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Einzelantrag

Priority Programme 2171 “Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces”

Dynamics of Wetting on Switchable and Adaptive Surfaces Based on Freely-Rotating Janus Particles

Dynamik der Benetzung auf schaltbaren und adaptiven
Oberflächen, basierend auf frei rotierenden Janus-Partikeln

Neuantrag

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Project Description

1 State of the art and preliminary work

Switchability is one of the most prominent properties of various biological molecular machines functioning in living organisms. Indeed, enzymes, RNA, ionic channels, molecular motors, etc. act not always and not everywhere, but only in a certain place and time. Being normally inactive, such machines transform (or reconform) in their active form when obtain the corresponding managing signal (e.g., upon interactions with ions, ATP, etc.). The switchability of biological elementary subunits is general principle of organization of matter, when it is necessary to achieve, for instance, a long-term co-existence and function of a great number otherwise incompatible species inside cells (e.g., RNA and RNase), or when it is necessary to initiate or terminate the desired process in certain time. Obviously, the **switchability is important mechanism for self-regulation of extremely complicated systems**.

In sharp contrast to natural organisms, man-made materials are significantly less “smart”. Further advances in material science impose requirements for dual surface properties that frequently are in conflict: a given material, depending on the conditions under which it is utilized, has to be hydrophobic or hydrophilic, acidic or basic, conductive or non-conductive, wettable or repellent. Investigation of the systems, able to reversibly change the surface properties began few decades ago as response on rising interest to the “smart” or “intelligent” materials.

Switchable/adaptive surfaces are the surfaces demonstrating considerable switching of their physico-chemical properties, for instance, wettability in response to small variations of external environmental conditions ¹. One possibility to design switchable surfaces is to **switch their surface chemical composition**. This can be realized by using surface immobilization of functional groups specifically sensitive to changes in pH, light, temperature, electric or magnetic fields¹. Another possibility consists in chemical immobilization of two sorts of incompatible polymer chains on one substrate ². Exposure to solvent selective to one of the polymers, results in switching of chemical composition in the topmost polymer layer³. Stimuli-responsive surface are, therefore, designed using mainly self-assembled monolayers or by surface immobilization with polymers - polymer brushes ⁴ metal oxides substrates ⁵. To date, stimuli-responsive polymer-brush modified surfaces sensitive to solvents ⁶, pH ⁷, salt concentration ⁷, electric ⁸ and magnetic ⁹ fields, light ¹⁰, as well as temperature ¹¹ have been applied to control wettability, adhesion, and surface charge ¹²⁻¹⁴. Thus, commonly surfaces with dynamic and switchable wettability are designed using substances with switchable hydrophilicity/hydrophobicity or by combining hydrophilic/hydrophobic materials, which are alternatively exposed to environment.

Another approach for design of surfaces with switchable wettability is based on **switching of their topography/morphology**. Different kinds of materials have been applied for design of surfaces with switchable topography including shape-memory polymers ¹⁵⁻¹⁶, liquid crystalline elastomers ¹⁷⁻¹⁸, rubbers with magnetic particles ¹⁹⁻²², hydrogels and semicrystalline polymers²³. These bulk materials can be structured using additive manufacturing techniques such as 3D printing that opens broad perspective for fabrication of structured materials with complex switching of wetting.

Recently, switching of position of colloidal particles at interfaces, which assumes of switching of chemistry and topography, has been used for design of surfaces with switchable wettability (Figure 1). For this, blends of wax and hydrophilic colloidal particles have been used ²⁴. It was found that hydrophilic silica particles almost completely immerse in wax after annealing in dry environment above wax melting point. On the other hand, the degree of particles immersion in wax decreases after annealing in aqueous environment. The surface properties of the particle-wax films are, therefore, switched between hydrophobic and hydrophilic states after annealing in air and in water, respectively. The hydrophilicity/hydrophobicity can be frozen by the cooling below the wax melting point. The possibility to produce hydrophilic/hydrophobic pattern on wax-particle films using local heating was also demonstrated. One advantage of particle-wax switchable materials approach is ability to recover their surface properties after mechanical damage, which is not intrinsic to polymer brushes and self-assembled monolayers. Once the wax-particle film is scratched, it easily recovers its switchable properties because colloidal particle hidden in bulk are able to migrate to newly appeared surface upon melting. Second, wax-particle

blends can easily be formulated/prepared in a variety of combinations that allow design of materials with different properties. Moreover, these materials can be easily 3D printed that opens broad possibilities in the future for design of smart materials and devices with switchable/adaptive wetting.

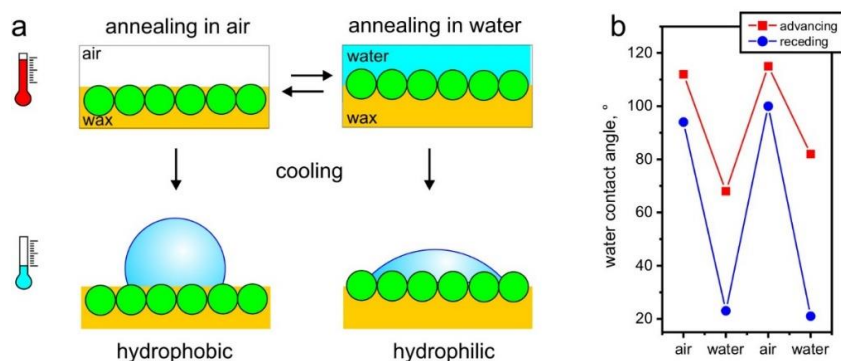


Figure 1. Scheme of switching of wax-particle surfaces. The hydrophilic particles are mixed with wax. Annealing in water and in air changes depth of immersion of the particles in oil layer that switches properties of the layer between hydrophilic and hydrophobic states. (a); Switching of advancing (red) and receding (blue) water contact angles on wax-silica surfaces after sequential annealing in water, in air and in water again (b)

Janus particles: Janus particles (JPs) are the colloidal particles having different properties (such as charge, hydrophobicity, optical and magnetic properties) at opposite sides²⁵. Combining of dissimilar properties in one material makes JPs unique among other colloidal particles²⁶⁻²⁸. Indeed, due to anisotropic properties, JPs are expected to be promising building blocks for design of smart materials²⁹⁻³¹. Mono- and bicomponent JPs based on different low- and high molecular weight materials were recently prepared using microfluidic technique³²⁻³⁷, controlled phase separation phenomena³⁸⁻⁴⁰, template-directed self-assembly⁴¹⁻⁴², controlled surface nucleation^{32, 43-45} and toposelective surface modification⁴⁶⁻⁵¹. A particularly interesting group of JPs comprises the ones specifically responding to change in environmental conditions. For example, immobilization of stimuli-responsive polymers on colloidal silica particles was recently used for synthesis of temperature/pH sensitive JPs⁵²⁻⁵⁴. Recently, JPs were demonstrated to be highly efficient as catalytic systems⁵⁵, as drug-carriers³⁶, as building blocks of self-assembling materials^{34, 56-64}, as optical⁶⁵ and rheological⁶⁶ probes as well as functional elements for design of electronic paper devices^{35, 67}. Investigation of behavior of JPs at interfaces is particularly interesting topic⁶⁸⁻⁷⁰. JPs have higher adsorption energy than homogenous particles do⁷¹⁻⁷². Moreover, JPs are able to segregate at interface between two liquids and to stabilize emulsions similarly to surfactants⁷²⁻⁷⁴. Their character of segregation can be precisely tuned by varying the ratio between two particle parts.

There are two remarkable properties of Janus particles: (i) they combine hydrophilic and a hydrophobic parts that was already used for emulsion stabilization and (ii) they are able to rotate at interfaces that was already used for fabrication of displaying elements.

