

Project description**Neuantrag im Schwerpunktsprogramm 2171:****“Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces“****Applicants**

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Title of the project

Dynamics of the coupled interaction of the three-phase contact line with electrokinetic and electrochemical processes on switchable surfaces

Proposal**1 Status Quo and Preliminary Work****1.0.1 Status Quo**

Electric fields for the manipulation of contact lines and drops are widely used in electrowetting [Mugele2005]. One basic element of such systems is a sheet of dielectric that separates the drop from an electrode embedded in the solid surface on which the drop resides. The dielectric prevents a direct current flow between the electrodes as well as electrochemical driven redox reactions at their surface. However, if the electrodes are operated in direct contact with the electrolyte electrochemical driven redox reactions may occur depending on the composition of the electrolyte and type of electrodes. One application of tremendous importance in energy economy is the generation of pure hydrogen and oxygen gas based on the electrochemical decomposition of water. In this process gas bubbles are formed at the individual electrodes if the applied voltage is in the order of their redox potential.

In the proposed project, we plan to investigate the fundamentals of how and under which conditions such bubbles can be productively used in the control of dynamic wetting at the electrodes which may in future be of interest in applications of paramount importance like electricity production.

In the standard electrowetting setup, a needle sticks into the droplet, while dielectrowetting setups are independent of such local geometry feature by using electrodes that are embedded in the solid surface the droplet sits on, like e.g. interdigitated electrodes. The switchable surfaces in the proposed project would be similar to those in dielectrowetting, but differ in the fact that the electrodes are in direct contact with the liquid. Dielectrowetting or liquid dielectrophoresis has been shown to be an attractive method to manipulate liquid interfaces [Edwards2018, Brabcova2016, McHale2013, McHale2011, Kaler2010]. It relies on the polarization of a dielectric liquid in a nonuniform electric field [Jones2001]. The employed electrodes produce a nonlinear electric field that create a nonuniform polarization of the liquid-air interface and thus leads to a force that can drive wetting processes. It is expected that a similar behavior also occurs in our system for the droplet-air interface. For the solid surface decorated with electrochemically created gas bubbles, it has to be investigated to what extend such forces can also act on the gas bubbles. If a bubble is introduced in a droplet, it exhibits polarization at the interface, but also on a more general level changes the electric field in direction and magnitude since it introduces a region of

different dielectric properties. It has to be investigated what electrical charges and hence which boundary conditions for the fluid apply on the gas bubble surfaces. Regarding the wetting behavior, the interplay of a moving three-phase contact line with the bubbles is also unknown. It is likely that electrodes being in direct contact with the droplet result in electroosmotic flows in the regions in between the electrodes [Squires2004], which could also influence the wetting behavior.

Electrochemical control of wetting could have especially large effects on superhydrophobic surfaces. Such surfaces have been extensively studied for their wetting properties, such as high contact angle and low hysteresis (e.g. [Ma2006]). They also provide an apparent slip boundary condition for the fluid that facilitates its motion. However, the performance is limited as soon as the Cassie state breaks down to the Wenzel state, i.e. when the air entrapped in the surface roughness features is pushed out. Stability of the Cassie state and triggering the reverse Wenzel-to-Cassie transition is still a challenge [Zhang2016].

For the above mentioned dielectrowetting, it has been shown that it can be combined with superhydrophobic as well as slippery surfaces, so that much larger drop mobilities and velocities on such surfaces can be reached [Torkkeli2001, Brabcova2017]. In these experiments, the electrodes were embedded underneath the surface structures, whereas in the proposed project, the electrodes would be positioned on top of the roughness features. This could potentially allow for a control of both wetting and slip along the surface. We would like to find out whether the gas bubbles can “lift up” the drop and thereby depin it from the surface. This could be of interest in all applications where drops are supposed to leave a certain spot, e.g. on solar cells or in fog harvesting. Wetting and slip properties could potentially be gradually controllable by using hierarchical structures.

Nanoporous electrodes for water splitting

Nanoporous electrodes gained great attention in the last years due to their unique electrochemical properties [Bae12]. They are used in a large number of applications like electrocatalysis [Siepenkoetter2016] and electroanalysis [Collinson2013, Hieda2004]. The enlarged electrode area of micropore (<2 nm) or mesoporous (2 – 50 nm) surfaces is an apparent feature of these electrodes. However, other phenomena like the nano-confinement, the discriminative current amplification or the overlapping of the electric double layer in pores lead to new phenomena [Park12].

In this project, the electrocatalytical water splitting reaction is envisioned to generate spatially separated hydrogen as well as oxygen bubbles at electrode surfaces. For this, the electrode material should reveal good corrosion resistance, high conductivity, and high catalytic efficiency. That is why pure noble metals are frequently used as electrode material. Electrocatalytic water splitting is still limited by the oxygen evolution reaction. Lim et al. demonstrated that electrodeposited microporous Pt electrodes with their high catalytic activity overcome this limitation of chemical oxygen reduction reducing concurrently the overpotential by 140 mV compared to solid Pt electrodes [Lim17]. Hydrogen oxidation was studied in frequent publications exploiting solid or nanoporous gold electrodes [Zheng2013]. Electrodes of both noble metals are stable in acid aqueous solutions [Sustersic2012].

For the production of microporous noble metal electrodes, a variety of bottom-to-top as well as top-to-bottom processes were developed [Kloke2011, Seker2009]. In this project we are solely interested in those processes compatible with microstructuring techniques excluding e.g. the deposition of nanoparticles for film formation. In case of platinum the chemical or electrochemical reduction of commercially available two- or four-valent platinum chloride salt was already used in early days of electrochemistry for the platinization of bulk Pt reference electrodes [Feltham71] and is still exploited for galvanic deposition of nanoporous Pt films on microstructured Pt electrodes [Pereira2013]. Varying the deposition parameter allows to tune the resultant nanopore size. Another widespread technique for both nanoporous gold and platinum electrodes employs the dealloying of metal alloy films that were sputtered from an alloy target of defined composition [Erlebacher2001]. An overview for the various fabrication processes of porous Pt electrodes is given by Kloke et al. [Kloke2011].

1.0.2 Preliminary work

1.0.2.1 Preliminary work (CS)

The working group Schoenecker deals with flow and wetting phenomena close to surfaces and interfaces. There is a strong expertise in theoretical and experimental investigation of multidisciplinary problems, like problems that involve a coupling of fluid dynamics and electrostatic forces.

In the past, a strong research field was the flow over and wetting of structured surfaces in the Cassie state, like superhydrophobic surfaces. An analytical model was developed that predicts both the flow field and the effective slip length of such surfaces for arbitrary combinations of Newtonian fluids acting as a lubricant and flowing over the surface. At the same time the model takes into account the topography of the surface microstructure [Schönecker2013, CS1], such that predictions of drag reduction capabilities of such surfaces can be made [Schönecker2015]. Theoretical methods employed during modeling were for example complex analysis, numerical calculations (finite element methods) and other techniques like the Lorentz theorem.

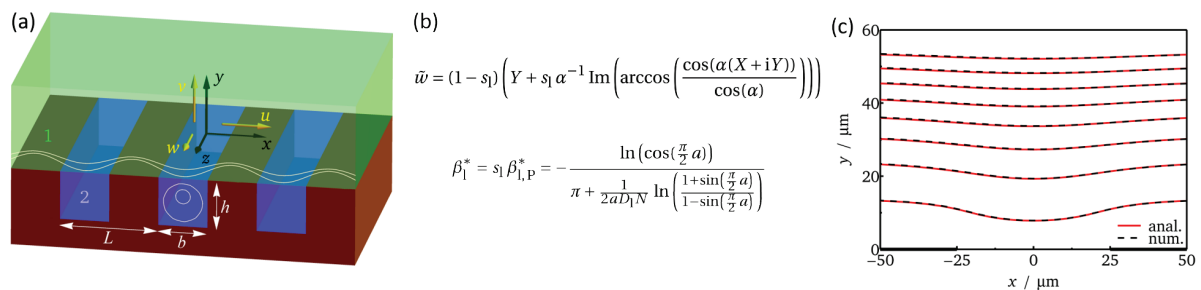


Fig.1: a) Sketch of the considered surface in the Cassie state with arbitrary Newtonian fluids 1 and 2 flowing over the surface and filling the rectangular grooves [CS1]; (b) explicit analytical expressions obtained for the velocity w in the z -direction and the effective slip length β in longitudinal direction along the grooves, nonspecified variables are parameters and functions defined in [CS1]; (c) analytical model and full numerical solution of the flow field show excellent agreement [CS1].

