

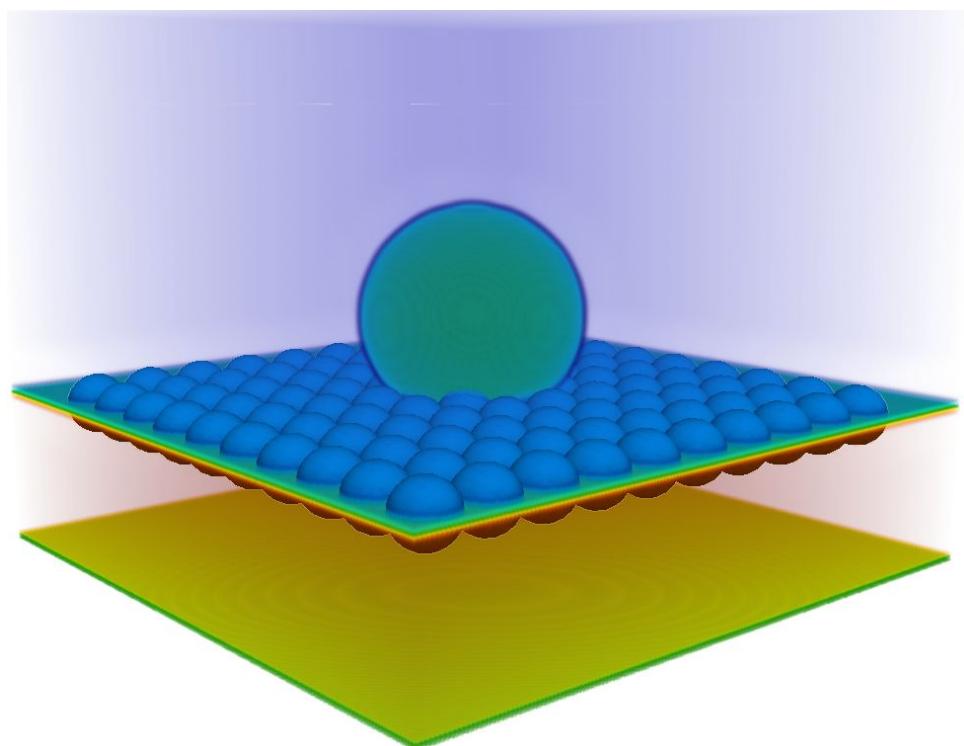
Project Description

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SPP 2171: Dynamic wetting of flexible, adaptive and switchable surfaces

Colloidal assembly as a tool for adaptive and switchable interfaces



Summary

This project will contribute to the fundamental understanding of dynamic wetting and dewetting processes on flexible, adaptive and even switchable substrates by means of lattice Boltzmann simulations and simple analytical models. Our aim is to propose strategies utilizing colloidal assembly at fluid interfaces to generate “substrates” with complex geometrical and wetting properties. We will base on recent advances in the synthesis and control of colloids which led to the availability of particles with highly specific features such as well-defined shapes and surface properties together with the ability to manipulate them by external forces and fields. An example for such particles are patchy particles or Janus particles which depict a variation of their surface properties in dependence on the position. They can even be stimuli responsive or react to external magnetic and electric fields, light or changes in the properties of the surrounding fluids. Attached to a fluid interface, these abilities render them interesting candidates to create interfaces which adopt to the surrounding liquid species or can be switched by means of external fields. For example, due to external forces, a collection of microscale Janus particles with hydrophobic and hydrophilic hemispheres might rotate at the interface and thus dynamically change the macroscale wetting properties of the interface. Alternatively, these particles might be let rotate freely at the interface so that they can optimize the wetting properties by simply minimizing their surface energy. We will investigate such systems systematically by simulating the spreading and wetting dynamics of droplets on various interfaces: A pure liquid interface, an interface covered with particles with defined homogeneous wettability and geometry, and particles with anisotropic shape and wetting properties. At last, we will investigate how to “switch” particle-laden interfaces by means of external fields.

Zusammenfassung

Ziel dieses Projekts ist ein fundamentales Verständnis dynamischer Benetzungsorgänge auf flexiblen, adaptiven oder schaltbaren Substraten. Mit Hilfe von Gitter-Boltzmann Simulationen und einfachen analytischen Modellen wollen wir neuartige Strategien zur Herstellung funktionaler Grenzflächen mit Hilfe von an Flüssigkeitsgrenzflächen angelagerten Kolloiden finden. Hierzu werden wir uns die großen Fortschritte, die die Teilchensynthese in den letzten Jahren verzeichneten konnte, zu Nutze machen. Es ist heute möglich, Partikel mit sehr spezifischen Eigenschaften, wie beispielsweise wohl definierten Formen und Oberflächeneigenschaften oder der Möglichkeit diese Teilchen durch externe Felder zu manipulieren, herzustellen. Ein Beispiel hierfür sind sogenannte Janusteilchen, welche unterschiedliche Eigenschaften an verschiedenen Positionen ihrer Oberfläche aufweisen. Diese Teilchen können sogar so hergestellt werden, dass sie auf externe Stimulationen (Licht, Wärme, externe Felder, etc.) reagieren und ihre Eigenschaften ändern. Lagert man sie an einer Flüssigkeitsgrenzfläche an, können sie vielversprechende Kandidaten zur Herstellung neuartiger adaptiver oder schaltbarer Grenzflächen sein. Zum Beispiel können Janusteilchen mit hydrophoben und hydrophilen Teilen ihrer Oberfläche an einer Grenzfläche rotieren und damit die Benetzungseigenschaften dieser Oberfläche dynamisch verändern. Haben solche Teilchen einen magnetischen Kern, lassen sie sich sogar mit angelegten magnetischen Feldern beeinflussen. Wir werden solche Systeme systematisch mit Hilfe von Computersimulationen untersuchen, wobei der Fokus auf der Adaptivität und Steuerbarkeit der Benetzungseigenschaften liegen soll. Am Beispiel eines Tropfens auf einer flüssig-flüssig Grenzfläche (“flüssiges Substrat”), sowie Grenzflächen, die mit homogenen und anisotropen Teilchen bestückt sind, werden wir verstehen, welchen Einfluss die Teilchen haben und wie sie mit Hilfe externer Felder “schaltbar” werden.

1 State of the art and preliminary work

State of the art

Dynamic wetting and dewetting processes on chemically or geometrically structured substrates are ubiquitous in many applications. While most research on this topic was performed for rigid and static substrates, many systems involve the transport of liquids on soft or flexible surfaces, such as 3D printing, the production of organic solar cells, or biological systems such as a droplet of sweat moving on the human skin. Many of these substrates might adopt to the presence of a liquid by means of elastic stresses, or even by chemical interactions [1–7]. Another common example of a deformable substrate is a wet or even liquid substrate, i.e. a solid surface covered by a liquid film [8–10]. While Young's law fails on any soft substrate, the balance equation of Neumann holds in the case of drops floating on another liquid [11, 12]. However, our fundamental understanding of dynamic wetting processes on flexible, liquid, and adaptive substrates is still limited. Furthermore, technological applications that efficiently utilize the abilities of such systems are sparse.