Summary of state of art: Surfaces with switchable topography and chemistry based on colloidal particles on waxy substrates are very interesting because they can allow broad variety of structures and transitions between different wetting regiments but remained out of scope of research. Due to their amphiphilic character Janus particles can be potentially used for design of switchable surfaces with complex and anisotropic wetting behavior. This was, however, not explored up to date and understanding of wetting in transition states is missing.

Own preliminary work

The Synytska group has strong competencies in all research areas, required for realization of this project: (1) synthesis of stimuli-responsive hybrid Janus particles with controlled chemical/morphological and geometrical design; (2) investigation of interactions between colloidal particles and their self-assembly at interphases and in bulk and (3) surface phenomena such as wetting and adhesion.

Synthesis and physical chemical property investigation of stimuli-responsive Janus particles: Synytska group has developed new synthetic routes for the controlled large-scale synthesis of libraries of core-shell Janus particles consisting of solid inorganic core and polymer

semi-shell possessing controlled chemical functionalities^{SY1, SY3, SY4}, Janus ratio^{SY8}, spherical and flat geometries^{SY2, SY6}, polymeric architectures and size^{SY4, SY8, SY10} (**Figure 2-3a**). Hereby, a chemical approach using a combination of Pickering emulsion with “grafting from” - “grafting to” methods for the fabrication of bifacial “hairy” Janus particles modified by two kinds of stimuli-responsive polymers was successfully established.^{SY10}

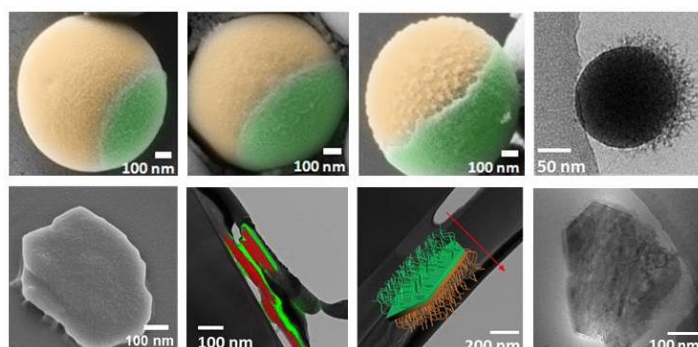


Figure 2. Representative SEM^{SY7} and cryo-TEM^{SY4} images of spherical polystyrene(PSt)-poly(2-dimethylaminoethyl methacrylate) PDMAEMA Janus particles with different Janus ratios^{SY7} (upper image); and SEM, EFTEM (FIB lamella) and cryo-TEM images of a PDMAEMA/poly lauryl methacrylate (PLMA) Janus platelets with a few layer thickness and (red and green are the signals of oxygen and carbon, respectively) (bottom image).

Topography investigations. The “Janus nature” of spherical particles^{SY1, SY3, SY7} (**Figure 2**, upper image) and Janus platelets^{SY2, SY6} (**Figure 2**, bottom image) was systematically proved by chemical and topographical mapping using fluorescence microscopy, ESEM, TEM, cryo-TEM, EFTEM as well as by measuring of interaction forces between them.^{SY1, SY2}

Nanoscale wetting. Moreover, we have employed a new methodology to measure directly and in situ the position/contact angle (nanoscale wetting) of such Janus microparticles at a water–oil interface. The approach is based on freeze-fracture, shadow-casting (FreSCa) cryo-scanning electron microscopy and makes use of unidirectional metal coating of particles protruding from a flash-frozen water–oil interface, after removal of the oil phase (**Figure 3**). In particular, our results extend to the colloidal domain previous results obtained with much larger JPs, which related the amphiphilic behavior of JPs at an interface to the Janus ratio and the wettability contrast between the two portions of the surface. We found that only in the case of large wettability contrasts, are our microparticles in a true Janus regime. In the case of smaller wettability contrasts, the particles behave like homogeneous objects, with a contact angle coinciding with the contact angle of one of the parts of the surface. The mono- and bifunctional polymeric coated core-shell Janus particles demonstrated stimuli-responsive and tunable self-assembling behavior^{SY3, SY6} in dispersions. Specifically, we established an easy and scalable bottom-up approach for the programmed assembly of hairy Janus particles based on electrostatic interactions mediated by polyelectrolytes grafted on their surface.^{SY4} Recently our group has demonstrated a potential application of stimuli-responsive Janus particles for interfacial catalysis. We demonstrated incorporation of catalytic nanoparticles in the polymer corona of Janus particles and possibility to stabilize/destabilize water-oil emulsions as well as to perform catalytic reactions in one of the phases^{SY3}.

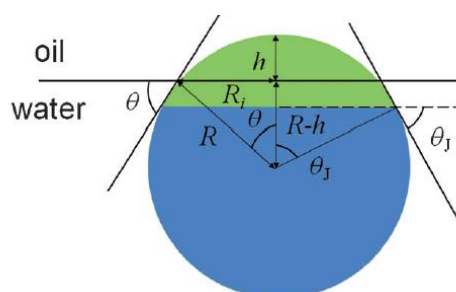
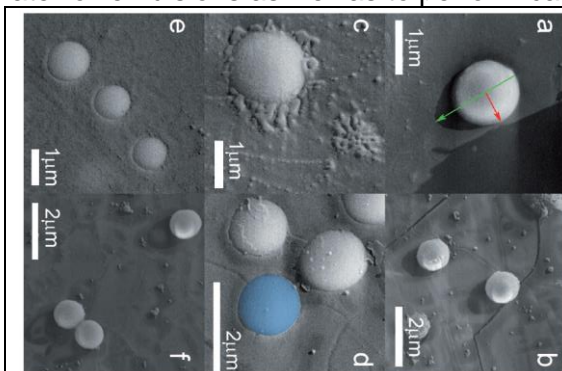


Figure 3. (left) FreSCa cryo-SEM images of the particles. a) b) c) JPs with different wettability contrasts; some frozen toluene residues are stuck around the particle contour at the interface; d) JP5; e) & f) non-JPs. On the JP1 (a) particle the shadow length and the particle radius are highlighted. On a JP4 (d) particle the cross-section at the interface is highlighted. In both cases, these quantities are used to measure the contact angles; (right) Schematic of a JP adsorbed at a water/oil interface. θ is the contact angle, while θ_J is the angle corresponding to the Janus boundary. If the two angles coincide, the contact

line is pinned at the Janus boundary and the particle behaves as a true amphiphilic object. Otherwise, the measured contact angle corresponds to the contact angle of the material that intersects the interface^{SY8}.

Macroscale wetting. Hydrophilic-hydrophobic Janus particles are able to spontaneously aggregate in a solvent selective to one of the sides. For example, such Janus particles dispersed in organic solvents tend to form controlled aggregates where hydrophobic sides of particles are exposed to environment and hydrophilic sides are hidden inside the aggregate. These aggregates being deposited on flat substrate form hierarchically rough surfaces with superhydrophobic behavior (**Figure 4**)⁷⁵

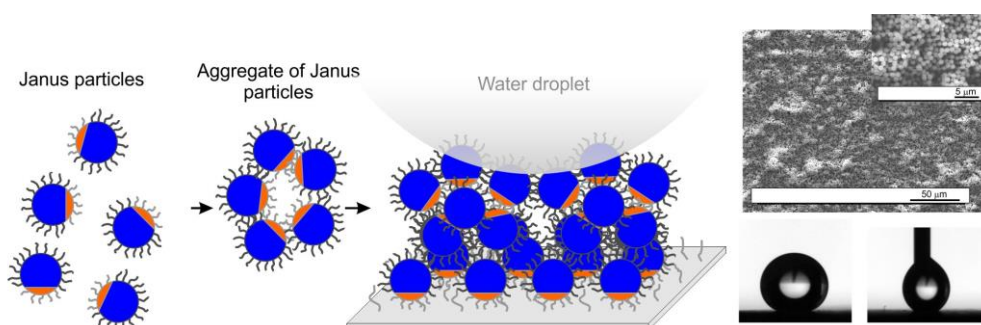


Figure 4. Schematic presentation of the design of functional surfaces using bi-component Janus particles. Janus particles form aggregates in solution, which being deposited on a supported substrate, possess ultra-hydrophobic properties. Topography (representative ESEM images) of bi-polymeric Janus particles on a substrate (a) as well as snapshots of static (b) and receding (c) water droplets on the Janus layer⁷⁵.