The specific case of slip on superhydrophobic surfaces was investigated experimentally. Using Fluorescence Correlation Spectroscopy, high resolution measurements of the flow field and the local slip length distribution on superhydrophobic surfaces could be obtained [CS2], which illustrate the influence of the flow field of the lubricating fluid as well as reveal a strong influence of surface-active substances on fluid motion along superhydrophobic surfaces.

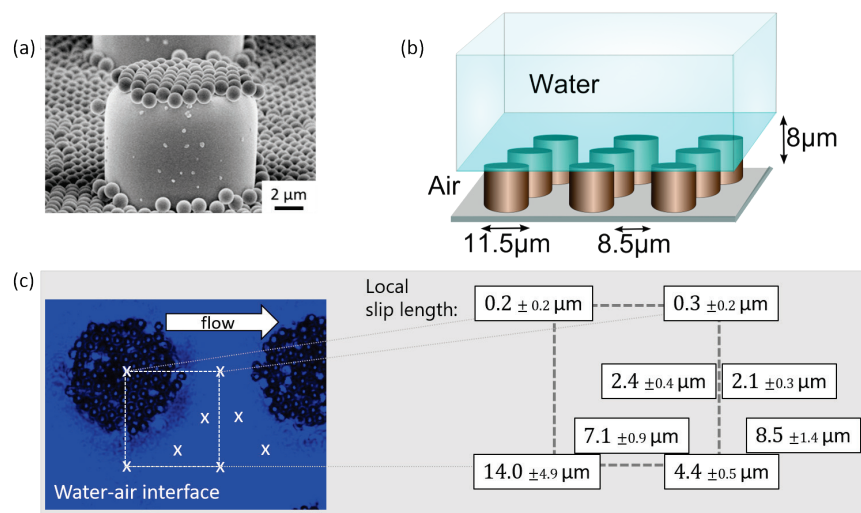


Fig.2: a) SEM image of a pillar of the superhydrophobic surface sketched in (b); (c) measured values of the local slip length by Fluorescence Correlation Spectroscopy on various measurement positions on the water-air interface (images adapted from [CS2]).

Flow over and wetting of surfaces in the Cassie state has also been investigated under the influence of electric fields. A principle for enhancement of electroosmotic flow on such surfaces

has been proposed. The principle is based on specific electrodes embedded within or underneath the surfaces microstructures. Electrical and flow fields were first modeled numerically [CS3]. Later, an analytical model was developed that provides an explicit analytical expression for the net electroosmotic flow along Cassie surfaces, again taking into account lubricant viscosity and the geometry of the surface structures [CS4].

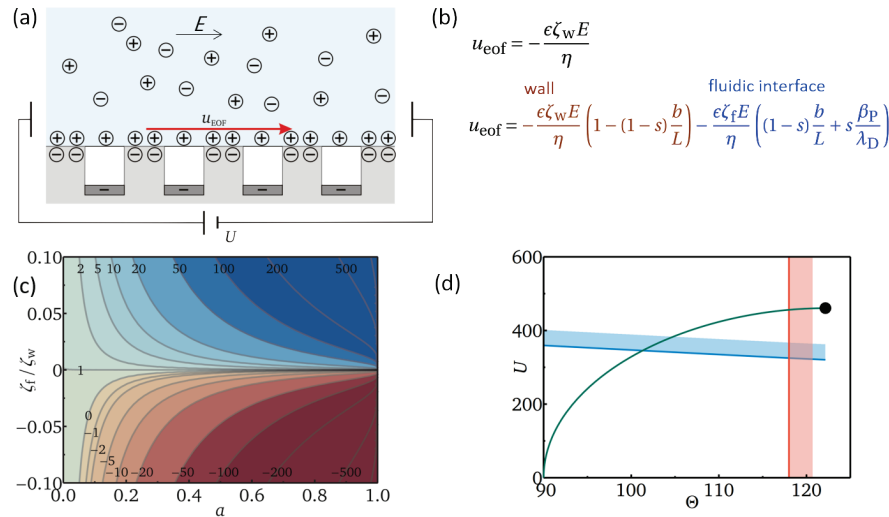


Fig.3: a) Principle of the proposed enhancement method for electroosmotic flows: surface in the Cassie state with electrodes being embedded in the surface structures [CS3] (b) comparison of the standard electroosmotically driven flow velocity and the newly derived analytical expression with contributions from the solid wall and fluidic interface regions [CS4], ζ refers to the electrical potentials on the wall w and fluid interface f , further variables are parameters and functions to be found in [CS4]; (c) theoretically predicted enhancement factor for the electroosmotic flow depending on the potentials of the different interfaces and the fluidic interface fraction α [CS4]; (d) Stability of the Cassie state under the influence of an electric field normal to the fluid-fluid interface. Example of a PTFE surface with air filling the grooves of width \times depth $50 \times 30 \mu\text{m}$. Green: deflection with applied voltage; blue: electrical breakdown limit; red: depinning limit; black point: surface instability limit [CS4].

Since the transition from Cassie to Wenzel state is a critical restriction for the functionality of such surfaces, wetting has always been in the focus of the group's research. The dynamics of the Cassie-Wenzel transition driven by an external electric field that is induced by surface electrodes have been modeled by energy arguments [CS4], showing different wetting modes for different types of surface microstructures. Wetting of lubricant infused surfaces was considered in [Liu2016].

A targeted wetting behavior is also the key point to work on enhancing CO_2 capture [CS5], where we experimentally employed superomniphobic membranes.

Modeling the dynamics of wetting over pre-existing liquid films by thin-film equations showed that at very low Capillary numbers, the height of the wetting film cannot entirely be explained by the classical Landau-Levich theory [Teisala2018].

1.0.2.2 Preliminary work (EO)

The working group Oesterschulze has a long-standing experience in the fabrication and characterization of micro- and nanostructures. In recent years one focus of the group was on Lorentz force actuated microresonators such as the so-called hybrid-bridge-resonator (HBR), that are suitable for *in-situ* mass detection in liquids with a sub-picogram mass resolution [EO1, EO2]. A column with an overhanging cap on top of the resonating bridge enables wetting in the Cassie-Baxter-state (CB-state), thus the most part of the HBR is oscillating in air (see Fig. 4 for details) [EO3]. This leads to an enhancement of the quality factor of at least one order of magnitude compared to a fully immersed bridge. By integrating the resonator into a closed feedback loop as a frequency determining element the quality factor was further raised to 10^5 . These resonators were later refined integrating a thin hydrogel layer on top of the overhang structure to obtain chemical selectivity (DFG project in collaboration with Prof. H.J. Bart) [EO4].

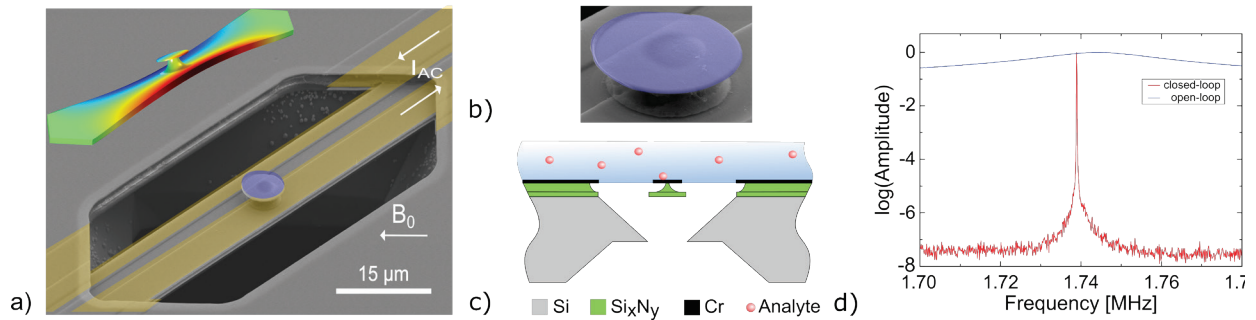


Fig. 4: a) SEM image of a hybrid bridge resonator [EO3]. The half-loop conducting path needed for the magnetic actuation is colorized in yellow, the overhanging cap in blue. The inset in the upper left corner shows the basic torsional mode (FEM simulation) of the bridge which is actuated by Lorentz force (static magnetic field orientation as indicated in the figure). b) SEM image of the column on top of the HBR carrying the plat-shape overhang structure. c) Sketch of the principle of mass sensing while wetting in the CB-state. d) Comparison of the resonant spectrum of a HBR during open- and closed-loop operation.

