Furthermore, we will be in close contact with the group of **Christian Brandl** (expert in computer modelling), who will support us with simulations and theoretical background for developing a theoretical framework for the obtained data.

Last not least, the framework of the SPP 2171 will also highly enrich the exchange between experimentalists and theorists working on a common theme by the joint events in form SPP workshops (1st and 2nd year), PhD workshops and advanced school (2nd and 1st year respectively) and an international conference (3rd year). These events will be important in strengthening the bonds between different projects and built a community that can even last into the future after the project runtime.

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.

[1] M. Hirtz, M. Lyon, W. Feng, A. E. Holmes, H. Fuchs, P. A. Levkin:
Porous polymer coatings as substrates for the formation of high-fidelity micropatterns by quill-like pens
Beilstein J. Nanotechnol. **2013**, *4*, 377.

[2] M. Hirtz, A. M. Greiner, T. Landmann, M. Bastmeyer, H. Fuchs:
Click-Chemistry Based Multi-Component Microarrays by Quill-Like Pens
Adv. Mater. Interfaces **2014**, *1*, 1300129.

[3] J. Li, L. Li, X. Du, W. Feng, A. Welle, O. Trapp, M. Grunze, M. Hirtz, P. A. Levkin:
Reactive Superhydrophobic Surface and Its Photoinduced Disulfide-ene and Thiol-ene (Bio)functionalization
Nano Lett. **2015**, *15*, 675.

[4] M. Hirtz, W. Feng, H. Fuchs, P. A. Levkin:
Click-Chemistry Immobilized 3D-Infused Microarrays in Nanoporous Polymer Substrates
Adv. Mater. Interfaces **2016**, *3*, 1500469.

[5] M. Hirtz, S. Varey, H. Fuchs, A. Vijayaraghavan:
Attoliter Chemistry for Nanoscale Functionalization of Graphene
ACS Appl. Mater. Interfaces **2016**, *8*, 33371.

[6] M. Davydova, A. de los Santos Pereira, M. Bruns, A. Kromka, E. Ukraintsev, M. Hirtz, C. Rodriguez-Emmenegger:
Catalyst-free site-specific surface modifications of nanocrystalline diamond films via microchannel cantilever spotting
RSC Adv. **2016**, *6*, 57820.

[7] S. Sekula-Neuner, M. de Freitas, L.-M. Tröster, T. Jochum, P. A. Levkin, M. Hirtz, H. Fuchs:
Phospholipid arrays on porous polymer coatings generated by micro-contact spotting
Beilstein J. Nanotechnol. **2017**, *8*, 715.

[8] J. Atwater, D. S. Mattes, B. Streit, C. von Bojničić-Kninski, F. F. Loeffler, F. Breitling, H. Fuchs, M. Hirtz:
Combinatorial Synthesis of Macromolecular Arrays by Microchannel Cantilever Spotting (µCS)
Adv. Mater. **2018**, *30*, 1801632.

[9] S. M. M. S. M. M. Dadfar, S. Sekula-Neuner, U. Bog, V. Trouillet, M. Hirtz:
Site-Specific Surface Functionalization via Microchannel Cantilever Spotting (µCS): Comparison between Azide-Alkyne and Thiol-Alkyne Click Chemistry Reactions
Small **2018**, *14*, 1800131.

1.1.2 Other publications

1.1.3 Patents

1.1.3.1 Pending

[1] U. Bog, M. Hirtz, H. Fuchs, J. Aghassi, C. Marques, S. Dasgupta, B. Breitung, H. Hahn:
„Verfahren zur Herstellung einer elektrisch leitfähigen Verbindung auf einem Substrat, mikroelektronisches Bauelement und Verfahren zu dessen Herstellung“
Submitted in September 2018

[2] M. Hirtz, H. Fuchs, K. Pantel, F. Brinkmann:
„Immobilization of Cells or Virus Particles on Protein Structures Using a Microfluidic Chamber”
Published, WO 2016/128125 A1. **2016**

1.1.3.2 Issued

2 Objectives and work programme

2.1 Anticipated total duration of the project

Three Years (36 months), starting from 01.10.2019

2.2 Objectives

For a better understanding of dynamics and mechanisms of (de)wetting processes in LIS, we want to:

- implement a new FluidFM based approach allowing for detailed monitoring of local adhesion forces with ‘liquid probes’, allowing measuring adhesion forces in static and dynamic modes (WP1)
- then apply this technique for detailed probing of a LIS system before, during, and after LIS formation (WP2)
- apply scanning probe lithography methods to locally tune the LIS model system (WP3) and probe these systems (WP2)
- use the obtained data as input for a model of dynamic (de)wetting (WP4)

2.3 Work programme incl. proposed research methods

For each applicant

<u>Schematic Workplan / Timeline:</u>

WP1: Development of a Liquid AFM Probe (LPFM)
WP1.1: Static Force Spectroscopy
WP1.2: Dynamic Force Spectroscopy

WP2: Characterization of a LIS/SLIPS model system by LPFM
WP2.1: Probing static SLIP surface properties
WP2.2: Dynamic Liquid Infusion and Exchange during SLIPS formation

WP2.3: Probing Friction
WP2.4: Droplet Formation on SLIPS

WP3: Tuning of SLIPS Systems
WP3.1: Local chemical Functionalization
WP3.2: Multiplexed Infusion Patterns

WP4: Data Analysis, Modelling, and Dissemination of Results
WP4.1: Data Evaluation and Software Development
WP4.2: Collaborative Modelling
WP4.3: Preparation of Publication for Journals and Conferences

Work Packages	Year 1				Year 2				Year 3			
WP1: Development of a Liquid AFM Probe (LPFM)	1.1											
		1.2										
WP2: Characterization of a LIS/SLIPS model system by LPFM		2.1										
			2.2									
					2.3							
						2.4						
WP3: Tuning of SLIPS Systems			3.1									
							3.2					
WP4: Data Analysis, Modelling, and Dissemination of Results	4.1											
	4.2											
			4.3				4.3				4.3	

Details on work package implementation:

WP1: Development of a Liquid AFM Probe (LPFM)

WP1.1: Static Force Spectroscopy

As first step in the development of the liquid probe force microscopy (LPFM) technique, static force microscopy will be addressed. This allows also to trial the basic requirements for probe generation and control.