The assembly of colloidal particles provides a promising alternative route to fabricate nano- and microstructured functional materials and substrates including flexible, soft, or adaptive substrates. Colloidal particles adsorb strongly at fluid-fluid interfaces. Detachment energies of spherical particles can be orders of magnitude greater than the thermal energy, $k_B T$. [13, 14] This means that colloidal particles can attach irreversibly to interfaces, and hence stabilize fluid interfaces better than surfactants, which are usually able to freely adsorb and desorb from an interface. [15] The shape and contact angle of the particle dictate how strongly it attaches for a given particle size: shapes that occupy smaller interface areas detach more easily than those occupying larger areas. Particles migrate to the interface to replace some fluid-fluid surface area with particle-fluid surface-area, reducing the free energy, $F_\gamma = \oint_{\partial A} \gamma dA$, where γ is the surface tension and ∂A the interface area.

Once colloidal particles adsorb at a fluid-fluid interface, particle-particle interactions caused by competing hydrodynamic, electromagnetic and capillary forces can lead to particles self-assembling into materials with specific mechanical, optical, or magnetic properties [16]. Capillary interactions arise when particles deform the fluid interface. These interface deformations can be induced by external forces and torques such as gravity, or even by particle shape alone [17]. Capillary interactions have attracted much interest in recent years for their role in, for example, the self assembly of anisotropic particles at fluid interfaces [14, 17–19] the suppression of the coffee ring effect [20] and the Cheerios effect [21].

Advances in materials science have enabled the production of anisotropic particles with precise shapes, sizes, and electromagnetic properties [22]. Particles can also be manufactured with embedded ferromagnetic [23] or (super)-paramagnetic dipoles [24] so that they are able to interact with external magnetic fields. This combination of particle shape and particle functionality, facilitated by the embedded dipoles, opens up a whole range of new ways to control particle self-assembly at fluid-fluid interfaces into two-dimensional structures.

Colloidal Janus particles have drawn special attention during the past two decades for their potential in materials science [25, 26]. Janus particles are characterized by anisotropic surface chemical (e.g. wetting or catalytic) or physical (e.g. optical, electric, or magnetic) properties at well-defined areas on the particle. Since the first synthesis of Janus particles three decades ago [27, 28], various methods have been developed to synthesize them. The synthesis of Janus particles can be classified into two categories: surface modification and compartmentalization.

Surface modification methods render initially homogeneous isotropic particles anisotropic on the surface [29–35], whereas compartmentalization methods assemble Janus particles from molecules or polymers and the synthesized particles have anisotropic compositions [36–38]. Fig. 1 depicts some examples of Janus particles created by our collaborator A. Synytska (Dresden) [34, 35].

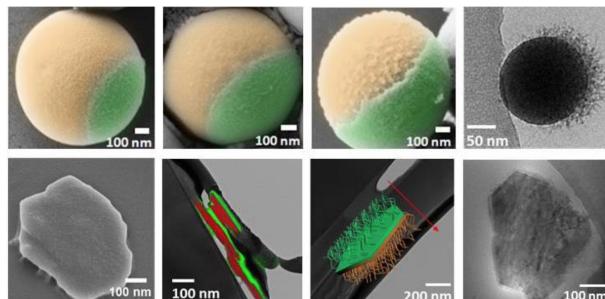


Fig. 1: Examples of Janus particles created by A. Synytska: the upper images show spherical polystyrene(PS)- poly(2- dimethylaminoethyl methacrylate) PDMAEMA Janus particles with different Janus ratios [35]. The bottom images depict PDMAEMA/poly lauryl methacrylate (PLMA) Janus platelets [34, 35].

This combination of chemical anisotropy and response to external fields makes Janus particles promising building blocks of reconfigurable and programmable self-assembled structures [39–43]. In a dilute particle suspension, the Janus particles mainly assemble into clusters [44, 45]. However, Janus particles strongly adsorb at liquid interfaces [13], and form networks or other 2D structures [46, 47].

Park et al. numerically calculate the interfacial energy of ellipsoidal and dumbbell Janus particles at a fluid-fluid interface and investigate the equilibrium angles [48, 49]. Rezvantalaba et al. used the surface evolver software package to study the capillary interactions between spherical Janus particles at fluid interfaces [50]. Surface evolver is based on an algorithm to minimize the surface area and is limited to systems with static particles. Later, the same group performed molecular dynamics (MD) simulations to understand the diffusion of Janus nanoparticles at a fluid-fluid interface [51] and the response of a single Janus nanoparticle adsorbed at an fluid-fluid interface to imposed shear flows [52]. However, MD simulations are too expensive if large numbers of particles need to be considered. Luu and Striolo used dissipative particle dynamics (DPD) simulations to investigate the equilibrium behavior of ellipsoidal Janus nanoparticles adsorbed at spherical oil/water interfaces [53]. Later Kobayashi and Arai also used the DPD method to study the rheological properties of Janus nano-particle solutions in nanotubes [54]. However, even with the degree of course-graining that DPD offers in comparison to MD, it is still too expensive to simulate a substantial number of Janus colloids.

Preliminary work

Our simulations require to resolve the hydrodynamics of the fluid together with the dynamics of the suspended particles. The applicant has collected more than fifteen years of experience with the simulation of multiphase or multicomponent fluid flows as well as particle-laden flows at different levels. To date a number of well-developed and massively parallel simulation codes exist in the group in Nuremberg. The most advanced simulation tool *LB3D* will be the starting point for the current project [55]. The code is based on the lattice Boltzmann (LB) method which can be seen as a discretized solver of the Boltzmann equation which in the limit of small Mach and Knudsen numbers recovers the Navier-Stokes equations [56]. It has become a successful tool

for modeling fluids in science and engineering. Compared to traditional Navier-Stokes solvers, it allows an easy implementation of complex boundary conditions and - due to the high degree of locality of the algorithm - is well suited for the implementation on parallel supercomputers. Our in-house LB code (LB3D) is formed by a collection of software packages for lattice-Boltzmann mesoscale fluid simulations designed for high performance computing. It was originally written for binary and ternary fluids and later extended to cover a wide range of physical applications such as colloidal suspensions [57–65], flows in porous media [66, 67], and more recently electrokinetics [68] or concentrated suspensions of deformable particles such as biological cells or polymeric particles [69–72]. The PI and his coworkers extended the method to particles suspended in *binary* fluid mixtures allowing to study interfacial stabilization and emulsification. This method has been used extensively to investigate particle-covered droplets, Pickering emulsions and so-called bicontinuous interfacially jammed emulsion gels (bijels) [61, 73, 74]. Additionally, the group focused on the interplay of capillary forces and particle anisotropy as a tool to direct the assembly of colloidal particles at fluid interfaces [63, 75]. LB3D is used by several groups inside and outside Germany and its versatility offers a wide range of applications to the users with excellent scalability on massively parallel computers [74]. The code is capable of handling suspensions with up to millions of particles, and has up to now led to more than 90 scientific publications. The availability of the simulation code will assure a jump start for the to be hired researcher since only very limited implementation work will be necessary.

