Priority Programme "Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces" (SPP 2171)

Title: Study of dynamic wetting on switchable surfaces at the micro and macroscale

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1. Project description

1.1 Summary

Smart surfaces with switchable dynamic wettabilities attract great interest because of their potential applications including, *inter alia*, microfluidic switches,[1] smart membranes,[2] controllable liquid separation[3] or water collection,[4] cell capture/release devices[5] or biosensors.[6] Reversible switching of wettability can be realized either by modifying surface with a responsive coating layer[5] or by using responsive bulk material.[6] Surfaces with switchable special wettability, such as superhydrophobicity, superoleophobicity or superhydrophilicity, represent a special case of switchable dynamic wettabilities with many potential applications.[7-9] However, despite the extensive studies on switchable surfaces and surfaces with special wettability, the switching of surface wettability is mostly characterized by standard contact angle measurements at the macroscale and, to the best of our knowledge, has never been investigated at the microscale in order to correlate the responsive properties of microstructures with the macroscopic responsiveness. The main reasons for this is the difficulty to create responsive microstructures with defined 3D shapes and to study wettability at the microscale.

As wetting is inherently a multi-scale phenomenon, physico-chemical interactions at the micro-scale solid-liquid interface determine dynamics of wettability at the macroscale. Therefore, it is of great importance to investigate wetting variations on switchable surfaces not only at the macroscopic length scale, for example, by measuring contact angles or sliding angles, but also on microscopic length scale to understand the intimate relationship between the micro and macroscale wetting dynamics. In this proposal, we aim to systematically investigate the dynamics of droplet adhesion to microstructures with defined 3D shapes build from a responsive polymer, such as poly(*N*-isopropylacrylamide) (polyNIPAAm) as a commonly used temperature responsive polymer material. In order to study wettability and its dynamics at the microscale, we will use a newly developed scanning droplet adhesion microscopy (SDAM) and compare these results with the macroscopic advancing and receding contact angle measurements on corresponding large flat as well as structured surfaces. There are several goals of this study. First of all, we would like to understand how the wettability switching can vary when microstructures are compared with large surfaces made of the same materials. We want to study the influence of different microstructure geometrical features as well as composition of the polymer microstructures on both micro- and macroscopic wettability. Finally, we want to bridge the dynamic liquid wetting processes on switchable surfaces at micro- and macro-length scales (Figure 1).

Aiming at revealing microscale spatial wetting heterogeneity on superhydrophobic or superoleophobic surfaces, SDAM´s unique advantage is that it can be used to characterize dynamic wetting events on individual microposts by measuring droplet adhesion force (snap-in and pull-off forces) with spatial resolution down to 10 µm and force sensitivity down to 5 nN[10]. SDAM also serves as a perfect tool to detect the subtle wettability variation on switchable surfaces, because the measurements of macroscopic contact angles are often very insensitive.[11] The SDAM technology has been recently developed by Prof.

Robin Ras and Prof. Quan Zhou at Aalto University (Finland). We have been successfully collaborating with both groups during the last several years [12, 13] and they agreed to collaborate also in this project to perform corresponding SDAM measurements (see collaboration support letter in the appendix).

We will also attempt to measure the microdroplet adhesion forces on switchable substrates using the fluid force microscopy (FluidFM) in collaboration with Dr. Michael Hirtz at INT (KIT), who is also applying for the SPP2171. Combing atomic force microscopy with nanofluidic system, FluidFM can precisely control the deposition and retraction of droplets on surface while simultaneously detect the adhesion force with resolution of nN, therefore providing us a new opportunity to measure the microdroplet adhesion force on switchable substrates.

To fabricate arrays of microstructures with reentrant geometry and made of polyNIPAAm of defined polymeric composition, we will adopt the direct laser writing (DLW) technique (commercial instruments from Nanoscribe GmbH).[14-16] Using DLW, microstructure arrays with well-controlled spatial chemical constitution and defined 3D geometry (features down to 100 nm) can be readily fabricated. This will enable us to systematically investigate the responsive wettability as a function of both polymer composition and microstructure 3D shape and size, which, to the best of our knowledge, has never been reported till now due to the difficulties in creating microstructures with such complex geometries and the lack of appropriate characterization methods. Over the last year, we have been successfully collaborating[12] with the group of Martin Wegener (APH, KIT), who co-developed the Nanoscribe´s DLW technology, and who agreed to collaborate within this project by providing his expertise in the DLW method (see support letter in the appendix).

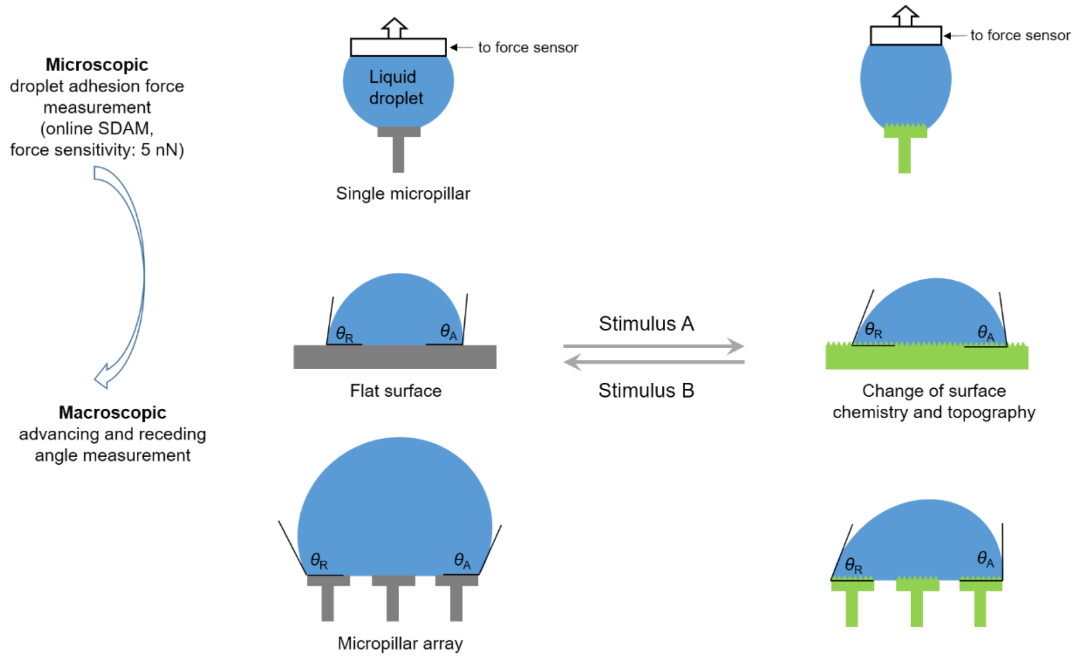

Figure 1. Scheme showing the investigation of the switchable wettability at the microscale using real-time SDAM and at the macroscale using advancing/receding contact angle measurements.

Zusammenfassung

Intelligente Oberflächen mit dynamisch-schaltbarer Benetzbarkeit ziehen großes Interesse auf sich aufgrund ihrer potentiellen Anwendungen in Bereichen wie u.a. mikrofluidische Schalter[1], intelligente Membranen[2], kontrollierbare Trennung von Flüssigkeiten[3] oder Wasseransammlungen[4], Erfassung und Freisetzung von Zellen[5] oder Biosensoren[6]. Das reversible Umschalten der Benetzbarkeit kann entweder durch Modifizierung der Oberfläche mit einer reaktiven Beschichtung[5] oder Nutzung von massiven reaktiven Materialien erreicht werden.[6] Oberflächen mit spezieller schaltbarer Benetzbarkeit wie superhydrophobie, superoleophobie oder superhydrophilie stellen einen Spezialfall der schaltbaren dynamischen Benetzbarkeit dar, der zahlreiche potentielle Anwendungen aufweist.[7-9] Dennoch wird die Benetzbarkeit einer Oberfläche, trotz intensiver Untersuchungen an schaltbaren und speziell benetzbaren Oberflächen, hauptsächlich durch Messungen des Kontaktwinkelns im Makromaßstab charakterisiert und wurde unseres Wissens nach noch nie auf der Mikroebene untersucht, um die Reaktivität der Mikrostrukturen mit denen der Makroebene zu verbinden. Einer der Hauptgründe hierfür ist die Schwierigkeit, reaktive Mikrostrukturen mit definierten dreidimensionalen Formen herzustellen und die Benetzbarkeit im Mikromaßstab zu untersuchen.