The basic idea of LPFM is shown in Figure 5. We will use a FluidFM tip and generate a femto- to nanoliter sized droplet by microfluidic pumping at the end of the tip. This is done while the tip is still far away from the surface. The tip with the terminating liquid droplet can now be brought into contact with the surface while force is constantly monitored and recorded. The will then be retracted to gain a full approach/retraction force-distance curve that can be evaluated with the well established methods from AFM force spectroscopy to gather information like adhesion forces, surface energies and information on the expected surface

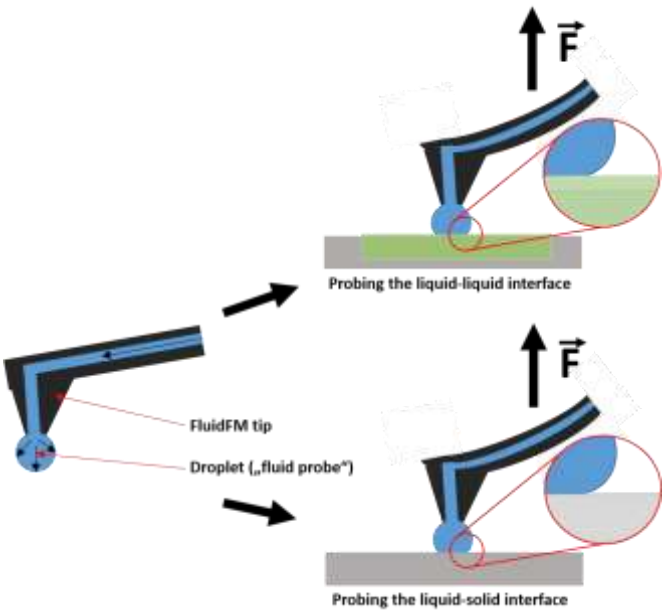

Fig.5: Concept of LPFM. A femto- to nanoliter sized droplet of liquid is generated by microfluidic pumping at the end of a FluidFM tip. The tip is then brought into contact with the surface while force is constantly monitored. This allows to probe the liquid-liquid and liquid solid interface of the SLIPS system.

contact angle.[46] The precise control over the tip will allow to gather maps of wetting properties, which will be especially interesting when combined with prestructured samples as produced in WP3.
The implementation of this method with the available technology is straightforward, as a similar concept to obtain wetting variation maps of biological surfaces was recently demonstrated for droplets of mm size attached to SU-8 plates connected to a force sensor.[19] The FluidFM based approach we want to develop will generate much higher spatial and force resolution as smaller droplets (micron-sized) and a more force sensitive setup will be employed. The FluidFM will also allow to regenerate the probes in-situ, as the liquid is delivered directly through the tip instead of being attached to the tip from the outside.
The miniaturizing of the droplet can potentially induce a new problem of liquid evaporation. For the mm sized droplets of the aforementioned approach it was reported that evaporation during measurement time (~20s) was less than 1%. As our approach can record measurements much faster (several Hz) and even regenerate liquid lost due to evaporation, we do not expect issues with drying. However, additional controls and feedback loops might be needed to be established in order to do this. The FluidFM control software will allow us to communicate over different application programming interfaces (APIs) to implement our own control software for this purposes in LabView and/or Visual Studio (WP4.1). To gain more control over the microfluidic setup, we will install a second microfluidic controller allowing easier switch between the regular FluidFM operation and the LPFM operation setup.

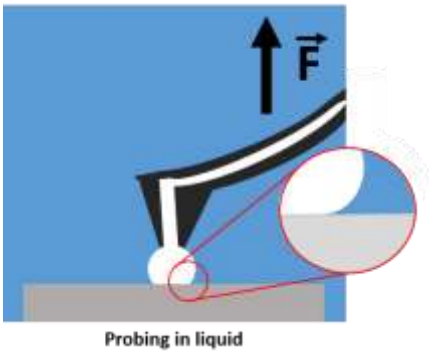

Fig.6: Air bubble probing. When measuring in liquid, also air as probing “liquid” can be employed.

In interesting additional option that will be explored in this work package is the probing of surfaces in liquid. As the FluidFM tip provides a closed channel, it can be used in liquid. All liquids non-miscible with the surrounding bulk liquid and even air could be used as probe under these conditions (Figure 6). This approach will allow to measure in particular high-energy surfaces that show zero contact angle for a standard “water probe in air” strategy to measure surface energies.

When the principal strategy for LPFM is implemented, several test surfaces of known surface energy will be measured with water as probing liquid to validate the method against the established methods like contact angle measurements. This will also allow us to build a library of other test liquids (especially hydrocarbons, e.g. alkenes of different lengths, chloroform) that will make the method also more flexible for other surfaces for future applications.