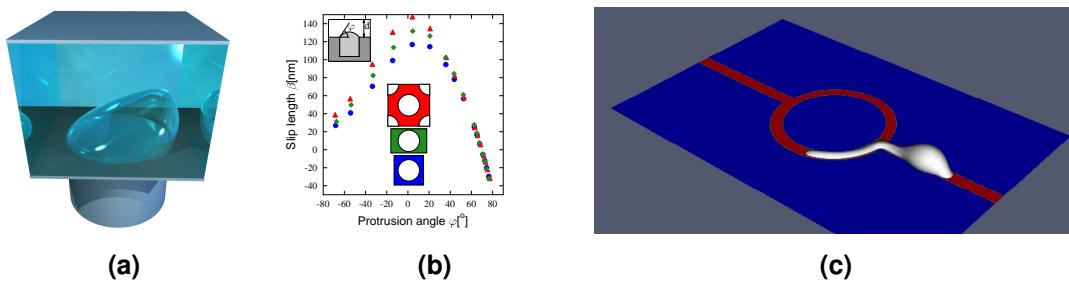


Fig. 2: a) A snapshot from a lattice Boltzmann simulation showing the deformation of a bubble on a geometrically and chemically structured substrate in a shear flow. b) The impact of the protrusion angle (here equivalent to the contact angle) on the measured slip length [76]. c) A droplet moving on a branched chemical pattern [77].

Within SPP1171 “Nano- and microfluidics” we investigated the impact of substrate properties on the effective transport of a fluid or a mixture of fluids in its vicinity. A particular focus was on the origin of an apparent nano- or microscale slippage that could be observed in numerous experiments [78–80]. At the starting time of the previous SPP, the origin of this “violation” of the no-slip boundary condition was not fully understood. We systematically investigated the impact of several properties of the experimental setup on the detected slip length and the wetting and transport of fluids by means of multiphase lattice Boltzmann simulations. These properties include hydrophobic interactions [81], surface roughness [82, 83], or bubble-mattresses leading to superhydrophobic behaviour [76] (see Fig. 2a-b). In particular the latter is of high interest to the current project: we demonstrated how the dynamic deformation of bubbles in combination with the wetting properties and geometrical structuring of the substrate influences the transport of fluid over such a substrate. We later extended these activities to open microfluidics applications and the directed transport of fluids on chemically patterned substrates (see Fig. 2c) [77]. The behaviour of droplets on a solid substrate, such as contact line pinning, spreading, coalescence, evaporation and condensation has been investigated extensively in the past. Recently, there has been much interest in studying a droplet sitting on an immiscible underlying lubricated

liquid layer. Some novel phenomena have been observed, such as the droplet can slide off at very small tilt angle [84] and there are non-monotonic interactions between droplets [8]. Such systems are also in the focus of the current SPP and will be investigated in this project. As a preliminary feasibility study and preparation of this proposal, we extended our code to investigate a ternary fluid system.

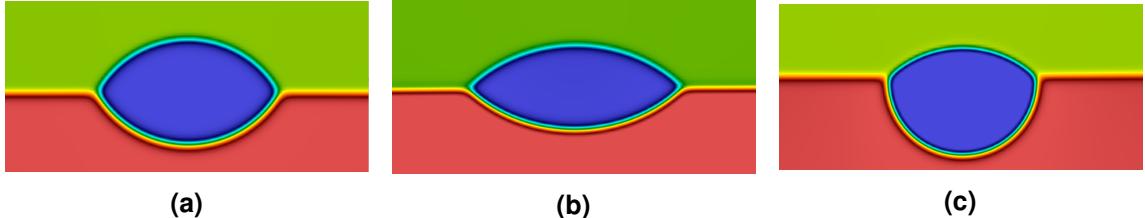


Fig. 3: Equilibrium shape of a droplet (blue) adsorbed at a fluid-fluid (red-green) interface with varying surface tensions. a) $\gamma_{bg} = \gamma_{br} = \gamma_{gr}$, b) $\gamma_{gr} > \gamma_{br} = \gamma_{bg}$, c) $\gamma_{bg} > \gamma_{br} = \gamma_{gr}$.

We initialized a droplet at a fluid-fluid interface to study the shape of the droplet with varying the surface tensions of the three fluids. Fig. 3a-3c depict snapshots from simulations with different surface tension ratios. The contact angle of the droplet can be calculated based on a Neumann construction [11]. In addition, we restrict ourselves to the surface tension dominated case, where the droplet surface forms a spherical cap shape. Then we can derive a theoretical prediction of the shape of the droplet with known surface tensions. Fig. 4 shows that our theoretical prediction is in good agreement with our simulation results.

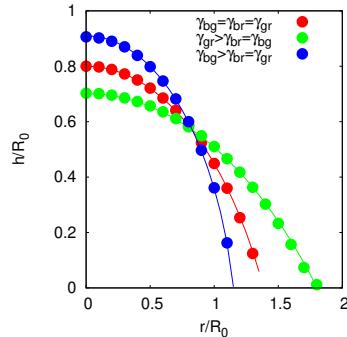


Fig. 4: Comparison of our simulation results (symbols) with the theoretical prediction (lines).

Then, we placed two droplets at a distance $L/R = 5$, where L is the droplet center to center distance, and R is the initial radius of the droplet. The droplets cause a deformation of the interface which leads to capillary attractions of the droplets, as shown in Fig. 5. Not shown are further preliminary studies of droplet-droplet interactions. An important parameter is the height of the interface h or the amount of “red” fluid present in the system. Depending on the interplay between chosen surface tensions and interface height, various states can be found ranging from droplet coalescence to stable side by side configurations or repulsion. In this project we aim at detailed studies of capillary interactions between droplets at fluid interfaces as outlined below. The energy required to detach a single particle from a fluid-fluid interface is an important parameter for designing certain soft materials including switchable and adaptive substrates based on particle-laden interfaces. For a fixed particle volume, prolate and oblate spheroids attach more strongly to interfaces because they have larger particle-interface areas. We developed a simplified detachment energy model for spheroids which depends only on the particle aspect ratio and the height of the particle centre of mass above the fluid-fluid interface.

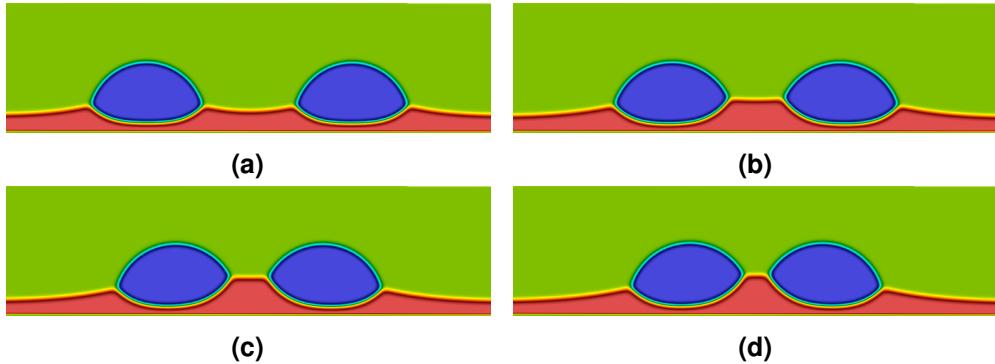


Fig. 5: Two droplets are placed with a center to center distance $L/R = 5$, where R is the initial radius of the droplet. The droplets cause the deformation of the interface causing the rise of capillary attraction which driving the droplets towards each other.