Die Benetzung einer Oberfläche ist von Natur aus ein Phänomen, das auf mehreren Größenebenen definiert wird: Durch physikalisch-chemische Wechselwirkungen im Mikromaßstab und durch die fest-flüssig Grenzflächen im Makromaßstab. Es ist daher von großer Wichtigkeit, Änderungen der Benetzbarkeit von schaltbaren Oberflächen nicht nur auf der makroskopischen Längenskala durch Kontaktwinkel und Abrutschwinkel zu messen, sondern auch mikroskopisch, um die enge Verbindung zwischen mikro- und makroskopischen Dynamiken zu verstehen.

In diesem Antrag ist es unser Ziel, systematisch die Dynamiken der Adhäsion von Tropfen an Mikrostrukturen mit definierten dreidimensionalen Formen, die mit Hilfe des häufig benutzten thermoresponsiven Polymers wie poy(N-isopropylacrylamide) (polyNIPAAm) hergestellt werden, zu untersuchen.

Um die Benetzbarkeit und deren Dynamik im Mikromaßstab zu untersuchen, werden wir die neu entwickelte Technologie der „scanning droplet adhesion microscopy (SDAM)“ verwenden und diese Ergebnisse mit den makroskopisch bestimmten voran- und zurückschreitenden Kontaktwinkeln auf größeren flachen und strukturierten Oberflächen vergleichen. Diese Studie hat mehrere Ziele: Zuerst möchten wir verstehen, wie die Benetzbarkeit zwischen Mikrostrukturen und großen Oberflächen aus dem gleichen Material variieren. Weiterhin wollen wir den Einfluss der geometrisch unterschiedlichen Mikrostrukturen und der Zusammensetzung des Polymers auf die mikro- und makroskopischen Benetzbarkeit untersuchen. Schließlich wollen wir die dynamischen Prozesse der Benetzung von schaltbaren Oberflächen mit einer Flüssigkeit im Mikro- und Makromaßstab verbinden. (Abbildung 1)

Darauf abzielend mikroskopisch kleine räumliche Heterogenitäten in der Benetzbarkeit von superhydrophoben und superoleophoben Oberflächen aufzudecken, ist der besondere Vorteil von SDAM, dass es dazu benutzt werden kann dynamische Benetzbarkeitsereignisse auf einzelnen Mikro-Pfosten zu charakterisieren, in dem Tröpfchen-Adhäsions-Kräfte („snap-in“- und „pull-off“-Stärke) gemessen werden können mit einer räumlichen Auflösung von bis zu 10 µm und einer Sensibilität von bis zu 5 nN Kraft. [10] SDAM dient ebenfalls als perfektes Mittel um feine Veränderungen in der Benetzbarkeit von veränderbaren Oberflächen zu detektieren, da hier die Messungen von makroskopischen Kontaktwinkel oftmals insensibel sind.[11] Die SDAM-Technologie wurde vor kurzem von Professor Robin Ras und Professor Quan Zhou and der Aalto Universität (Finnland) entwickelt. Wir haben erfolgreich mit beiden Gruppen währen der letzten Jahre kooperiert und sie haben sich einverstanden erklärt ebenfalls in diesem Projekt mit uns zu kooperieren, um entsprechende SDAM Messungen durchzuführen (siehe den Unterstützungsbrief im Appendix).

Wir streben ebenfalls an die Adhäsionskräfte von Mikro-Tröpfchen auf veränderbaren Oberflächen durch „Fluid Force Microscopy (FluidFM)“ zu messen in Kollaboration mit Dr. Michael Hirtz am INT (KIT), dessen Gruppe sich ebenfalls für das SPP2171 bewirbt. Indem es atomare Kräftemikroskopie mit

nano-fluidischen System kombiniert, kann das FluidFM präzise die Ablage und das Zurückziehen von Tropfen auf Oberflächen kontrollieren, während es simultan die Adhäsionskräfte mit einer Auflösung von nN detektiert, wodurch es uns mit einer neuen Möglichkeit ausstattet die Adhäsionskraft von Mikro-Tröpfchen auf veränderbaren Oberflächen zu messen.
Um Array-Systeme mit "re-entrant"-Geometrie-Mikrostrukturen herzustellen, die aus polyNIPAAm mit definierter polymerischer Komposition bestehen, werden wir die direkte Laser-Schreibung (DLW) Technik adaptieren (kommerzielle Instrumente werden von Nanoscribe GmbH bereitgestellt).[12-14] Durch DLW können Mikrostruktur-Arrays mit genau kontrollierter räumlich chemischer Beschaffenheit und definierter 3D-Geometrie (Merkmale mit einer Auflösung von bis zu 100 nm) einfach fabriziert werden. Dies wird uns erlauben systematisch die reaktionsfähige Benetzbarkeit als Funktion von sowohl der Polymer-Beschaffenheit und der Mikrostruktur-3D-Formen und -Größe zu studieren, was – soweit uns bekannt ist – bisher noch nicht publiziert wurde wegen der Schwierigkeit, die darin liegt Mikrostrukturen mit solcher Komplexität herzustellen und zu charakterisieren. Innerhalb des letzten Jahres, haben wir erfolgreich mit der Gruppe von Martin Wegener (APH, KIT) kooperiert, der die Nanoscribe DLW Technologie entwickelt hat und der sich Einverstanden erklärt hat innerhalb dieses Projektes zu kollaborieren, in dem er seine Expertise in der DLW Methode zur Verfügung stellt (siehe den Unterstützungsbrief im Appendix).

1.2 State of the art

Controlling surface wettability is important in numerous industrial applications such as microfluidics,[17] coatings,[18] heat transfer[19] and liquid manipulation.[20] Reversible control of the surface wettability can be realized either by modifying the surface with stimuli-responsive compounds or by using responsive bulk materials. Various responsive functionalities have been used, for example, light responsive azobenzene,[21] temperature responsive polyNIPAAm ,[22] pH-responsive carboxylic acid,[23] and various other systems.[24] By combining the change in surface chemistry with surface micro- and nano-structure, which can enhance stimuli-responsive wettability, reversible switching between superhydrophilicity and superhydrophobicity has been realized.[25]

However, despite a lot of research over the fabrication and application of switchable substrates, the precise mechanism by which a liquid advances and recedes on switchable surfaces is only partially understood. Thus, our ability to predict dynamic wetting behaviour and model processes on switchable substrates is significantly restricted.[26] This incomplete understanding originates from the fact that dynamic wetting process operates on a scale that extends from the macroscopic to the microscopic and molecular,[27] while our observations are usually limited to the macroscopic measurements such as apparent advancing and receding contact angels or sliding angles, with the macroscopic contact angles measured by sessile drop method at a resolution of no better than several millimeters.[28, 29] As the measurement is based on observing the movement of contact line on a macroscopic view, it is inherently unsuitable for characterization of microscale wetting variations.[30] Besides, the sessile drop method is strongly influenced by the details of the experiment setup,[11, 31] e.g., even a tiny deviation of the base line could result in significant changes in the measured contact angles, therefore lacking the accuracy and sensitivity to characterize the subtle wettability variation on switchable substrates sometimes with contact angle change less than 10°.[21]

As wetting is inherently a multi-scale phenomenon, the contact line motion is ultimately determined by physicochemical interactions of the liquid with the substrate.[32] For example, the hydrophobicity of an impacting sphere, which can be altered by a coating of a few nanometers thick, controls the outcome of a macroscopic splash.[33] Therefore, it is of great importance to investigate wetting variations on switchable surfaces not only on macroscopic length scale, but also on microscopic length scale to understand the intimate relationship between the micro and macroscale wetting dynamics. It has long been proposed that macroscopic contact angles during dynamic wetting process are strongly influenced by interactive forces between the liquid and solid at the microscale and nanoscale.[34, 35] However, because most existing contact angle and force-based measurements lack sensitivity and spatial resolution,[28, 31, 36] it remains a great challenge to characterize the liquid-solid interactions in dynamic wetting at the micro scale.