Similar HBR's were arranged in a periodic array (see images in Fig. 5a)-b)). [EO5]. The main goal was to study the damping mechanism of the vibrating columns in contact with the water meniscus of a droplet resting on them in more detail. The surface structure was designed in such a way that droplets placed on them were in the CB-state without any need for a superhydrophobic coating. However, by disturbing the droplet, a transition from the CB-state into the fully wetted Wenzel-state was provoked (Fig. 5c). Because of the stronger damping in the Wenzel state compared to the CB-state, the resonator experienced both a negative frequency shift and a decreasing quality factor during this wetting transition. In this way we were able to determine the wetting state of each HBR and also to gain access to the amount of energy dissipation without the need to perform conventional contact hysteresis measurements that are prone to various artefacts.

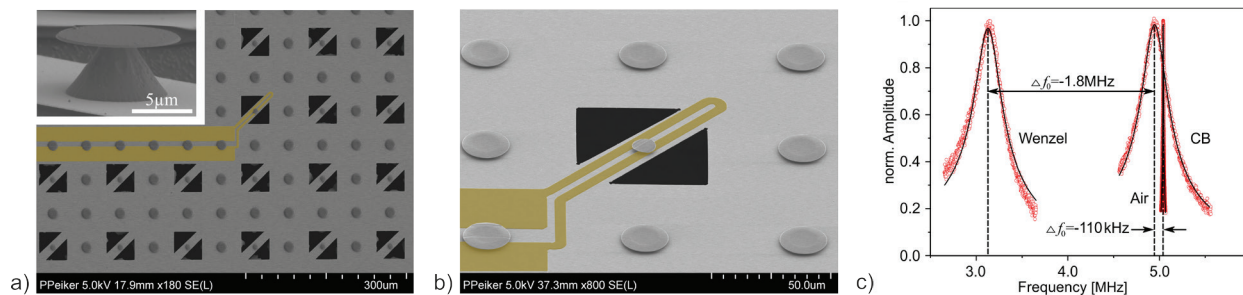


Fig. 5: a) SEM image of a periodic array of HBR's [EO5]. The conducting path is colorized in yellow. All of the bridges could potentially be used as a resonator by embedding a conducting path into them, which was done at 16 bridges per structure. The inset shows a single column with overhang structure, b) SEM image of a single HBR with integrated actuator. c) Comparison of the frequency shift in the CB- and Wenzel-state relative to the resonators frequency in air.

On the base of this work on HBR's, most recently we focused on the fabrication and investigation of re-re-entrant surface geometries that provide a stable CB-state also for low surface-tension liquids such as alcohols and even perfluorinated alkanes without superhydrophobic coatings (Fig. 6a) and b)). Such superomniophobic structures were first realised using UV-lithography and dry-etching on rigid silicon substrates.

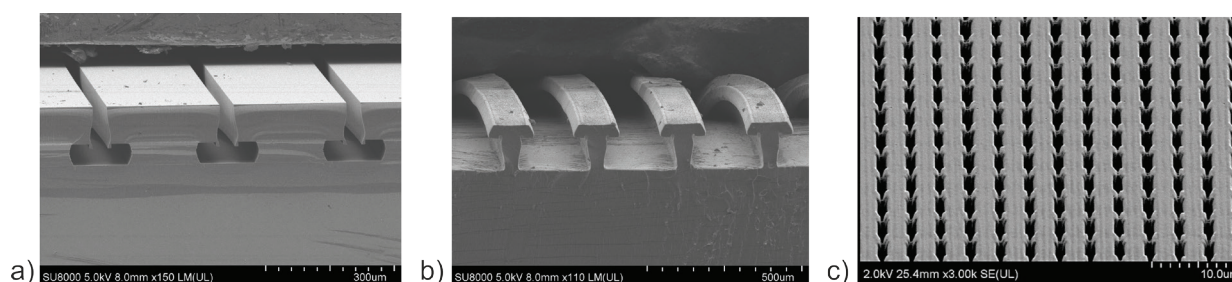


Fig. 6: a) SEM image of a mold made from silicon and photoresist used to fabricate re-re-entrant polymer structures employing a dry etching process. b) SEM image of a re-re-entrant PDMS structure molded from a structure similar to that shown in a). c) Direct laser written photoresist structure used for the fabrication of an optimized condensation plate with hierarchical surface structure.

By slightly modifying the fabrication process a mold made from silicon and a photoresist layer was developed that was used to receive a re-re-entrant structure made entirely from polydimethylsiloxane (PDMS). The PDMS structures not only showed the same wetting behavior as the ones made from silicon but are mechanically flexible as well. If the substrate is thin enough, the structure can be placed on various objects like a film and act as a superomniphobic surface itself. Meanwhile, Direct Laser Writing (DLW) was identified and used as very flexible tool to design and fabricate surface structures for condensation plates with hierarchical surface structure (Fig. 6b)). Here will use this method to generate 3D surface structures in WP5.

In a first attempt to generate 100 nm thin nanoporous Au films, we followed a recipe for dealloying Au by electrochemical means from the literature [Erlebacher2001]. To end up with pores of roughly 5-20 nm lateral size we used a sputter target with 60% Ag and 40% Au. The target composition strongly affects the resulting pore distribution. After applying a wet chemical etch, Ag was selectively removed from the deposited film and a nanoporous Au film remained (Fig. 7)).

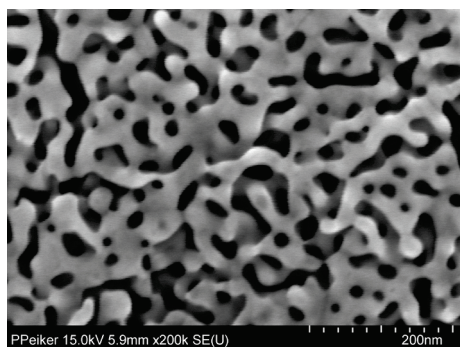


Fig. 7: SEM image of a 100 nm thin nanoporous Au electrode from the top obtained by first sputtering a ca. 100 nm thin homogeneous film using an Au/Ag alloy sputter target and second removing Ag selectively by its electrochemical dissolution.

Another topic of interest of EO is the investigation of new electrochromic (EC) devices like switchable irises and graduated optical filters that show unique filter characteristics. In one of these devices two complementary EC molecules (viologen and phenacine) are solved in the electrolyte that is sandwiched between two glass substrate each carrying a structured ITO electrode. When applying a voltage in the order of the redox potential of these molecules to the ITO electrodes viologen molecules are colored blue at the cathodic electrode and phenacine molecules green at the anodic electrode. After they undergo the redox process at the electrodes they move back along the field lines into the solution. When they meet halfway in the electrolyte they recombine by intermolecular charge transfer and switch back to the colorless state. This coloring process can be seen in Fig. 8 spatially separated that shows the colored state of a cell with parallel ITO stripes on each glass substrate where the two substrates forming the cell are rotated by 90° against each other. Each individual electrode shows the color of one sort of molecule that was colored there by redox reactions.

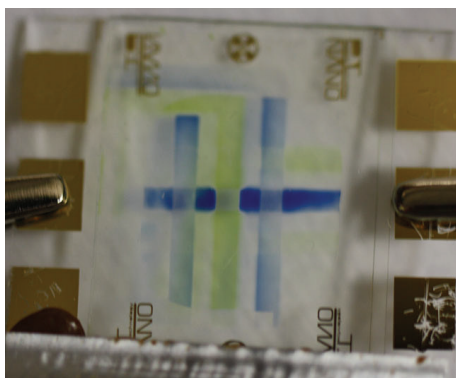


Fig. 8: Transparent EC device consisting of two stripe structured thin film ITO electrodes on a glass substrate. The two substrates were rotated by 90° against each other during device fabrication: the blue (greenish) stripes show the cathodic (anodic) electrode reaction with colored viologen (phenacin) molecules.