We tested our theoretical model by detaching spheroidal particles from liquid-liquid interfaces using our lattice Boltzmann model, finding good quantitative and qualitative agreement [85]. Since anisotropic particles have more than one possible orientation at an interface, how does the free energy of the particle change as its orientation at the interface changes? To answer this question, We simulated ellipsoidal particles adsorbed at a liquid–liquid interface influenced by an external magnetic field using lattice Boltzmann simulations, which include the effect of interface deformations arising from the local fulfillment of Young’s equation around the particle. We showed that interface deformation significantly contributes to the observed tilt angle for a given dipole-field strength and accounts for the observed deviations between simulations and the planar interface approximation adopted in previous publications. We showed that the particle tilting deforms the interface in a dipolar manner, creating capillary charges which lead to capillary interactions between particles [62].

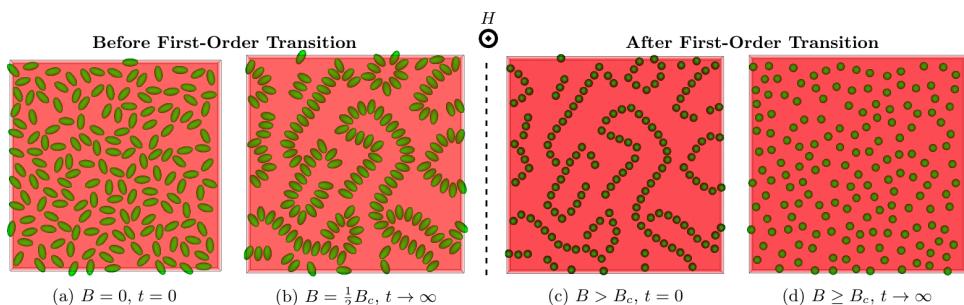


Fig. 6: (a) The particles are distributed randomly in their equilibrium orientations. (b) Applying a magnetic field parallel to the interface normal causes them to self-assemble due to dipolar capillary interactions. (c) Once the critical field strength is reached, particles transition to the vertical state, halting dipolar capillary interactions. (d) Once capillary interactions have been turned off, the particles may order randomly [63].

By using magnetic anisotropic particles interacting with external magnetic fields, we have shown how to dynamically tune dipolar capillary interactions between particles by varying the dipole-field strength, and how to switch these dipolar capillary interactions on and off by making the particles undergo a first-order orientation transition, as shown in Fig. 6. Our simulations reveal novel self-assembled structures that depend on the surface coverage of particles and the dipole-field strength. We observed the formation of “capillary caterpillars”, in which particles align in side-side configurations, and “capillary couples” where particles in individual caterpillars align in tip-tip chains with particles in other caterpillars, due to the anti-symmetric menisci formation [63]. In the current project we plan to build on these findings and investigate how to utilize such

interfacial structures obtained from anisotropic particles as adaptive or switchable substrates. In a series of papers, we investigated the behavior of magnetic Janus particles adsorbed at fluid-fluid interfaces [64]. The Janus particles consist of a hydrophilic and a hydrophobic hemisphere. They have a dipole moment orthogonal to their Janus boundary and are influenced by an external magnetic field directed parallel to the interface. The field causes the particles to experience a magnetic torque, but surface tension opposes this torque, and the particles therefore tilt with respect to the interface, resulting in a deformation of the interface. We derived analytical models to calculate the free energy for a single magnetic Janus particle. Using lattice Boltzmann simulations, we tested the model predictions. Our analytical model that includes small interface deformations captures the behaviour of the particle. We further showed that the interface deformations around such Janus particles are dipolar in nature (as shown in Fig. 7a) and can be dynamically tuned by altering the external field strength.

Then, we developed a pair-interaction model for two tilted magnetic Janus particles using the superposition and small interface deformation approximations [86]. Our model predicts that these particles should arrange into a side-side configuration, which was confirmed by our simulation results. When many magnetic Janus particles adsorb at the interface, we found that the particles arrange into long, straight chains exhibiting little curvature (as shown in Fig. 7b-f). We further found a regime in which highly ordered, lattice-like monolayer structures form, which can be tuned dynamically using an external magnetic field.

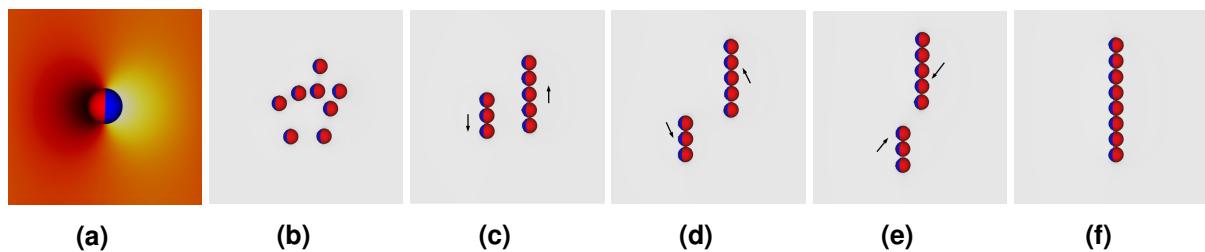


Fig. 7: (a): Snapshot of the relative height of the interface. Influenced by a magnetic torque, the Janus particle reorients, leading to dipolar interface deformations: the interface is depressed on one side of the particle (black) and raised on the other side (yellow). These dipolar interface deformations are dynamically tunable, providing a route to generate capillary-driven assemblies at fluid interfaces.

(b)–(f): Snapshots of the assembly process of 8 Janus particles adsorbed at a fluid-fluid interface. (b) Particles are initially placed randomly distributed. (c) The parallel external field is switched on, causing capillary interactions between the particles, leading them to assemble into two separate chains. Particles arrange side-by-side. (d), (e) The chains move relative to one another in the direction shown by the arrows and merge into a single one (f) [86].

To go beyond flat fluid-fluid interfaces, a situation that is quite artificial in the real world where most fluid-fluid interfaces exhibit some degree of curvature, we investigated the assembly of particles in a drying droplet [75]. We exploited the combination of particle chemical anisotropy and particle response to both an external magnetic field and a curved interface by studying the magnetic Janus particles adsorbed at a surface droplet. The particles organized in reconfigurable hexagonal lattice structures and could be directed to assemble at desirable locations on the droplet interface by simply varying the magnetic field direction, as shown in Fig. 8.