To this end, we aim to combine a newly developed scanning droplet adhesion microscopy (SDAM) with and macroscopic advancing/receding contact angle measurements to understand how the microscale liquid-solid interactions influence the macroscopic dynamic wetting on switchable substrates. As an effective way of characterizing the interactions between liquid and solid surfaces, SDAM measures tensile adhesion forces with spatial resolution down to 10 μm and three orders of magnitude better force sensitivity than current tensiometers.[30] Thus, SDAM provides an effective tool to detect subtle changes of liquid-solid interactions on switchable substrates by measuring adhesion force at the microscale, and how this adhesion force can be correlated to the macroscopic change of dynamic contact angles.

It is well known that both surface chemical composition and micro-topography govern the surface wettability of solid substrates.[37] For example, it has been reported that both the variation of micro-post shape and distance could result in a significant change of receding contact angles on superhydrophobic surfaces.[38] Therefore, it is of importance to systematically study the kinetics of responsive wettability as a function of both composition of a responsive material and the 3D shape of microstructures. DLW is an additive manufacturing technique based on two-photon absorption polymerization, which offers the true freedom for 3D fabrication, as well as the high spatial resolution in sub-micrometer range.[14-16] In DLW, microstructures with various well-defined 3D topography can be printed in a microarray format, and the chemical constituent of the microstructures can be controlled by using different compositions of prepolymer mixtures.[16] Therefore, DLW in combination with the SDAM serve as perfect tools to investigate the stimuli-responsive wettability at the microscale and to correlate this behavior with the macroscopic dynamic wettability.

1.3 Preliminary work

Previously we have successfully used the DLW for rapid prototyping and systematic investigation of arrays of hierarchical doubly re-entrant micropillars with or without nanopillars on their top surfaces (collaboration with Martin Wegener's research group at APH (KIT) (Figure 2).[12] By infusing a lubricant into the nanopillared surface on top of the doubly re-entrant micropillars, we could combine the slippery low adhesion effect of lubricant-infused surfaces with the superoleophobicity of doubly re-entrant microstructures, leading to the "Cassie state" where a liquid droplet is located on the lubricant–air composite interface, avoiding direct contact between droplet and solid interface (Figure 3).

We used the scanning droplet adhesion microscopy (SDAM) to demonstrate that the dynamic, ultra-smooth slippery layer indeed reduced the adhesive force of water droplets on individual micropillars (collaboration with the research groups of Robin Ras and Quan Zhou at Aalto University) (Figure 4). In addition, the adhesion force measurements confirmed the need for the nanoroughness in order to stabilize the lubricant layer on the tops of the doubly re-entrant micropillars.

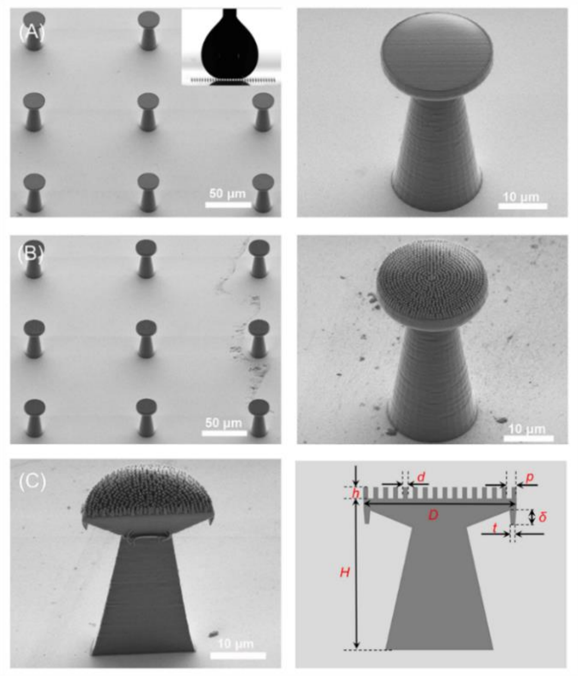

Figure 2. SEM images of doubly re-entrant micropillars with flat and nanopillared (nanorough) tops. (A) 45° view of doubly re-entrant micropillars with flat tops. The insert picture shows a 6 μL ethanol drop deposited on a surface composed of the doubly re-entrant micropillars with static contact angle of 158 ± 5°. (B) 45° view of doubly re-entrant micropillars with nanorough tops. (C) Cross-sectional view of a doubly re-entrant micropillar with a nanorough top.[12]

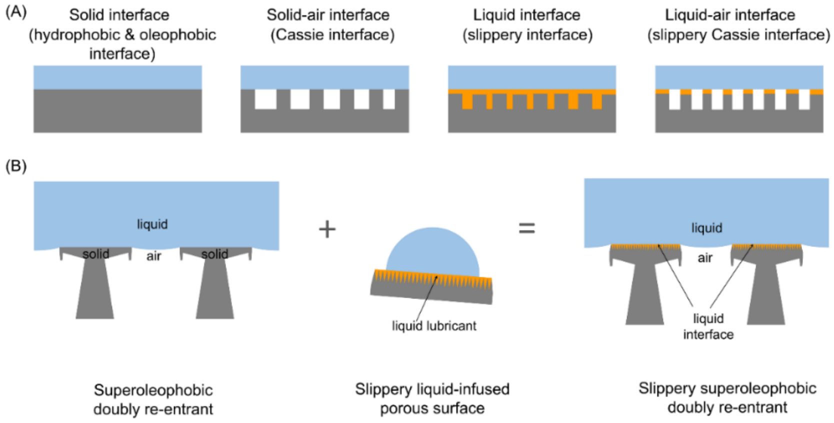

Figure 3. (A) Schemes showing liquid on a hydrophobic & oleophobic, superhydrophobic & superoleophobic, slippery and slippery superhydrophobic & superoleophobic surfaces possessing different contact interfaces. (B) Blueprint for a slippery superoleophobic surface formed via combination of a doubly re-entrant structure and a slippery liquid-infused porous surface.[12]

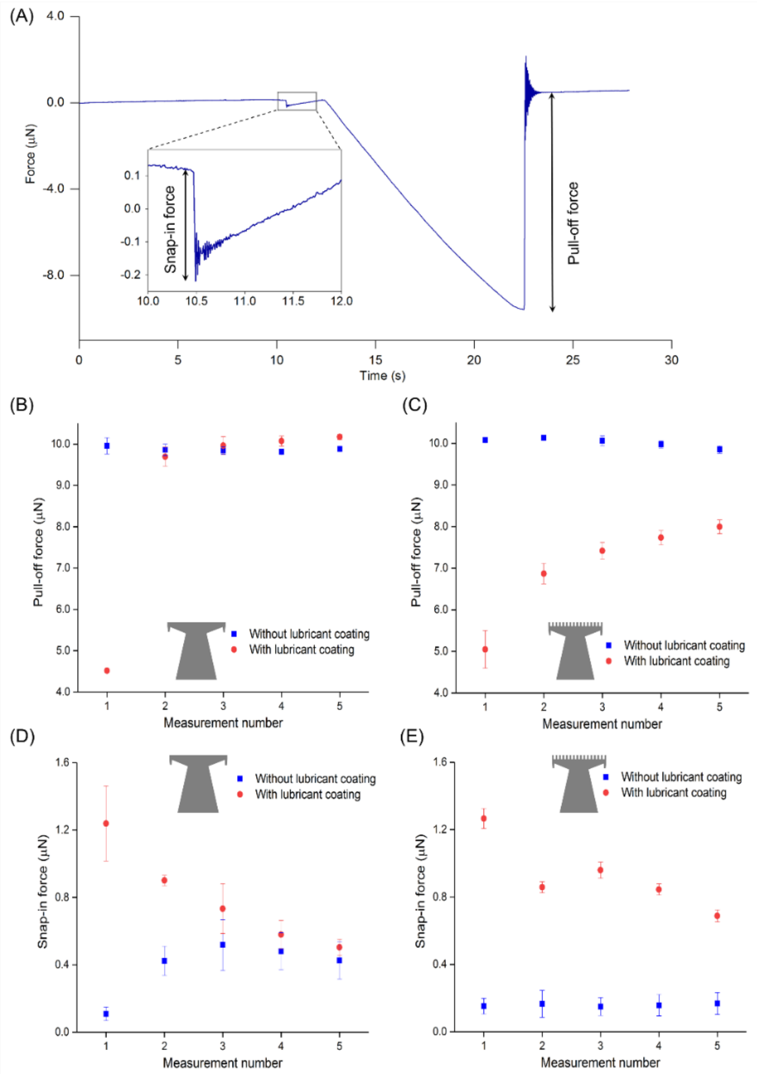

Figure 4. Microscopic droplet adhesion force measurements on individual micropillars. (A) A representative force curve for a single 50 µm diameter uncoated micropillar with a flat top using a 1.5 µL water droplet. (B-C) Pull-off forces and (D-E) snap-in forces on 50 µm diameter micropillars with (red circles) and without (blue squares) lubricant coating. B and D: pillars with flat top surfaces; C and E: pillars with nanorough top surfaces. The error bars represent standard deviations based on 5 independent measurements on 5 individual micropillars.[12]