Self-assembly of Janus particles at interfaces: Another important achievement of the group is developed strategies for application of hairy Janus particles for a rational design of multi-functional surfaces and interfaces with controlled wettability^{SY9, SY10} and adhesion behavior^{SY1, SY2, SY6} under different environmental conditions. We address fundamental questions concerning the molecular origins of wetting and adhesion as well as their correlation to surface energy/ chemical functionality^{SY5}, surface charge, and structural features of designed materials for understanding of properties of interfaces.

Wetting phenomena on structured surfaces: Our group has an extensive expertise in experimental investigation and simple modelling of wetting on structured surfaces. As an example, we fabricated well-ordered and fully disordered surfaces using spherical colloidal particles. We experimentally investigated wetting of the regular and irregular particle layer using water-methanol mixture with different surface tension. We have also analyzed these results according to the Wenzel⁷⁶, Cassie-Baxter⁷⁷ (contact area approach), and Extrand⁷⁸⁻⁷⁹ (structure of contact line approach) models as well as minimal and maximal possible contact angles introduced by Shuttleworth and Bailey⁸⁰⁻⁸¹ (**Figure 5**).

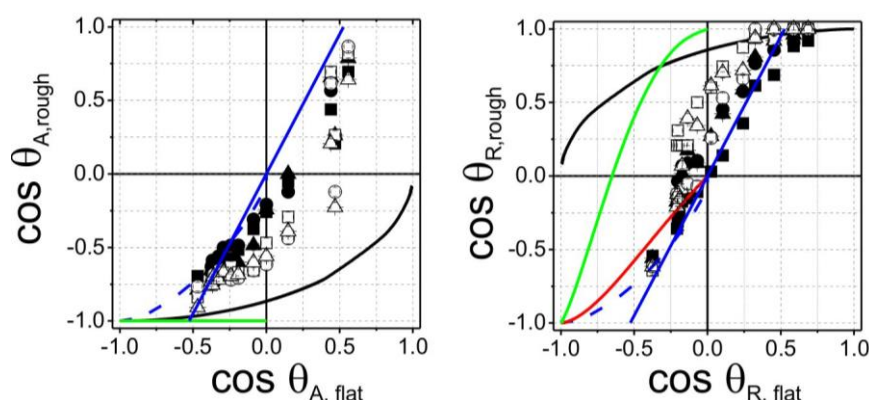


Figure 5. Wetting behavior of the water/methanol mixtures on the regular layers prepared from fluorosilane - coated particles of different size. The lines on the plots correspond to the minimum of the global energy and to minimum and maximal contact angles.⁸²⁻⁸³

Preliminary work towards proposed project – estimation of behavior of Janus particles at oily surfaces

Behavior of highly fluorinated (PTFE) – hydrophilic (SiO₂) symmetric Janus particles at molten wax-air and oil-water interfaces is theoretically simulated in order to explore orientation of the

Janus particles in different environment (**Figure 6**). The simulations are based on calculation of free energy and are very similar to the consideration presented in Ref ⁸⁴, (the results are unpublished). Modeling show that the degree of particle immersion and their orientation at oil-air and oil-water interfaces is different. This, as expected, can change wetting properties of wax surface after cooling below melting point.

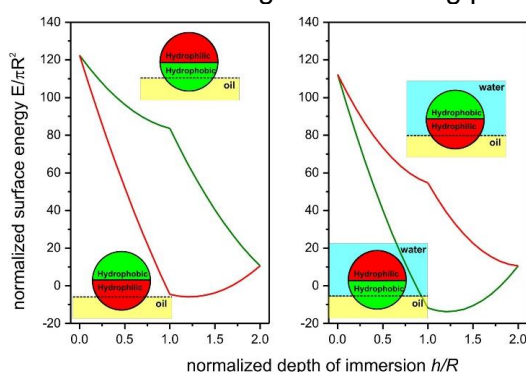


Figure 6. Simulated energy of hydrophobic (PTFE) /hydrophilic (SiO₂) Janus particle at oil-air and oil(wax)-water interface. The orientation of particles depends on the environment. (similar to the consideration presented in Ref ⁸⁴, own results - unpublished)

Summary: Our group has strong expertise in the synthesis of Janus particles of various topologies and their physico-chemical characterization. Preliminary work shows that Janus particles must be able to rotate at oil interface when they are exposed to either water or air that makes design of switchable surfaces using Janus particles feasible.

1.1 Project-related publications

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

- [SY1] A. Kirillova, L. Ionov, I. Roismann, **A. Synytska***, "Hybrid Hairy Janus Particles for Anti-Icing and De-Icing Surfaces: Synergism of Properties and Effects", *Chem. Mater.* **2016**, 28, 6995–7005.
- [SY2] A. Kirillova, C. Marschelke, J. Friedrichs, C. Werner, **A. Synytska***, "Hybrid Hairy Janus Particles as Building Blocks for Antibiofouling Surfaces", *ACS Appl. Mater. Interfaces*, **2016**, 8, 32591–32603.
- [SY3] A. Kirillova, G. Stoychev, **A. Synytska***, "Programmed assembly of oppositely charged homogeneously decorated and Janus particles", *Faraday Discussions* **2016**, 191, 89-104.
- [SA4] **A. Synytska***, L. Ionov, V. Dutschk, M. Stamm, K. Grundke, Wetting on Regularly Structured Surfaces from "Core-Shell" Particles: Theoretical Predictions and Experimental Findings. *Langmuir* 2008, 24 (20), 11895-11901.
- [SY5] A. Kirillova, C. Schliebe, G. Stoychev, A. Jakob, H. Lang, **A. Synytska***, "Hybrid Hairy Janus Particles Decorated with Metallic Nanoparticles for Catalytic Applications", *ACS Appl. Mater. Interfaces* **2015**, 7, 21218–21225.
- [SY6] A. Kirillova, G. Stoychev, L. Ionov, **A. Synytska***, "Self-Assembly Behavior of Hairy Colloidal Particles with Different Architectures: Mixed versus Janus", *Langmuir* **2014**, 30, 12765-12774.
- [SY7] A. Kirillova, G. Stoychev, L. Ionov, K.-J. Eichhorn, M. Malanin, **A. Synytska***, "Platelet Janus Particles with Hairy Polymer Shells for Multifunctional Materials", *ACS Applied Materials and Interfaces* **2014**, 6, 13106-13114.
- [SY8] **A. Synytska***, A. Kirillova, L. Isa, "Synthesis and Contact Angle Measurements of Janus Particles", *ChemPlusChem* **2014**, 79, 656-661.
- [SY9] **A. Synytska***, L. Ionov, "Stimuli-Responsive Janus Particles", *Particle & Particle Systems Characterization* **2013**, 30, 922-930.
- [SY10] S. Berger, L. Ionov, **A. Synytska***, "Engineering of Ultra-Hydrophobic Functional Coatings Using Controlled Aggregation of Bicomponent Core/Shell Janus Particles", *Advanced Functional Materials* **2011**, 21, 2338–2344.