We developed an interface energy model to reveal the underlying mechanism and found good agreement with simulation results. During the drying process of the droplet, we found that the external magnetic field allows to tune the deposition of the particles, as shown in Fig. 8b. Our results open a possible way of creating highly ordered and – more importantly – tunable or

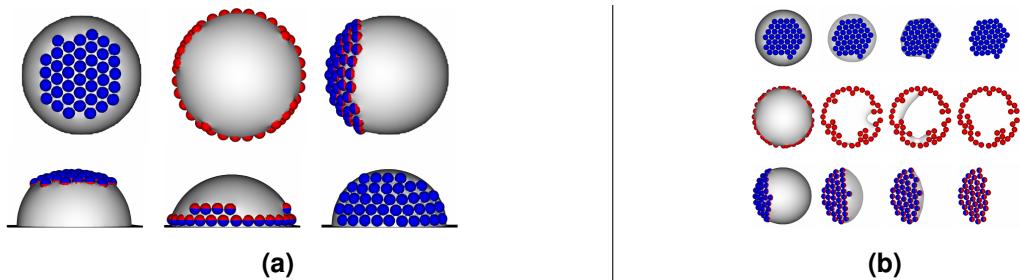


Fig. 8: a) Top (1st row) and side view (2nd row) of Janus particles adsorbed at a droplet interface under upward (1st column), downward (2nd column), left horizontal (3rd column) magnetic field directions. The particles relocate and form differently ordered structures depending on the direction of the magnetic field. b) Snapshots of the assembled structures during droplet evaporation and with an upward (1st row), downward (2nd row) and left horizontal (3rd row) applied magnetic field. Influenced by an upward magnetic field, the particles remain at the top of the droplet while the contact line decreases before it de-pins. Under a downward magnetic field, the particles form a ring-like structure that self-pins the contact line, and the contact line decreases continuously. Finally, in a horizontal magnetic field the particles migrate in the field direction and cause self-pinning on one side of the droplet.

switchable structures for hierarchical materials assembly or as a basis for switchable substrates. We studied the behavior of a single ellipsoidal Janus particle at a flat fluid-fluid interface. The equilibrium angle depends on the interplay between the particle shape and the wettability contrast. For weakly anisotropic particles with a strong wettability contrast, the equilibrium orientation is an upright orientation with respect to the interface. For highly anisotropic Janus particles the equilibrium state is a tilted orientation. This effect allows the assembly of complex structures depending on particle shape and wettability contrast [87].

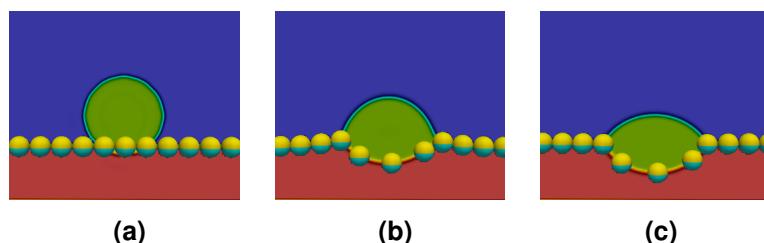


Fig. 9: Spreading of a droplet on a Janus particle laden interface. Time progresses from left to right¹.

The current project focuses on dynamic wetting on substrates obtained from colloidal assembly and particle-laden fluid interfaces. During the preparation of this proposal we extended our simulation method to already handle three fluid components and Janus particles. An example from such a lattice Boltzmann simulation is shown in Fig. 9 which depicts snapshots of a droplet spreading on a Janus particle laden fluid-fluid interface. It will be of great advantage for the to be hired researcher that the project does not require any method or code development. Instead, the candidate will be able to perform simulations directly from the start.

¹The orientation of the particles is properly taken care of in the simulation, but our visualization software is not yet able to do so.

1.1 Project-related publications

1.1.1 Articles published by outlets with scientific quality assurance

1. N. Rivas, S. Frijters, I. Pagonabarraga, and **J. Harting**
Mesoscopic electrohydrodynamic simulations of binary colloidal suspensions
Journal of Chemical Physics 148, 144101 (2018), doi:10.1063/1.5020377 [68]
2. Q. Xie and **J. Harting**
From dot to ring: the role of friction on the deposition pattern of a drying colloidal suspension droplet
Langmuir 34, 5303 (2018), doi:10.1021/acs.langmuir.8b00727 [88]
3. Q. Xie, G.B. Davies, and **J. Harting**
Direct assembly of magnetic Janus particles at a sessile droplet interface
ACS Nano 11, 11232 (2017), doi:10.1021/acsnano.7b05550 [75]
4. Q. Xie, G.B. Davies, and **J. Harting**
Controlled capillary assembly of magnetic Janus particles at fluid-fluid Interfaces
Soft Matter 12, 6566 (2016), doi:10.1039/C6SM01201A [86]
5. Q. Xie, G.B. Davies, F. Günther, and **J. Harting**
Tunable dipolar capillary deformations for magnetic Janus particles at fluid-fluid interfaces
Soft Matter 11, 3581 (2015), doi:10.1039/C5SM00255A [64]
6. G.B. Davies, T. Krüger, P.V. Coveney, **J. Harting**, and F. Bresme
Assembling Ellipsoidal Particles at Fluid Interfaces Using Switchable Dipolar Capillary Interactions
Advanced Materials 26, 6715 (2014), doi:10.1002/adma.201402419 [63]
7. T. Krüger, B. Kaoui, and **J. Harting**.
Interplay of inertia and deformability on rheological properties of a suspension of capsules
Journal of Fluid Mechanics 751, 725, (2014), doi:10.1017/jfm.2014.315 [72]
8. H. Mehrabian, **J. Harting**, and J.H. Snoeijer
Soft particles at a fluid interface
Soft Matter 12, 1062-1073 (2016), doi:10.1039/C5SM01971K [89]
9. C. Kunert, **J. Harting**, and O.I. Vinogradova
Random-roughness hydrodynamic boundary conditions
Physical Review Letters 105, 016001 (2010), doi:10.1103/PhysRevLett.105.016001 [83]
10. J. Hyväläluoma and **J. Harting**
Slip flow over structured surfaces with entrapped microbubbles
Physical Review Letters 100, 246001 (2008), doi:10.1103/PhysRevLett.100.246001 [76]

2 Objectives and work programme

2.1 Anticipated total duration of the project

The project is supposed to start on 01.10.2019 and shall take 36 months.

2.2 Objectives

This project aims at an understanding of how colloidal particles can be utilized to assemble adaptive and switchable substrates. We will work towards the following objectives by means of state of the art computer simulations and analytical modelling.

- O1:** Understand and control the spreading and transport of droplets attached to a fluid interface and how droplets interact via capillary interactions. Investigate the influence of limited film thicknesses on the spreading behaviour.
- O2:** Adaptive interface: add particles to the ternary fluid system and understand the impact of particle shape and wettability on the assembly and transport. Determine how the particle arrangement influences the droplet shape.
- O3:** Adaptive interface with Janus particles: Understand the equilibrium position of Janus particles in the presence of a droplet and determine how they adopt by rotation and collective assembly.
- O4:** Switchable interfaces: Apply external magnetic fields to create a torque on the particles and understand if the known behaviour for binary fluids does extend towards ternary systems.