Project related publications

1.4.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published

- Dong, Z.; Schumann, M, F.; Hokkanen, M, J.; Chang, B.; Welle, A.; Zhou, Q.; Ras, R. H. A.; Xu, Z.; Wegener, M.; Levkin, P. A. Superoleophobic Slippery Lubricant-Infused Surfaces: Combining Two Extremes in the Same Surface. *Adv. Mater.* **2018**, 1803890.
- Li, L.; Feng, W.; Well, A.; Levkin, P. A. UV-Induced Disulfide Formation and Reduction for Dynamic Photopatterning. *Angew. Chem. Int. Ed.* **2016**, 55, 13765–13769.
- Feng, W.; Li, L.; Du, X.; Welle, A.; Levkin, P. A. Single-Step Fabrication of High-Density Microdroplet Arrays of Low-Surface-Tension Liquids. *Adv. Mater.* **2016**, 28, 3202–3208.

- Du, X.; Li, J.; Welle, A.; Li, L.; Feng, W.; Levkin, P. A. Reversible and Rewritable Surface Functionalization and Patterning via Photodynamic Disulfide Exchange. *Adv. Mater.* **2015**, 27, 4997–5001.
- Li, J.; Li, L.; Du, X.; Feng, W.; Welle, A.; Trapp, O.; Grunze, M.; Hirtz, M.; Levkin, P. A. Reactive Superhydrophobic Surface and Its Photoinduced Disulfide-ene and Thiol-ene (Bio)functionalization. *Nano Lett.* **2015**, 15, 675−681.

1.4.2 Other publications

- Neto, A. I.; Demir, K.; Popova, A. A.; Oliveira, M. B.; Mano, J. F.; Levkin, P. A. Fabrication of Hydrogel Particles of Defined Shapes Using Superhydrophobic-Hydrophilic Micropatterns. *Adv. Mater.* **2016**, 28, 7613–7619.
- Du, X.; Li, L.; Li, J.; Yang, C.; Frenkel, N.; Welle, A.; Heissler, S.; Nefedov, A.; Grunze, M.; Levkin, P. A. UV-Triggered Dopamine Polymerization: Control of Polymerization, Surface Coating, and Photopatterning. *Adv. Mater.* **2014**, 26, 8029–8033.
- Feng, W.; Li, L.; Yang, C.; Welle, A.; Oliver, T.; Levkin, P. A. UV-Induced Tetrazole-Thiol Reaction for Polymer Conjugation and Surface Functionalization. *Angew. Chem. Int. Ed.* **2015**, 54, 8732–8735.
- Popova, A. A.; Schillo, S. M.; Demir, K.; Ueda, E.; Mueller, A. N.; Levkin, P. A. Droplet-Array (DA) Sandwich Chip: A Versatile Platform for High-Throughput Cell Screening Based on Superhydrophobic–Superhydrophilic Micropatterning. *Adv. Mater.* **2015**, 27, 5217–5222.
- Li, L.; Li, J.; Du, X.; Welle, A.; Grunze, M.; Oliver, T.; Levkin, P. A. Direct UV-Induced Functionalization of Surface Hydroxy Groups by Thiol–Ol Chemistry. *Angew. Chem. Int. Ed.* **2014**, 53, 3835–3839.

1.4.3 Patents

1.4.3.1 Pending

(NA)

1.4.3.2 Issued

(NA)

2. Objectives and work program

2.1 Anticipated total duration of the project

36 months

2.2 Objectives

The goal of this project is to investigate the temperature responsive behavior and wettability of reentrant polyNIPAAm-based microstructures with different three-dimensional geometries produced by direct laser writing. The scanning droplet adhesion microscopy (SDAM) technology will be used to study the responsive behavior at the microscale and contact angle measurements will be used for correlating the microscale behavior with that at the macroscale. The objectives can be summarized as following:

- Investigate the possibility of using real-time SDAM to identify the temperature responsive behavior of polyNIPAAm-derived reentrant microstructures at the microscale. Examples of responses of reentrant polyNIPAAm structures are illustrated in Figure 5;

- Investigate the responsive behavior (including response kinetics) of polyNIPAAm derived reentrant microstructures as a function of the composition of the polymer (e.g. concentration of *N*-isopropyl acrylamide in the polymer) and degree of cross-linking (e.g. controlled by laser intensity);
- Investigate the responsive behavior of polyNIPAAm derived microstructure as a function of their 3D shape including the top disk thickness, diameter and roughness (Figure 5);
- Investigate the dynamic wettability of both arrays of polyNIPAAm-derived reentrant micropillars and a smooth flat surface at the macroscale by using contact angle measurements. Correlate these results with the microscale responses and water adhesion forces measured by SDAM.

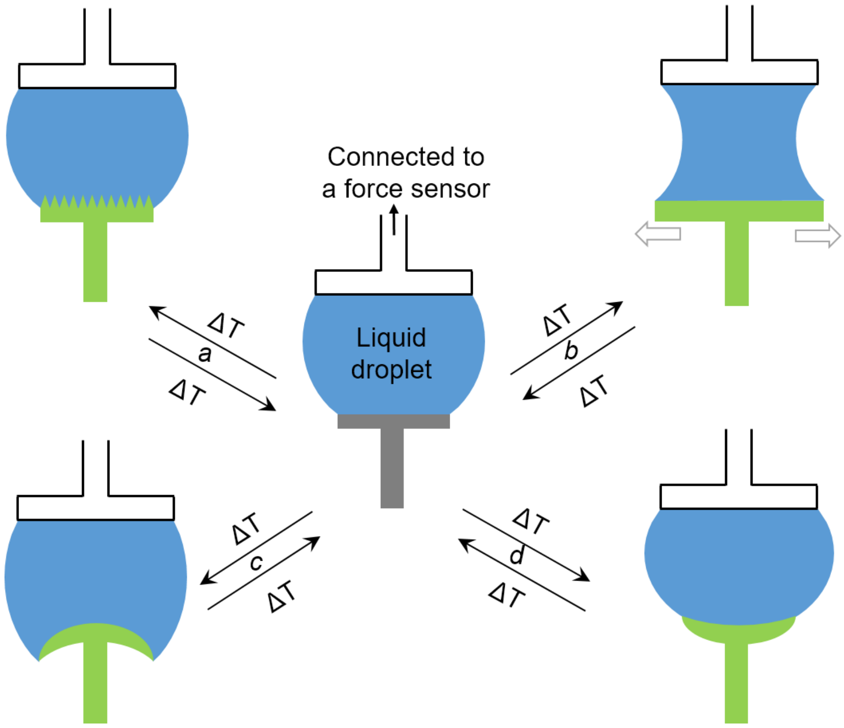

Figure 5. Examples of possible responses of reentrant polyNIPAAm microstructures and schematic showing the real-time measurement of the kinetics (and droplet adhesion: snap-in and pull-off forces) of the responsive behavior: (a) possible response in case of the swelling of the upper surface of the top disk; (b) possible response (increase of diameter) in case of the swelling of the whole top disk; (c) possible response in case of shrinkage of the upper surface (bending downwards); (d) possible response in case of shrinkage of the upper surface (bending upwards). The advantage of the DLW is the possibility to create arrays of different microstructures, which can be screened for their responses.