Project relevant publications

1.1.1 Peer reviewed publications

Publications CS

- [CS1] C. Schönecker, T. Baier and S. Hardt, Influence of the enclosed fluid on the flow over a microstructured surface in the Cassie state, *Journal of Fluid Mechanics*, 740, 168-195, 2014
- [CS2] D. Schäffel, K. Koynov, D. Vollmer, H.-J. Butt and C. Schönecker, Local flow field and slip length of superhydrophobic surfaces, *Physical Review Letters*, 116, 134501, 2016
- [CS3] C. Steffes, T. Baier and S. Hardt, Enabling the Enhancement of Electroosmotic Flow over Superhydrophobic Surfaces by Induced Charges, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 376, 85-88, 2011
- [CS4] C. Schönecker and S. Hardt, Electroosmotic flow along superhydrophobic surfaces with embedded electrodes, *Physical Review E*, 89, 063005, 2014
- [CS5] F. Geyer, C. Schönecker, D. Vollmer and H.-J. Butt, Enhancing CO₂ Capture Using Robust Superomniphobic Membranes, *Advanced Materials*, 2016

(Steffes = maiden name of C. Schönecker)

Publications EO

- [EO1] P. Peiker, E. Oesterschulze, Semi-analytical modeling of a partially wetted resonant mass sensor operated in a low-loss localized eigenmode, *J. Appl. Phys.*, 115, 183510, 2014.
- [EO2] P. Peiker, E. Oesterschulze, Geometrically tuned wettability of dynamic micromechanical sensors for an improved in-liquid operation, *Appl. Phys. Lett.* 107, 101903, 2016.
- [EO3] P. Peiker, E. Oesterschulze, Virtual mass effect in dynamic micromechanical mass sensing in liquids, *Appl. Phys. Lett.*, 108, 241904, 2016.
- [EO4] J. Menges, P. Kleinschmidt, H.-J. Bart, E. Oesterschulze, A precision structured smart hydrogel for sensing applications, *Appl. Phys. Lett.*, 122, 134501, 2017.
- [EO5] S. Klingel, E. Oesterschulze, Investigating the wetting behavior of a surface with periodic reentrant structures using integrated microresonators, *Appl. Phys. Lett.*, 111, 061604, 2017.

1.1.2 Other publications

Not apply

1.1.3 Patents

Not apply

2. Objectives and work program

2.1 Anticipated total duration of the project

The project scope is defined for three years' duration and is planned to begin on 01.10.2019.

2.2 Objectives

The goal of this project is the fundamental understanding of the interaction of the dynamics of the three-phase contact line with electrochemical phenomena induced by electric fields in droplets of simple liquids like water. Such phenomena change the boundary conditions at the surface-droplet interface by generating gas bubbles via electrolysis. They can be operated at much lower voltages compared to electrowetting. Additionally, they are associated with electrokinetic effects that may act on the contact line directly as well as on the wetted surface. This problem involves dynamical processes related to the gas bubble generation, the flow inside the droplet, and the wetting dynamics of the moving contact line. As a means of creating these effects, we employ controllable surfaces electrode structures that are in direct contact with the droplet (see Fig. 9).

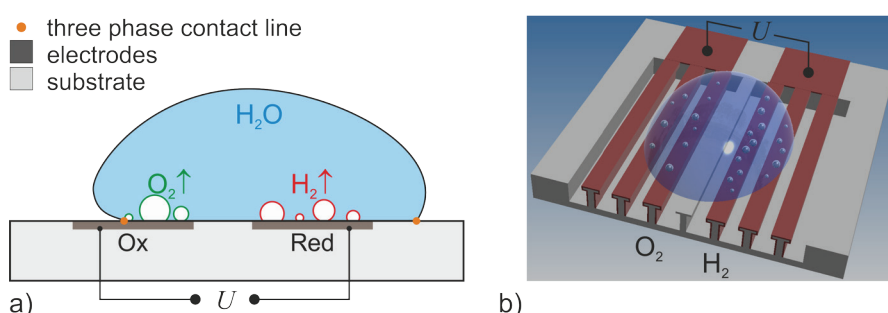


Fig. 9: a) Impact of in-plane electric fields between electrodes on the droplet including gas generation by electrochemical redox reactions. b) 3D stripe structure with integrated electrodes for gas generation.

The project is subdivided into three stages of rising complexity:

- 1) Electrokinetic phenomena within the droplet arise from the electric field between the surface electrodes (Fig. 9a)). Additionally, electrical charges are generated on the distinct interfaces of the drop that will vary dynamically upon (de)wetting of surfaces areas. This already occurs at voltages below the potential above which bubbles are generated. For the visualization of these phenomena, we will employ redox mediated coloring of molecular species at single electrodes.
- 2) Gas generation is obtained from the electrolytic decomposition of water ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2(\text{g}\uparrow) + \text{O}_2(\text{g}\uparrow)$) at inert metal surface electrodes (or catalysts thereon). This will significantly change the boundary shape as well as the mobility at the boundary since it introduces an apparent slip at the surface of the bubbles. A controlled actuation procedure by optimizing the surface electrode structure will ideally allow to continuously vary the slip length of the surface structure by electrical means without changing the surface topography.
In case of a moving droplet the gas layer has to be dynamically generated. Hence, the effective wetting behavior of the droplet will depend on the interplay of physico-chemical processes with different time scales (time constant of electrolytic gas generation, time scale of (de)wetting dynamics, etc.) and additionally different length scales (e.g. slip length, mean drop size, double layer thickness). We like to understand how the outer contact line interacts with the interior contact lines of the gas bubbles, whether dynamically created surface bubbles can lift and consequently manipulate the contact line and to what extent contact line friction is varied.
- 3) Electrochemical control is in particular promising for the wetting behavior of superhydrophobic 3D structured surfaces that already support the Cassie-Baxter state (Fig. 9b)). Such surfaces decorated with electrodes will potentially allow a continuous control of both (de)wetting and also transport of individual drops by increasing / decreasing the local effective gas layer thickness on top of the surface microstructure and thus the slip length, respectively. With an appropriate local electrode configuration, a control of dynamic wetting is envisioned both for droplets and advancing wetting fronts, e.g. switchable wetting barriers or a massive dewetting of wetted surfaces by facilitating roll-off by reduction of the water-surface contact area.

This project is a close collaboration of two groups with complementary scientific/technical experiences: The detailed modelling of the physics of the wetting behavior and the complex interaction at the three-phase contact line requires thorough background in fluid motion and electrokinetic flow phenomena. This is available in the group of Prof. Schönecker. All technological preparation of samples with the different electrode arrangements will be performed in the group of Prof. Oesterschulze. The characterization of the dynamic wetting process of droplets on various surface configurations will be performed by both groups using optical coherence tomography, wetting angle and hysteresis measurements as well as confocal microscopy and fluorescence correlation spectroscopy (the latter in close collaboration with MPI-P Mainz (Prof. Butt)).

Time schedule of work packages

| WP | Year 1 | | | | Year 2 | | | | Year 3 | | | |
|----|--------|----|----|----|--------|----|----|----|--------|----|----|----|
| | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 |
| 1 | | | | | | | | | | | | |
| 2 | | | | | | | | | | | | |
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| 4 | | | | | | | | | | | | |
| 5 | | | | | | | | | | | | |

Color coding of main tasks in the work packages: EO ■, CS ■, collaborative tasks ■

2.3 Work program incl. proposed research methods

The following work packages are assigned to the responsible applicant adding the abbreviation CS for C. Schönecker and EO for E. Oesterschulze

WP 1: Preliminary work for the choice / preparation of adapted gas generating electrodes and the improvement of the existing hysteresis measurement set-up

WP1.1) Preparation of adapted plane and nanoporous electrodes for gas generation (EO)

As already mentioned in Sec. 1.0.1, the use of two different electrode materials is advantageous for the decomposition of water to receive oxygen (platinum) and hydrogen (gold). Plane structured electrodes of desired geometry are routinely fabricated employing UV-lithography, sputter or electron beam deposition of the desired metal and subsequent etching processes. However, to control the gas bubble size distribution on each electrode, it is desirable to control the topology of the electrodes by nanoporification. In case of Pt electrodes, the galvanic deposition of nanoporous Pt thin layers will be implemented and optimized following the recipes in the literature [Kloke2011].

We will investigate the surface of these samples by scanning electron microscopy (SEM) and control their cross sectional properties by focused ion beam (FIB) milling / imaging and atomic force microscopy measurements. To obtain an overall flat surface for droplet propagation, 50-100 nm of Pt will be galvanically deposited into cavities that are defined by UV lithography and obtained by plasma etching of a 100 nm thin film dielectric material (preferably low stress silicon nitride made by plasma enhanced physical vapor deposition)). Prior to this process the substrate is coated with a thin Pt layer that is used as seed layer for the galvanic Pt growth. Nanoporous gold electrodes will be fabricated following the preparation procedure of dealloying of sputtered Au-Ag alloy films removing Ag (see Status Quo 1.0.2.2 for details).

WP1.2) Characterization of gas bubble size distribution (EO)

The manipulation of both the three-phase contact line and the amount of the solid/fluid contact area via gas generation demands its experimental investigation. Gas bubble formation is a statistical process with an almost unknown gas bubble size distribution. The latter depends on the topology and porosity of the thin film electrodes as well as on the chosen galvanic process condition (pulsed current versus continuous current). The bubble size distribution will be investigated using optical microscopy (for bubble diameters larger than 1 μm). Additionally, optical coherence tomography (OCT) will be used to study the topology of the bubble surface.