1.1.2 Other publications

none

1.1.3 Patents

1.1.3.1 Pending

none

1.1.3.2 Issued

none

2 Objectives and work programme

2.1 Anticipated total duration of the project

Tentative project starting date 1.10.2019, duration 36 months

2.2 Objectives

This project aims at understanding and correlation the time-depending reorientation, self-organization and switching of individual Janus particles and formed Janus-particle structured layers at fusible wax-air/fusible wax-water interfaces with a complex non-equilibrium wetting response in transition states. *Switchable surfaces will be formed by fusible waxy materials and hydrophilic/hydrophobic Janus particles (JPs) of varied topology and anisotropy (spherical and rod-like).* Janus particles will be mobile inside wax and on its surface when wax is molten. Janus particles will be immobile when wax is solid. Predictions show that Janus particles are able to segregate at the interface between wax and environment, which can be either air or water (**Figure 6**). The orientation and degree of immersion of Janus particles in molten wax must depend on environment (water or air) (**Figure 7**). Therefore, we expect that hydrophobic or hydrophilic sides of Janus particles must be exposed when molten wax contacts air or water, respectively. Cyclical change of environment must result in rotation of Janus particles i.e. they will adapt themselves to changing environment due to surface tension forces. Solidification of molten wax by crystallization shall freeze states of Janus particles, when either hydrophobic or hydrophilic sides are exposed. The formed wax-Janus particle surfaces can be either hydrophilic or hydrophobic depending on orientation of Janus particles. Thus, the *Janus particle-wax surfaces are adaptive (adapt to environment - either to air or water) when wax is molten and crystallization/melting of wax allow deactivation/activation of this adaptive behavior. In other words, these are surfaces with switchable adaptivity.*

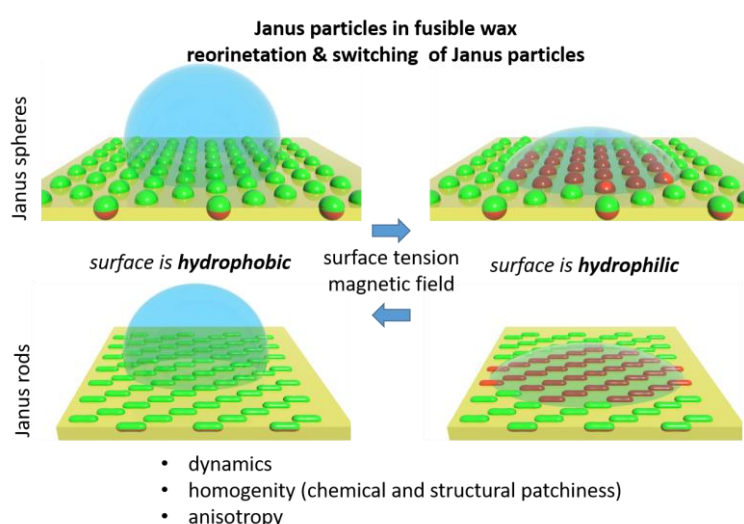


Figure 7. Schematic illustration for switchable/adaptive surfaces formed by fusible wax and Janus particles. JPs are able to rotate at fusible wax interface when it is molten. Orientation of JPs can be frozen by crystallization of wax. Formed surfaces can be either hydrophilic or hydrophobic depending on orientation of JPs. Rod-like JPs are expected to assemble in more complex structures which will lead to anisotropic behavior of water droplet. The key questions on the effects of time of (re)-orientation and switching of individual JPs and formed of them structured substrates on non-equilibrium wetting response will be addressed.

We aim to prove our hypothesis that Janus particles will be able to rotate at oil/water interfaces and the time of their rotation and switching will affect non-equilibrium wetting properties of water on these surfaces. The wetting properties and their dynamics will depend on the time of self-organization and switching of Janus particles and resulted complex structures, which is affected by JP form and anisotropy (spherical, rods), Janus balance (hydrophilic/hydrophobic contrast on individual JPs) and size (sub- μm and μm -large). We expect to demonstrate **a causal link between time-dependent orientation and switching behavior of individual JPs at fusible oil/water interfaces and cumulative effect of multiple JPs structured layers on dynamics**

of macroscopic wetting during their rotation and assembly and afterwards when the switching state is “frozen” and adaptation to water droplet is proceeded. The project is organized in three work packages (WPs, **Figure 8**). First, we will synthesize a library of hydrophilic/hydrophobic Janus particles with controlled topologies and forms (WP1). Second, we will explore kinetics of the reorientation process of JPs, its spatial homogeneity and its dependency on external parameters like the phase above the wax (air or water). We expect to visualize the time-depending switching protocol and formed complex structures with total reflection microscopy as well as confocal microscopy and high-speed imaging (WP2). Then, we will investigate the dynamics of water droplet during the time-depending switching and formation of either homogeneous or heterogeneous (depending on above addressed factors - chemically or topographically) structures during advancing and receding cycles – dynamic wetting behavior (WP3). Together with our cooperation partners within this SPP (**Harting, Berger & Butt, Harth, Auernhammer and Gurevich & Heuer**) we anticipate explaining processes involving time-depending switching and related to this non-equilibrium response and dynamics of three-phase contact lines on switchable JPs-based substrates.

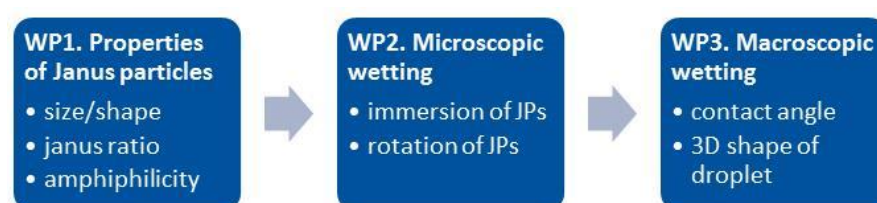


Figure 8. Envisioned structure of project, which will allow elucidation of casual link between properties of Janus particles of dynamics of switching of wetting behavior.

2.3 Work programme incl. proposed research methods

WP 1: Synthesis of Janus particles with controlled topology

In this project we will use Janus particles with two shapes: spherical and rods. Spherical Janus particles are fully symmetric, while rod-like Janus particles can be of two sorts: border between two sides goes either transversely or longitudinally in respect to long axis. In this funding period, we plan to investigate longitudinal cylindrical Janus particles (**Figure 9**). Transverse one will be investigated in the second funding period.

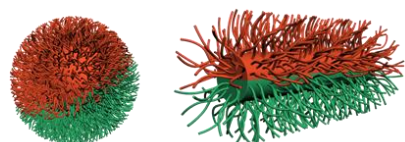
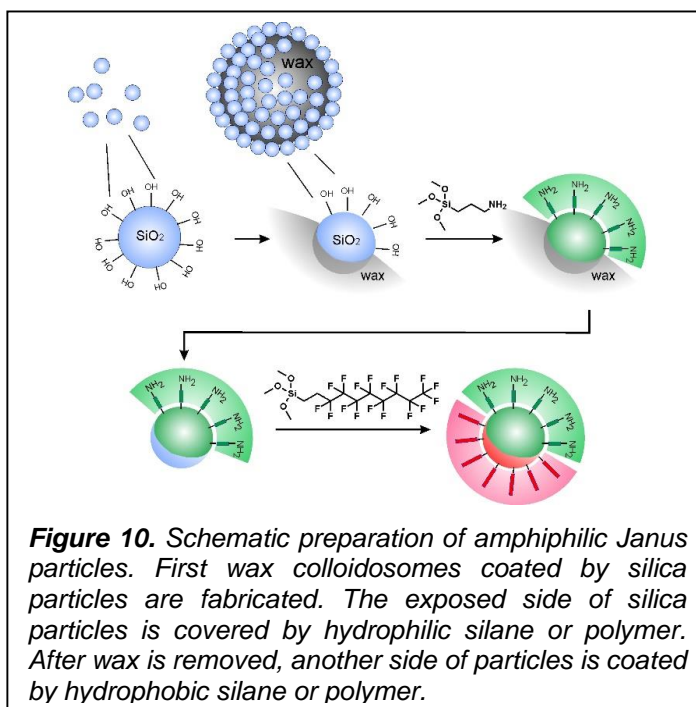


Figure 9. Schematic representation of spherical and rod-like Janus particles, which will be synthesized and investigated in this project.