2.3 Work program incl. proposed research methods

Work package 1: Optimization of fabrication of reentrant poly NIPAAm microstructures by DLW

The aim of this work package is to optimize the DLW procedure and to identify compositions of pre-polymer mixtures based on *N*-isopropylacrylamide (NIPAAm) monomers that can be used to reproducibly form reentrant microstructures using DLW. DLW fabricated structures with varying chemical composition and crosslinking degree will be screened for their temperature responsiveness. We will utilize the new Nanoscribe instrument Photonic Professional GT (available for our use at the KIT).

WP 1-1: Identify the pre-polymer mixture compositions containing NIPAAm monomers suitable for DLW fabrication.

The commercially available DLW setup Photonic Professional GT (Nanoscribe GmbH, Germany) will be used. The instrument is equipped with a high-numerical aperture (NA = 1.4, ×63) oil immersion objective lens.

Reentrant micropillars with a diameter D of 50 μm, disk thickness δ of 5 μm and height h of 50 μm will be programmed in the print preparation software described for the DLW. The reentrant geometry of the micropillars (Figure 5) is necessary in our case because the polyNIPAAm is relatively hydrophilic and therefore simple micropillars can be completely wetted by water. Therefore, we will use reentrant micropillars in order to confine water droplets used in the following SDAM measurements to the upper surface of the pillars. It will be also possible to use doubly reentrant structures in order to further increase the water repellency of these micropillars. [12, 39]

To identify the pre-polymer mixtures suitable for DLW fabrication, mixtures containing different ratios of thermoresponsive moieties will be screened. NIPAAm will be used as a standard thermoresponsive monomer, however, various other temperature responsive monomers can be used as well if necessary. Pentaerythritol tetraacrylate (PETA), a widely used crosslinker in two-photo polymerization,[40] will be used as the crosslinker in order to improve the compatibility with the DLW system. 7-Diethylamino-3-thenoylcoumarin (DETC) will be used as the photoinitiator for DLW, since its absorption spectrum matches well with the DLW laser wavelength at 780 nm. The ratio of the NIPAAm monomer in the pre-polymer mixture will be increased from 0 wt% up 90 wt% to vary the chemical composition of the DLW fabricated reentrant micropillars, and the writing power during DLW process will be varied from 20 to 100% dose to control the crosslinking degree of the obtained micropillars.

WP 1-2: Screen the DLW fabricated polyNIPAAm derived microstructures for their temperature responsiveness

To identify whether the DLW microstructures fabricated in WP 1-1 possess temperature responsiveness, the swelling behavior of the reentrant micropillars with different chemical composition and crosslinking degree will be evaluated under a high-resolution optical microscope (Keyence BZ-9000, Germany) available in the group. Briefly, micropillars with a diameter of 50 μm produced by DLW will be immersed in a temperature controlled water bath. The temperature of the bath will be increased slowly from 20 ℃ to 40 ℃ and the diameter of the micropillars will be measured at different temperatures using the optical microscope. For each measurement, the temperature will be maintained for 10 mins to allow the samples to attain equilibrium. The onset point of the change of micropillar diameter will be determined as the LCST of the micropillar.

Milestone: DLW fabricated reentrant microstructures with 10~15 different chemical compositions and crosslinking degrees are found to possess temperature responsive properties.

WP 1-3: Characterization of the DLW fabricated polyNIPAAm derived microstructures

The DLW fabricated microstructures showing temperature responsiveness will be characterized by X-ray photoelectron spectroscopy (XPS) to check their surface chemical compositions, by SEM to evaluate their 3D shape and geometry. A K-Alpha+ XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK) will be available for us at IFG, KIT. ToF-SIMS analysis is also available for surface characterization.

Work package 2: Investigation of the response kinetics of polyNIPAAm derived reentrant microstructures at the microscale using real-time SDAM

The aim of this work package is to investigate the wettability, responsive behavior, including response kinetics, of polyNIPAAm derived reentrant microstructures at the microscale using standard SDAM measurements (snap-in and pull-off forces) and using real-time SDAM. We will investigate the response behavior as a function of chemical composition (percentage of NIPAAm) and crosslinking degree and the 3D shape and size of the reentrant micropillars. The SDAM instrument available at the Aalto University in the group of Robin Ras and Quan Zhou will be used (see support letter from Quan Zhou).

WP 2-1: Use of SDAM with temperature control device for real-time characterization of the responsive behaviors and kinetic of polyNIPAAm derived microstructures.

The current SDAM device consists of a micro-force sensing probe for force measurement, a motorized high-precision positioning stage for sample movement, a data acquisition board for data collection and a high-speed camera for visualization.[30] For real-time characterization of the thermo responsiveness of PNIPAAm derived microstructures, the SDAM device will be placed in a chamber with well-controlled temperature unit, and the TEC 400 /TC 400 electrical temperature control unit (DataPhysics GmbH, Germany) will be used for the temperature control. The TEC 400 /TC 400 electrical temperature control unit mainly consists of a thermal chamber with three optical windows, two electrical heaters, connectors for air or nitrogen cooling and two resistance thermometers Pt 100 as measuring and control sensor. As the TEC 400 /TC 400 unit is originally designed for temperature controlled measurements of the interfacial properties, therefore could be an ideal device for the temperature control during real-time SDAM measurement.

The real-time SDAM measurement on PNIPAAm derived reentrant microstructures will be performed as follows: briefly, a water droplet (1.5 μL) suspended from a force sensor modified with a hydrophilic disc will be brought to the sample surface. The automated sample stage will be moved up towards the droplet at a constant speed (2 $\mu m\ s^{-1}$) until the droplet touches the surface (snap-in force is measured), i.e., a discontinuous decrease is detected in the force. After the snap-in force is detected, the droplet will be incubated while in contact with the micropillars to equilibrate any polymer swelling effects. The stage will then continue moving upwards for a fixed time after snap-in and then stops at a fixed position. Then, the temperature in the SDAM chamber will be varied in the range of 20~40 °C by TEC 400 /TC 400 electrical temperature control unit, and the real-time force variation during the temperature change will be recorded. As an example, if the temperature is increased above the LCST, the upper part of the micropillars might shrink leading to a decrease of the surface area being in contact with water, thereby generating upward force, which should be detectable by the SDAM´s force sensor. Many different possibilities for the response in this case are imaginable (Figure 5).

PolyNIPAAm demonstrates temperature responsiveness only while wetted with water or aqueous buffers. Therefore, we expect that only the areas of the reentrant microstructures in contact with a water droplet will demonstrate temperature responsive behavior. In addition, the degree of swelling of the pillars in water after being placed in contact with the water droplet will also affect the response behavior. Therefore, degree of crosslinking, the fraction of the NIPAAm in the polymer as well as the thickness of the top disk of the micropillars can influence the response of the microstructures to water temperature, and eventually lead to a force change detected by the real-time SDAM. As the temperature variation of the water droplet itself will result in a change of surface tension of the droplet and different evaporation kinetics and therefore a change of the force exerted on the sensor, a control experiment will be performed on a non-responsive micropillar with identical structure but without NIPAAm to compensate the temperature effect on the force deviation.

Milestone: The real-time SDAM is successfully implemented to characterize the temperature responsive behaviors and kinetics of polyNIPAAm derived reentrant micropillars.

WP 2-2: Investigate the responsive kinetics of polyNIPAAm derived microstructures as a function of chemical composition and crosslinking degree of the microstructures using SDAM

There are two straightforward ways of changing the responsive properties of the polyNIPAAm: the percentage of the NIPAAm monomers in the total polymerization mixture and the degree of crosslinking. In order to investigate the composition-response relationship, we will create reentrant micropillars of the same geometry (selected based on the results in WP1) but by using prepolymer mixtures containing various concentration of NIPAAm from 0% wt. up to 90% wt. The other components of the polymerization mixtures will be pentaerythritol tetraacrylate (PETA) and DETC initiator often used for the DLW. The laser intensity and other parameters of the DLW will be kept constant in this case.