2.3 Work program incl. proposed research methods

The lattice Boltzmann method for particles and interfaces

We use the lattice Boltzmann (LB) method as the basis for our simulation combined with the discrete element method (DEM) to describe the motion of solid particles in complex flow situations. Here, we implement the pseudopotential multicomponent LBM method of Shan and Chen [90] with a D3Q19 lattice [91] and review some relevant details in the following. Each fluid component is modelled by the evolution equation of a distribution function discretized in space and time according to the lattice Boltzmann equation

$$f_i^c(\vec{x} + \vec{e}_i \Delta t, t + \Delta t) = f_i^c(\vec{x}, t) + \Omega_i^c(\vec{x}, t), \quad (1)$$

where $i = 1, \dots, 19$, $f_i^c(\vec{x}, t)$ are the single-particle distribution functions for fluid component c , \vec{e}_i is the discrete velocity in the i th direction, and

$$\Omega_i^c(\vec{x}, t) = -\frac{f_i^c(\vec{x}, t) - f_i^{\text{eq}}(\rho^c(\vec{x}, t), \vec{u}^c(\vec{x}, t))}{(\tau^c / \Delta t)} \quad (2)$$

is the Bhatnagar-Gross-Krook (BGK) collision operator [92]. τ^c is the relaxation time for component c . The macroscopic densities and velocities are defined as $\rho^c(\vec{x}, t) = \rho_0 \sum_i f_i^c(\vec{x}, t)$, where ρ_0 is a reference density, and $\vec{u}^c(\vec{x}, t) = \sum_i f_i^c(\vec{x}, t) \vec{e}_i / \rho^c(\vec{x}, t)$, respectively. Here, $f_i^{\text{eq}}(\rho^c(\vec{x}, t), \vec{u}^c(\vec{x}, t))$ is a second-order equilibrium distribution function [93]. When sufficient lattice symmetry is guaranteed, the Navier-Stokes equations can be recovered from Eq. (1) on appropriate length and time scales [56]. For convenience we choose the lattice constant Δx , the timestep Δt , the unit mass ρ_0 and the relaxation time τ^c to be unity, which leads to a kinematic viscosity $\nu^c = \frac{1}{6}$. For fluids to interact, we introduce a mean-field interaction force between components c and c' following Shan and Chen [90]. This leads to diffuse fluid interfaces with a width of $\approx 5\Delta x$. Suspended particles are discretized on the fluid lattice and coupled to the fluid species by means of a modified bounce-back boundary condition as pioneered by Ladd and Aidun [65, 94, 95].

Lubrication forces between particles are properly reproduced by the LB method if the particles are more than one lattice constant Δx apart. As soon as there is a direct particle-particle interface without intermediate fluid nodes, a short-range lubrication correction is applied [60, 94]. Recently, the particle-fluid coupling was extended to the Shan-Chen multicomponent method by our group [61, 71, 73, 74, 96] and applied to particle-laden fluid interfaces, particle-stabilized emulsions or dynamic particle wetting problems.

WP1: Droplets on a wet substrate: control the spreading and transport of droplets attached to a fluid interface

A fluid film on a solid substrate is the basis for the systems of interest in this proposal. At such a “wet substrate”, particles can be adsorbed and manipulated. Depending on the application, the fluid film can either stay liquid or after assembly of the particles, a liquid-solid phase transition can be triggered to fix the particles in space. This is for example the case in the wax based systems of our experimental collaborator A. Syntska, where the initially liquid wax is cooled down to ascertain a static configuration of Janus particles adsorbed to this interface. In addition, the understanding of “wet substrates” is of importance for numerous other projects in the SPP focusing on liquid infused substrates or droplet impact on wet films.

In the first work package, we will benchmark our simulation package which was recently extended to three fluid components and systematically study the deposition, spreading, receding and interaction of droplets at such interfaces. In all cases described below, it is planned to combine our simulations with analytical computations based on energy balances or thin film dynamics. We plan to collaborate with U. Thiele (Münster)/J. Snoeijer (Twente) on the theory, with K. Harth (Twente/Magdeburg) to compare our simulations to her experimental measurements, with G. Lecrivain (Dresden-Rossendorf) on benchmarking droplet spreading at a liquid interface, and with M. Sega (Nürnberg) on droplet dynamics on soft/wet substrates.

1. We will investigate how a droplet behaves at a fluid interface and how the interplay of the involved surface energies between the different fluids determines the shape of the attached droplet. In our summary of the preliminary work (Sec. 1) we already showed some feasibility studies of a three-fluid system which were performed at the time of writing of this proposal. Already there, we demonstrated that we can recover the expected shapes including the analytically computed Neumann angles for a very specific set of surface tensions and droplet sizes (see Fig. 5d). While the preliminary studies were in 2D, here, we will extend our work to three dimensions and systematically change the parameters of the system (surface tensions, droplet size, system size, etc.).
2. We will then investigate the spreading dynamics of droplets adsorbing to the interface for different surface tension ratios and understand how the properties of the surrounding fluid influences the spreading dynamics.
3. We will study the transport of droplets by adding a pressure gradient to the upper surrounding fluid or a shear gradient. Questions to be answered involve the influence of the “wet substrate” on the dynamic transport, as well as the impact on the difference between advancing and receding contact angles.
4. We will limit the thickness of the liquid film h . In the case where the droplet radius is much smaller than the film height ($R \ll h$), we expect the influence of the solid substrate to be negligible. Once $R \approx h$ or even $R > h$, the picture changes. Due to the limited available

volume below the fluid interface and the limited amount of fluid forming the wet film, the deformation of the droplet at the interface and the interface itself will adopt.

5. Due to the droplet-induced deformation of the liquid film (see Fig. 5), the droplets feel capillary interactions leading to an attraction or repulsion. This in turn causes the droplets to propel at the interface. We already found in our preliminary work that depending on the surface tension ratios and fluid volumes involved, this can lead to complex behaviour: the droplets might or might not coalesce, depending on the pressure balance between the droplet interfaces. We will study the dynamic interactions and coalescence of multiple droplets on a liquid film by means of lattice Boltzmann simulations and combine our findings with analytical estimates based on pressure balances.

WP2: Adaptive interfaces based on interfacially assembled colloids

When particles are brought in contact with a fluid interface, they adsorb and reduce the interface free energy of the system. In the case of perfectly smooth and non-interacting hard spheres, the level of immersion is solely determined by the contact angle of the particles with the fluid interface. The interface does not deform and no capillary interactions exist. However, if the particles are geometrically anisotropic or interact for example via electrostatic or magnetic forces, capillary interactions can appear. Those can cause a highly complex time dependent dynamics of a particle ensemble at an interface and lead to the formation of 2D particle networks with specific geometrical properties. An example of such a system are the magnetic ellipsoidal particles we studied in the preliminary work in Sec. 1. Fig. 6 depicts how the dipolar capillary interactions between particles can be switched on or off by varying the external field and how ellipsoids form “capillary caterpillars”, i.e. well-defined and highly tunable structures.

Depositing a droplet of a third fluid on such a particle-laden interface adds an additional level of complexity. Depending on the interplay between the involved surface tensions and the wettability of the particles, the effective interactions between the particles will change leading to the interface structure to adapt to the presence of the droplet. As such, particle-laden interfaces might be a simple way to create adaptive surfaces with well-defined properties. The current WP aims at a detailed fundamental understanding of capillary particle assembly at interfaces in the presence of three fluid components. Furthermore, we will investigate how such adaptive interfaces can be utilized to tune the wetting properties of a substrate.