Janus particles will be prepared using topo selective methods recently reported by Granick and adopted by our group for the synthesis of polymer-modified hairy Janus particles⁴⁹. The method is based on the fabrication of wax colloidosomes covered by silica particles (**Figure 10**). Variations of the Janus ratio of particles will be performed by controlling the depth of penetration of silica particles in the wax phase during the preparation of the oil–water emulsion. For this purpose, variations of the pH value of the boiling water will added to the mixture as was already demonstrated in our own work^{SY8} (**Figure 3**). The exposed part is used for immobilization of a silane or polymer. The rear side of the particles can be modified by after wax is dissolved. We will use this method for synthesize Janus particles coated by silanes from both sides, two polymers or polymer at one side and silane at opposite one. To graft different silanes, spherical native SiO₂ particles synthesized by Stöber⁸⁵ method (hydrolysis of tetraethyl orthosilicate with ammonium hydroxide in ethanol) will be used. Cylindrical SiO₂ particles will be synthesized by hydrolysis of tetraethyl orthosilicate in the presence of polyvinylpyrrolidone and sodium citrate⁸⁶. We will use particles with the size ranging from 100 nm to ca 1 μm, rods will be prepared with different aspect ratio in the range between 1 and 10. Wax- particles colloidosomes will be prepared in water emulsion of molten wax. Colloidosomes will be isolated and first silane will be immobilized on exposed side of SiO₂ particles. Silane will be removed and second silane will be immobilized on rear side.

For grafting of two polymers, we will first modify surface of SiO₂ particles using (3-aminopropyl)triethoxysilane and α -bromoisobutyryl bromide in order to introduce initiator groups for atom transfer radical polymerization. Modified particles will be used as compatibilized for emulsion consisting of water solution of hydrophilic monomer and solution of hydrophobic monomer in organic solvent. During polymerization hydrophobic and hydrophilic polymers will be grafted on opposite sides of modified SiO₂ particles.

Polymer- or silane-modified Janus particles will be synthesized by using a combination of two methods. First one silane will be immobilized on one side of SiO₂ particles assembled around wax droplets. Next, (3-aminopropyl)triethoxysilane and α -bromoisobutyryl bromide will be immobilized on opposite side and, finally, polymer will be grafted on this side using atom transfer radical polymerization.



We will synthesize Janus particles, which are fluorescently labelled at one side. This, as expected, will allow tracing of their rotation using confocal microscopy. Fluorescence labelling will be achieved by copolymerizing rhodamine acrylate.

Synthesis of magnetic Janus particles. We will also synthesize Janus particle, which are magnetic at one side. The orientation of such particles can be manipulated using magnetic field. For this, we will use spherical and rod-like SiO₂ particles synthesized using Stöber method discussed above. The particles will be deposited on a solid substrate such as glass or silica wafer. Then, Ni will be sputtered on the top of particles using physical vapor deposition. Amount of deposited Ni will be controlled by conditions of deposition. The Ni-modified side of particles will be chemically modified by thiols, non-modified SiO₂ side will be modified silanes.

Polymers can be grafted on particles surface as follows. First, SiO₂ particles with Ni side are modified by thiol with amino group (3-amino-1-propanethiol) and then with α -bromoisobutyryl bromide to introduce groups, which are able to initiate polymerization, on Ni side. First polymer will be grafted on Ni side by ATRP. Next, SiO₂ side will be modified by (3-aminopropyl)triethoxysilane and α -bromoisobutyryl bromide introduce groups, which are able to initiate polymerization. Second polymer will be grafted on SiO₂ side by ATRP.

We will graft following polymers or silanes:

- **Hydrophobic:** polystyrene, poly(pentafluorostyrene), pol(yalkylmethacrylates) poly(perfluoroalkylmethacrylates), alkyl silane, perfluoroalkyl silane.
- **Hydrophilic:** polyethylene glycol (PEG) and polyacrylic acid (PAA). PEG will be grafted in the form of poly(polyethylene glycol methacrylate) (PEGMA), which is polymer with methacrylate backbone and PEG side groups. PAA will be first grafted in the form of poly(tert butyl acrylate) (PtBA), which is hydrolysed in acidic environment. Pegulyted and (3-aminopropyl) triethoxysilanes will be used as hydrophilic silanes.
- For the study of assembly and wetting behavior will use fluorescent, confocal, and total reflection microscopies (WP2). For this, we will use solid substrates such as glass (transparent) and silicon oxide wafer (reflecting). Both these materials are intrinsically hydrophilic that may lead to dewetting of wax film on their surface. In order to minimize chances for dewetting, the surface of glass and silicon oxide wafer will be modified using hydrophobic silanes with alkyl chains.

Finally **amphiphilic Janus particles with following controlled parameters will be designed:**

- Chemical composition on opposite sides with strong wettability contrast (intrinsic contact angle for hydrophilic and hydrophobic parts between 20 and 40° and 90-115°, respectively);
- Janus balance (1:3; 1:1, and 3:1 between hydrophilic and hydrophobic polymers);
- shape and anisotropy: spherical and rod-like topologies;
- magnetic sensitive shells;
- size between 200 nm and 1 μm
- fluorescent polymeric “shell” or core for further visualization via FL or CLMS.

Expected output from WP1: Library of Janus particles with tunable topologies, form and anisotropy (spherical and rod-like), and hydrophobic/hydrophilic contrast (Janus balance).

WP2: Investigation of kinetics of (re-)orientation and switching behavior of JPs at oil-air and oil-water interfaces

In this part of the project the rotational behavior of Janus particles at oil-air and oil-water interfaces will be investigated. The simulation predicts that JPs shall migrate to interface and orient there in order to minimize free energy (**Figure 6**). This behavior will be investigated on the example of mixtures of JPs and low-melting point waxy solids or polymer with low melting point (**Table 1**). The main parameters, which affect behavior of particles, are surface tensions at interfaces determined by the chemical structure of substrates on the surface of Janus particles (see WP1, will be varied in synthesis) and chemical nature of waxy oils. Another parameter is the properties (hydrophilicity/hydrophobicity) of waxy substances. We will not use hydrophilic fusible materials such as polyethylene glycol because of their solubility in water. We will use hydrophobic waxes with relatively low molecular weight as well as fusible polymers. We will test polymers listed in **Table 1** with different molecular weight to investigate effect viscosity on ability of Janus particles to rotate when environment changes. We will also use silicone oils with different viscosity as reference material and will compare kinetics of rotation of Janus particles with kinetics of their rotation on surface of liquid molten wax (low viscosity oil).

JPs will be mixed with waxes, deposited on substrate and annealed at temperature above the melting point of the wax. Some particles will segregate at solid-air interface and occupy it. Other particles will stay in bulk because of unavailability of vacant area at solid-air interface. Availability and density of the particles at interface will be investigated using AFM, SEM and optical microscopy. Orientation of particles will be investigated using Janus particles whose one side is selectively labeled with fluorescent dyes such as rhodamine derivatives. “Memory effects” – irreversible switching of particle orientation and migration, which may be caused by large hysteresis of contact angle at border line between particles, wax and environment (water or air), will be investigated as well.

Special emphasis will be given to experimental *in situ* investigation of switching of orientation of single Janus particles upon change of environment from dry to wet and vice versa. Specifically, in cooperation with the group of **Auernhammer** (IPF Dresden) we will investigate the time-depending switching protocols of individual Janus particles as well as formed Janus particles layers at fusible water/oil and air/oil interfaces, yielding a complex non-equilibrium dynamics of water droplets and wetting response. For this, we plan to explore *in-situ* (re-)orientation of rhodamine-labelled (either in core or in the polymeric shell) Janus particles with spherical and rod-like shapes, varied intrinsic wettability contrast (hydrophilic and hydrophobic polymeric shells with equilibrium CAs between 20-40° & 90-115°, respectively), and Janus balance (ratio between hydrophilic and hydrophobic patterns) using fluorescent and laser confocal microscopy. We want to understand (i) how fast the reorientation and switching of surface will happen; (ii) if all JPs will be reoriented in similar fashion and then exposed to the environment (either air or water) by one side; (iii) if not all JPs will reoriented in similar fashion – to which level of chemical patchiness (less wettable and more wettable regions) it would lead; and (iv) which kind of complex geometrical patterns and structures will be created by spherical (presumably hexagons) and rod-like (presumably stripes) JPs. Finally, we will experimentally explore and address the question what happens with the dynamics of water droplet during the time-depending switching and formation

of either homogeneous or heterogeneous (depending on above addressed factors - chemically or topographically) structures (as a next step in **WP3**).