Important is also to investigate the temporal dynamics of the gas formation process that is governed by the time constant of the galvanic process at the electrodes compared to the transient time necessary for a droplet to pass over a given electrode area. Besides gas bubble formation, also coalescence of bubbles will be investigated because it may influence gas film preparation.

WP1.3) Possible impact of polarization effects (EO)

Electrowetting experiments are typically performed covering the electrodes with a dielectric layer avoiding electrochemical processes and the flow of free charges applying voltages of some ten to some hundred volts. Here, we will study the impact of an external voltage and thus also polarizing effects keeping it well below the electrochemical redox potentials of the involved materials (some volts). In this way, we like to distinguish between the impact of polarizing effects on the contact line compared to those driven by electrochemical processes in later experiments. For this purpose we will use either an arrangement of in-plane electrodes (in-plane electric field) or a single electrode on the substrate and an additional wire that sticks straight into the droplet's top surface (perpendicular electric field) to apply the voltage.

WP1.4 Extension of the hysteresis measurement set-up

With the available wetting angle measurement system (DataPhysics OCA 15EC) we can detect only the advancing and receding angle from the droplet profile to evaluate the hysteresis of the given surface. If we manipulate the shape of the droplet by means of spatial gas generation, it is important to profile the droplet also in the two other orthogonal directions. Therefore, we will install two additional cameras in our existing set-up.

WP 2: Modeling of wetting phenomena (CS)

Any generation of gas bubbles at the electrode surfaces has a significant influence on the surface properties, such as boundary conditions for the fluid and the contact line. In this work package, we hence aim at developing the theoretical framework for understanding the wetting processes, which will be observed in the other WPs.

The theoretical description will be developed in close comparison with experimental observations of the dynamic wetting behavior throughout the whole duration of the project.

WP2.1) Electrokinetic effects below the gas generation potential

We will explore the base situation before gas bubble generation analogous to WP3. This includes the characterization of forces on the contact line by liquid dielectrophoresis as well as the investigation of flow processes close to the solid surface. In our specific case, the electrodes are in direct contact with the water. This can lead to electroosmotic flows being induced inside the droplet. These flows could potentially also act on the contact line.

Electrokinetics inside the droplet: We will model the electric field and flow distribution inside the droplet on a continuum level on the scale of the droplet, starting from Poisson and (Navier-)Stokes equations. For simplicity, the equations will be solved numerically in order to obtain the amount of polarization charges on the distinct surfaces and to predict flow patterns inside the droplet.

Near-Electrode region: We will investigate the electric field and distribution of charged species in the near-electrode region in order to find out about charge layer formation, times scales of these processes and to what extent conservation equations of charged species have to be considered in the simulations on the scale of the droplet. These calculations will be performed on the basis of existing analytical models for induced-charge electroosmosis near parallel electrodes, and can likely be analytically solved.

Contact line: We will check to what extent existing analytical models for liquid dielectrophoresis forces in dielectrowetting can be applied to our scenario. If necessary, these models will be modified, aiming at an analytical expression for the force on the contact line induced by polarization effects.

WP2.2) Modeling of the gas bubbles

This section accompanies WP4 and 5. It aims at understanding the processes at the gas bubble interfaces, their time evolution and the conditions they offer to the bottom of a moving droplet or an approaching contact line. This is a prerequisite for the understanding of the motion on the scale of the droplet. Questions to be answered are such as: What is the amount of net charge

induced on the bubble interfaces and is does this lead to a significant electroosmotic flow along the bubble interfaces? What is the shape of the bubbles under influence of the electric field? What are the time scales of charge formation vs. bubble evolution? What is the boundary condition for the water on the bubble-water interfaces? Depending on the bubble distribution obtained experimentally in WP1: is it possible to model the mixed boundary conditions on the switchable surface-water interface by an averaging, macroscopic boundary condition? What would such a boundary condition look like depending on gas bubble distribution, gas bubble size compared to the droplet size, electric field, etc.?

In order to answer these questions, we will build on analytical modeling and numerical simulations we previously developed to characterize the physical picture on air pockets in superhydrophobic surfaces. The processes take place on different length scales, so we will develop descriptions on these scales electric field, charge distribution and flow will first be modeled on the scale of the bubbles (i.e. starting from Poisson, Stokes equations). Solution of these equations will be analytical if possible and otherwise numerical. In order to capture time dependent effects, we will in the same manner consider the processes on the scale of the charge layer (conservation equations for ions). After describing a single bubble, it will be investigated to what extent these findings can be extended to a bubble distribution. To reduce complexity, bubble generation will not be calculated, but assumed as given from the experimental observations in WP1.

WP2.3) Modeling of the Cassie surfaces

Analogously to WP2.2, we will aim at investigating the boundary condition on the bubble decorated Cassie surfaces. This additionally introduces the air-water interfaces created by the Cassie state. If a stable air layer is observed in the experiments that “lifts” the drop upwards, it may be necessary to divide the boundary description in two parts: before and after lift-off.

WP2.4) Modeling of contact line motion

This section also accompanies the experimental sections WP4 and WP5 and builds on the previous finding in WP2.2 and 2.3.

If we find in the previous part of the work package that the surface decorated with bubbles can be modeled by a macroscopic boundary condition, e.g. similar to a slip or electroosmotic-slip condition, we will use this expression to consider the motion of a contact line or drop. This could especially explain the phenomena we expect for a droplet motion over an inhomogeneously patterned surface.

We are interested to what extent such a boundary condition is applicable to the contact line in general and to specific positions to the contact line in particular. It is expected that, for example for a moving drop, the front and back sides have to be treated differently as the bubbles as well as the charges on the individual air-water interfaces have to be built up. For this, we will consider the different time scales for contact line motion, building up of the charge layers, generation of the bubbles, etc., and to which effects this leads in the motion of the contact line.

WP3 Investigation of electrokinetic effects in droplets on plane electrode structures (EO/CS)

As a prerequisite we will first study the impact of electric fields on plane electrode arrangements keeping the fields well below the redox potential necessary for the decomposition of water.

WP3.1) Contact line motion

Contact angle and hysteresis measurements will be conducted to identify the impact of static in-plane or out-of-plane fields on the shape of the droplet and on the contact line behavior. Here we will investigate plane metal electrodes as well as electrodes covered with a thin dielectric layer to identify differences to the dielectrowetting case.

WP3.2) Visualization via electrochromic molecules

Although fields are rather small compared to those in EWOD experiments, we expect flow fields to occur in the droplet. We suggest a new method to experimentally observe these flow fields

employing electrochromic molecules solved therein. The latter are colored during charge transfer at the electrode surfaces which is ascribed to the corresponding oxidation or reduction process. After coloring molecules move back into the body of the droplet following the flow fields therein which can then be detected by optical imaging. When two complementary molecules meet midway in the droplet, they are bleached owing to intramolecular charge transfer. Owing to our experiences with EC devices we will use viologen and phenacine as complementary EC molecules solved in water (see Status Quo). Observation is done in a high resolution optical microscope (Zeiss Axioskop).

WP3.3) Confocal Microscopy and Fluorescence Correlation Spectroscopy

Processes in the droplet and moving of the contact line will be investigated via confocal microscopy. These experiments will be carried out in collaboration with Hans-Jürgen Butt and Kaloian Koykov at the Max-Planck-Institute for Polymer Research in Mainz, where CS has access to confocal microscopy and fluorescence correlation spectroscopy. The group has a large experience in imaging wetting phenomena via confocal microscopy techniques as well as measuring flow in extreme proximity to the surface. We aim at detecting flows inside the droplet and close to the surface electrodes via fluorescence correlation spectroscopy. This technique is capable of detecting flows with a high local resolution in very close proximity to surfaces. We will use transparent ITO electrodes, so that the inside of the droplet is optically accessible.

WP4: Investigation of the dynamic wetting of a droplet on flat surfaces with integrated gas generating electrodes (EO/CS)

In this work package electrodes are designed in such a way that we can study the dynamic wetting of a flat surface if gas generation takes place at all electrodes it is residing on. First we will investigate a sessile droplet on a symmetric electrode arrangement that avoids force gradients perpendicular to the direction of motion. Gas generation on the electrodes will change the interaction between the droplet and the underlying surface and thus vary the slip length. For comparison with our switchable surface, we will also investigate nanoporous silicon from the project of Patrick Huber (TU Hamburg) as an electrode material.