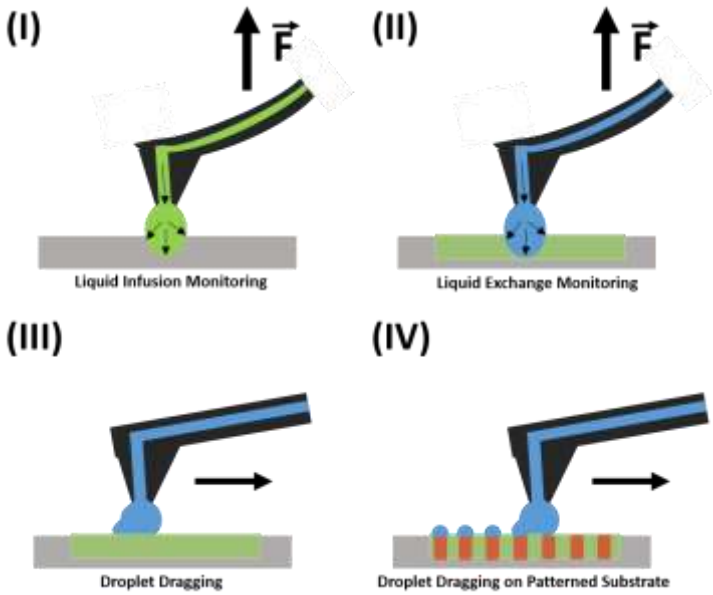

Fig.7: Dynamic Force Spectroscopy Modes. The LPFM will also allow monitoring forces during dynamic processes, e.g. (I) the infusion of the LIS liquid, (II) the exchange of liquids in a LIS/SLIPS system, (III) dragging of a probe droplet over a LIS/SLIPS, and (IV) droplet formation on patterned LIS/SLIPS.

WP1.2: Dynamic Force Spectroscopy

With the experience from implementation of the static force spectroscopy for LPFM (WP1.1),

a more sophisticated dynamic force spectroscopy mode will implemented. Here, either the liquid probe will consist of fluids that will infuse into a porous surface (forming a LIS/SLIPS system), exchange with the liquid already present in the LIS/SLIPS (Figure 7, (I) and (II)), or the tip is used to drag the probe droplet over the surface and monitor friction/adhesion forces or processes like droplet formation on patterned LIS/SLIPS surfaces (Figure 7, (III) and (IV)). In the dynamic processes that are connected to a loss of probe fluid (Figure 7 (I), (II), (IV)), two different sub-modes will be developed. Either the depletion in probe fluid is accepted and the force-time curve is recorded as it evolves, or the probe liquid is constantly replenished by the microfluidics in a controlled rate to keep up with the loss. As swelling or shrinking of the droplet will be reflected in the force curve, a feedback loop can be established tuning the microfluidic supply according to the current loss.

WP2: Characterization of a LIS/SLIPS model system by LPFM

As an interesting LIS to apply the LPFM method developed in WP1 we chose the SLIPS system established in the Levkin group at KIT. This makes it easy to obtain sufficient amounts of samples without establishing the production in our own group while at the same time having chemical expertise nearby to inform us in our experiments. This SLIPS system consists of a porous poly(2-hydroxyethyl methacrylate-co-ethylene dimeth-acrylate) (HEMA-EDMA) film (Figure 40) in-fused with a fluorinated liquid (perfluoro-polyether, PFPE) and was already demonstrated by the Levkin group in various applications.[5,6] The pore sizes of the HEMA-EDMA films can be adjusted and will be tuned to about 150nm for our experiments.[40]

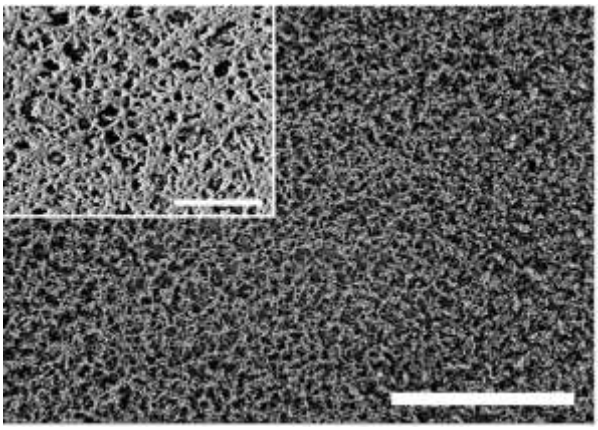

Fig.8: SEM image of a porous HEMA film. Scale bar equals 10µm in the main image and 2µm in the inset. From [40].

WP2.1: Probing static SLIP surface properties

The first measurements on the SLIPS system, which can also already run in parallel with the method development in WP1.1 are the measurement on static properties. This will on the one hand enable the researcher to familiarize with the SLIPS system and on the other hand will give feedback needed for the further development of the LPFM method. Adequate probing liquids will be chosen (e.g. water on PFPE infused porous polymer film) to obtain microscopic contact angles, values for the surface energy, adhesion forces and the software developed for data evaluation and mapping (WP4.1) can be tested here on comparable simple systems. These experiments will also produce the first data to inform model development (WP4.2).

WP2.2: Dynamic Liquid Infusion and Exchange during SLIPS formation

When the procedures and software for dynamic LPFM measurements are developed (WP1.2) dynamic processes during SLIPS formation and fluid exchange can be elucidated. In extension to the static measurements implemented in WP2.1, this workpackage will produce the data on dynamic processes in formation of the SLIPS, i.e. the process of liquid infusion and on the exchange of liquids in a SLIPS, which on the one hand is the hallmark of SLIPS failure / break-down, but can also be used for constructive purposes as controlled fabrication of droplet arrays (which will be examined in WP2.4). For monitoring the formation process of a SLIPS, a liquid probe of PFPE will be produced and interfaced with the porous HEMA-EDMA film as schematically visible in Figure 7 (I). On contact, the PFPE will infuse into the porous film while forces on the droplet probe can be monitored. One possibility is to obtain time-resolved force

data exclusively from the preformed droplet on the tip, which will rather quickly be depleted by infusion into the substrate. As alternative mode of characterization, different flow rates of the infusion liquid through the FluidFM tip will be trialed. This will allow characterizing the infusion process as a depletion or swelling of the droplet will become obvious in the obtained force-time-curves, hence the rate of imbibement and liquid spreading in the porous polymer can be monitored.
The same approach to measurement can be used in the case of liquid exchange, meaning a process in which the probe liquid is displacing the prior infused SLIPS liquid (Figure 7, (II)). Here, especially patterned surfaces produced in WP3 are of interest, as they allow for consecutive experiments on the differently functionalized areas of such a sample, e.g. to repeatedly study the exchange process of PFPE with water on adjacent features with underlying superhydrophilicity. The in-situ renewability of the liquid probe will allow for rapid repetition of infusion experiments on the features to obtain sufficient statistics or (in the case of gradient / multiplexed substrate patterns) probe different surface chemistries and wetting gradients with high efficiency.