Experimentally, optical microscopy allows simultaneous observation of multiple particles in air and aqueous environments that allows observation of switching in air and water. On the other hand, optical microscopy possesses insufficient resolution to observe small particles. Moreover, since the particles are transparent determination of orientation of particles is challenging. We will try to use chemical substances, which in contact with water change their properties. These can be, for example, pH sensitive fluorescent molecules, which in contact with water with certain pH will change their color. As result, we will know that is orientation of particles – whether side with fluorescence labels faces wax or water. Additionally, we plan to use confocal microscopy and high-speed imaging (home-built laser scanning confocal microscope (LSCM)) to follow in-situ the reorientation of the Janus particles on the fusible wax surface, which allows better quality of images from point of view of signal to noise ratio. The maximal resolution of confocal microscopy in x,y plane is ca. 300 nm (for oil immersion 100x objective, depends on wavelength) and ca 800 nm in z direction. We will use air objectives to avoid cooling of the sample due to the heat capacity of the objective. In these experiments, we will determine the time-dependency/kinetics of the reorientation process, its spatial homogeneity and its dependency on external parameters like the phase above the wax (air or water).

Table 1. List of polymers and low-molecular weight substances with low melting point, which might be used.

Substance	Melting point	Substance	Melting point
poly(butyl vinyl ether)	64°C	poly(trans-Isoprene)	65°C
poly(ethylene adipate)	54°C	poly(vinyl butyral)	49°C
paraffin	50 - 80°C	1-iodo-1H,1H,2H,2H-perfluorodecane	54 - 58°C

It is expected that rotational behavior of spherical and rod-like Janus particles will be different: spherical particles are able to rotate in all directions, while rod-like particles, which lay at the interface, are able to rotate only along long axis (like a barrel in water). We also expect that colloidal particles will be able to self-organize at interfaces. Due to their geometrical symmetry, increase of density of spherical particles will lead to their denser packing and dense hexagonal packing will be achieved at the maximal density. Self-organization of rod-like particles at interfaces is more complicated. Rod-like particles at high density behave similar to liquid crystals – they start to spontaneously align parallel to each other like nematic liquid crystals. We will investigate how particles align in switching cycles upon advancing and receding of liquid front (due to non-equilibrium of surface forces, moving liquid droplet will generate shear force, which will cause alignment of particles) using optical microscopy.

Moreover, close cooperation with the theoreticians group of **Harting** is essential for understanding of dynamics of self-ordering of Janus particles at interfaces. Specifically, Harting's group will model and simulate self-organization and orientation of Janus particles at water/oil and air/oil interfaces depending on their Janus balance (similar to the classical hydrophile-lipophile balance of small surfactant molecules) and anisotropy induced either by their chemical design, shape and complex form (Janus rods). This knowledge might further help to predict which kind of complex structures and patterns from those individual Janus particles can be created and how these surface structures and anisotropy will influence wettability under dynamic conditions (in the next step within WP3). This will allow predicting the strength (surface tension or capillary forces) of interaction between individual Janus particles as well as surface and water droplet. We expect to find a relation between switching, wetting dynamics and reversibility of the transitions induced by the heating of the substrate or applying magnetic field. We foresee quantitative comparison and correlation between our experimental results with numerical predictions from Harting's group.

Expected output from WP2: Understanding of kinetics of reorientation and switching protocols of Janus particles at fusible wax/air and fusible wax/water interfaces. Understanding of impact of chemical (intrinsic wettability as well as wettability contrast/ Janus balance) and topological design (spherical and rod-like) on complex structure formation (homogeneous or patchy,

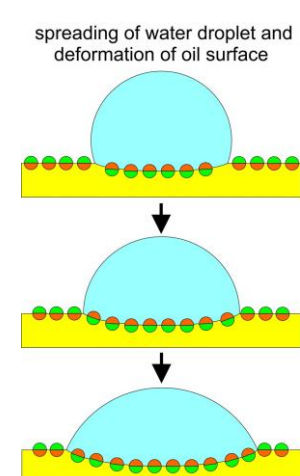
hexagonal or stripes-like structures) and its dependency on external parameters like the phase above the fusible wax (air or liquid).

WP3: Investigation of switching, wetting dynamics and reversibility of the transitions

In this part of the project, we will experimentally investigate and understand wetting behavior of particle – wax surfaces. We plan two kinds of wetting experiments. In the first set of experiments, we will switch the surface at elevated temperature to hydrophobic and hydrophilic states and then test wetting properties of obtained surfaces by measuring static contact angle, advancing/receding contact angle and sliding contact angle. This is a classical switching experiment when wetting behaviors in two states is tested.

The more interesting is, however, to investigate dynamics of switching of macroscopic wetting (**Figure 11**). Therefore, in second set of experiments, we will perform *in situ* switching. For switching from hydrophobic to hydrophilic state we will deposit a droplet on the surface, melt wax and will measure evolution of droplet shape with the time. The similar experiment will be performed for investigation of switching from hydrophilic to hydrophobic state. For this surface with a hole will be immersed in water and air bubble will be formed by a needle inserted in the hole. Afterwards, the surface will be melted and we will investigate evolution of bubble shape with the time.

It is very important to consider difference in density of wax and testing liquid (water) in contact angle measurements experiments. Wax has lower density (0.9 g/cm^3) than water (1 g/cm^3) does. It means that deposition of water droplet on fusible wax surface may result in migration of water down and molten oil to the top.



during measurements to consider this difference in densities (turn sample upside down) or impregnate porous hydrophobic substrates such as polypropylene fibrous film (liquid infused surfaces). Capillary forces will then hold wax and will not allow gravity forces to cause migration of materials.

Since wax in molten state is liquid with a relatively low viscosity (ca 3-6 mP s), we can expect deformation of wax layer at the edge of the water drop. We also expect that this deformation will be affected by interfacial activity of Janus particles. Since Janus particles reduce interfacial tension, we can expect that Janus particles will enhance deformation of wax. We will investigate shape of meniscus at the three-phase contact line (wax with JPs/air/liquid).

Figure 11. Expected spreading of water droplet and deformation of molten wax

We plan also to cooperate with **Auernhammer** and **Harth** and groups to investigate the contact between water droplet and surface made of Janus particles as well as tracking of Janus particles at oil/water interfaces. Their expertise in confocal and total internal reflection microscopy is important for this. Together with the Auernhammer group we will experimentally determine the spreading dynamics of liquid droplets during the time-dependent reorientation and switching process of JPs. Advancing and receding contact angles will be measured optically using a high speed camera by extrapolating the contour of the meniscus to the contact line. In cooperation with the **K. Harth** we expect to visualize the time-dependent water drop spreading during the reorientation and switching of Janus particles at fusible waxy surfaces. For this we will apply high-speed total reflection microscopy or an different appropriate bottom / top view based experimental technique combined with side view imaging. This allows direct visualization of the interaction of the substrate's interaction with moving liquid interfaces in a wide range of velocities. We want to explore and understand the water drop dynamics and non-equilibrium wettability response depending on the kinetics of reorientation process, its spatial homogeneity (depending on JPs form - spherical and rod-like; wettability contrast on the opposite sides and ratio between hydrophilic and hydrophobic patterns on JPs-Janus ratio) and its dependency on external parameters like the phase above the fusible wax (air or water).