WP4.1) Contact line motion under various conditions: macroscopic viewpoint

WP4.1.1) The basic electrode set-up consists of at least two parallel stripe shaped electrodes necessary for the redox reaction. First, we will study, how the motion of the contact line changes with the generation of gas bubbles compared to voltages below the gas generation voltage (AP 1.4). We will also perform dynamic switch-on and –off experiments to explore the time-dependent wetting behavior.

WP4.1.2) If the electrodes are short-circuited after gas generation, a fraction of the oxygen and hydrogen gas below the droplet chemically react reversibly to form water again in the presence of catalytic materials on the surface. The impact of the shrinking gas volume on the propagation will be measured.

WP4.1.3) We will exploit redox reactions where gas generation is restricted to only one of two electrodes while at the other electrode material is deposited onto the electrode (mass transfer).

WP4.2) Contact line motion: microscopic viewpoint

Similar to WP3.3, we will explore fluid motion close to the switchable surface and close to the contact line using confocal microscopy and fluorescence correlation spectroscopy in cooperation with the MPI for Polymer Research in Mainz. In addition, we plan to image the interplay of gas bubble and contact line dynamics using confocal microscopy.

WP5: Dynamic wetting on structured surfaces: Wenzel versus Cassie-Baxter state (EO/CS)

The goal of this work package is the investigation of the influence of forces on droplets (and their three-phase contact line) resting on a 3D structured surface either in the Wenzel or Cassie-Baxter state. Electrodes will be integrated into these structures to allow electrical excitation of the droplet or gas generation through redox reactions.

WP5.1) Fabrication of striped electrodes

To achieve this goal, a structure of parallel stripes is generated either on solid substrates such as silicon by using lithographic methods or on soft polymers by molding or hot embossing from a silicon master. In a second process step electrodes are generated via electron beam evaporation. Because of the unidirectional flow of the evaporated material it is possible to deposit the electrodes on top of the stripes and between them in one step without risking a shortcut at the side walls of the structure.

Another fabrication strategy relies on the application of Laser Direct Writing (see Fig. 6c)). This technique allows to generate almost arbitrary surface structures with a resolution of 100 nm. In contrast to conventional microfabrication tools, DLW allows very easily to generate overhang structures that might be useful for the fabrication of superomniphobic structures and electrodes thereon.

WP5.2) Impact of gas generation of droplets in CB state

At first droplets are investigated that are resting on top of the stripes in the Cassie-Baxter state. The electrodes are then used to study three-phase contact line effects similar to the ones described in WP3 to WP5 but with the additional aspect that a gas layer is already trapped underneath the droplet. How does the contact line vary if additional gas is generated? How much of the droplet can be lifted up compared to the conventional Cassie-Baxter state (with no fields)? Therefore, we will study the droplet shape using an optical imaging set-up with at least two cameras (WP1).

The roll-off behavior and hysteresis of the droplet in the actuated CB state compared to that in the conventional CB state will be substantially altered if additional gas generation takes place. However, the gas generation process is governed by the time constant of the underlying chemical redox process. Therefore, the impact of this process will depend on the amount of the droplet's acceleration that needs to be studied.

We will also study if these relatively loosely bonded droplets can be excited to one of their resonances if we apply an additional AC voltage of adapted amplitude and frequency.

WP5.3) Switching capability between Wenzel / CB state

If the droplet wets the complete surface structure in the Wenzel state, the electrodes on top of the structure as well as the ones on the bottom can be used to apply forces and thus to manipulate actively the droplet. This leads to a series of questions that we like to address:

Is it possible to switch between the CB and Wenzel state by virtue of the gas generation process? During this process the liquid/electrode contact area is reduced and thus the gas generation process underlies self-regulation. How does this phenomenon alter the three-phase-contact line dynamically?

WP5.4) Impact of electrode structure on droplet dynamics

We like to investigate how the geometry of the surface electrodes effects the shape and dynamics of a droplet. For this we will vary the electrode arrangement going from the parallel stripe geometry of constant width and pitch used in WP5.1 to WP5.3 to a configuration where the complete electrode arrangement is tapered reducing both width and pitch.

2.4 Data handling

Scientific data will be presented during national / international conferences and published in journal papers. This may be the source of emerging collaborations with other groups/institutions worldwide. The measured/simulated data will be separately stored on synchronized servers to be long term available.

2.5 Other information

Not apply

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern Not apply

2.7 Information on scientific and financial involvement of international cooperation partners Not apply

2.7.1 Information on scientific cooperation within SPP 2171

Within the SPP 2171, we will have a strong cooperation with Hans-Jürgen Butt at the MPI for Polymer Research in Mainz. Through this collaboration, we will have access to the experimental facilities at the MPI, especially confocal microscopy and fluorescence correlation spectroscopy. One PhD student of our project will regularly visit the MPI in order to perform measurements of the flow close to the solid surface and of contact line motion. Secondly, we will also cooperate with the project of Ralf Müller, Hans Hasse, Kai Langenbach and Sergiy Antonyuk (TU Kaiserslautern), who will provide us access to a high-speed long-distance microscope system, such that observation of contact line motion will be possible at a high resolution of about 1µm. In exchange, we will provide switchable surfaces for their project that can be used as an alternative method for droplet excitation. Thirdly, we will cooperate with the project of Patrick Huber at TU Hamburg. They will use samples of our switchable surfaces to investigate under which conditions and to what extent imbibition of water into the porous electrode structure occurs in our setup. This information can for example be used in the theoretical modeling of our surfaces in WP2. Furthermore, in our project, we will use nanoporous silicon electrodes from their project as an additional electrode material to be compared to our materials (Pt and Au). In our project, we will then be able to investigate gas bubble distribution and corresponding wetting behavior based on the underlying nanoporous structure. For example, their nanoporous silicon exhibits a regular geometry of vertical tubes, while our Pt and Au exhibit an irregular porosity. Fourthly, we will theoretically cooperate with the project of Christian Holm, University of Stuttgart. Since our modeling approaches are complementary (we use continuum models whereas they use Lattice Boltzmann and Molecular Dynamics to simulate electric field driven wetting), we hope to exchange information and results on the conditions and fluid motion in the vicinity of a surface electrode. Overall, we hope to provide valuable insight in the principles of dynamic wetting under electrical field for any member of the SPP that works with electrically switchable surfaces.

3. Bibliography

- [Bae2012] J. H. Bae, J. H. Han, T. D. Chung, Electrochemistry at nanoporous interfaces: New opportunity for electrocatalysis, *Phys. Chem. Chem. Phys.* 14, 448-463, 2012.
- [Brabcova2016] Z. Brabcova, G. McHale, G. G. Wells, Near Axisymmetric Partial Wetting Using Interface-Localized Liquid Dielectrophoresis, *Langmuir*, 32, 10844–10850, 2016.
- [Brabcova2017] Z. Brabcova, G. McHale, G. G. Wells, C. V. Brown, M. I. Newton, Electric field induced reversible spreading of droplets into films on lubricant impregnated surfaces, *Appl. Phys. Lett.* 110, 121603, 2017.
- [Collinson2013] M. M. Collinson, Nanoporous Gold Electrodes and Their Applications in Analytical Chemistry, *ISRN Analytical Chemistry*, 2013, 1-21, 2013.
- [Edwards2018] A.M.J. Edwards, C.V. Brown, M.I. Newton, G. McHale, Dielectrowetting: The past, present and future, *Current Opinion in Colloid & Interface Science*, 36, 28–36, 2018.
- [Erlebacher2001] J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Evolution of nanoporosity in dealloying, *Nature*, 410, 450-453, 2001.
- [Feltham1971] A. M. Feltham, M. Spiro, Platinized platinum electrodes, *Chemical Reviews*, 71, 177-193, 1971.
- [Hieda2004] M. Hieda, R. Garcia, M. Dixon, T. Daniel, D. Allara, M. H. W. Chan, Ultrasensitive quartz crystal microbalance with porous gold electrodes, *Appl. Phys. Lett.*, 84, 628-630, 2004.
- [Jones2001] T.B. Jones, Liquid dielectrophoresis on the microscale, *Journal of Electrostatics* 51-52, 290-299, 2001.
- [Kaler2010] K. V. I. S. Kaler, R. Prakash, D. Chugh, Liquid dielectrophoresis and surface microfluidics, *Biomicrofluidics*, 4, 022805, 2010.
- [Kloke2011] A. Kloke, F. von Stetten, R. Zengerle, S. Kerzenmacher, Strategies for the