The results of this work package can be compared to the experiments done by A. Synytska (Dresden). In addition, we plan to build an analytical theory for droplets on particle-laden interfaces in collaboration with U. Thiele (Münster). Further links will be formed with J. Snoeijer (Twente) building on an ongoing collaboration on soft particles at interfaces, and P. Huber (Hamburg) on fluid transport on nanoporous/structured surfaces.

1. We will focus on homogeneous spheres at an interface and understand the interplay of interfacial tensions, particle wettability, particle concentration, and particle/droplet size ratio on the dynamics of a droplet deposited on such a particle-laden interface. The droplet will deform the original interface and form a Neumann triangle similar to WP1. However, the induced curvature of the interface leads to capillary interactions leading to a collective motion and modified geometrical particle assembly. This in turn will influence the dynamic wetting properties of the droplet and lead to a different droplet shape.
2. If the size of the particles is not neglectable in comparison to the size of the droplet, a particle-laden interface will appear like a rough surface. Contact lines moving on such a

"substrate" will perform a stick-slip motion, but depending on the strength of the capillary forces, might also "drag" particles around. We will investigate this effect depending on particle size, wettability, concentration and mobility (i.e. ratio of fluid viscosities) and study how the presence of particles influences the spreading and receding of droplets.

3. We will move from spheres to geometrically anisotropic particles such as prolate and oblate ellipsoids or rod-like particles. The anisotropic shape of the particles might improve the appearance of capillary interactions leading to stronger ordering effects. A question to be answered is if anisotropic particles allow to create adaptive surfaces with non-trivial position dependent adaptivity.

WP3: Adaptive interfaces based on Janus particles

This work package focuses on Janus particle attached to the fluid interface. A spherical Janus particle with hydrophobic and hydrophilic hemispheres behaves in many respects similar to a particle with an anisotropic geometry and we have studied such a system in detail in the past (see preliminary work, Sec. 1 and Figs. 7 and 8. However, a substantial difference is their ability to reorient in order to minimize their interaction with the surrounding fluids. A Janus particle with two equally sized sides at a water-oil interface will thus rotate until the hydrophobic part is immersed in the oil and the hydrophilic part is immersed in the water. If a droplet of a third fluid is deposited on an interface covered by such particles, the situation becomes less clear: It is the interplay between the interfacial energies of all involved surfaces and fluids that determines the equilibrium particle orientation. Eventually, the energetically most favourable configuration might involve a deformed fluid interface leading to capillary interactions and thus again assembly and ordering of the particles.

Our simulations and analytical calculations based on free energy minimization shall be closely synchronized with the experiments of A. Syntska (Dresden) on Janus particle-laden surfaces and the measurements of K. Harth (Twente/Magdeburg). In addition, they shall be linked to the analytical work of U. Thiele (Münster).

As in the experimental counterpart of this proposal, we aim at the understanding of two different scenarios: the Janus particles might rotate freely at the fluid interface or their orientation might be fixed in space leading to inhomogeneous wetting with a droplet deposited on top of such an interface. The latter causes additional interface deformation and capillary interactions leading to a change of the spreading dynamics of the droplet.

1. We will extend our previous analytical work on capillary interactions between Janus particles (see preliminary work in Sec. 1). In the small deformation regime, we were able to compute the actual value of the force between particles in dependence on the Janus ratio and amphiphilicity. Good agreement was found with our lattice Boltzmann simulations. Here, we will extend our theoretical approach to a third fluid phase.
2. We will repeat the studies performed for particles with homogeneous surfaces in order to understand the impact of the Janus character on the wetting properties. For this, we will again vary the interfacial tensions, the particle/droplet size ratio, and the particle concentration for different particle amphiphilicities. The additional parameters to be studied are the freedom of the particles to rotate or not, the wettability contrast and the Janus ratio, i.e. the ratio of the hydrophobic and hydrophilic areas of the particle surface.
3. Ellipsoidal or rod-like Janus particle have an additional rotational degree of freedom which has an impact on their equilibrium position at a fluid interface. For example, a rod-like

particle will – depending on the amphiphilicity – find itself in a tilted state. We will determine the equilibrium orientation of geometrically anisotropic Janus particles at fluid interfaces and in the presence of a third fluid by means of analytical models and lattice Boltzmann simulations. We will then study the impact of the particles on the spreading dynamics of droplets deposited at such an interface.

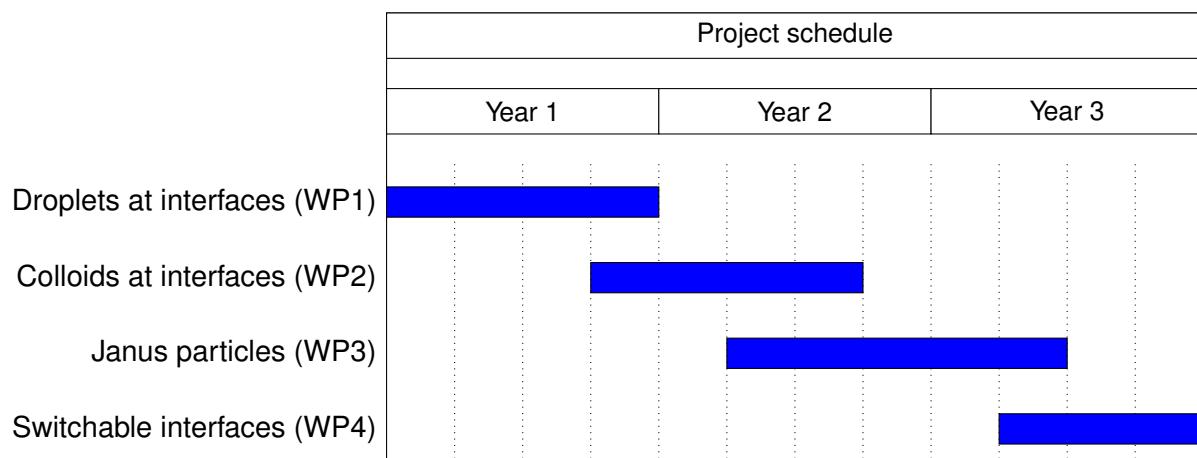
WP4: Switchable interfaces and external fields

In our previous work, we investigated the interplay of particle anisotropy (geometrical or Janus-like) on the occurrence of capillary interactions leading to assembled 2D structures at a fluid interface (see Sec 1 for details). Here, we will extend this work towards the presence of a third fluid and the dynamic wetting of droplets on particle-laden interfaces in external fields. For simplicity, we will restrict ourselves to particles interacting with magnetic fields which effectively only leads to a torque on the particles.

Again, we plan to closely collaborate with A. Syntska (Dresden) who plans to synthesize and study magnetic Janus particles in her project. On magnetically actuated systems, we plan to collaborate with J. Hussong and E. Gurevich (Bochum).