Together with the group of **Berger/ Butt**, who has developed drop adhesion force methodology - DAFI, we will investigate a change of forces acting on the drop when the contact angles change during the adaption process. Specifically, we will measure the advancing (Θ_a) and receding (Θ_r) contact angles of the moving water drop at different velocity on switchable surfaces realized by freely rotating Janus-particles. We will address the question how fast does the surface structure of Janus particle layer, which depends on the dynamics of (re)-orientation of individual Janus particles, change when it is exposed to the water or, vice versa, when it becomes dry again. For instance, one can suppose that measured force will be large if JPs have enough time to reorient (surface become hydrophilic an adhesive). In the case when JPs don't have enough time to reorient, surface will stay hydrophobic and less adhesive. From these experiments we will get an insight into the strength of interaction between surface and water droplet and in this way will verify together a theoretical description of adaptive wetting on switchable surfaces realized by freely rotating Janus-particles. These dynamic wetting experiments performed with DAFI methodology will help us to quantify adaptation kinetics of switchable surfaces realized by freely rotating Janus-particles.

Special emphasis in this WP will be given to investigation of correlation between microscopic wetting of individual Janus particles with oil and water (WP2) and macroscopic wetting of wax surfaces with multiple Janus particles. We will apply existing models for description of wetting on structured surfaces (Marmur, Extrand and others^{78-79, 87}) to describe wetting of wax-Janus particle surfaces. Cooperation with the groups of physicists and theoreticians **Gurevich/Heuer** group will help to develop of advanced approaches for modelling of wetting on such structured surfaces. For this, the different numerical/theoretical approaches, and the multi-scale techniques to bridge between them on a quantitative level will be applied (**Gurevich/Heuer**). Together we plan to analyze and to understand the time-depending switching dynamics of structured substrates based on freely rotating Janus particles with the resulted non-equilibrium wetting behavior of water. We expect that JPs will build up structured surfaces with different complex geometries (hexagonal or stripes), patchiness, and wettability (less wettable or more wettable) depending on JP topologies (spherical or rod-like) as well as hydrophobic/hydrophilic contrast (Janus balance). The key questions: (i) how fast will (re)-orientation of JPs and switching take place; (ii) what happens with the dynamics of water droplet during this dynamic process; (iii) what happens with dynamics of droplet if formed surface from JPs will be chemically homogeneous (all JPs will be exposed by one side to environment); (iv) what happens with dynamics of droplet if formed surface from JPs will be chemically pre-structured (not all JPs will be exposed by one side to environment – this can lead to the chemical patchiness); (v) what happens with the dynamics of droplet if formed surface from JPs will be topographically pre-structured (Janus rods can form stripes). The multi-scale simulation results will be compared with our experimental findings.

Investigation of anisotropy of wetting is particular interesting. We do not expect anisotropic wetting on surfaces with spherical particles. On the other hand, spontaneous alignment of rod-like particles may result in wetting anisotropy. Moreover, sliding water droplet as well as advancing and receding droplets can cause alignment and orientation of rods on molten wax in the direction of movement. We will investigate these effects by doing cyclical wetting measurements (multiple advancing and receding cycles).

In the end of the project, we will explore possibilities to switch wetting locally. The local heating will be realized by using a laser. Since melting points of waxes and polymers, which are planned to be used, are slightly above ambient temperature, low power LED lasers (100 mW-500 mW) can be used. It is expected that local switching will open broad possibilities for investigation of dynamics of reorientation of Janus particles and dynamics of switching o wetting behavior.

Expected output from WP3 and project output: The major project output will be the understanding of correlation between behavior and dynamics of self-assembly and organization of individual Janus particles at interfaces, cumulative effect of multiple Janus particles layers on macroscopic dynamic wetting and reversibility of the transitions induced by the temperature and magnetic field.

Project outlook: In the first application period we will investigate effects of switching of orientation of Janus particles with spherical and longitudinal rod-like topologies on switching and dynamics of wetting. In the second application period we plan to investigate the interfacial

and dynamic wetting behavior and effects of Janus particles with more complex forms such as conical and transverse rod-like. We also plan to introduce possibility to switch the orientation of individual Janus particles by heating with laser beam to fabricate surfaces with switchable local surface pattern. Moreover, we plan to use wax-Janus particle blends to create structured surfaces with complex topography using 3D printing and investigate their dynamic wetting properties.

Table 1. Description of work packages and time schedule

Year	Year 1				Year 2				Year 3			
Quarter	1	2	3	4	1	2	3	4	1	2	3	4
WP1: Synthesis of JPs with varied topologies												
WP2: Exploring kinetics of (re)-orientation of JPs and switching protocols at oil/water & oil/air interfaces												
WP3: Determination of liquid droplet dynamics & non-equilibrium wettability response during switching and formation of structures. Comparison of experimental findings with multi-scale simulations												

2.4 Data handling

All data developed in this project will be stored on our institute's raid systems, which are connected to our own backup-systems. Raw simulation data (time series) will be back-uped on external storage media in order to keep them available for longer times. High level data and graphs from the simulations will be secured by the IT-system of the Leibniz Institute of Polymer Research Dresden for at least 10 years.

2.5 Other information

Please use this section for any additional information you feel is relevant which has not been provided elsewhere.
none

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

none

2.7 Information on scientific and financial involvement of international cooperation partners

none

2.8 Information on scientific cooperation within SPP 2171

The SPP 2171 consists of cooperative and individual projects in the fields of (i) design of switchable, adaptive or flexible surfaces, (ii) development and application of methods for investigation of dynamic wetting with simple liquids, and (iii) understanding of wetting phenomena by correlating experiment and modelling. **This proposal is positioned in the category of fundamental understanding of time-dependent switching protocols and the resulted dynamics of three phase contact lines on switchable and adaptive JPs substrates.** Cooperation with scientist/groups with expertise in complex methods for investigation of wetting as well as in modelling of dynamic wetting is required to get a full understanding into the complex non-equilibrium wetting response on Janus particles substrates during the switching. Therefore, in the first phase of the project we will establish close cooperation with **5 of our key partners** within the SPP:

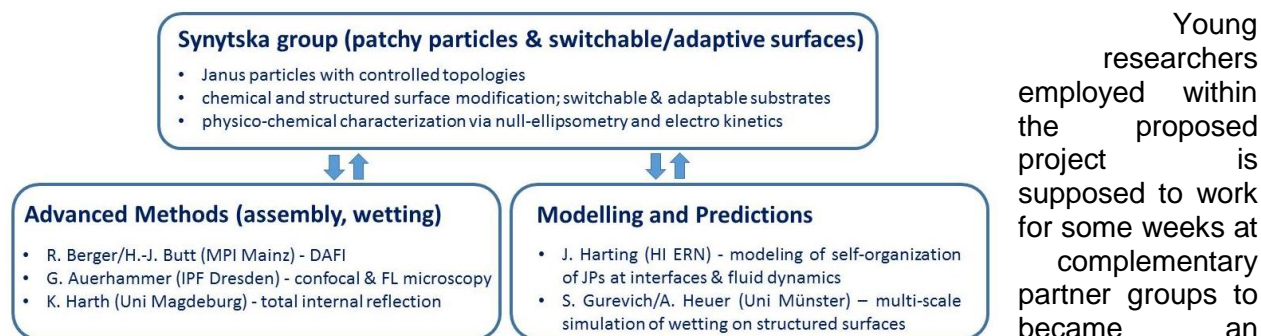
In cooperation with the group of **Auernhammer** we will determine the time-dependent reorientation process of JPs (WP2), its spatial homogeneity (WP2) and its dependency on external parameters like the phase above the wax (air or water) (WP3) using confocal and fluorescence microscopy.

Together with the group of **Harting** we will get fundamental understanding of dynamics of reorientation of JPs and their organization into complex structures and patterns (within WP2). This knowledge might further help to predict how these surface structures and anisotropy will

influence wettability under dynamic conditions (within **WP3**). We foresee quantitative comparison and correlation between our experimental results with numerical predictions from Harting's group. Together with the group of **Harth** we will investigate the time-depending water drop spreading during the reorientation and switching of Janus particles at fusible waxy surfaces. (**WP3**). For this high-speed total reflection microscopy will be used.