- fabrication of porous platinum electrodes, *Advanced Materials*, 23, 4976-5008, 2011.
- [Lim2017] T. Lim, M. Sung, J. Kim, Jongwon, Oxygen Evolution Reaction at Microporous Pt Layers: Differentiated Electrochemical Activity between Acidic and Basic Media, *Scientific Reports*, 7, 5-10, 2017.
- [Liu2016] Y. Liu, J. Wexler, C. Schönecker and H. Stone, Effect of viscosity ratio on the shear-driven failure of liquid-infused surfaces, *Physical Review Fluids*, 1, 074003, 2016.
- [Ma2006] M. Ma, R. M. Hill, Superhydrophobic Surfaces, *Current Opinion in Colloid & Interface Science* 11, 193–202, 2006.
- [McHale2011] G. McHale, C.V. Brown, M.I. Newton, G.G. Wells, N. Sampara, Dielectrowetting Driven Spreading of Droplets, *PRL* 107, 186101, 2011.
- [McHale2013] G. McHale, C.V. Brown, N. Sampara, Voltage-induced spreading and superspreading of liquids, *Nature Communications*, 10.1038/ncomms2619, 2013.
- [Mugele2015] F. Mugele, J.-C. Baret, Electrowetting: from basics to applications, *J. Phys.: Condens. Matter*, 17, R705–R774, 2015.
- [Park12] S. Park, H. Ch. Kim, T. D. Chung, Electrochemical analysis based on nanoporous structures, *Analyst*, 137, 3891-3903, 2012.
- [Pereira2013] R. Pereira, L. F. Marchesi, R. G. Freitas, R. Matos, E.C. Pereira, A low-cost platinum film deposited direct on glass substrate for electrochemical counter electrodes, *Journal of Power Sources*, 232, 254-257, 2013.
- [Schönecker2013] C. Schönecker and S. Hardt, Longitudinal and transverse flow over a cavity containing a second immiscible fluid, *Journal of Fluid Mechanics*, 717, 376-394, 2013.
- [Schönecker2015] C. Schönecker and S. Hardt, Assessment of drag reduction at slippery, topographically structured surfaces, *Microfluidics and Nanofluidics*, 19, 199-207, 2015.
- [Seker2009] E. Seker, M. L. Reed, M. R. Begley, Nanoporous gold: Fabrication, characterization, and applications, *Materials*, 2, 2188-2215, 2009.
- [Siepenkoetter2016] T. Siepenkoetter, U. Salaj-Kosla, X. Xiao, S. Belochapkin, E. Magner, Nanoporous Gold Electrodes with Tuneable Pore Sizes for Bioelectrochemical Applications, *Electroanalysis*, 28, 2415-2423, 2016.
- [Squires2004] T. M. Squires, M. Z. Bazant, Induced-charge electro-osmosis, *J. Fluid Mech.*, 509, 217–252, 2004.
- [Sustersic2012] M. G. Sustersic, N. V. Almeida, A. E. von Mengershausen, S. M. Esquenoni, Hydrogen oxidation on gold electrode in sulphuric acid solution, *International Journal of hydrogen energy*, 37, 14747-14752, 2012.
- [Teisala2018] H. Teisala, C. Schönecker, A. Kaltbeitzel, W. Steffen, H.-J. Butt, D. Vollmer, Wetting over pre-existing liquid films, *Physical Review Fluids*, 3, 084002, 2018.
- [Torkkeli2001] A. Torkkeli, J. Saarihahti, A. Haara, H. Harma, T. Soukka, P. Tolonen, Electrostatic transportation of water droplets on superhydrophobic surfaces, *Micro electro mech. syst.*, 475–8, 2001.
- [Zheng2013] L. T. Zheng, Y. L. Wei, H. Q. Gong, L. Qian, Application progress of nanoporous gold in analytical chemistry, *Chinese Journal of Analytical Chemistry*, 41, 137-144, 2013.
- [Zhang2016] B. Zhang, X. Chen, J. Dobnikar, Z. Wang, X. Zhang, Spontaneous Wenzel to Cassie dewetting transition on structured surfaces, *Phys. Rev. Fluids* 1, 073904, 2016.

4. Requested modules/funds

This section was separated into two parts: 4.1 for Clarissa Schönecker and 4.2 for Egbert Oesterschulze.

4.1 Necessary funding for the group of Jun.-Prof. Schönecker:

4.1.1 Basic Module (Basis Modul)

4.1.1.1 Funding for Staff (Personalmittel)

4.1.1.1.1 Research Staff (Wissenschaftliche Mitarbeiter)

| | |
|--|------------------|
| Ph.D. student TV-L E13 (100%) for 3 years | € 193,500 |
| The person is responsible for the modeling and calculation of the wetting processes as sketched out in WP2. The person will also perform fluorescence correlation spectroscopy and confocal microscopy measurements in the group of Prof. Butt at the MPI for Polymer Research in Mainz. Being allocated in the Mechanical and Process Engineering, where 100% employment is standard, finding an appropriately qualified person, who can both handle the theoretical as well as the experimental part, is only possible if the position is the usual 100% TV-L E13. | |

4.1.1.1.2 Non-academic staff not apply

4.1.1.1.3 Student assistants (Studentische Hilfskräfte)

| | |
|---|-----------------|
| Student assistant for 3 years (10 h / week) | € 15,000 |
| Involving students in research projects has proven to be very helpful. They can perform routine measurements and help with data analysis. | |

4.1.1.2 Direct project costs

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

Equipment up to 10,000€

| | |
|-------------------------------------|----------------|
| Workstation for Comsol Computations | € 6,500 |
|-------------------------------------|----------------|

Explanation for the equipment

The coupled fluid-electrodynamic problems have to be solved on a powerful workstation. The computations especially require a large RAM of 128GB and fast processors.

Software

| | |
|--|----------------|
| Comsol license extension: chemical reaction engineering module | € 2,500 |
|--|----------------|

Explanation for the software

An extension of Comsol is required to calculate the processes on the level of the Nernst-Planck equations. License Costs are 1800 for the first year and 350€ for each following year.

Consumables

| | |
|--|----------------|
| 1. Consumables for microscopy (reference media, chambers for calibration, fluorescent dyes, cover slips, Chemicals for cleaning) (2500 per year for 2 years) | € 5,000 |
|--|----------------|

4.1.1.2.2 Travel Expenses

| | |
|--|----------------|
| The results of the project will be presented by the PI and coworkers at national and international conferences related to the project topic. These conferences are also important to stay in touch with current status and developments with respect to the topics of the project and the SPP. We will also exchange with the other members of the SPP during the meetings of the SPP and within the planned cooperations. During the measurement phases, the PhD student performing the measurements at the MPI for Polymer Research will have to travel to Mainz on a regular basis. | € 8,000 |
|--|----------------|

4.1.2.3 Visiting Researchers (excluding Mercator-Fellow)

Not apply

4.1.2.4 Expenses for Laboratory Animals

Not apply

4.1.2.5 Other costs

Not apply

4.1.2.6 Project related publication expenses

| | |
|---|----------------|
| Results are published in international peer review journals and demand costs of approximately 750 € per year. | € 2,250 |
|---|----------------|

4.2 Necessary funding for the group of Prof. Oesterschulze**4.2.1 Basic module****4.2.1.1 Funding for Staff****4.2.1.1.1 Research Staff**

| | |
|--|------------------|
| Ph.D. student TV-L E13 (75%) for 3 years | € 145.125 |
| The person is responsible for the layout, fabrication and structuring of the electrode structures including their nanoporous variants in the cleanroom facility of the Nano-Structuring Center (TU Kaiserslautern). This also includes their characterization (wetting angle + hysteresis, optical coherence tomography, scanning electron microscopy etc.) and their application. | |

4.2.1.1.2 Non-academic staff

not apply

4.2.1.1.3 Student assistants

| | |
|--|-----------------|
| Student assistant for 3 years (10 h / week) | € 15,000 |
| Our last projects have proven that it is very helpful to involve students in the project because they get already in this phase of their studies in touch with experiments. Furthermore, the experience shows that in most cases very motivated and skillful students ask for this kind of laboratory work which is also very helpful for the project. | |

4.2.1.2 Direct project costs**4.2.1.2.1 Equipment up to 10,000 Euro, Software and Consumables****Equipment up to 10,000€**

| | |
|--|-----------------|
| 1. High speed camera for 3D wetting angle characterization (DataPhysics GmbH). | € 5,800 |
| 2. Rotation Stage U-651 (Physik Instrumente GmbH) | € 6,000 |
| 3. USB-based 16 channel voltage controller (Measurement Computing) | € 610 |
| total | € 12,410 |

Explanation for the equipment

ad 1) and 2): For *in-situ* 3D imaging of a droplet an available HexPod system (H-824 Physik Instrumente, 6 axis system) will be extended installing three high speed camera. One below and the other above the pivot point of the Hexpod are used to image the droplet's contact area and the other the lateral extent of the droplet. The third camera will be installed on a rotational stage. This allows to image the droplet's contour from any desired azimuth angle with respect to the substrate surface.

ad 3): This device offers 16 analog output channels and will be used to control the potentials of complex electrode set-up's.