WP2.3: Probing Friction

Another interesting use case for the dynamic LPFM methods developed in WP1.2 is the probing of friction. Here a droplet generated by the FluidFM tip will be dragged over the surface of a SLIPS while monitoring the adhesion force. Forces will be monitored by moving the FluidFM cantilever perpendicular to its axis over the sample while measuring the twist in the cantilever (analog to contact mode friction measurements in AFM). The forces will be correlated with macroscopic data of tilting-angles for droplet roll-off in SLIPS systems (WP4.1) and can act as basis for models introducing external forces for dynamic processes in SLIPS (WP4.2). The experience in control of tip movement via software will be fed into the droplet formation study to be conducted in WP2.4.

WP2.4: Droplet Formation on SLIPS

A very interesting dynamic process observed in a SLIPS system is the droplet formation on a SLIPS by liquid exchange.[6] Here, the SLIPS system has been patterned with superhydrophobic and superhydrophilic areas before infusion of PFPE as “slippery” liquid component. If such a system is wetted by dragging a matching liquid across the surface, liquid exchange takes place in the superhydrophilic areas, leading to the formation of separated liquid droplets (Figure 9).

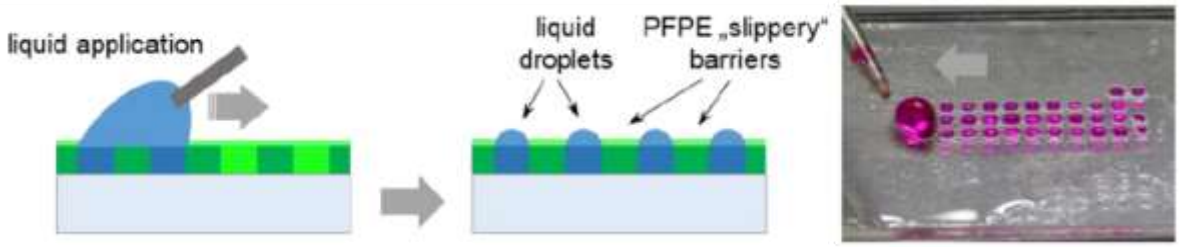

Fig.9: Droplet formation on a patterned SLIPS. A liquid droplet is dragged over a SLIPS based on a superhydrophilc and superhydrophobic (darkgray) patterned porous surface (left). This results in the formation of droplets on the superhydrophilic areas, where liquid exchange takes place (middle). An actual realization of this system is seen on the right. Adapted from [6].

This dynamic process will be a perfect use case for dynamic force spectroscopy with the FPFM technique. As currently, the obtained patterns are all of mesoscopic (µm to mm) scale and application of the exchange liquid is done manually via pipettes, only very limited information on the dynamics of this process is available. The miniaturization of the pattern of superhydrophilic / superhydrophobic patterns in the porpous substrate into the µm scale (WP3.1) will allow to probe the system by dragging a microdroplet over the surface with a FluidFM tip (Figure 7, (IV)). With the experiences and data obtained from the dynamic liquid exchange experiments (WP2.2)

the role of droplet volume, dragging speed and exchange liquid can be systematically elucidated and a model for the system developed (WP4.2).

WP3: Tuning of SLIPS Systems

WP3.1: Local chemical Functionalization

As detailed in section 1, our group has a strong track record in chemical surface modification and functionalization with scanning probe lithography methods. Here, we will employ our expertise to prepare microstructured porous films with high-density features of specific chemical functionalization (Figure 10). While standard photolithography with a mask can be used for some of the measurements in WP2, the size of the features currently produced with these (~hundreds of µm) is not well suited for rapid sampling and high repetition rates of force measurements with the LPFM approach. In addition, the photomask approach does not allow for multiplexing and only to a limited degree for gradient surfaces. Thus, we will employ µCS and (for some higher-resolution structures to challenge the resolution limit of the envisioned LPFM mapping) DPN and structuring of surfaces by FluidFM itself to miniaturize the surface patterning. The patterned surfaces will be crucial for the WP2, especially WP2.4 were the formation of droplet arrays by liquid exchange in a SLIPS will be studied. Here, a high density of alternating superhydrophilic/superhydrophobic features will be crucial to ensure that the LPFM probe can scan over sufficient amounts of features at a time. µCS will be used to deliver hydrophilic precursors (e.g. thiol alcohols) and hydrophobic precursors (e.g. fluor-thiols) at the desired areas of the porous films that can then bind to the HEMA-EDMA by thiol-ene click-chemistry under UV irradiation.[41] Afterwards the porous films can be infused with PFPE as usual to obtain the SLIPS as needed for experimentation. The same approach can also be used to obtain patterns of gradient hydrophilicity, e.g. by vaying the concentration of the precursor deposited on the surface.