Together with the group of **Berger / Butt** we will determine the advancing (Θ_a) and receding (Θ_r) contact angles of the moving water drop at different velocity on switchable surfaces realized by freely rotating Janus-particles. From these experiments we will get an insight into the strength of interaction between surface and water droplet and in this way will verify together a theoretical description of adaptive wetting on switchable surfaces realized by freely rotating Janus-particles (**WP3**). These dynamic wetting experiments performed with DAFI methodology will help us to quantify adaptation kinetics of switchable surfaces realized by freely rotating Janus-particles.

Cooperation with the group of **Heuer/ Gurevich** will allow comparison of our experimental findings with modeling (microscopic and macroscopic scale simulation on structured surfaces) and understanding the time-depending switching dynamics of switchable structured substrates based on freely rotating Janus particles with the resulted non-equilibrium wetting behavior of water (**WP3**).



complementary expertise in advanced methods such as DAFI (**Berger/Butt**), confocal microscopy (**Auerhammer – expertise inside of IPF**) or total reflection microscopy (**Harth**) as well as to work with the groups of theoreticians to get an insight into simulations and predictions (**Hartings** and **Gurevich/ Heuer**). **Synytska** group will provide an expertise and experimental training in the chemical and topographical modification of surfaces and designing of switchable and adaptable substrates based on polymeric brushes (via grafting to, grafting through and grafting from approaches) and colloidal systems. Also training and support in null-ellipsometry technique for the characterization of dynamics of water uptake and swelling behavior in polymeric brush systems will be provided. Participation in summer schools organized in the frames of SPP in the fields of materials, colloids and interfacial phenomena is also planned. We also plan to prepare hands-on tutorials for graduate (MS and PhD students) explaining behavior of colloidal particles at interfaces, which allows design and fabrication of surfaces with switchable and dynamic wetting.

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4 Requested modules/funds

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

4.1 Basic Module

4.1.1 Funding for Staff

	Staff	Wage group	Position (month)	Standard sum
1	PhD student (chemistry)	TV-L E13	75% position, 36 Months	48.375 €/year
1	Student assistant (SHK)*			6.000 €/year
	Total			54.375 €/year

N.N, PhD student: The new doctoral candidate should have a background in physical and polymer chemistry and will perform the work outlined in WP1–3 and support collaborations with the other groups listed in WPs as well as in Section 2.8 of this project.

SHK (student assistant) students will prepare hand-on tutorials

Total Costs Personnel

163.125 €

4.1.2 Direct Project Costs

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

Description	Costs
Chemicals for the Janus particle synthesis: for the synthesis of JPs expensive starting materials and solvents are needed.	8.000 EUR/year
Lab consumables: glass ware, filters, vials, seals;	1500 EUR/year
Grids for TEM and SEM, AFM probes, wafers	500 EUR/year
Total	30.000 EUR

4.1.2.2 Travel Expenses

Conferences	Expenses
1 SPP workshop	800 EUR/year
1 International/national Conference (e.g. ACS National Meeting, MRS)	1000 EUR/year
1 Visits to other groups, summer school and SPP meetings*	800 EUR/year
Total	8.400 EUR

* The following SPP meetings are planned

- * 1st and 2nd year: one SPP workshop (4 days)
- * 1st year: Advanced School (5 days)
- * 2nd year: PhD-candidate workshop (4 days)
- * 3rd year: international conference - (5 days)

4.1.2.3 Visiting Researchers (excluding Mercator Fellows)

none

4.1.2.4 Expenses for Laboratory Animals

none

4.1.2.5 Other Costs

none

4.1.2.6 Project-related publication expenses

We plan to publish in open Source journals which require page charges

750 EUR/year

4.1.3 Instrumentation

4.1.3.1 Equipment exceeding Euro 10,000

none

4.1.3.2 Major Instrumentation exceeding Euro 50,000

none

5 Project requirements

5.1 Employment status information

Dr. Alla Synytska is a Head of Department of Polymer Interfaces, Research Group Leader (Group of Functional Particles and Interfaces) at the Leibniz Institute of Polymer Research Dresden and private dozen at the TU Dresden (defense of habilitation thesis is upcoming on 13.11.2018). Dr. Alla Synytska has shown to exhibit strong competencies in 3 key research areas: (1) synthesis of organic-inorganic hybrid particles (incl. Janus colloids) with controlled topological design; (2) characterization of their physical and chemical property in bulk and at interfaces; as well as (3) exploration of self-assembly of particles at interfaces and surfaces for material design that are vigorous for the implementation and success of the envisaged project. Dr. Synytska is permanently employed.

5.2 First-time proposal data

None

5.3 Composition of the project group

Dr. Alla Synytska is the principal investigator of the project. She will supervise and coordinate the work of the PhD student. She will guide the student during the course of the PhD. She will also be assist for all necessary collaborations planned within the consortium. She will participate in regular discussions of the results obtained in the project.

Dr. Petr Formanek will support this project with electron microscopy measurements.

Dipl.-Ing. Andreas Janke will support this project with Atomic Force microscopy measurements.

Dipl.-Ing. Stephan Michel will support this project with pendant drop tensiometry measurements.

5.4 Cooperation with other researchers

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

- Prof. Jens Harting (Forschungszentrum Jülich GmbH, Helmholtz-Institut Erlangen-Nürnberg) - Dynamics of Complex Fluids and Interfaces
- Dr. R. Berger/ Prof. H.-J. Butt (MPI Mainz) - force measurements of moving droplets, DAFI
- Dr. Günter K. Auernhammer (Leibniz Institute of Polymer Research, Dresden) – a home-built laser scanning confocal microscope (LSCM)
- Dr. Kirsten Harth (University of Twente) - high-speed total reflection microscopy
- PD Dr. Svetlana Gurevich/ Prof. Andreas Heuer (University of Münster) – multi-scale simulation of wetting behavior on structured surfaces

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

Prof. L. Isa (ETH Zürich), Prof. C. Creton (ESPCI Paris), Prof. H. Lang (Technische Universität Chemnitz), Prof. M. Kampremann (Wageningen University), Prof. A. del Campo (INM Saarbrücken), Prof. E. Arzt (INM Saarbrücken), Dr. J. Borst (Wageningen University), Dr. F. Wurm (MPI-P Mainz), Prof. A. Fery (IPF Dresden), Prof. L. Ionov (University of Bayreuth), Prof. S. Kaskel (Technische Universität Dresden).

5.5 Scientific equipment

- Home-built laser scanning confocal microscope (LSCM) (details on the apparatus are described in the proposal of Auernhammer/Fery)
- Confocal Microscope μ Surf with Software μ Measure and μ Analyze (NanoFocus, Oberhausen, Germany)
- Atomic Force Microscopes (Dimension Icon & V, Bruker; MFP-3D-BIO, Asylum Research; Nanowizard Ultra & IV, JPK Instruments)
- X-Ray Photo Electron Spectrometer Amicus (Kratos Analytical, Manchester, United Kingdom)
- Transmission Electron Microscope, Libra120 and Libra 200 Cs-STEM (Carl Zeiss AG, Jena, Germany)
- Scanning Electron Microscope / Focused Ion Beam Neon 40 (Carl Zeiss AG, Jena, Germany)

- Null-ellipsometer with variable measurement angles and with cells for measurements in liquids and in dry state (Multiscope, Optrel Berlin, Germany).
- Sessile, pendant drop and captive (adhering) bubble techniques (DataPhysics OCA35L, DataPhysics OCA40 micro)

5.6 Project-relevant cooperation with commercial enterprises

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

none

5.7 Project-relevant participation in commercial enterprises

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

none

6 Additional information

Third-party funding for this project has not been applied for.