Another way to control the chemical constitution of the polymer structures formed by DLW is the laser intensity used during the writing process, which changes the degree of polymerization. We will use the same microstructures made with several different compositions and will vary the laser intensity in order to create a range of structures with different degree of polymerization (DP). The DP affects the swellability and might influence the temperature responsive behavior of the microstructures. The DLW method has also a unique possibility of writing the same microstructures using different laser intensity in different parts of the structures, which can lead to the different temperature responsive swelling behavior as was recently shown by Eva Blasco and colleagues (ITCP, KIT) (unpublished data).

The produced collection of reentrant structures with different compositions and DPs will be characterized for their response to temperature first using microscopy by measuring the dimensions of the structures at different temperatures.

We will then characterize them by using the real-time SDAM measurements at varying temperatures as well as using the standard SDAM method to measure both snap-in and pull-off forces at different temperatures. For the control of temperature in the SDAM experiments, see section WP 2-1.

WP 2-3: Investigate the responsive properties of polyNIPAAm derived microstructures as a function of 3D topography using real-time SDAM.

The response of the reentrant microstructures to water (swelling) and to water temperature (temperature responsiveness due to the LCST of polyNIPAAm) also depends on the 3D shape and size of the micropillars. Therefore, we will also investigate the influence of the following parameters on the temperature responsiveness as shown in Figure 6:

a. Diameter of the top disk (*D*): 30 µm, 40 µm 50 µm, 60 µm and 70 µm
b. Thickness of the top disk (δ): 1 µm, 5 µm, 10 µm, 15 µm, 20 µm

The height of the pillar stem *h* and the center to center pitch distance *p* will be kept the same and will be 50 µm, 200 µm, respectively. The stem diameter *d* will be adjusted to 30 % of the top disk diameter *D* in order to avoid the mechanical deformation of the reentrant top.

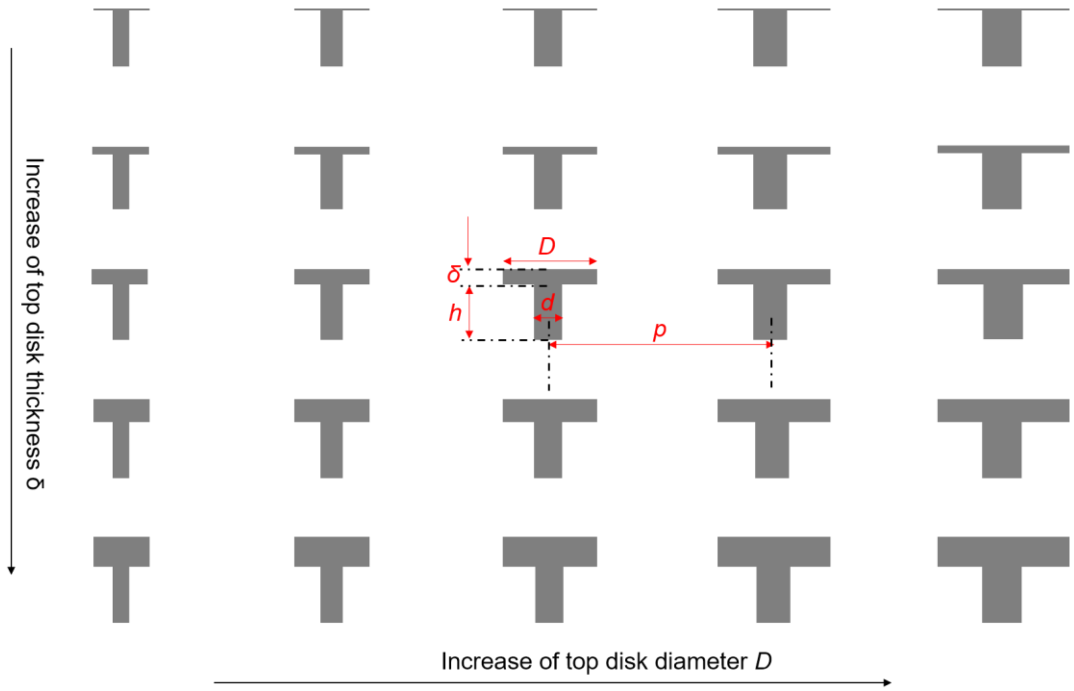

Figure 6. Scheme showing the DLW fabricated reentrant micropillars with different top disk thickness and diameter: from left to right, the disk diameter *D* increases from 30 to 70µm; from top to bottom, the disk thickness δ increases from 1 to 20 µm.

All these structures will be printed on each glass slide in order to be able to characterize all of them using a single sample by SDAM and by microscopy measurements.

We will then characterize them by using the real-time SDAM measurements at varying temperatures as well as using the standard SDAM method to measure both snap-in and pull-off forces at different temperatures. For the control of temperature in the SDAM experiments, see section WP 2-1.

The changes of the adhesion forces (real-time measurement) as well as both snap-in and pull-off forces will be plotted as a function of water temperature for various micropillars (diameter, thickness, composition and degree of polymerization/laser intensity).

Work package 3: Investigation of the dynamic wettability of polyNIPAAm derived reentrant microstructures at the macroscopic level using advancing and receding contact angle measurements

The aim of this work package is to investigate the wettability of both polyNIPAAm derived arrays of reentrant microstructures and flat polyNIPAAm surfaces produced by photopolymerization of thin prepolymer layers. The surfaces will be characterized by using advancing and receding contact angles measured at different temperatures. The results will be correlated with the results obtained for the individual micropillars using the SDAM method.

In this case we will not be able to characterize all the different geometries, compositions and structures with different degree of polymerization. Representative microstructures selected in the WP 2-2 and 2-3 will be used in these experiments. Advancing and receding contact angles will be measured. The DLW method allows us to create arrays of micropillars of about 5x5 mm within reasonable time. 5x5 mm area is enough for the contact angle measurements.[12] The new instrument, available at the KIT, is even faster and should probably permit even larger areas.

Work package 4: Analysis of the results

The main goal here is to analyze whether and how the microscopic temperature responsiveness of the individual reentrant micropillars correlates with the macroscopic changes of the contact angles on such structures as well as on the flat polyNIPAAm surfaces. Examples of questions, *inter alia,* that we would like to answer in this analysis are:

a. Is the kinetics of the response different between the responses of the microstructures and macroscopic measurements.
b. Can we identify all possible dynamic responses listed in Figure 5. Are there any unexpected responses?
c. Can we use macroscopic advancing and receding contact angles to realistically assess the dynamics and type of responses happening at the microscale.
d. Can we identify interesting (fast, strong) macroscopic switching of wettability by screening arrays of micropillars with variable properties by the SDAM method.
e. How do the temperature-dependent changes of contact angles of flat polyNIPAAm surfaces correlate with the microscale responsive effects.

Time schedule

	Timeline											
	Year 1				Year 2				Year 3			
Work packages (WP)	I	II	III	IV	I	II	III	IV	I	II	III	IV
1: Optimization of fabrication of reentrant polyNIPAAm microstructures by DLW												
1-1 Identify the pre-polymer mixture compositions containing NIPAAm monomers suitable for DLW fabrication.												
1-2 Screen the DLW fabricated polyNIPAAm derived microstructures for their temperature responsive properties												
1-3 Surface characterization of the DLW fabricated polyNIPAAm derived microstructures												
2: Investigation of the response kinetics of polyNIPAAm derived reentrant microstructures at the microscale using real-time SDAM												
2-1 Use of SDAM with temperature control device for real-time characterization of the responsive behaviors and kinetic of polyNIPAAm derived microstructures with temperature change												
2-2 Investigate the responsive kinetics of polyNIPAAm derived microstructures as a function of chemical composition and crosslinking degree of the microstructures												
2-3 Investigate the responsive kinetics of polyNIPAAm derived microstructure as a function of 3D topography												

3: Investigation of the dynamic wettability of polyNIPAAm derived reentrant microstructures at the macroscopic level using advancing and receding contact angle measurements												
4: Analysis of the results												

2.4 Data handling

(NA)

2.5 Other information

(NA)

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals

(NA)

2.7 Information on scientific and financial involvement of international cooperation partners

(NA)

2.8 Information on scientific cooperation within SPP~2171 and embedment of the project into SPP

The goal of the project integrates well into the topic of the SPP 2171 and the results of our investigations will be useful for the members of the SPP. In addition, the methods used in the project and associated expertise accumulated during the project, DLW and SDAM, will be of benefit for at least several other SPP projects. Although this proposal is focused on the polyNIPAAm based microstructures, the material is chosen as a model responsive polymer with proven behavior and applicability to make responsive microstructures by DLW. Other polymers can be used for the formation of 3D microstructures with defined geometries and investigated by SDAM. Light-responsive properties can be incorporated into the system or DLW technology can be also used for surface modification of the 3D microstructures in spatially controlled way. Therefore, I envision many more possibilities for collaborations within the SPP 2171.