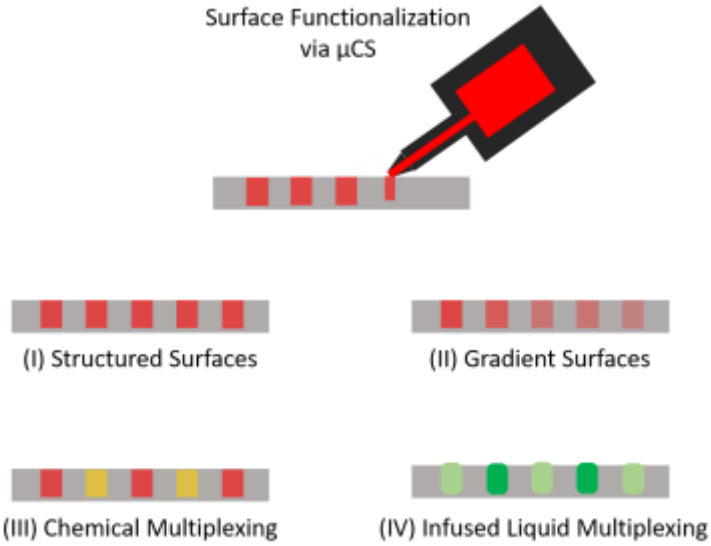

Fig.10: Functionalization of the porous film substrate. Spotting of chemicals in the microscale will allow defining the surface chemistry of the films prior to fluid infusion. This includes (I) simple single component structures, (II) gradient structures e.g. of varying hydrophilicity, and (III) chemically multiplexed structures, e.g. with alternating chemical make-up. The techniques can also be used to locally infuse a porous substrate with different liquids to build “micro-SLIPS” (IV).

Another crucial application of pre-patterning will be to allow the modelling results to feedback into experimental systems by realize custom-made boundary conditions in form of wetting contrasts and geometry suggested by theorists (WP4.2). This experimentation informed by theory/model will be able to validate models by realizing predictions or toy cases, and – in case of mismatch – provide direct new input for the modelling.

WP3.2: Multiplexed Infusion Patterns

In addition to the approach of tuning the substrate hydrophilicity to obtain structured SLIPS, the scanning probe lithography also offers the option to structure SLIPS with different infusion liquids (Figure 10, (IV)). Here, a (chemically structured or plain) porous substrate is – instead of a bulk infusion of PFPE – only locally infused via µCS or FluidFM. This will enable us to generate “micro SLIPS” that can vary in their infused fluid composition to their neighbors, e.g. to

screen the influence of infusion liquid surface tension on SLIPS formation and stability in dynamic modes like WP2.3 and WP2.4.

WP4: Data Analysis, Modelling, and Dissemination of Results

WP4.1: Data Evaluation and Software Development

As much of the obtained data will be used in collaborative efforts with other partners (WP4.2) an efficient gathering, systematic ordering and evaluation of data will be crucial for the project. Thus, we envision building a library of the data obtained in WP1/WP2 that would allow sharing data (e.g. adhesion forces, surface energies, force curves) easily and transparently with colleagues, thus enabling a close collaboration over different groups and labs.
The systematic library of results will also make it easier to validate the liquid probe data, by checking for consistency with the results of macroscopic probing (which will be at minimum possible at least for the static case) from contact angle measurements and results in the existing literature (especially crucial during WP1 to establish the LPFM method).
In order to gather and evaluate the data, software programming will be realized (I) to control the FluidFM setup directly over an API, control tip movements and microfluidics and read-out data directly, and (II) to unify data treatment e.g. for generating force maps of surfaces and systematically evaluation of force curves. These programs will be implemented in LabView and Microsoft VisualStudio.

WP4.2: Collaborative Modelling

The data obtained in WP2 will be basis for collaborative modelling of the SLIPS system we chose as first use case for our LPFM method. Here, we plan to benefit from expertise of existing collaborators as well as new partners that will be identified during the SPP 2171 joint activities during the planned workshops and PhD events.

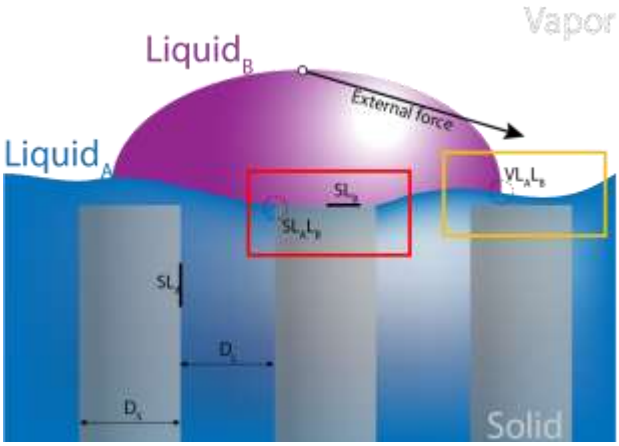

Fig.11: Schematics of a droplet on a LIS/SLIPS with a mesoscale solid scaffold with characteristic length scales infused with a liquid A (blue). Microscopic processes are investigated at the contact lines (indicated by dashed circles) to reveal the local (de)wetting dynamics additionally to the global (ir)reversible dynamics of the liquid B droplet. The red box demarks a place of the LIS/SLIP were liquid B exchanges liquid A, the yellow box a place were no exchange takes place.