Consumables

| | |
|---|-----------------|
| 1. 90 Si-wafers (Microchemicals) currently ca. 15 € / piece | € 1,350 |
| 2. Chemicals (acetone, isopropanol, DMSO, PDMS for molding, KOH for Si etching), safety gloves, dry etching gas (experience from other project: 70 € / month) | € 2,520 |
| 3. Only third year: Liquid N ₂ for cryogenic dry etching (ICP etching) one to two cans (each 120 l) per month (1 l is 0,64 € / l at present) ca. 150 € per month | € 1,400 |
| 4. Au-Ag sputter target for the generation of silver nanoporous electrodes | € 1,600 |
| 5. Au for E-beam evaporation 15 gr/year, currently 34 € / gr | € 1,530 |
| 6. Quartz Photomasks for Lithography, 3 masks per year, currently 700 € per 5"-mask | € 6,300 |
| 7. 2 x 5 gr platinum salt (Sigma-Aldrich) for 1 l platinum electrolyte needed for the galvanic generation of nanoporous platinum electrodes | € 1,500 |
| total | € 16,200 |

4.2.1.2.2 Travel expenses

| | |
|---|----------------|
| The results of the project will be presented by the PI and coworkers at national and international conferences related to the project topic. These conferences are also important to stay in touch with current status and developments with respect to wetting phenomena on electrodes and their active control. | € 6,000 |
|---|----------------|

4.2.1.2.3 Visiting Researchers (excluding Mercator-Fellow)

Not apply

4.2.1.2.4 Expenses for Laboratory Animals

Not apply

4.2.1.2.5 Other costs

Costs for the work in the cleanroom of the Nano Structuring Center at TU KL

| | |
|---|----------------|
| From similar projects supported by the DFG with comparable amount of technological work we estimate the clean room costs of ca. 200 € / month and person or total cost of 7,200 € for the whole funding period. | € 7,200 |
|---|----------------|

4.2.1.2.6 Project related publication expenses

| | |
|---|----------------|
| Results are published in international peer review journals and demand costs of approximately 750 € per year. | € 2,250 |
|---|----------------|

4.2.1.3 Instrumentation

Not apply

5. Project requirements

This section was separated into 5.1 (5.2) containing the information of CS (EO).

5.1 Information for Clarissa Schönecker**5.1.1 Employment status information**

Schönecker, Clarissa, Jun.-Prof.

Fixed-term contract until 05/2020, prolongation expected until 05/2023 + extension because of parental leave, funding: public

5.1.2 First-time proposal data

Schönecker, Clarissa

5.1.3 Composition of the project group

| Name | Academ. Title | Employment | Financing | Site |
|---------------|-----------------------|---------------------------|-----------|-------------------|
| Sushmita Vini | MSc Nanotechnology | Scholarship (until 10/21) | Public | TU Kaiserslautern |

5.1.4 Cooperation with other researchers

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

Prof. Hans-Jürgen Butt, MPI for Polymer Research Mainz
 Dr. Kaloian Koynov, MPI for Polymer Research Mainz
 Prof. Patrick Huber, TU Hamburg
 Prof. Christian Holm, Universität Stuttgart
 Prof. Sergiy Antonyuk, TU Kaiserslautern
 Jun.-Prof. Kai Langenbach, TU Kaiserslautern
 Prof. Hans Hasse, TU Kaiserslautern
 Prof. Ralf Müller, TU Kaiserslautern

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

There are close collaborations with the group of Hans-Jürgen Butt (MPI-P, Mainz), where Clarissa Schönecker is a guest scientist. Topics are experiments and theory of wetting and the physics of flows near surfaces (especially fluorescence correlation spectroscopy). Furthermore, there are collaborations with Howard Stone (Princeton) and members of his group, especially Bhargav Rallabandi (now Riverside), regarding flows near structured surfaces and elasticity influence on particles near surfaces. Some of this work was also together with the group of L. Mahadevan (Harvard) and with Thomas Salez (Bordeaux). Also, in the last 3 years, there has been theoretical work with Steffen Hardt (Darmstadt) on surfaces in the Cassie state.

5.1.5 Scientific equipment

Comsol license for basic module, CFD and particle tracking module.

Through the collaboration with the MPI for Polymer Research: access to facilities of the MPI-P, especially confocal microscopy and fluorescence correlation spectroscopy (e.g. Zeiss Axiovert 200M + LSM 510 + ConfoCor 2)

5.1.6 Project-relevant cooperation with commercial enterprises Not apply

5.1.7 Project-relevant participation in commercial enterprises Not apply

5.2 Information for Egbert Oesterschulze

5.2.1 Employment status information

Oesterschulze, Egbert, Prof. Dr., permanent at TU KL

5.2.2 First-time proposal data Not apply

5.2.3 Composition of the project group

| Name | Academ. Title | Employment | Financing | Site |
|-----------------|---------------|-----------------------------------|-----------|-------------------|
| Hans Molter | Technician | permanent | Public | TU Kaiserslautern |
| Steffen Klingel | Dipl. Phys. | non-permanent until 30.09.2019 | Public | TU Kaiserslautern |

5.2.4 Collaboration with other Scientists

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

see comments in Sec. 5.1.4.1

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

There are close collaborations with Prof. Dr. M. Haase and Prof. Dr. L. Walder (both Universität Osnabrück, Germany) on the printing / doctor-blading of nanoparticle layers with the interest to study their wetting behavior when applying electrolytes on their surface and their impact as electrodes for electrochromic devices.

5.2.5 Scientific equipment (Apparative Ausstattung)

Most of these apparatus are available in the Nano-Structuring Center at TUK.

| | | |
|------------------------|---|--|
| Lithography | <ul style="list-style-type: none"> - Mask aligner (EVG, EVG 620) - Electron beam writer +EDX (Raith, eLiNe) | <ul style="list-style-type: none"> - Photoresist Spin Coater - Photoresist Spray Coater (EVG) |
| Subtractive Techniques | <ul style="list-style-type: none"> - RIBE Plasma etcher (Roth & Rau, IonLAB) - ICP RIE Plasma Etching Oxford Instruments Plasmalab Syst.100 | <ul style="list-style-type: none"> - ECR-RIE Plasma etcher (Roth & Rau, MicroSys 500) - Equip. for silicon KOH wet etching - ECR-RIE Plasma etcher (Roth & Rau, MicroSys 500) |
| Additive Techniques | <ul style="list-style-type: none"> - Oxidation oven BEO603 (ATV) - Thermal Deposition. Pfeiffer (Vak. Classics 500L) - Sputter deposition Univex 450C (Oerlikon Leybold Vacuum) | <ul style="list-style-type: none"> - PECVD of SiO_x, amorphous Si, SiN_x, PlasmaLab 80 Plus (Oxford) - Parylene PVD Deposition (Cookson Electronics SCS PDS 2010) |
| Charact. / Analytics: | <ul style="list-style-type: none"> - SEM Hitachi S8400 / DSM 960 (Zeiss) - Confocal Microscope (WiTec, a-SNOM) - 3 opt. Microscopes for Wafer inspection (Zeiss Axioskop 2MAT) | <ul style="list-style-type: none"> - AFM Dimension 3100 (Veeco) / AFM (WiTec GmbH) - Profiler (Dektak, Dektak 8) 4 point measurement |
| Others | <ul style="list-style-type: none"> - Anodic Bonding (EVG, Bonder 501) - Critical Point Dryer (CPD 030, Baltec) - Wetting angle/hysteresis measurement set-up OCA 15EC (DataPhysik) - Optical Coherent Tomography (OCT) Thorlabs | <ul style="list-style-type: none"> - Wafer saw (Disco, DAD321) - Wire bonder (TPT, HB16) - Bond Aligner (EVG 620) - Bipotentiostat (Gamry) for electrochemical charact. / spectroscopy |

5.2.6 Project-relevant cooperation with commercial enterprises

Not apply

5.2.7 Project-relevant participation in commercial enterprises

Not apply

6. Additional information

Both applicants have not applied for or received funding of this topic elsewhere.