Groups who applied for the SPP and with whom we plan to actively collaborate include the group of Dr. **Michael Hirtz** (Institute of Nanotechnology, KIT) and Prof. **Steffen Hardt** (Institute for Nano- and Microfluidics, Center of Smart Interfaces, TU Darmstadt). With **Michael Hirtz** we plan to evaluate the possibility of using his newly installed FluidFM system that allows the deposition of sub-micron sized droplets of different liquids while being a full-fledged atomic force microscope (AFM) capable of highly sensitive force measurements. This will allow us to approach surfaces locally with a liquid droplet dispensed from a hollow AFM tip as probe while simultaneously recording adhesion forces. He also possesses various micrometer and submicrometer patterning techniques that might be very interesting to use for surface functionalization of our 3D-DLW printed microstructures. With **Steffen Hardt** we will collaborate in the area of liquid-infused interfaces and will share experimental data on wetting on 3D microstructured surfaces. Calculation and modelling of wetting on our 3D microstructures will be another possibility to collaborate with PI Hardt.

Other potential (envisioned) collaborations might include inter alia:
Stanislav Gorb: tribology, rheometry, spectroscopy on 3D printed microstructures
Regina v. Klitzing: effect of the swelling ability of a polymer substrate and its static and dynamic wetting behavior

Jeanette Hussong and Evgeny Guerevich (Bochum): Wetting of switchable surfaces through magnetically-actuated structures.

Last but not least, we will be interested to collaborate with groups from SPP who actively work with simulations and modeling of solid-liquid interactions.

3. Bibliography

[1] C. Yu, S. Mutlu, P. Selvaganapathy, C. H. Mastrangelo, F. Svec, J. M. J. Fréchet, *Anal. Chem.* **2003**, *75*, 1958.

[2] H. Che, M. Huo, L. Peng, T. Fang, N. Liu, L. Feng, Y. Wei, J. Yuan, *Angew. Chem., Int. Ed.* **2015**, *54*, 8934.

[3] D. Tian, X. Zhang, Y. Tian, Y. Wu, X. Wang, J. Zhai, L. Jiang, *J. Mater. Chem.* **2012**, *22*, 19652.

[4] Y. Huang, B. B. Stogin, N. Sun, J. Wang, S. Yang, T.-S. Wong, *Adv. Mater.* **2016**, *29*, 1604641.

[5] H. Liu, X. Liu, J. Meng, P. Zhang, G. Yang, B. Su, K. Sun, L. Chen, D. Han, S. Wang, L. Jiang, *Adv. Mater.* **2012**, *25*, 922.

[6] M. Xiong, B. Gu, J.-D. Zhang, J.-J. Xu, H.-Y. Chen, H. Zhong, *Biosens. Bioelectron.* **2013**, *50*, 229.

[7] A. de Leon, R. C. Advincula, *ACS Appl. Mater. Interfaces* **2014**, *6*, 22666.

[8] Y. Lv, Y. Cao, F. Svec, T. Tan, *Chem. Commun.* **2014**, *50*, 13809.

[9] J. Li, Q. Han, Y. Zhang, W. Zhang, M. Dong, F. Besenbacher, R. Yang, C. Wang, *ACS Appl. Mater. Interfaces* **2013**, *5*, 9816.

[10] V. Liimatainen, M. Vuscovac, V. Jokinen, V. Sariola, M. Hokkanen, Q. Zhou, R. H. A. Ras, *Nature Communications* **2017**, *8*, DOI: 10.1038/s41467.

[11] T. Huhtamäki, X. Tian, J. T. Korhonen, R. H. A. Ras, *Nat. Protoc.* **2018**, *13*, 1521.

[12] Z. Dong, M. F. Schumann, M. J. Hokkanen, B. Chang, A. Welle, Q. Zhou, R. H. A. Ras, Z. Xu, M. Wegener, P. A. Levkin, *Adv. Mater.* **2018**, *0*, 1803890.

[13] B. Chang, O. Kivinen, I. Pini, P. A. Levkin, R. H. A. Ras, Q. Zhou, *Soft Matter* **2018**, *14*, 7500.

[14] J. Fischer, M. Wegener, *Laser Photonics Rev.* **2012**, *7*, 22.

[15] O. Tricinci, T. Terencio, B. Mazzolai, N. M. Pugno, F. Greco, V. Mattoli, *ACS Appl. Mater. Interfaces* **2015**, *7*, 25560.

[16] C. Barner-Kowollik, M. Bastmeyer, E. Blasco, G. Delaittre, P. Müller, B. Richter, M. Wegener, *Angew. Chem., Int. Ed.* **2017**, *56*, 15828.

[17] P. Lam, K. J. Wynne, G. E. Wnek, *Langmuir* **2002**, *18*, 948.

[18] R. Blossey, *Nat. Mater.* **2003**, *2*, 301.

[19] A. R. Betz, J. Jenkins, C.-J. C. Kim, D. Attinger, *Int. J. Heat Mass Transfer* **2013**, *57*, 733.

[20] X. Hou, Y. Hu, A. Grinthal, M. Khan, J. Aizenberg, *Nature* **2015**, *519*, 70.

[21] K. Ichimura, S.-K. Oh, M. Nakagawa, *Science* **2000**, *288*, 1624.

[22] Y. G. Takei, T. Aoki, K. Sanui, N. Ogata, Y. Sakurai, T. Okano, *Macromolecules* **1994**, *27*, 6163.

[23] C. D. Bain, G. M. Whitesides, *Langmuir* **1989**, *5*, 1370.

[24] L. Heng, Y. Dong, J. Zhai, B. Tang, L. Jiang, *Langmuir* **2008**, *24*, 2157.

[25] F. Xia, H. Ge, Y. Hou, T. Sun, L. Chen, G. Zhang, L. Jiang, *Adv. Mater.* **2007**, *19*, 2520.

[26] H.-J. Butt, R. Berger, W. Steffen, D. Vollmer, S. A. L. Weber, *Langmuir* **2018**, *34*, 11292.

[27] J. H. Snoeijer, B. Andreotti, *Annu. Rev. Fluid Mech.* **2013**, *45*, 269.

[28] S. Srinivasan, G. H. McKinley, R. E. Cohen, *Langmuir* **2011**, *27*, 13582.

[29] F. Schellenberger, N. Encinas, D. Vollmer, H.-J. Butt, *Phys. Rev. Lett.* **2016**, *116*, 096101.

[30] V. Liimatainen, M. Vuckovac, V. Jokinen, V. Sariola, M. J. Hokkanen, Q. Zhou, R. H. A. Ras, *Nat. Commun.* **2017**, *8*, 1798.
[31] H.-J. Butt, I. V. Roisman, M. Brinkmann, P. Papadopoulos, D. Vollmer, C. Semprebon, *Curr. Opin. Colloid Interface Sci.* **2014**, *19*, 343.
[32] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, E. Rolley, *Rev. Mod. Phys.* **2009**, *81*, 739.
[33] C. Duez, C. Ybert, C. Clanet, L. Bocquet, *Nat. Phys.* **2007**, *3*, 180.
[34] T. D. Blake, J. De Coninck, *Adv. Colloid Interface Sci.* **2002**, *96*, 21.
[35] H.-J. Butt, D. Vollmer, P. Papadopoulos, *Adv. Colloid Interface Sci.* **2015**, *222*, 104.
[36] B. Samuel, H. Zhao, K.-Y. Law, *J. Phys. Chem. C* **2011**, *115*, 14852.
[37] B. Xin, J. Hao, *Chem. Soc. Rev.* **2010**, *39*, 769.
[38] D. Öner, T. J. McCarthy, *Langmuir* **2000**, *16*, 7777.
[39] T. L. Liu, C.-J. C. Kim, *Science* **2014**, *346*, 1096.
[40] D. W. Yee, M. D. Schulz, R. H. Grubbs, J. R. Greer, *Adv. Mater.* **2017**, *29*, 1605293.