The main focus in our own efforts will be the study of liquid exchange processes in SLIPS, and we will be guided in the theoretical modelling by our collaborator Christian Brandl. The approach as envisioned so far is as follows: The exchange between the infused liquid A in a porous surface by another liquid B droplet is the limit of the anticipated tuning of the reversibility and associated dynamics of the wetting and dewetting processes. In this irreversible wetting limit, a SLIPS infused with a liquid A is wetted with a liquid B, which under certain circumstances replaces liquid A at places of the SLIPS with specific properties (Fig. 11). By increasing the inclination of the SLIPS - akin direction of external driving force relative to the substrate - the dynamics towards the reversible (de)wetting dynamics limit is probed on intrinsic heterogonous substrate with a multiscale structure/morphology – this can be probed with the dynamic force spectroscopy as described in WP2.3.
The associated (de)wetting mechanisms with dynamics at interface and contact lines are governed by the interaction of the tunable external driving force with the internal driving forces at different time and length scales. Internal driving forces include interface/surface of/in the substrate (chemical composition, surface energy, morphology, pore size) and bulk and surface

properties of liquid A and liquid B (density, viscosity, surface tension, etc.) which can be tuned e.g. by the film production process (pore size) or chemical modifications of the substrate to tune hydrophilicity (WP3.1). The detailed balance of internal and external driving forces contributing to the effect of liquid exchange on the LIS/SLIPS system can be additionally tuned by changing the involved surface energies, e.g. by changes in surface chemistry, surfactants, and exchange of used liquids (WP3.1 and WP3.2). Most of these variables can be potentially changed/controlled via using external stimuli to realize controllable transition between wetting/dewetting of two liquids on the LIS/SLIPS switchable and on-demand in future applications.

In the forming process of the SPP we also identified already Uwe Thiele as potential collaborator in this matter, as his group has previously developed models for two-liquid film systems[44,45] that could – as of personal communication – potentially be adjusted readily to the SLIPS system we focus in our proposal.

The planned activities in the first two years (the joint SPP workshops and PhD workshop) will give many opportunities to connect with additional groups and built bridges for exchange of expertise and results. Especially, when the capabilities of the LPFM technique (WP1) become clearer and first results can be presented, we can reach out on these events to offer experimental support and test our technique on other systems.

WP4.3: Preparation of Publication for Journals and Conferences

For efficient communication of results in between the members of the SPP 2171, regular meetings and workshops are planned (c.f. WP4.2). Additionally, results will also be prepared for dissemination over (in addition to the 3rd year SPP conference) at least one additional international conference not organized by the SPP and in high impact international journals to ensure communication to the wider scientific community. When possible, open access publication options will be preferred, therefore budget for gold open access and publication fees is allocated.

2.4 Data handling

All data obtained during the project will be handled in accordance to DFG guidelines for best practices. Appropriate measures for data security, backups and structured archiving is implemented at our institute and long term storage for 10 years can be guaranteed in collaboration with the Steinbuch Centre for Computing (SCC) at KIT as provider of IT solutions.

2.5 Other information

Please use this section for any additional information you feel is relevant which has not been provided elsewhere.

none

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern

none

2.7 Information on scientific and financial involvement of international cooperation partners

none

3 Bibliography

[1] P. Zhang, F. Y. Lv, *Energy* **2015**, *82*, 1068.
[2] A. K. Epstein, T.-S. Wong, R. A. Belisle, E. M. Boggs, J. Aizenberg, *Proc. Natl. Acad. Sci.* **2012**, *109*, 13182.
[3] C. Howell, A. Grinthal, S. Sunny, M. Aizenberg, J. Aizenberg, *Adv. Mater.* **2018**, 1802724.
[4] I. Sotiri, J. C. Overton, A. Waterhouse, C. Howell, *Exp. Biol. Med.* **2016**, *241*, 909.
[5] J. Bruchmann, I. Pini, T. S. Gill, T. Schwartz, P. A. Levkin, *Adv. Healthc. Mater.* **2017**, *6*, 1601082.
[6] D. Paulssen, W. Feng, I. Pini, P. A. Levkin, *Adv. Mater. Interfaces* **2018**, *5*, 1800852.
[7] A. N. Lupas, *Science (80-.).* **2014**, *346*, 1455.
[8] A. Meister, M. Gabi, P. Behr, P. Studer, J. Vörös, P. Niedermann, J. Bitterli, J. Polesel-Maris, M. Liley, H. Heinzelmann, T. Zambelli, *Nano Lett.* **2009**, *9*, 2501.
[9] T. Zambelli, M. Aebersold, P. Behr, H. Han, L. Hirt, O. Guillaume-gentil, J. Vörös, *Open-SpaceMicrofluidics Concepts, Implementations, Appl.* **2018**, 295.
[10] H. Heinzelmann, A. Meister, P. Niedermann, J. Bitterli, J. Polesel-maris, M. Liley, M. Gabi, P. Behr, P. Studer, J. Vörös, T. Zambelli, *Microsc. Anal.* **2009**, *23*, 11.
[11] E. Potthoff, O. Guillaume-Gentil, D. Ossola, J. Polesel-Maris, S. LeibundGut-Landmann, T. Zambelli, J. a Vorholt, *PLoS One* **2012**, *7*, e52712.
[12] O. Guillaume-Gentil, E. Potthoff, D. Ossola, P. Dörig, T. Zambelli, J. a. Vorholt, *Small* **2012**, n/a.
[13] P. Dörig, P. Stiefel, P. Behr, E. Sarajlic, D. Bijl, M. Gabi, J. Vörös, J. a. Vorholt, T. Zambelli, *Appl. Phys. Lett.* **2010**, *97*, 023701.
[14] O. Guillaume-Gentil, E. Potthoff, D. Ossola, C. M. Franz, T. Zambelli, J. A. Vorholt, *Trends Biotechnol.* **2014**, *32*, 381.
[15] P. Stiefel, T. Zambelli, J. a Vorholt, *Appl. Environ. Microbiol.* **2013**, *79*, 4895.
[16] P. Stiefel, F. I. Schmidt, P. Dörig, P. Behr, T. Zambelli, J. a Vorholt, J. Mercer, *Nano Lett.* **2012**, *12*, 4219.
[17] R. R. Grüter, J. Vörös, T. Zambelli, *Nanoscale* **2013**, *5*, 1097.
[18] L. Fabié, P. Agostini, M. Stopel, C. Blum, B. Lassagne, V. Subramaniam, T. Ondarçuhu, *Nanoscale* **2015**, *7*, 4497.
[19] V. Liimatainen, M. Vuckovac, V. Jokinen, V. Sariola, M. J. Hokkanen, Q. Zhou, R. H. A. Ras, *Nat. Commun.* **2017**, *8*, 1.
[20] R. D. Piner, J. Zhu, F. Xu, S. Hong, C. A. Mirkin, *Science (80-.).* **1999**, *283*, 661.
[21] F. Huo, Z. Zheng, G. Zheng, L. R. Giam, H. Zhang, C. A. Mirkin, *Science (80-.).* **2008**, *321*, 1658.
[22] M. Hirtz, A. M. Greiner, T. Landmann, M. Bastmeyer, H. Fuchs, *Adv. Mater. Interfaces* **2014**, *1*, 1300129.
[23] M. Hirtz, A. Oikonomou, S. Varey, H. Fuchs, A. Vijayaraghavan, T. Georgiou, H. Fuchs, A. Vijayaraghavan, *Nat. Commun.* **2013**, *4*, 2591.
[24] M. Hirtz, S. Varey, H. Fuchs, A. Vijayaraghavan, *ACS Appl. Mater. Interfaces* **2016**, *8*, 33371.
[25] M. Hirtz, A. Oikonomou, N. Clark, Y.-J. Kim, H. Fuchs, A. Vijayaraghavan, *Nanoscale* **2016**, *8*, DOI 10.1039/c6nr04615k.
[26] N. Willems, A. Urtizberea, A. F. Verre, M. Iliut, M. Lelimousin, M. Hirtz, A. Vijayaraghavan, M. S. P. Sansom, *ACS Nano* **2017**, *11*, 1613.
[27] H.-Y. Chen, M. Hirtz, X. Deng, T. Laue, H. Fuchs, J. Lahann, *J. Am. Chem. Soc.* **2010**, *132*, 18023.
[28] M. Davydova, A. de los Santos Pereira, M. Bruns, A. Kromka, E. Ukraintsev, M. Hirtz, C. Rodriguez-Emmenegger, *RSC Adv.* **2016**, *6*, 57820.
[29] S. M. M. S. M. M. Dadfar, S. Sekula-Neuner, U. Bog, V. Trouillet, M. Hirtz, *Small* **2018**, *14*, 1800131.
[30] E. Oppong, P. N. Hedde, S. Sekula-Neuner, L. Yang, F. Brinkmann, R. M. Dörlich, M. Hirtz, H. Fuchs, G. U. Nienhaus, A. C. B. Cato, *Small* **2014**, *10*, DOI 10.1002/smll.201303677.
[31] A. Angelin, S. Weigel, R. Garrecht, R. Meyer, J. Bauer, R. Kumar, M. Hirtz, C. M.