1. In line with the first task of the previous WP3, we will investigate the influence of a torque imposed by an external magnetic field on the capillary interactions between Janus particles and in the presence of three fluids.
2. By means of computer simulations we will then investigate how the switching of the particle orientation and thus the properties of the particle-laden interface can be utilized to manipulate the dynamic properties of a droplet present on such an interface.

Anticipated project schedule



2.4 Data handling

The knowledge gained from this project will be shared through presentations at SPP meetings, further international scientific meetings and publication in peer-reviewed journals. The simulation data will be stored according to good scientific practice for at least 10 years, either on the storage facility of the group in Nuremberg or centrally at the facilities of Forschungszentrum Jülich.

2.5 Information on scientific cooperation within SPP 2171

This project closes the loop between wetting on soft (soft), adaptive and switchable substrates and is thus at the core of the SPP. Our computer simulations can be closely linked to numerous further projects that are planned within the SPP. Most of these will be actively pursued by the to be hired PhD student, but some are more related to the projects of other members of staff at our institute. Here, the SPP shall be the platform to build and maintain regular contacts. At the point of writing, contacts and collaborations already exist with the following PIs and we agreed to collaborate in case our proposals get funded:

- The current proposal is a tandem proposal with **A. Syntska (Dresden)** who will synthesize Janus particles and experimentally investigate their ability to form switchable substrates. We will link her experiments with our simulations and provide a microscopic understanding of the physical effects relevant to control Janus-particle laden interfaces (WP1-WP4).
- Our simulations shall be compared to the thin-film gradient dynamics models for adaptive substrates of **U. Thiele (Münster)** (WP1-WP3).
- We plan to extend our long-standing collaboration on (soft) particles at liquid interfaces with **J. Snoeijer (Twente)** [89] (WP1-WP3).
- The spreading and receding of contact lines on liquid and adaptive substrates shall be investigated in collaboration with the experiments of **K. Harth (Twente/Magdeburg)** (WP1-WP3).
- A cooperation with **G. Lecrivain (Dresden-Rossendorf)**, will involve benchmark tests involving the joint simulation of a liquid droplet at rest on a thin oil-film (WP1).
- We will collaborate with **P. Huber (Hamburg)** on liquid imbibition in porous media [67]. Our recently developed coupled multiphase LB and Nernst-Planck solver for electrokinetic problems shall be utilized to collaborate on electrowetting on nanoporous substrates [68, 97] (WP2).
- We plan to exchange with **J. Hussong** and **E. Gurevich (Bochum)** on magnetically actuated surfaces (WP4).
- With **M. Sega (Nürnberg)** close links exist on simulation methodologies and the physics of soft and wet substrates.
- We plan to exchange with **C. Holm** and **K. Jain (Stuttgart)** on the development and application of multiphase LB solvers for complex fluids.

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4 Requested modules/funds

4.1 Basic module

4.1.1 Funding for staff

4.1.1.1 Research staff

The project demands both, a high level of training in theoretical physics (for numerical modeling of

hydrodynamic problems), and the capacity to work at the interface of physics and computational sciences, which requires the ability to manipulate a highly complex simulation framework and to perform the simulations and data analysis on state of the art supercomputing facilities. We are applying for funding for one doctoral researcher for the entire duration of the project (E13, 75%). The candidate will be hired by the Research Centre Jülich and shall be a member of staff of the Helmholtz Institute Erlangen-Nürnberg in Nürnberg. According to the current DFG recommendations, this amounts to an annual cost of €48,375.

4.1.1.2 Student assistant

The project requires a very large number of simulations to be run and labour intensive analysis to be performed. Funding is requested for a student assistant to assist the researcher in these tasks and to implement analysis and visualization tools to be used for data post processing. Furthermore, within the SPP hands on tutorials on specific techniques shall be prepared. Within this project we plan to create such tutorials on lattice Boltzmann based simulation techniques. The related work shall be supported by the student assistant. (10h/Week, €6000 per year).

Total: €163,125

4.1.2 Direct project costs

4.1.2.1 Equipment up to €10,000, software and consumables

While the basic equipment and access to supercomputing facilities are secured by the PI, preserving the data associated with the simulations increases the need for data storage. Consequently, we are applying for a funding of €3,000 to increase the capacity of the RAID storage system of the group and for consumables such as portable hard drives, etc..

Total: €3,000

4.1.2.2 Travel expenses

SPP Workshop (4 days), Year 1, PI+PhD student	€1,500
SPP Workshop (4 days), Year 2, PI+PhD student	€1,500
Advanced SPP School (1 week), Year 1, PhD student	€1,300
SPP PhD-candidates Workshop (4 days), Year 2, PhD student	€700
International Conference (5 days), Year 1, PI	€2,000
International Conference (5 days), Year 2, PI + PhD student	€4,000
International Conference (5 days), Year 3, PI + PhD student	€4,000

Total: €15,000

4.1.2.3 Project-related publication expenses

It is expected that the results will likely yield three scientific publications of high quality. For their open access publication in well-reputed scientific journals of the field (e.g. Physical Review, New Journal of Physics, Journal of Fluid Mechanics, Physics of Fluids, Scientific Reports), €750/year are requested.

Total: €2,250

5 Project requirements

5.1 Employment status information

Prof. Dr. Jens Harting is W2 professor at the Department of Chemical and Biological Engineering, Friedrich-Alexander-University Erlangen-Nürnberg. Permanently on leave to head the research unit “Dynamics of Complex Fluids and Interfaces” at the Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IEK-11) / Research Centre Jülich (Permanent employment with civil servant status, “Jülicher Modell”). Further, Jens Harting is Associate Professor (20% FTE) at the Department of Applied Physics, Eindhoven University of Technology, The Netherlands.

5.2 Composition of the project group

The project leader has more than 15 years of experience with the computer simulation of particle-laden and multiphase flows and will be the daily supervisor of the scientist. Furthermore, several postdocs and PhD students working on lattice Boltzmann simulations of particle-laden multiphase flows (Dr. O. Aouane, Dr. A. Sukhov, Dr. Q. Xie, O. Ronsin, B. König, M. Wouters, G. Venditti) will be able to support the project. A software developer (M. Zellhöfer) will be available to help with the code development, simulation setup and data organization. Additional Master and Bachelor students and student workers will further participate in the project in both groups with appropriate research subprojects.

5.3 Cooperation with other researchers

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

Dr. T. Krüger (Edinburgh), Dr. C. Misbah (Grenoble), Dr. B. Kaoui (Compiegne), Prof. P. Coveney (London), Prof. J. Snoeijer, Prof. D. Lohse, Prof. S. Luding (all Twente), Prof. O. Vinogradova (Moscow), Prof. A. Darhuber (Eindhoven), Prof. H. Steeb (Stuttgart), Prof. U. Rüde, Prof. A.-S. Smith (all Erlangen-Nürnberg), Prof. L. Mahadevan (Harvard)

5.4 Scientific equipment

The simulations will be carried out on the compute cluster at the Helmholtz Institute Erlangen-Nürnberg, the supercomputing facilities of the Research Center in Jülich (JURECA and JUWELS), as well as on the supercomputing facilities of FAU Erlangen-Nürnberg.

6 Additional information

This proposal has not been submitted to any other national or international funding body.