4. Requested modules/funds

Basic Module
Funding for Staff

One postdoc (Zheqin Dong) will work on this interdisciplinary project.
The fabrication of micropillar arrays by the DLW, SDAM measurements as well as the macro/micro dynamic contact angle and microscopic adhesion force characterization part in the project will be performed by Mr. Zheqin Dong (full-time). Mr. Dong has been working in the lab of Pavel Levkin for 2 years and acquired strong expertise in fabrication and characterization of surfaces with special wettability. He performed various preliminary experiments to test the feasibility of the SDAM method and DLW method and published our preliminary results in a recent Advanced Materials paper. The project is very interdisciplinary and requires strong expertise in polymer materials, wettability, DLW and SDAM. Therefore, Mr. Dong is will be an ideal candidate for this position. is going to graduate at the end of 2018.
Total: 209700€

Funds for student helpers (SHK, HiWi):
3 months/450€ per year
Total: 4050€

Personnel (costs in €) (DFG-Vordruck 60.12 – 01/18)	Year 1	Year 2	Year 3
Postdoc, Zheqin Dong	69,900	69,900	69,900
Sum 3 years (Levkin, ITG)	**209,700**		

Direct Project cost

Consumables and small investment (costs in €)	Year 1	Year 2	Year 3
WP1: Consumables for direct laser writing of reentrant microstructures			
- Plastics and glassware, pipette tips and gloves (VWR GmbH)	400	400	400
- ITO Glass slides (Nanoscribe GmbH)	600	600	600
- NIPAAm (Sigma Aldrich GmbH)	250	250	250
- Pentaerythritol tetraacrylate (Sigma Aldrich GmbH)	200	200	200
- DETC (Chemos GmbH)	260	260	260
- Isopropanol for wash of microstructures (Sigma Aldrich GmbH)	120	120	120
WP2: Instrumentation for real-time SDAM characterization		4000	
- TEC 400 / TC 400 electrical temperature control unit (DataPhysics GmbH)			
WP3: Consumables for advancing and receding contact angle measurements on flat and structured polyNIPAAm surface			
- Glass slides (Schott)			200
- Deep UV bulb for preparation of flat polyNIPAAm thin layers	1300	1300	1300
Sum	**3330**	**3130**	**3330**
Sum 3 years	**13790**		

Travel Expenses

Total for 3 years: **7520 €**

Year 1:

a) SPP2171 workshop attendance: PI Levkin, employed researcher (4 days: 80 Euro/person = 640€ + 200 Euro/person travel expenses) = 1040 Euro

b) Advanced SPP School for employed researcher (5 days: 80 Euro/person + 200 Euro travel expenses) = 600 Euro

c) Travel of the employed researcher to the Aalto University for doing SDAM measurements (3 times, 3 days each: 80 Euro/night + 300 Euro/ flight) = 540 Euro

Year 2:

a) SPP2171 workshop attendance: PI Levkin, employed researcher (4 days: 80 Euro/person = 640€ + 200 Euro/person travel expenses) = 1040 Euro

b) PhD-Workshop organized by SPP researchers, where all employed researchers should be present. Attendance: employed researcher. (4 days: 80 Euro/person + 200 Euro travel) = 520 Euro

c) Attendance of the Symposium on Wettability organized by Prof. Robin Ras at Aalto University: 1500 Euro

d) Travel of the employed researcher to the Aalto University for doing SDAM measurements (3 times, 3 days each: 80 Euro/night + 300 Euro/ flight) = 540 Euro

Year 3:

a) International conference organized by the SPP. Attendance: PI, employed researcher (5 days) = 1200 Euro

b) Travel of the employed researcher to the Aalto University for doing SDAM measurements (3 times, 3 days each: 80 Euro/night + 300 Euro/ flight) = 540 Euro

Expenses for Laboratory Animal
-NA

Other costs

Overheads (Programmpauschale) need to be added, which amounts to 20% of total funding requested.

Project-related publication expenses

Publication expenses: **750 Euro / year** (color figures, open access)
Total for 3 years (year 2 and 3): **2250 Euro**

Instrumentation
(NA)

Equipment exceeding Euro 10000
(NA)

Major Instrumentation exceeding Euro 10000
(NA)

5. Project requirements

a. Employment status information

Priv.-Doz. Dr. **Pavel Levkin**, Institute of Toxicology and Genetics, KIT. Group leader, permanent position. Research group of Biofunctional polymer materials.
Tasks of PI: supervision and coordination of the project.

b. First-time proposal data (NA)

c. Composition of the project group

Dr. Pavel Levkin (KIT, ITG):

- Supervisor of the surface functionalization, and the microscopic adhesion force and micro/macro dynamic contact angles characterization part of the project
- Help with project planning, design of experiments, and constructive feedback
- Expertise in surface functionalizing and characterization with novel photochemical strategies

Mr. M.Sc. Zheqin Dong (finalizing PhD in chemical engineering):

- Performing the surface functionalization, and the microscopic adhesion force and macro dynamic contact angles characterization part of the project
- Expertise in fabrication, functionalization and characterization of surfaces with special wettability including superhydrophobic, superoleophobic and SLIPS surfaces

d. Cooperation with other researchers

i. Researchers with whom you have agreed to cooperate on this project

Prof. Dr. Martin Wegener, Institute of Applied Physics, Karlsruhe Institute of Technology:
Dr. Wegener will provide his expertise in direct laser writing of micro-nano structured materials.

Dr. Michael Hirtz, Institute of Nanotechnology, Karlsruhe Institute of Technology
Dr. Hirtz will provide his expertise in the operation of FluidFM instrument.

Prof. Dr. Robin H. A. Ras, Department of Applied Physics, Aalto University School of Science, Finland.
Prof. Dr. Quan Zhou, Department of Electrical Engineering and Automation, Aalto University School of Electrical Engineering, Finland:
Dr. Ras and Dr. Zhou will provide their expertise in the design and handling of the SDAM device.

Prof. Steffen Hardt, Institute for Nano- and Microfluidics, Center of Smart Interfaces, TU Darmstadt

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

Prof. Dr. Ras. H. A. Robin, Department of Applied Physics, Aalto University School of Science, Finland

Prof. Dr. Quan Zhou, Department of Electrical Engineering and Automation, Aalto University School of Electrical Engineering, Finland

Prof. Dr. Martin Wegener, Institute of Applied Physics, KIT

Prof. Dr. Thomas Schwartz, Institute of Functional Interfaces, KIT

e. Scientific equipment

The following equipment will be available at the KIT:

- Project infrastructure including workspace at the office, PCs and necessary software and workspace in laboratories for chemical work will be provided by the institutes (ITG).
- Microstructure fabrication by DLW: The KIT possesses the required infrastructure for the direct laser fabrication of thermal-responsive microstructures. A commercial DLW equipment Photonic Professional GT is available at the KIT (for our group).
- Macroscopic contact angle measurement: The ITG/KIT possesses the required infrastructure for measuring the macroscopic advancing/receding contact angles. A commercial contact angle goniometer Krüss DSA 25 is available in the group of Dr. Pavel Levkin.
- FluidFM: The INT/KIT possesses the FluidFM and can be used as an alternative to measure droplet adhesion force on switchable substrates.

The following equipment will be available in the group of our collaborators at the Aalto University, and the employed researcher will travel to the Aalto University 3 times every year for doing SDAM measurements:

- Microdroplet adhesion force measurement (SDAM): A scanning droplet adhesion microscopy which can measure tensile adhesion force with sensitivity of several nN was recently developed by Prof. Ras Robin and Prof. Quan Zhou at the Aalto university.

f. Project-relevant cooperation with commercial enterprises (not planned)
g. Project-relevant participation in commercial enterprises (not planned)

6. Additional information (not applicable)