Niemeyer, *Angew. Chemie Int. Ed.* **2015**, *54*, 15813.
[32] F. Brinkmann, M. Hirtz, A. Haller, T. M. Gorges, M. J. Vellekoop, S. Riethdorf, V. Müller, K. Pantel, H. Fuchs, *Sci. Rep.* **2015**, *5*, 15342.
[33] R. Kumar, S. Weigel, R. Meyer, C. M. Niemeyer, H. Fuchs, M. Hirtz, *Chem. Commun.* **2016**, *52*, 12310.
[34] R. Kumar, A. Bonicelli, S. Sekula-Neuner, A. C. B. Cato, M. Hirtz, H. Fuchs, *Small* **2016**, *12*, 5330.
[35] J. Atwater, D. S. Mattes, B. Streit, C. von Bojničić-Kninski, F. F. Loeffler, F. Breitling, H. Fuchs, M. Hirtz, *Adv. Mater.* **2018**, *30*, 1801632.
[36] P. Rath, M. Hirtz, G. Lewes-Malandrakis, D. Brink, C. Nebel, W. H. P. Pernice, *Adv. Opt. Mater.* **2015**, *3*, 328.
[37] U. Bog, T. Laue, T. Grossmann, T. Beck, T. Wienhold, B. Richter, M. Hirtz, H. Fuchs, H. Kalt, T. Mappes, *Lab Chip* **2013**, *13*, 2701.
[38] U. Bog, F. Brinkmann, H. Kalt, C. Koos, T. Mappes, M. Hirtz, H. Fuchs, S. Köber, *Small* **2014**, *10*, 3863.
[39] U. Bog, F. Brinkmann, S. F. Wondimu, T. Wienhold, S. Kraemmer, C. Koos, H. Kalt, M. Hirtz, H. Fuchs, S. Koeber, T. Mappes, *Adv. Sci.* **2015**, *2*, 1500066.
[40] M. Hirtz, M. Lyon, W. Feng, A. E. Holmes, H. Fuchs, P. A. Levkin, *Beilstein J. Nanotechnol.* **2013**, *4*, 377.
[41] J. Li, L. Li, X. Du, W. Feng, A. Welle, O. Trapp, M. Grunze, M. Hirtz, P. A. Levkin, *Nano Lett.* **2015**, *15*, 675.
[42] M. Hirtz, W. Feng, H. Fuchs, P. A. Levkin, *Adv. Mater. Interfaces* **2016**, *3*, 1500469.
[43] S. Sekula-Neuner, M. de Freitas, L.-M. Tröster, T. Jochum, P. A. Levkin, M. Hirtz, H. Fuchs, *Beilstein J. Nanotechnol.* **2017**, *8*, 715.
[44] A. Pototsky, M. Bestehorn, D. Merkt, U. Thiele, *J. Chem. Phys.* **2005**, *122*, 224711.
[45] A. Pototsky, M. Bestehorn, D. Merkt, U. Thiele, *Europhys. Lett.* **2006**, *74*, 665.
[46] B. Cappella, G. Dietler, *Surf. Sci. Rep.* **1999**, *34*, 1.

4 Requested modules/funds

Explain each item for each applicant (stating last name, first name).

The overall funding (3 Year period) requested is tabulated below and detailed in the following specific sections.

Staff (PhD student)	145.125€
Small Equipment and Consumables	30.400€
Travel Expenses	5.400€
Publication Costs	2.250€
Total (whole 3 year period)	**183.175€**

4.1 Basic Module

4.1.1 Funding for Staff

We propose to have one PhD student (n.n.) focusing on the

Year 1	PhD student (75% position)[2]	48.375€
Year 2	PhD student (75% position)	48.375€
Year 3	PhD student (75% position)	48.375€
	Total	**145.125€**

4.1.2 Direct Project Costs

4.1.2.1 Equipment up to Euro 10,000, Software and Consumables

Software (Labview, Visual Studio)

Year 1	Microfluidic Equipment (Controller, Pressure Sensors, tubing) Software (LabView) Consumables (Chemicals, FluidFM tips)	9.000€ 400€ 7.000€
Year 2	Consumables (Chemicals, FluidFM tips)	7.000€
Year 3	Consumables (Chemicals, FluidFM tips)	7.000€
	Total	**30.400€**

4.1.2.2 Travel Expenses

We estimate the average cost for travel events with 80€ per person per day, 200€ for travel within Germany, 600€ for international travel.

Year 1	SPP Workshop, 4 days (1 PhD + 1 PI)	1.040€
	Advanced School, 5 days (1 PhD)	600€
Year 2	SPP Workshop, 4 days (1 PhD + 1 PI)	1.040€
	PhD workshop, 4 days (1 PhD)	520€
Year 3	SPP conference 5 days (1 PhD + 1 PI)	1.200€
	International conference, 5 days (1 PhD)	1.000€
	Total	**5.400€**

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

none

4.1.2.4 Expenses for Laboratory Animals

none

4.1.2.5 Other Costs

none

[2] Costs as defined in „Personalmittelsätze der DFG für das Jahr 2018“, 64.500€/annum

4.1.2.6 Project-related publication expenses

Year 1	Open Access publication cost	750€
Year 2	Open Access publication cost	750€
Year 3	Open Access publication cost	750€
	Total	**2.250€**

4.1.3 Instrumentation

No additional large instrumentation needed (FluidFM is already available).

5 Project requirements

5.1 Employment status information

For each applicant, state the last name, first name, and employment status (including duration of contract and funding body, if on a fixed-term contract).

Name	Employment Status	Funding
Michael Hirtz	permanent	KIT

5.2 First-time proposal data

Only if applicable: Last name, first name of first-time applicant

n/a

5.3 Composition of the project group

List only those individuals who will work on the project but will not be paid out of the project funds. State each person's name, academic title, employment status, and type of funding.

Name	Title	Employment Status	Funding	
Michael Hirtz	PD Dr. Dr.	permanent	KIT	**PI**
Navid Hussain	Master	PhD student (contract till 31.5.2021)	KIT	
N.N.		Master Student (no contract)	KIT	

5.4 Cooperation with other researchers

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

For the detailed description of collaboration plans, please refer to section 1 and specific mentions in the workplan. In short, following researchers have already agreed on collaboration:

- Pavel Levkin (KIT) will provide porous polymer films for our project and we will provide experimental characterizations with LPFM for their SPP project
- Jacco Snoeijer (University of Twente)/Uwe Thiele (WWU Münster) will be additional partners in the exchange of experimental data and theoretical expertise / modelling in the SPP framework
- Christian Brandl (KIT) will support us in the modelling of our SLIPS system

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

National	International
Prof. Andrew Cato (KIT)	Prof. Andrea Holmes (Doane University)
Prof. Christof Niemeyer (KIT)	Prof. Ronnie Willaert (VBU)
Prof. Klaus Pantel (UKE)	Prof. Lifeng Chi (Soochow University)
Prof. Wolfram Pernice (WWU)	Prof. Chad Mirkin (Northwestern University)
Prof. Christoph Nebel (IAF)	Dr. Aravind Vijayaraghavan (Manchester University)
Prof. Thomas Schimmel (KIT)	
Dr. Cesar Rodriguez-Emmenegger (RWTH)	

5.5 Scientific equipment

List larger instruments that will be available to you for the project. These may include large computer facilities if computing capacity will be needed.

Scanning Probe Lithography

Our group has high end scanning probe lithography equipment available. We are equipped with a DPN 5000 and a NLP 2000 system (NanoInk, USA). In addition, we have several self-built setups that can be used for different scanning probe lithography techniques as DPN, PPL and µCS.

FluidFM

Our newly installed FluidFM (Cytosurge/Nanosurf, Switzerland) is an unique tool for aspiration or deposition of small liquid volumes. Simultaneously, the FluidFM allows normal AFM operation, thus enabling force measurements and imaging. It can be operated in air and liquid environments.

Atomic Force Microscopy, Scanning Electron Microscopy

The INT as hosting institute offers joint facilities for AFM (Dimension Icon & Multimode, Bruker, Germany) and SEM (Leo, Zeiss, Germany) that are available to the project when needed.

Karlsruhe Nano Micro Facility (KNMF)

In addition to equipment directly available to our group or available in-house in INT, we can also rely on the support of the KNMF, a user facility that offers 26 different technologies in characterization and nano/microfabrication free of charge. Details on the offered technologies can be found under https://www.knmf.kit.edu/

5.6 Project-relevant cooperation with commercial enterprises

If applicable, please note the EU guidelines on state aid or contact your research institution in this regard.

none

5.7 Project-relevant participation in commercial enterprises

Information on connections between the project and the production branch of the enterprise

none

6 Additional information

If applicable, please list proposals requesting major instrumentation and/or those previously submitted to a third party here.

none